BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1928.

General, Physical, and Inorganic Chemistry.

True and apparent width of spectral lines. P. H. van Cittert and H. C. Burger (Physica, 1927, 7, 149—156).—If s is the apparent width of a spectral line in a Fabry–Perot interferometer. a the apparent width for monochromatic light, and b the actual width, for $b > 0{\cdot}42a$, $s^- = a + 2{\cdot}15b^2$; for $0{\cdot}46a > b < 2a$, $s = 0{\cdot}80a + 0{\cdot}81b$. Also, $a = \varepsilon\lambda^2 2\pi d t^{\frac{1}{2}}$ for $\varepsilon = 1 - t$, t being the reflexion coefficient of the silver layer.

Chemical Abstracts.

Continuous spectra in hydrogen. G. Herzberg (Physikal. Z., 1927, 28, 727—728).—The continuous limit of the Balmer series, hitherto observed in emission only in solar prominences etc., has been produced in the laboratory with the aid of the electrodeless ring discharge. The continuous spectrum observed by Stark with canal rays is not the continuous limit in question. The work of Oldenburg (A., 1927, 177) on the ordinary hydrogen continuum and the many-lined spectrum is in general confirmed. Various hypotheses for the origin of the continuum have been suggested (cf. Schuler and Wolf, A., 1926, 213; Blackett and Franck, A., 1925, ii, 1097), but these are regarded as erroneous. The emission of the continuous spectrum is in some way connected with the decomposition of the H_2^+ ion, possibly as follows, $H_2^+ + H_2 = H_3^+ + H$ (Dorsch and Kallmann, A., 1927, 1001).

R. A. Morton.

Secondary spectrum of hydrogen and other spectra. H. Deslandres (Compt. rend., 1927, 185, 905—909).—The author's simple relationship between the number of atoms in a molecule and the frequency of the most intense radiation of each of the groups of bands emitted by the molecule (A., 1925, ii, 1114) is applied to results recently obtained for the intense radiations of the secondary spectrum of hydrogen. These radiations are due to H_3 molecules rather than to groups of three H_2 molecules, since the latter cannot exist at the high temperatures concerned and, moreover, have been identified with weaker radiations of the same spectrum. Similarly, the effect of a diatomic molecule (probably oxygen) is detectable in the ultra-violet band spectrum of water vapour. The universal constant $d(=1062{\cdot}5)$ in the formula is also intimately connected with the principal bands of the absorption spectra of oxygen and the light gases, with the emission spectra of nitrogen, carbon, carbon dioxide, and cosmic bodies, and with many line spectra.

J. Grant.

Structure of the O II spectrum. C. Mihul (Compt. rend., 1927, 185, 937—939).—The terms of the O II spectrum derived from the normal electronic configuration of the O III spectrum are made up of systems a of quadruplets and of doublets corresponding with the O III multiplet ^3P, and of two systems a' of doublets corresponding with the O III terms ^1D and ^1S, respectively. A list of new terms and their combinations is given, thus completing the groups of the terms of the doublet system a', corresponding with the $3p$ and $3d$ orbits of the emissive electron. The results are confirmed by the Zeeman effect.

J. Grant.

Arc and spark spectra of scandium (Sc I and Sc II). H. N. Russell and W. F. Meggers (U.S. Bur. Standards Sci. Paper 558, 1927, 22, 329—373).—The arc and spark spectra have been analysed and spectral term combinations have been assigned to 353 lines of Sc I and 142 of Sc II. Nearly all the observed lines in both spectra have been thus classified. In the spark spectrum (Sc II), which is the simplest, the terms with lowest energy content are ^3D, ^1D, arising from the electron configuration $3d\,.\,4s$, and these and other terms combine with spectral terms associated with the configurations $3d\,.\,4p$, $3d\,.\,4d$, and $3d\,.\,5s$. The ionisation potential of the Sc^+ atom is calculated to be 12·8 volts. The arc spectrum (Sc I) is much more complex. In this case, the lowest-energy term, representing the normal state of the scandium atom, is -D, originating with the three-electron configuration $3d\,.\,4s\,.\,4s$. This term and a $^4F'$ term arising from $3d\,.\,3d\,.\,4s$ begin two series from which an ionisation potential of 6·7 volts is calculated for the neutral scandium atom. Energy-level diagrams and tables are given for both spectra, and it is shown that in each case all details are in complete agreement with Hund's theory, which derives one or more specific spectral terms from each possible configuration of the electrons not in completed groups.

G. A. Elliott.

Analysis of the copper spectrum. II. Complex separations and quadruplet relations. W. M. Hicks (Phil. Mag., 1927, [vii], 4, 1161—1227).—Previous work on the copper spectrum (A., 1926, 766) is extended. An examination of the inverse D-lines indicates the possibility that these and the line at 5105 Å. with the frequency separation 2042 may not, as generally supposed, belong to the doublet system. Evidence is adduced for the existence of quadruplet systems depending on d terms with separations 2042, 1412, 894 and with these completely in accord with Lande's separation rules. The quadruplet systems are discussed in detail.

A. E. Mitchell.

Reversed spectra of metals produced by explosion under increased pressure. M. FUKUDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 1—47).—Fine wires or strips of copper, silver, gold, mercury, calcium, zinc, cadmium, thallium, and tin were exploded in an enclosure under pressures of 1 and 8 atm. In general, the widths of the absorption and emission lines were found to be increased with the pressure. Forbidden lines were found in emission and absorption, their intensity increasing with the pressure. The characters of the lines obtained in explosion under two pressures are tabulated. The appearance of the lines could be correlated with the series classification of the ordinary type, but no satisfactory agreement was found between the theoretical classification of the copper, gold, and tin multiplets except in a few cases with copper. C. J. SMITHELLS.

Arc spectrum of bismuth. G. R. TOSHNIWAL (Phil. Mag., 1927, [vii], **4**, 774—787).—The spectrum of bismuth has been examined in the heavy-arc and in the under-water spark. 183 lines in the region 1900—3550 Å. have been measured. The results are in general agreement with those of other observers, but include 57 lines not previously reported. The structure of the spectrum, from the point of view of theories of complicated spectra, is discussed, and it is shown that owing to the large atomic number of bismuth terms arising from the same level are widely separated; this increases the difficulty of interpretation.
A. E. MITCHELL.

Classical theories of absorption and refraction of X-rays. F. K. RICHTMYER (Phil. Mag., 1927, [vii], **4**, 1296—1302).—Although the relation between the index of refraction and atomic absorption coefficient of X-rays which may be developed by the classical method agrees in order of magnitude with the experimental data, the latter is too scanty to permit of an exact verification, and it seems quite probable that the relation applies to scattering rather than to fluorescent absorption. The equations of classical optics also lead to equations for scattering.
R. CUTHILL.

Vacuum spectrograph and its use in the long X-ray region. J. SHEARER (Phil. Mag., 1927, [vii], **4**, 745—753).—A description is given of an X-ray spectrograph employing a common vacuum in the X-ray tube and spectrograph, which permits of the rotation through known angles of the crystal and photographic film from outside the spectrograph while it is evacuated. Thus the difficulties, inherent in work with long X-rays, of absorption in the window between the spectrograph and the X-ray tube, of absorption in the air between the slit and the crystal and between the crystal and the photographic plate, and of the absorption in the covering over the photographic plate or film are obviated. The wave-length of the Ni $L\alpha$ line determined with this instrument is 14·5720 Å., which is in disagreement with the value of 14·528 Å. given by Thoræus. A determination of the $2d$ spacing of sucrose gave the value 21·1519 whilst that reported by Stenstrom is 21·141 Å.
A. E. MITCHELL.

X-Ray spectra of long wave-length. T. H. OSGOOD (Physical Rev., 1927, [ii], **30**, 567—573).—A photographic method of obtaining X-ray spectra of wave-length greater than 20 Å. is described. About 15 lines have been measured between 40 and 200 Å., but as it is not yet possible to obtain a pure spectrum of any one element, the interpretation of the lines is uncertain. A. A. ELDRIDGE.

L X-Ray absorption edges of tin, indium, cadmium, silver, palladium, rhodium, and ruthenium. G. D. VAN DYKE and G. A. LINDSAY (Physical Rev., 1927, [ii], **30**, 562—566).—Values of the wave-length, ν/R, and $(\nu/R)^{\frac{1}{2}}$ for the L-absorption limits of the above elements are tabulated, together with energy level values. A. A. ELDRIDGE.

Spectra of tin and their Zeeman effects. J. B. GREEN and R. A. LORING (Physical Rev., 1927, [ii], **30**, 574—591).—The spectra of tin in the neutral state and in two stages of ionisation have been classified. The spectrum of neutral tin has five low levels, ${}^3P_{0,1,2}$, ${}^1D_2'$, ${}^1S_0$, due to the configuration $5_2 5_2$. The configuration $5_2 6_1$ yields ${}^3P_{0,1,2}'$ and ${}^1P_1'$. The configuration $5_2 5_1$ yields 12 terms, of which the lowest four are definitely established. The ionisation potential of Sn I calculated from the value of the ${}^2p^3P_0$ term is 7·37±0·05 volts, and the resonance potential computed from the resonance line 2863 Å. is 4·30 volts. The spectrum of Sn II is a doublet spectrum like that of In I. Several series are noted, including lines due to abnormal states, the electrons having the configuration The ionisation potential of Sn II is 14·5 volts, and the resonance potential 6·5 volts. The spectrum of Sn III consists of singlets and triplets, like that of Cd I. The ionisation potential is calculated to be about 30 volts, and the resonance potential 6·81 volts.
A. A. ELDRIDGE.

Zeeman effect in the band spectra of AgH, AlH, ZnH, and MgH. W. W. WATSON and B. PERKINS, jun. (Physical Rev., 1927, [ii], **30**, 592—597).—The AgH bands exhibit no Zeeman effect. With AlH bands, only the first lines in each branch show an effect, in quantitative agreement with Van Vleck's predictions. With ZnH bands, the wide doublets found by Hulthen for the Q and R lines are shown to be quadruplets. With magnesium hydride bands, all the lines show broadening with a field of 10,000 gauss. There is no evidence of the existence of satellites splitting off from the main lines under the influence of the magnetic field. A. A. ELDRIDGE.

Stark effect for the spectra of silver, copper, and gold. Y. FUJIOKA and S. NAKAMURA (Astrophys. J., 1927, **65**, 201—213).—For silver the Stark effect of the doublet diffuse series lines was observed up to $2p-7d$. These and known data are discussed, and the components are classified as forbidden combinations. For copper, the effect was observed up to $2p-6d$; none of the $2p-mp$ combinations was observed. For gold, the effect was observed only for the $2p-4d$ lines. A. A. ELDRIDGE.

Multiple ionisation in X-ray levels. H. R. ROBINSON (Phil. Mag., 1927, [vii], **4**, 763—774).—A general discussion of work on X-ray measurement and multiple ionisation effects in X-ray levels.
A. E. MITCHELL.

Thermionic work function of tungsten. C. DAVISSON and L. H. GERMER (Physical Rev., 1927, [ii], **30**, 634—638).—Corrected values are obtained; the conduction electrons within the filament do not possess normal thermal energies.

A. A. ELDRIDGE.

Properties of atomic hydrogen. J. KAPLAN (Physical Rev., 1927, [ii], **30**, 639—643).—Atomic hydrogen was passed from a discharge-tube into a 3-litre glass bulb, its presence being indicated by glowing thoria. The glow persisted for 3 sec. after interruption of the discharge, and white action spots on the glass for 6 sec. after interruption. Possibly atomic hydrogen can exist for 10 sec.

A. A. ELDRIDGE.

Active nitrogen. IV. Independence of the afterglow and the chemical properties of active nitrogen. E. J. B. WILLEY (J.C.S., 1927, 2831—2842; cf. A., 1926, 893; 1927, 431, 635).—Four methods are described by which it is shown that chemically active nitrogen which exhibits no visible luminosity may be prepared. "Active" nitrogen has probably a metastable diatomic or acetylenic molecule, since, when it reacts with other substances, it gives rise to compounds which, on hydrolysis, liberate ammonia. Substances of this type are produced in the few reactions of ordinary inert nitrogen, so that the two cannot be very different in structure.

M. S. BURR.

Electrodeless discharge through gases. (SIR) J. J. THOMSON (Phil. Mag., 1927, [vii], **4**, 1128—1160).—The theory of the electrodeless discharge, produced when a vessel containing gas at a low pressure is placed inside a solenoid through which rapidly alternating currents are passed, is discussed. It is shown that the discharge requires a maximum magnetic force inside the solenoid depending on the nature of the gas, its pressure, the frequency of the currents, and the size of the vessel. The force is infinite when the pressure is either infinite or zero, and is a maximum when the pressure is such that $\lambda p=c$, where λ is the free path of the electron in the gas, p the frequency of the alternating current, and c the electron velocity when its energy is that required for ionisation of the gas. Thus it follows that there is a critical pressure when the discharge passes most easily. It is shown also that in the electrodeless discharge very heavy currents may pass through the gas without producing visible luminosity. The effects produced on the discharge by placing certain solids at the centre of the ring discharge are discussed.

A. E. MITCHELL.

Spectroscopic determination of e/m. W. V. HOUSTON (Physical Rev., 1927, [ii], **30**, 608—613).—The wave-lengths of the hydrogen lines at 6563 and 4861 Å., respectively, measured with reference to the helium line 5015·6750 Å. are 6562·7110±0·0018, 6562·8473±0·0009; 4861·2800±0·0013, 4861·3578±0·0022, and those of the ionised helium line 4686 are 4685·7030±0·0012, 4685·8030±0·0026. The Rydberg constant for hydrogen is thence computed as 109677·759±0·008, and that for helium 109722·403±0·004. The ratio e/m is evaluated as 1·7606±0·0010±10^7 *E.M.U.* per g.

A. A. ELDRIDGE.

Diffraction of cathode rays by thin films of platinum. G. P. THOMSON (Nature, 1927, **120**, 802).—Previous work on celluloid (A., 1927, 605) has been extended to platinum, as well as to gold and aluminium.

A. A. ELDRIDGE.

Duration of the existence of doubly-charged positive ions in gases and their detection. L. B. LOEB (Proc. Nat. Acad. Sci., 1927, **13**, 703—707).—Theoretical. It is concluded that the experimental evidence for the existence of doubly-charged positive gas ions is not conclusive.

W. E. DOWNEY.

Ionisation by collision. L. G. H. HUXLEY (Phil. Mag., 1927, [vii], **4**, 899—902).—A reply to Taylor's criticisms (A., 1927, 1001).

C. J. SMITHELLS.

Atomic structure and the magnetic properties of co-ordination compounds. II. L. C. JACKSON (Phil. Mag., 1927, [vii], **4**, 1070—1080).—The previous discussion on uninuclear co-ordination compounds (A., 1926, 773) has been extended to the multinuclear co-ordination compounds. It is concluded that the scheme proposed by Cabrera is better able to account for the magnetic properties of co-ordination compounds than those of Welo and Baudisch or of Bose.

A. E. MITCHELL.

Preparation of radiothorium. D. K. YOVANOVITCH (Arh. Hemiju, 1927, **1**, 89—94).—A preparation extremely rich in radiothorium is obtained by repeated precipitation with concentrated hydrochloric acid from concentrated solutions of mesothorium-1. This preparation is freed from traces of barium, mesothorium-1, and radium by fractional crystallisation.

R. TRUSZKOWSKI.

Behaviour of small quantities of radon at low temperatures and low pressures. A. F. KOVARIK (Phil. Mag., 1927, [vii], **4**, 1262—1275).—The vapour pressure, P, of radon has been measured between 79° and 114° Abs., and found to be connected with the temperature, T, by the expression $\log P=-968{\cdot}479/T+0{\cdot}3021 \log T+1{\cdot}158$. Considerable irregularities were, however, observed, suggesting that the product of condensation may be in the form both of small frozen drops and of a monatomic layer on the cooled surface. The volatilisation temperature of small amounts of radon condensed in a glass tube is apparently either 116° or 121° Abs.

R. CUTHILL.

Effect of radon on the solubility of lead uranate. A. HOLMES (Phil. Mag., 1927, [vii], **4**, 1242).—A misinterpretation by Bailey (A., 1927, 928) of the author's previous statements (A., 1926, 654) is corrected.

A. E. MITCHELL.

Efficiency of β-recoil of thorium-*B*. K. DONAT and K. PHILIPP (Physikal. Z., 1927, **28**, 737).—Barton (A., 1926, 553) found the efficiency of β-ray recoil of radium-*C* from radium-*B* to be not more than 6%, and only 2% with a perfectly clean surface; Muszkat (Phil. Mag., 1920, [vi], **39**, 690) found much higher values. Thorium-*B* has certain advantages as a test-substance for this problem, and investigation shows the efficiency to be between 2% and 6·5%. Gurney (A., 1926, 990), however, has shown that the primary β-particles from thorium-*B* have smaller velocities than those from radium-*B*; thus the

β-recoil should show a smaller efficiency. The present work is therefore not completely in agreement with that of Barton. The discrepancy may be due to reflexion of recoil atoms from the collecting surface.

R. A. MORTON.

Half-period of radium-*E*. L. F. CURTISS (Physical Rev., 1927, [ii], **30**, 539—542).—An extension of previous work (A., 1926, 771). The mean value given by new preparations is 4·975 days.

A. A. ELDRIDGE.

Radioactivity of potassium. G. HEVESY (Nature, 1927, **120**, 838—839).—In order to ascertain which of the isotopes of potassium is responsible for the emission of β-rays, 1 litre of the metal was submitted to ideal distillation, the distance between the hot and cold surfaces being less than 1 cm. The at. wt. of the residual fraction was reported by Honigschmid to be 0 005 ($\pm$1) unit greater than the normal value. Using Hofmann's vacuum electrometer method, the difference between the feeble radioactivities of the heavy fraction and ordinary potassium (as chloride) was determined as $4\cdot2\pm0\cdot7\%$. This result is in accord with the at. wt. determination if the radioactivity is assumed to be due to the isotope of at. wt. 41. It is concluded that this isotope is mainly, if not solely, responsible for the observed radioactivity of potassium. Cæsium, a pure element, does not exhibit radioactivity, whilst if the radioactivity of rubidium (85, 87) is due to the heavier isotope, the greater activity of rubidium is quantitatively accounted for. Holmes and Lawson's value (A., 1926, 554) of $1\cdot5\times10^{12}$ years as the half-value period of potassium now requires correction to their alternative value, $7\cdot5\times10^{10}$ years (A., 1927, 86), since before the consolidation of the earth's crust about 2% of the potassium isotope 41 has disintegrated. If it is assumed that the emission of β-rays effects an alteration in the nuclear charge, the transformation product will be a calcium isotope of at. wt. 41; the maximum amount of this which has accumulated in potassium minerals during the whole of geological time will thus be 0·1% of the potassium content, an amount which should permit of detection.

A. A. ELDRIDGE.

Collision of α-particles with helium atoms. S. GHOSH (Bull. Calcutta Math. Soc., 1926, **17**, 99—104).—Of 1203 Wilson cloud photographs of α-particle tracks in helium, 44 were forked. The range of the recoil atoms was 0·94—3·2 cm., and the angle between the tracks was 1° 23′—6° 17′. It is concluded that the helium nucleus is oblate spheroidal in shape, and (since the recoil tracks were not longer than the original α-particle tracks) the recoil atoms do not exist as singly-charged particles during the whole course of their existence as ionising agents.

CHEMICAL ABSTRACTS.

Accurate determination of ion-formation by single α-particles and detection of new activities. G. HOFFMANN (Physikal. Z., 1927, **28**, 729—731).—The formation of ions by α-particles in the neighbourhood of metal surfaces has been investigated and the statistical results of a large number of α-ionisations are expressed by plotting the number of ions formed against the number of collisions per unit time. Both by electrometric readings and by a specially designed recording instrument, the curves show sharp maxima corresponding with uranium I and uranium II, using uranium as the source of α-particles. Ion-formation is at a maximum at the saturation potential. Metal surfaces of lead, gold, aluminium, zinc, copper, and brass have been studied, and particularly interesting results obtained with a copper surface coated with zinc residues left after treating the metal with sulphuric acid. A large number of maxima are observed in the ionisation, and these may be due to α-particles of very short range or else to another phenomenon, possibly H-rays.

R. A. MORTON.

Determination of the range of the α-particles of uranium I and II. G. C. LAURENCE (Proc. Nova Scotian Inst. Sci., 1927, **17**, 103—106).—The ranges of the α-particles of uranium I and II have been redetermined by the Wilson cloud chamber method. The value 2·72 cm. for uranium I, with a probable error of 1·5%, falls on the Geiger–Nuttall curve within the limits of experimental error and is close to Geiger and Nuttall's value of 2·67 cm. The value 3·29 cm. for uranium II, with a probable error of 1%, is, however, considerably greater than Geiger and Nuttall's value of 3·07 cm. Neither is it in agreement with that deduced from measurements of pleochroic haloes. The disintegration constant of uranium II, calculated by applying the Geiger–Nuttall relationship to the range 3·29 cm., is $2\cdot1\times10^{-11}$ per sec.

M. S. BURR.

Ionisation and stopping power of various gases for α-particles from polonium. I. G. E. GIBSON and E. W. GARDINER (Physical Rev., 1927, [ii], **30**, 543—552).—Determinations of the differential ionisations and stopping powers of hydrogen, neon, nitrogen, oxygen, argon, and methyl iodide for α-particles from polonium indicate that the energy lost by the α-particle per ion is nearly independent of the speed throughout the range. A. A. ELDRIDGE.

Ionisation and stopping power of various gases for α-particles from polonium. II. G. E. GIBSON and H. EYRING (Physical Rev., 1927, [ii], **30**, 553—561).—The molecular ionisation and stopping power of cyanogen, hydrogen cyanide, carbon monoxide, carbon dioxide, nitrous oxide, methyl iodide, oxygen, nitric oxide, and azomethane and the stopping power of hydrogen for α-particles from polonium are tabulated. Such unstable molecules as nitric oxide and azomethane give strictly additive stopping powers. Values are obtained of α for air in the straggling equation $y—e^{-(x/\alpha)^2}/\pi^{\frac{1}{2}}\alpha$ which agree with those given by other methods.

A. A. ELDRIDGE.

Atomic disintegration. G. STETTER (Physikal. Z., 1927, **28**, 712—723).—A review. See A., 1927, 494, 495.

R. A. MORTON.

Scattering of radiation from atoms. I. WALLER (Phil. Mag., 1927, [vii], **4**, 1228—1237).—Mathematical.

A. E. MITCHELL.

Structure of an atom of nitrogen. V. H. COLLINS (Chem. News, 1927, **135**, 341—346).—Speculative.

Quantum emission and stationary states. N. H. KOLKMEIJER (Z. physikal. Chem., 1927, **130**,

95—99).—Mathematical. Space–time considerations are applied to certain aspects of the Bohr atom.

L. L. BIRCUMSHAW.

Light quanta and interference. A. J. DEMPSTER and H. F. BATHO (Physical Rev., 1927, [ii], 30, 644—648).—By means of interference experiments with the helium line 4471 Å. it is shown that a single quantum of radiation obeys the classical laws of partial transmission and reflexion at a half-silvered mirror and of subsequent combination with the phase difference required by the wave-theory of light.

A. A. ELDRIDGE.

Experimental technique of photochemistry. IV. Critical examination of certain filters for the 365 mercury line. L. T. M. GRAY (J. Physical Chem., 1927, 31, 1732—1736).—Winther's filter (A., 1913, ii, 458) and the Luther–Forbes G1 filter (A., 1909, ii, 632) are both shown to be efficient filters for the mercury line 365 $\mu\mu$, measurements of transmission having been made. Both filters are very sensitive to hydrogen-ion concentration, addition of acid to the latter moving the bands towards the visible end of the spectrum, and addition of alkali in the opposite direction. The Goerz glass filter has also been examined. With all three filters, however, measurements of transmission before and after use should be made. L. S. THEOBALD.

Metals as semi-transparent layers in the interferometer. P. ZEEMAN (Z. physikal. Chem., 1927, 130, 237—240).—The behaviour of transparent layers of silver, treated in various ways, of platinum, copper, and gold, and of gold alloys is described.

L. S. THEOBALD.

Absorption experiments on excited molecular hydrogen. L. A. SOMMER (Nature, 1927, 120, 841).—Search has been made for a metastable state of H_2, corresponding with the 2^3S state in the helium spectrum, by absorption experiments in excited molecular hydrogen. A number of intense lines located in definitely bounded regions show self-reversal, whilst other intense lines scattered over the whole spectrum do not show any absorption. A. A. ELDRIDGE.

Absorption of ultra-sonic waves by hydrogen and carbon dioxide. T. P. ABELLO (Proc. Nat. Acad. Sci., 1927, 13, 699—701).—An ultra-sonic beam, generated by a piezo-electric crystal, was passed through a mixture of air and carbon dioxide (or hydrogen). The energy of the emergent beam was measured by the pressure it exerted on a torsion vane.

W. E. DOWNEY.

Absorption spectra of chromic acid, potassium chromate and dichromate in aqueous solution. E. VITERBI and G. KRAUSZ (Gazzetta, 1927, 57, 690—703).—The extinction coefficients of these substances have been determined for 0·001M- and 0·0001M-solutions. The absorption of chromic acid is similar to that of potassium dichromate, and solutions of these substances obey Beer's law whilst a solution of potassium chromate does not. It is thought, therefore, that in potassium dichromate solution only a little dichromate ion is dissociated into chromate or $HCrO_4'$ ions, and that in potassium chromate solution the failure of Beer's law is due to the formation of dichromate ions. R. W. LUNT.

Absorption spectra of various alkaloids and their salicylates and of other derivatives of salicylic acid. J. E. PURVIS (J.C.S., 1927, 2715—2719; cf. A., 1926, 108, 557; 1927, 496).—The absorption spectra of the following substances have been examined and the results compared with previous data relating to other derivatives of salicylic acid: salicylamide, salicylanilide, benzene-5-azosalicylic acid, *o*-salicyloyloxybenzoic acid, the alkaloids atropine, pilocarpine, colchicine, and eserine and their salicylates. The specific absorptive capacity of compounds containing centres of different chemical type, *e.g.*, acid and basic, appears to depend not only on their chemical nature, but also on the more or less intimate chemical combination of the various centres. When the chemical combination is not so close, as in the salicylates of the alkaloids, both the acid and basic nuclei retain their own specific absorption to a considerable extent. In such compounds as salicylanilide, or benzene-5-azosalicylic acid, where, on the contrary, there is closer chemical combination of the absorbing centres, each centre is influenced by the other to a much greater extent and the specific absorption of each is not so sharply defined.

M. S. BURR.

Absorption spectra of some anthocyanidins. S. A. SCHOU (Helv. Chim. Acta, 1927, 10, 907—915).—The absorption spectra of pelargonidin, cyanidin, delphinidin, pæonidin, syringidin, and syringidin diglucoside (malvin) in the visible and ultra-violet regions have been investigated and the results correlated with the structure of these compounds. In addition to the absorption maximum in the visible region, all these substances exhibit a band at about 2700 Å. The absorption spectra of alkaline solutions of syringidin diglucoside are quite different from those of neutral solutions, and it is suggested that in alkaline media the substance has a quinonoid structure.

J. S. CARTER.

Fluorescence in mixtures of ammonia and mercury vapour. A. C. G. MITCHELL (J. Amer. Chem. Soc., 1927, 49, 2699—2703).—Mercury atoms excited by the absorption of the resonance line 2537 Å. of mercury are necessary for the production of the above fluorescence band having a maximum at 3370 Å. (cf. A., 1927, 217). Ammonia and mercury atoms in the 2^3P_1 or 2^3P_0 states are necessary for the production of the ultra-violet portion of the band. The intensity of the diffuse band varies with the ammonia and hydrogen pressure in the same manner as the rate of sensitised decomposition of ammonia, which is readily explained on the assumption that the emitter is an ammonia molecule activated by a collision of the second kind with an excited mercury atom. S. K. TWEEDY.

Ionisation of hydrogen chloride by electron impacts. H. A. BARTON (Physical Rev., 1927, [ii], 30, 614—633).—By a mass-spectrographic method, the products of electron impact ionisation in hydrogen chloride were found to be: H^+, H_2^+, $(H_2O)^+$, $(HCl)^+$, and Cl_2^+. The type Cl_2^+ is considered to be a secondary product, and the hot tungsten filament in the hydrogen chloride produced molecular hydrogen in quantities sufficient to account for the hydrogen

ions. When further resolved, the peak ascribed to $(HCl)^+$ was found to consist of peaks corresponding with the ions $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, $(HCl^{37})^+$. Hydrogen ions were not observed when time was given for the water vapour adsorbed by the walls of the vessel to be removed. Negative ions can be formed in hydrogen chloride without electron impacts of more than 2—3 volts energy. The results indicate the process of ionisation of hydrogen chloride by electron impacts to be $W+HCl \longrightarrow (HCl)^+ + e$, and not $W+HCl \longrightarrow H^+ + Cl^-$. A. A. ELDRIDGE.

Band spectra and dissociation of iodine monochloride. G. E. GIBSON and H. C. RAMSPERGER (Physical Rev., 1927, [ii], **30**, 598—607).—The wave-lengths and frequencies of 33 band-heads of iodine monochloride are tabulated, and the frequencies are arranged in two series; two faint heads of a third series were also observed. The maximum of continuous absorption is about 4800 Å. The variation of intensity with wave-length accords with Franck's theory; hence iodine monochloride dissociates in light into unexcited atoms, and into an unexcited iodine atom and a chlorine atom in the 2^2P_1 state. The results require an evolution of 3·8 kg.-cal. for the reaction $ICl=0{\cdot}5I_2+0{\cdot}5Cl_2$. Thermodynamic calculations support the former process, so it is concluded that dissociation by the former process takes place with greater intensity than by the latter. A. A. ELDRIDGE.

Excitation of the spectra of carbon monoxide by electronic impacts. O. S. DUFFENDACK and G. W. FOX (Astrophys. J., 1927, **65**, 214—237).—The ionisation potential of carbon monoxide, as determined by the low-voltage arc, is 14·3 volts. For the neutral molecule, two sets of levels were determined as 6·0, 10·34, 11·35 and 8·0, 10·73 volts, and the band systems are correlated to transitions between these levels. Deslandres' third positive carbon bands are due to carbon monoxide. The ionised carbon monoxide molecule has three levels at 16·9, 20·0, 22·9 volts, and the negative band systems have been correlated to transitions between these levels. A. A. ELDRIDGE.

Absolute measurement at high frequency of the dielectric constants of liquids. R. DARBORD (Compt. rend., 1927, **185**, 1193—1195).—The new type of condenser described for the measurement of ε by the Wheatstone bridge method consists of a cylindrical vessel divided into an upper and a lower portion, the latter containing two shaped, horizontal armatures, one of which is fixed, whilst the other rotates inside it. If c_1 and c_2 are the capacities of the empty lower portion for the two extreme positions of the armatures, and εc_1 and εc_2 are the corresponding capacities after the addition of the liquid, then $\varepsilon=(\varepsilon c_2-\varepsilon c_1)/(c_2-c_1)$. If the armatures are fixed, the instrument must be standardised against a liquid of known ε. The apparatus avoids the influence of dispersion of the lines of force, and may be used with liquids for the vapours of which ε is nearly unity. J. GRANT.

Variation of the specific inductive capacity of fluids in intense electric fields. L. CAGNIARD (Compt. rend., 1927, **185**, 1195—1197).—Herweg's calculations of electrical induction (Z. Physik, 1920, **3**, 36) are extended to include the effect of electrostriction, and it is shown that for an isothermal transformation there is an increase in the dielectric constant. The calculations do not apply to liquid dielectrics and do not afford evidence for or against the existence of dipoles. J. GRANT.

Contraction in the formation of volatile hydrides. C. DEL FRESNO (Anal. Fís. Quím., 1927, **25**, 363—368).—The contraction in the formation of the volatile hydrides increases with diminution in the atomic number of the negative element present. Within each period, the contraction varies approximately inversely with the atomic number of the negative element and directly with the number of hydrogen atoms in the hydride. G. W. ROBINSON.

Refractive index of sulphur trioxide. R. NASINI (Gazzetta, 1927, **57**, 667—669).—Attention is directed to certain errors in the data in Abegg's "Handbuch" relating to the refractive index of this substance and notice is given of a forthcoming paper on this subject. R. W. LUNT.

Magnetic rotation in optically active substances. G. CALCAGNI (Gazzetta, 1927, **57**, 713—716).—The change in rotation of a number of optically active substances produced by an external magnetic field depends on the direction of the field and is independent of the concentration of the solution in the cases examined. R. W. LUNT.

Dispersion of methane. T. H. HAVELOCK (Phil. Mag., 1927, [vii], **4**, 721—725).—A comparison is made of the approximate dispersion formulæ for neon, hydrogen fluoride, water, ammonia, and methane. It is shown that methane does not belong to this sequence and that its molecule is not equivalent to a C^{----} ion with four hydrogen nuclei. This argument is substantiated by an examination of the ionisation potentials. It is shown that the dispersion formula is in support of a molecular structure with a C^{++++} ion and four H^- ions. A. E. MITCHELL.

Thermal degeneration of the X-ray haloes in liquids. C. V. RAMAN (Nature, 1927, **120**, 770).—The predicted degeneration of the diffraction halo with rise of temperature has been demonstrated experimentally. A. A. ELDRIDGE.

Crystal structure of Cu_3Sn and Cu_3Sb. W. M. JONES and E. J. EVANS (Phil. Mag., 1927, [vii], **4**, 1302—1311).—When the crystal structure of alloys corresponding in composition with the above formulæ is examined by X-ray methods, the results are the same as would be obtained with a pure metal possessing a close-packed hexagonal structure, so that it is not possible from these experiments to decide whether the alloys are true compounds or merely solid solutions. In each instance, the shortest interatomic distance is equal to the sum of the atomic radii of the component elements. R. CUTHILL.

Crystal structure of some of the alums. J. M. CORK (Phil. Mag., 1927, [vii], **4**, 688—698).—X-Ray measurements of a number of alums have yielded the following values (in Å.) for the dimensions of the unit cubic cell: 12·18 for $NH_4Al(SO_4)_2,12H_2O$,

12·14 for $KAl(SO_4)_2,12H_2O$ and for $KCr(SO_4)_2,12H_2O$, 12·20 for $RbAl(SO_4)_2,12H_2O$, 12·31 for $CsAl(SO_4)_2,12H_2O$, and 12·21 for $ThAl(SO_4)_2,12H_2O$. Four molecules are ascribed to the unit cell. The eight metal atoms take positions at the corners, centre, centre of faces, and mid-points of edges of the cell, making a rock-salt arrangement of univalent and tervalent metals. The space-group is T_h^6. From a Fourier analysis of the electron distribution and a critical survey of the atomic absorption coefficients, alternative arrangements of the atoms along the trigonal axis have been deduced.

A. E. MITCHELL.

Structure of the isomorphic substances tetramethylammonium iodide, bromide, and chloride. L. VEGARD and K. SOLLESNES (Phil. Mag., 1927, [vii], **4**, 985—1001).—The dimensions of the unit cell and the space-group D_{4h}^7 previously found for tetramethylammonium iodide by Bragg's method (*ibid.*, 1917, [vi], **33**, 395) have been confirmed by the powder method. The investigation of the chloride and bromide compounds has made it possible to fix the position of the nitrogen and carbon atoms more accurately. They form groups NC_4, where nitrogen is at the centre of a tetrahedron of carbon atoms. The centre distance of these groups is 1·50 Å. Regarding the crystal as a packing of spheres, it is assumed that there is one group of 8 and one group of 16 hydrogen atoms in a unit cell. The diameter of the hydrogen atom is 1·70 Å. The arrangement of the atoms suggests that the crystal has an ionic constitution $NMe_4^+Cl^-$ (or Br^- or I^-).

C. J. SMITHELLS.

New kinds of mixed crystals. V. D. BALAREV [with R. KAISCHEV] (Z. anorg. Chem., 1927, **167**, 237—240).—It is suggested that in the mixed crystals of barium sulphate and potassium permanganate prepared by Geilmann and Wünnenberg (A., 1927, 120) the permanganate was merely held in capillaries in the sulphate. The possibility of the formation of such crystals and of the removal of the permanganate from them with oxalic and sulphuric acids will depend on the experimental conditions. In the co-precipitation of zinc and copper sulphides, where a similar explanation has been advanced (A., 1927, 925), the amount of the former sulphide present in the precipitate has been found to depend on the temperature and acidity of the solution.

R. CUTHILL.

Change of ionic refraction in crystal lattices. K. FAJANS (Z. physikal. Chem., 1927, **130**, 724—731).—An attempt has been made to obtain a quantitative expression for the change of the refraction of ions when composing a crystal lattice. For the change ΔR_a of the refraction R_a of the anion of the alkali halides the equation $\Delta R_a = CR_a^2/r^4$ (r the distance between the positive and negative ions and C a constant) should be valid. For the lithium halides, a fairly satisfactory constant is obtained. Calculations for the other alkali halides indicate qualitatively that ΔR_c, the change of refraction of the cation, increases for a given cation as the distance between the ions decreases, and for different cations increases with their ease of deformation.

H. F. GILLBE.

Temperature variation of the elasticity of Rochelle salt. E. P. HARRISON (Nature, 1927, **120**, 770).—Attention is directed to the analogy between piezo-electric phenomena and the reciprocal relations between strain and magnetic properties shown by ferromagnetic metals.

A. A. ELDRIDGE.

Temperature–electrical resistivity relationship in certain copper α-solid solution alloys. A. L. NORBURY and K. KUWADA (Phil. Mag., 1927, [vii], **4**, 1338—1341).—The electrical resistivity, R, of alloys of copper with aluminium, tin, and silicon has been determined between $-191°$ and 438°, the results showing that R is related to the resistivity at 0°, R_0, and the temperature, t, by the equation $R = R_0 + \alpha t$, where α is a linear function of R_0, and increases with it. Alloys of copper with nickel or manganese deviate somewhat from this relationship.

R. CUTHILL.

Iron carbide (Fe_3C). G. TAMMANN and K. EWIG (Z. anorg. Chem., 1927, **167**, 385—400).—The temperature–magnetisation curves of steels containing 0·15—3·9% of carbon show that the magnetisation decreases sharply between 200° and 220° by an amount which is proportional to the carbon content, and increases with it. Since the steels which are richer in carbon contain carbide formed from the molten metal as well as from the γ-mixed crystals, the two forms must be identical. A sample of cementite lost its magnetisation completely at 210°, but after having been heated at 500° for 5 hrs., there was no change in the magnetisation at 200—215°, and the magnetisation–temperature curve corresponded with that of pure iron. This relatively low decomposition temperature, however, appeared to be due to the presence of occluded gases. A cooling curve showed no irregularity at the transition point at 210°, but a volume change could be detected dilatometrically. Aluminium and titanium do not affect the transition temperature, but silicon, manganese, and boron depress it considerably, the effects increasing in this order.

R. CUTHILL.

Theory of the magnetic properties of iron and other metals. R. H. DE WAARD (Phil. Mag., 1927, [vii], **4**, 641—667).—A mathematical theory of magnetism based on the result obtained by Barkhausen (Physikal. Z., 1919, **20**, 401) that during the magnetisation of a body the magnetic moment changes partly discontinuously, and the extension of Barkhausen's work by van der Pol to show that hysteresis curves in iron wires show discontinuities.

A. E. MITCHELL.

Magnetic properties of thin films of electrolytic iron. E. P. T. TYNDALL (Physical Rev., 1927, [ii], **30**, 681—691).—Magnetisation curves and hysteresis cycles were obtained for films of iron electrolytically deposited on brass tubes.

A. A. ELDRIDGE.

Production of metallic single crystals. J. A. M. VAN LIEMPT (Amer. Inst. Min. Met., Tech. Pub., 1927, No. 15, 8 pp.).—Four methods are reviewed, viz., from the liquid state, from the gaseous state, electrolytically, and by recrystallisation in the solid state.

CHEMICAL ABSTRACTS.

Photo-electric threshold of single bismuth crystals. T. J. PARMLEY (Physical Rev., 1927, [ii], **30**, 656—663).—The photo-electric threshold of single-crystal bismuth after a new surface had aged for 1 hr. at 10^{-6} mm. was 2567 Å., and immediately after a new surface had been cut in a vacuum of the order of 10^{-7} mm. was 2835 Å. Values for the polycrystalline form were 2560 and 2830 Å.

A. A. ELDRIDGE.

Photo-electric effect and surface structure in zinc single crystals. E. G. LINDER (Physical Rev., 1927, [ii], **30**, 649—655).—The photo-electric current obtained varies when the surface of a single crystal of zinc, illuminated with ultra-violet light, is rotated; it is maximal when the hexagonal axis is normal to the illuminated surface and minimal when parallel.

A. A. ELDRIDGE.

Photo-electric conduction in selenium. R. J. PIERSOL (Physical Rev., 1927, [ii], **30**, 664—672).—With the aid of a specially constructed cell, a linear relation between the square of the photo-current and the light intensity is established; hence photo-conduction in selenium is due to a photo-electric liberation of electrons rather than to an allotropic change. Experiments on the effect of immersing a cell in liquid air indicate that the mechanism of the current conduction under dark conditions is entirely different from that of the photo-conduction.

A. A. ELDRIDGE.

Cohesion at a crystal surface. J. E. LENNARD-JONES and (MISS) B. M. BENT (Trans. Faraday Soc., Nov. 1927, advance proof).—Theoretical. A mathematical investigation of the cohesive forces outside a (100) surface plane of a crystal of the rock-salt type, the problem being idealised in the sense that the boundary is assumed to be perfectly plane and unlimited in extent. The cohesive forces between an outside particle and the (100) surface plane are dealt with under four headings. (1) If the outside particle is charged there is an electrostatic force between the particle and the valency charges of the ions in the crystal. At a given distance from the plane surface this force is a maximum above the lattice points of the crystal, and is zero at all points of those planes normal to the surface which bisect the lines joining adjacent ions. An expression is deduced for this force which diminishes rapidly with the distance from the surface; thus with sodium chloride the maximum forces on a charge ε at distances 2·815 and 5·63 Å. are $8{\cdot}46\times10^{-5}$ and $9{\cdot}87\times10^{-7}$ dynes, respectively. (2) If a neutral atom approaches the crystal surface, there is no direct electrostatic attraction, but an induced attraction is set up owing to the polarisation of the atom by the charged ions in the crystal. An expression is deduced for this effect, which is much less than the electrostatic force in (1), and falls off much more rapidly with increasing distance. Thus in the case of a neutral atom of argon approaching the (100) surface of sodium chloride, the forces at distances 2·815 and 5·63 Å. are $8{\cdot}19\times10^{-6}$ and $1{\cdot}1\times10^{-9}$ dynes, respectively. (3) Attractions similar to those of van der Waals exist between neutral atoms and similar forces are supposed to exist in the case of charged particles in addition to the forces in (1) and (2). An expression is deduced for this attraction, which, in the case of an argon atom, at distances 2·815 and 5·63 Å., amounts to $1{\cdot}92\times10^{-5}$ and $3{\cdot}04\times10^{-7}$ dynes, respectively. This attraction thus falls off much less rapidly with distance, and the van der Waals' forces may thus act as the first agents in the process of adsorption. (4) The fourth problem is the polarisation of a crystal by a charge outside it, and the difficulties in the solution are indicated.

W. HUME-ROTHERY.

Cohesion in the crystalline state. F. I. G. RAWLINS (Trans. Faraday Soc., Nov. 1927, advance proof).—The applications of the new wave mechanics to ionic or heteropolar crystals (cf. Pauling, A., 1927, 399), and the work of Hund (Z. Physik, 1925, **34**, 833) on "stratified" lattices are briefly reviewed. An explanation of the cohesion in other special crystal lattices may be sought in a combination of the theories valid for truly heteropolar and truly homopolar lattices.

W. HUME-ROTHERY.

Effect of rolling on single crystals of aluminium. S. TANAKA (Mem. Coll. Sci. Kyoto, 1927, **10**, 303—309).—Single crystals of aluminium, in the form of plates 1 mm. thick, were rolled to varying degrees, and the orientations of the small crystals produced by the destruction were investigated by *X*-ray methods. Three types of fibrous structures were observed. In the first type the fibre axes correspond with the [110] direction, and most of the (001) planes are nearly parallel to the rolled surface. The maximum deviation from this orientation, which is produced by rotation of the crystals about the fibre axis, is about 26°. The second type has an orientation of the micro-crystals such that the fibre axis corresponds with the [112] direction, and the (110) planes coincide with the rolled surface; the maximum deviation from this orientation is about 28°. In the third type, the [111] direction and the (110) planes are nearly parallel to the fibre axes and the rolled surface, respectively; the deviation is here about 10°. Another arrangement similar to the third type but with the (112) plane parallel to the surface may exist, but the proof is incomplete. No simple relation could be traced between the initial orientation of the single crystal, the direction of rolling, and the final state of the fibrous structure.

W. HUME-ROTHERY.

Effect of grain boundary on the hardness of aluminium. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 271—300).—Aluminium test pieces cut from sheet 1 mm. thick were strained by a tensile load of 5 kg./mm.^{2} and annealed at 600° to form large crystals occupying the full cross-section of the material. Reference lines were drawn at intervals of 1 mm. at right angles to the major axis, from which the extension in different parts of the test piece, when loaded in tension, could be determined. The elongation took place almost entirely in the crystals and diminished rapidly in the neighbourhood of a grain boundary. The percentage elongation varied widely in crystals of different orientation. The results are in agreement with the slip-interference theory of hardening.

C. J. SMITHELLS.

Deformation, rupture, and hardening of crystals. M. Pólanyi (Trans. Faraday Soc., Nov. 1927, advance proof).—The deformation and rupture of crystals of zinc, cadmium, tin, and other metals with special reference to the work of the author and his collaborators (cf. A., 1923, ii, 768; 1924, ii, 298; 1925, ii, 252, 370, 371; 1926, 666) is described. The mechanism of the strengthening and weakening of crystals by deformation is described, and the theory of the "bent crystal" is discussed.

W. Hume-Rothery.

Effect of iron and oxygen on the electrical conductivity of copper. R. P. Heuer (J. Amer. Chem. Soc., 1927, **49**, 2711—2720).—Thermodynamic calculations indicate that the effect of the presence of oxides on the conductivity of copper cannot be neglected (cf. Hanson and Ford, B., 1924, 833, whose copper is shown to have contained ferrous oxide). The conductivity of copper is reduced at the rate of 630% of the standard value for 1% of iron. Iron, also, may be completely oxidised in alloys containing cuprous oxide eutectic. S. K. Tweedy.

Hall effect and resistance in sputtered tellurium films. F. W. Warburton (Physical Rev., 1927, [ii], **30**, 673—680).—Except when the film is heated in a gas, and apart from an ageing process, the Hall *E.M.F.* is proportional to the resistance of the film. A. A. Eldridge.

Hall effect in aluminium crystals in relation to crystal size and orientation. (Miss) P. Jones (Phil. Mag., 1927, [vii], **4**, 1312—1322).—Determinations of the Hall coefficient with aluminium crystals have given the absolute value $3{\cdot}44\times10^{-4}$, this being independent of the crystal size and of the direction of the primary current in relation to the lattice planes. R. Cuthill.

Magnetic differentiation of hydrated ferric oxides. II. E. Wedekind and W. Albrecht (Ber., 1927, **60**, [*B*], 2239—2243; cf. A., 1926, 1196).—Examination of the susceptibility of hydrated ferric oxides indicates a probable maximum in specimens containing less than 22% of water. Such specimens cannot be prepared below 45° or by means of acetone. Dehydration under water at 100° in sealed tubes or open vessels yields products which have maximum susceptibility when containing 14—15% and 10—11% of water, respectively, but the experiments are not strictly reproducible and the process is complicated by ageing phenomena which occur slowly even at the atmospheric temperature. It appears valid to conclude that at least one definite hydrate is responsible for the high magnetic susceptibility of the products. Ageing of the specimens is accompanied by the appearance of interference lines in their *X*-ray spectra. A hydrate, obtained by ultrafiltration of a solution of ferric chloride which had been dialysed as far as possible and subsequently dried by acetone and ether, was not remarkably magnetic. Further specimens were obtained by the interaction of iron pentacarbonyl with hydrogen peroxide in alcoholic solution and by the addition of anhydrous ferric sulphate or ferric ammonium sulphate to 35% ammonia solution. Although having almost identical water content, the hydrates differ greatly in their magnetic properties. H. Wren.

Magnetic susceptibilities of positive vanadium ions. S. Freed (J. Amer. Chem. Soc., 1927, **29**, 2456—2468).—The magnetic susceptibilities of quadrivalent, tervalent, and bivalent positive vanadium ions, measured by a null method, indicate that these ions contain 1, 2, and 3 Bohr magnetons, respectively. This is not in agreement with published theories based on the quantum theory and the anomalous Zeeman effect on atomic ions, possibly because the latter should be replaced by magnetic influences on band spectra (molecular ions). Measurements on sodium perchlorate, sodium chloride, perchloric acid, and sulphuric acid solutions are recorded.

S. K. Tweedy.

Liquid wires and their surface films. W. B. Pietenpol and H. A. Miley (Physical Rev., 1927, [ii], **30**, 697—704).—When a wire of a metal of low m. p. is heated in air or oxygen, it may glow without breaking, owing to the support afforded by a thin oxide film of considerable strength. Wires with clean surfaces when heated in nitrogen break at the m. p. of the metal. Experiments with sulphide, bromide, and chloride films indicate that (*a*) if there is not a firm coat at the m. p. of the metal the wire breaks at that temperature, (*b*) if the m. p. of the coat is between the m. p. of the metal and the glowing temperature the wire breaks at the m. p. of the coat, (*c*) if the m. p. of the film is above the glowing point, the wire can be made to glow when freely suspended. A. A. Eldridge.

Thermal expansion of cobalt–nickel, cobalt–iron, and iron–nickel alloys. A. Schulze (Physikal. Z., 1927, **28**, 669—673).—The measurements have been carried out for the complete series of these alloys, using the glass-tube method of Henning, and operating within the range from the ordinary temperature to 100°. In each case, the expansion–composition curves for these metal pairs show remarkable peaks corresponding with the compositions of intermetallic compounds which were detected previously from measurements of electrical conductivities (A., 1927, 196), or otherwise. The results are of special interest, since non-ferromagnetic alloys do not give expansion curves of this type.

G. A. Elliott.

Thermal expansion at low temperatures of metals crystallising in regular systems. W. H. Keesom (Z. physikal. Chem., 1927, **130**, 658—661). —The cubical expansion coefficients of silver and copper have been calculated according to Grüneisen's formula, and although the results in general show fair agreement with observed values, at the lowest temperature-intervals considerable discrepancies occur. H. F. Gillbe.

Theory of specific heat, with consideration of the latent heat of fusion and vaporisation. V. Doi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 129—147).—The latent heat accompanying the change of state of a substance is treated from the point of view of the quantum theory. By regarding the thermal agitation of an atom of a non-gaseous substance as being composed of simple

harmonic motions, and giving it an expression analogous to that of the energy of the Bohr atom, the following approximate expression is deduced for the latent heat of vaporisation: $L=3Nph\nu/2J$, where N is Loschmidt's number, J the mechanical equivalent of heat, h is Planck's constant, and ν the frequency of atomic oscillation in the state corresponding with the quantum number p. ν is given by $2^{\frac{1}{2}}N_0^{\frac{1}{3}}V/2\pi$, V being the velocity of propagation of longitudinal waves along a thin rod of the substance under consideration and N_0 the number of atoms contained in a unit cube of the substance. It is further shown that the product of the latent heat of vaporisation L, and the temperature coefficient of linear expansion α, equals a constant, and by calculation for a number of metals, using data for L and α taken from the tables, it is found that $\alpha L=1$ approx. By means of this relation, the following expressions are obtained: $x=\sqrt{3Nm_H\alpha AV^2/1\cdot008J}$, where x is the ratio of the mean distance between two neighbouring atoms to the mean amplitude of the supposed simple harmonic motions executed by the atoms, A is the at. wt., and m_H the mass of the hydrogen atom; and $p=2\sqrt{2}\,.\,\pi mV/x\cdot N_0^{\frac{1}{3}}h$, m being the mass of the atom under consideration. x and p are calculated for fourteen metals. In every case, x is greater than 2, or the mean value of the amplitude of the thermal oscillations of an atom in a non-gaseous substance is less than half the mean distance between two neighbouring atoms. L. L. BIRCUMSHAW.

Electrical conductivity and specific heat of solid metals, and the occurrence of transition points. C. DRUCKER (Z. physikal. Chem., 1927, **130**, 673—690).—The method described previously (A., 1925, ii, 24) for the determination of the ratio between the temperature coefficient a of the electrical resistance and the specific heat c has been applied to bismuth and nickel. The method forms a very sensitive test for the occurrence of transition points. Direct determination of a not only demonstrates the influence of impurities and of the previous treatment of the metal, but also exhibits anomalous variations in the neighbourhood of the transition point. H. F. GILLBE.

Heat capacities of acetaldehyde and paraldehyde and the heat of transformation of acetaldehyde into paraldehyde. D. LEB. COOPER (Proc. Nova Scotia Inst. Sci., 1927, **17**, 82—90).—The mean specific heats of acetaldehyde and paraldehyde, between 17° and temperatures ranging from −182·5° to −47·0° in the first case, and from −78·5° to 100° in the second, have been determined. From the curves obtained by plotting heat capacity against temperature, the latent heat of fusion of paraldehyde is found to be 25·2 g.-cal. per g. and of acetaldehyde 17·6 g.-cal. per g. The heat of polymerisation of acetaldehyde into paraldehyde, catalysed by sulphuric acid, is given as 20,495 g.-cal., which is 4850 g.-cal. less than that calculated from the heats of combustion. The density–composition curve of mixtures of acetaldehyde and paraldehyde is plotted, and also the heat capacity curve between −182·5° and 100° for the "pyrex" glass used in the experiments. A curve of the existing data for the variation of the equilibrium composition of mixtures of acetaldehyde and paraldehyde with temperature is given. M. S. BURR.

Change of properties of substances on drying. H. B. BAKER (J.C.S., 1927, 2902—2903).—The view of Balarev (cf. A., 1927, 613) that the rise in b. p. of substances dried over phosphorus pentoxide may be due to the presence of phosphoric acid or of its esters is shown to be untenable. O. J. WALKER.

Transition point of zinc at 175°. G. I. PETRENKO (Z. anorg. Chem., 1927, **167**, 411—412; cf. A., 1927, 615).—The existence of a transition point of zinc at 175° has now been confirmed by microscopical examination. R. CUTHILL.

Vapour pressures of methylene chloride. J. H. PERRY (J. Physical Chem., 1927, **31**, 1737—1741; cf. Rex, A., 1906, ii, 342).—The vapour pressures of purified methylene chloride have been measured over the temperature range 186·1—311·5° Abs., giving a pressure range from less than 1 to 715·8 mm. The extrapolated value of the normal b. p. is 40·67° and the latent heat of vaporisation, calculated from the modified Clapeyron equation, is 7020 g.-cal./g.-mol. at this temperature. Trouton's constant is 22·4 and the ratio of the temperatures Abs. corresponding with vapour pressures of 760 mm. and 200 mm. is 1·114. The value of T_c calculated from the relation given by Prud'homme (A., 1921, ii, 376) is 215·7°, which may be compared with Nadejdine's (J. Russ. Phys. Chem. Soc., 1882, **14**, 157) experimental value of 245·1°. L. S. THEOBALD.

Physical properties of vinyl chloride. L. I. DANA, J. N. BURDICK, and A. C. JENKINS (J. Amer. Chem. Soc., 1927, **49**, 2801—2806).—The vapour pressure of vinyl chloride, f. p. −159·7°, b. p. −13·9°, is given to within 0·3% by $\log p(\text{atm.})=0\cdot8420-1150\cdot9/T+1\cdot75\log T-2\cdot415\times10^{-3}T$ between 245° and 333° Abs. The density (g./c.c.) of the liquid between −13° and 60° is $0\cdot9471-1\cdot746\times10^{-3}t-3\cdot24\times10^{-6}t^2$, where t is in °C. The critical pressure is estimated to be 52·2 atm. and the critical temperature 142°. Probable values of the vapour density and latent heat of evaporation are tabulated.

S. K. TWEEDY.

Influence of grain size on the dissociation pressure of solids. M. CENTNERSZWER and J. KRUSTINSONS (Z. physikal. Chem., 1927, **130**, 187—192).—The influence of grain size of crystals on the dissociation pressure has been examined for silver carbonate and mercuric oxide, the dissociation pressures being measured by the improved dynamic method previously described (A., 1927, 21). The pressure for the yellow oxide of mercury is higher than that for the red (cf. Schoch, A., 1903, ii, 428), and a darker-coloured yellow oxide, prepared from the red by grinding, gave an intermediate value. The effect of grain size of the crystals on the temperature of dissociation is expressed by the equation $dT/dr=-2\sigma MT/\lambda dr^2$, where r is the radius of the particle and λ the heat of dissociation. The surface tension at the gas–solid boundary is also calculated from the data obtained. L. S. THEOBALD.

Constancy of pressure during isothermal condensation or vaporisation as a criterion of purity.

E. W. WASHBURN (Z. physikal. Chem., 1927, **130**, 592—600).—Constancy of pressure during the isothermal evaporation of a liquid is not a general criterion of purity. For cases in which the principle is applicable, equations are derived for calculating the quantity of impurity present, provided that it consists of only one substance and that certain data regarding it are known. H. F. GILLBE.

Entropy at infinite pressure and the equation of state of solids. G. N. LEWIS (Z. physikal. Chem., 1927, **130**, 532—538).—An attempt is made to find a theoretical method of extrapolating data regarding interatomic forces at high pressures to much greater pressures. By assuming that at all temperatures the entropy of a pure solid is zero at infinite pressure, the following partly empirical equations are derived: $S_0=\alpha/n\Pi^n$, $(\delta V/\delta T)_{p=0}=\alpha/\Pi^{1+n}$, where Π is the internal pressure of a substance at zero external pressure and α and n are constants. Good agreement is found between these equations and Bridgman's values of $(\delta V/\delta P)_T$ for lithium, sodium, and potassium. H. F. GILLBE.

Internal energy, maximum work, and free energy of the elements. R. D. KLEEMAN (J. Physical Chem., 1927, **31**, 1669—1673).—The values of the internal energies, referred to a temperature of 298° Abs. and to the volumes possessed at 0° Abs., have been obtained graphically for certain elements, and show a periodicity similar to the entropies as calculated by Lewis and Gibson (A., 1918, ii, 29). The maximum work has been calculated using the same values for the entropies, and gives results which are numerically similar to those obtained for the internal energies. The change which a complex substance may undergo at 0° Abs. is shown to have an important bearing on the calculation of the internal energy, and the case of white and grey tin is discussed in this connexion. L. S. THEOBALD.

Surface tension of rock salt. G. N. ANTONOV (Phil. Mag., 1927, [vii], **4**, 792—800).—A modification of the method for the determination of the surface tensions of solids described previously (A., 1926, 671) has been employed for the determination of the surface tension of rock salt. The value 315 dynes/cm. has been obtained. In support of the method, it is claimed that it is in no way dependent on the molecular structure of the material under examination. A. E. MITCHELL.

Surface tension of liquid carbon dioxide. E. L. QUINN (J. Amer. Chem. Soc., 1927, **49**, 2704—2711). —The surface tension of liquid carbon dioxide, which was measured between −52·2° and 25° by the capillary-rise method, is given by $0{\cdot}0653(31{\cdot}35-t)^{1{\cdot}21}$ dynes/cm., except at the lowest temperatures. The internal pressure is calculated to be about the same as that of toluene, chloroform, and carbon tetrachloride. The density of saturated carbon dioxide vapour between 0° and 25° is given by d(g./c.c.)$=1{\cdot}936p^n/(273+t)$, where $n=0{\cdot}737+0{\cdot}0048t$, and p is in atm. S. K. TWEEDY.

Viscosity of metals. Bismuth. G. SUBRAHMANIAM (Nature, 1927, **120**, 770).—The coefficient of viscosity of bismuth at 23·7° is computed from known data to be $13{\cdot}71\times10^8$ poises. A. A. ELDRIDGE.

Sutherland's viscosity constant and its relation to the molecular polarisation. F. G. KEYES (Z. physikal. Chem., 1927, **130**, 709—714).—For a large number of gases Sutherland's constant C increases progressively with the Lorenz–Lorentz polarisation constant P_0. The majority of gases exhibit a linear relationship between $T^{\frac{1}{2}}/\eta$ and T^{-1}, T being the temperature, as required by Sutherland's formula. Helium, except possibly at high temperatures, forms an exception. H. F. GILLBE.

Internal friction of mercury. G. TAMMANN and and J. HINNUBER (Z. anorg. Chem., 1927, **167**, 230—236).—Determinations of the viscosity of mercury by experiments on the rate of flow through capillary tubes of glass appear to be vitiated by the mercury slipping over the surface of the glass. Using copper capillaries, the true value of the viscosity is found to be 0·04931±78 g./cm. sec. at 13·5°, with a temperature coefficient of −0·0012±2 per 1°. The viscosity at 10° is increased by 12·4% by 0·114% of gold. R. CUTHILL.

Dielectric constants of binary mixtures. Application of the method of partial molal quantities. J. W. WILLIAMS and J. H. MATHEWS (Z. physikal. Chem., 1927, **130**, 277—285).—When a liquid is placed between parallel plates, 1 cm. apart, of dimensions such as to contain between them 1 g.-mol. of liquid, the dielectric capacity is defined as the molal inductive capacity. This equals $M(\varepsilon-1)/d$, where M is the mol. wt. of the liquid. The application of this concept to dielectric constant data is discussed, and the association factor for ethyl alcohol has been calculated from the known data for the system ethyl ether–ethyl alcohol. L. S. THEOBALD.

Solid solutions between compounds of elements of different valency. G. BRUNI and A. FERRARI (Z. physikal. Chem., 1927, **130**, 488—494).—The grating constants of ferrous, zinc, manganous, and cadmium chlorides have been determined. The ratio c/a is a function of the radius of the metal ion which lies on a smooth curve for magnesium, ferrous, manganous, and cadmium chlorides, whilst that for zinc chloride lies somewhat below the curve. These results are discussed with reference to the author's work on the mixed crystals formed by lithium and magnesium chlorides (cf. A., 1926, 236). R. W. LUNT.

Viscosities of chromic anhydride solutions. J. R. PARTINGTON and S. K. TWEEDY (J.C.S., 1927, 2900—2902).—The viscosities of chromic anhydride solutions between 0° and 40° are recorded. The chromic anhydride (cf. A., 1926, 697) has m. p. 193° and exhibits no supercooling. The absolute viscosities are calculated from Leroux's values for the absolute viscosity of water, η, which can be represented between 10·9° and 30° by the expression $[0{\cdot}633161/(T-241{\cdot}307)]-0{\cdot}00207155$, where T is the absolute temperature. O. J. WALKER.

Densities of co-existing liquid and gaseous carbon dioxide and solubility of water in liquid carbon dioxide. H. H. LOWRY and W. R. ERICKSON (J. Amer. Chem. Soc., 1927, **49**, 2729—2734).—The densities of the isobaric phases at t° C. are given

by $d_l=0·4683+0·001442(31-t)+0·1318(31-t)^{\frac{1}{3}}$ and $d_g=0·4683+0·001442(31-t)-0·1318(31-t)^{\frac{1}{3}}$, where 0·4683 is the critical density derived from the law of rectilinear diameters. Within the limits of error, the presence of water vapour does not affect the density of saturated carbon dioxide vapour, so that the solubility of water in the liquid is probably less than 0·05% by weight over the range −5·8° to 22·9°.

S. K. Tweedy.

Solubility of barium *n*-butyrate. H. J. Wing (J. Amer. Chem. Soc., 1927, **49**, 2859—2861).—The solubility of barium *n*-butyrate is 37·0 g. in 100 g. water at 0·06°; it decreases to a minimum of about 34·8 g. at about 30°, and then increases to 48·1 g. at 94·96°. The anhydrous salt is in equilibrium with the solution throughout.

F. G. Willson.

Solubility of the barium salts of α-sulphocarboxylic acids. H. J. Backer (Z. physikal. Chem., 1927, **130**, 177—183).—Solubility data at 25° are given for the barium salts of the α-sulpho-aliphatic acids and of their halogenated derivatives. These salts are less soluble in water than are the corresponding salts of the fatty acids, and the smaller solubility appears to be connected with the formation of a stable, six-membered ring structure in the barium salt. The introduction of a methyl group or of a halogen increases the solubility of the barium salt, but the introduction of a halogen in the barium α-sulphopropionate lowers the solubility. The bromo-compounds are more soluble than the chloro-derivatives.

L. S. Theobald.

Partition of lactic acid between water and ether and between water and amyl alcohol. W. U. Behrens (Biochem. Z., 1927, **189**, 348—349).—A reply to Dietzel and Rosenbaum (A., 1927, 820).

P. W. Clutterbuck.

Condensation of vapours of certain substances at temperatures below their m. p. N. V. Tancov and T. Chodalevitsch (J. Russ. Phys. Chem. Soc., 1927, **59**, 631—638).—The vapours of camphor, borneol, and *iso*borneol were cooled in a specially devised apparatus by means of a stream of cold air. Care was taken to avoid contact of the vapours with any crystalline substance or dust. It is found that the supersaturated vapours of all these substances condense to liquids when cooled below their m. p.

A. Ratcliffe.

Velocity of dissolution of solid substances. W. Jacek and Z. Lehr-Spławinska (Rocz. Chem., 1927, 7, 309—333).—Spheres cut out of crystals of sodium chloride and uniformly agitated in water dissolve uniformly, no deformation of the spherical shape being noticeable even after prolonged immersion. The following formula is deduced : $-dr/dt-k_1(c+r^3)$, where r is the radius of the sphere at time t, c the difference between the cubes of the original radius of the sphere and of the radius of a sphere large enough to saturate the volume of water used, and $k_1=\frac{4}{3}-k$, where k is the velocity coefficient. For irregularly-shaped bodies, the formula : $-dr/dt=(P/4-r^2).k_1(c+r^3)$ where P is the surface area of the body in question, is found to hold. The value of k is given by $k=\rho\times$ unit surface $-\frac{4}{3}\pi a_1^3$, where ρ is the thickness of the layer of salt dissolved in unit time from the surface of the sphere; k depends on the temperature and on the velocity of translation of the sphere in the solvent, but is independent of its radius and of the volume of solvent used.

R. Truszkowski.

Crystal crusts. H. Erlenmeyer (Helv. Chim. Acta, 1927, **10**, 896—900; cf. Washburn, A., 1927, 931).—Creeping occurs mainly with solutions of simple salts, crystallisation commencing at the periphery of the liquid surface. Double salts do not, in general, exhibit creeping and crystallisation usually commences at the bottom of the containing vessel. It is suggested that in solutions of simple salts undissociated molecules predominate at the surface and that on slow evaporation crystallisation begins in the peripheral capillary film. Capillary layers between the crystals and in the space between the crystals and the walls of the container are responsible for the propagation of the crystal crust. With solutions of double salts, it is assumed that the undissociated molecules of the simple constituent salts are not present at the surface in the requisite proportions, and that on evaporation the solubility of the double salt is not exceeded at the periphery, but in the main body of the solution. Quantitative measurements of the creeping of solutions of a number of salts have been made and the data tabulated.

J. S. Carter.

Causes of solubility: surface forces in a system constituting a pair of partly miscible liquids. R. M. Woodman (J. Physical Chem., 1927, **31**, 1742—1745).—Measurements have been made, at 25°, of the surface tensions between air and the separate layers of various equilibrium mixtures of the system water–acetic acid–toluene, together with measurements of the interfacial tension between the layers themselves. The tensions of the aqueous layers, which decrease rapidly as the critical point is approached, are, up to a point, greater than those of the toluene layers, which decrease but little, the two tensions tending to coincide as the critical point is reached. The system obeys the Antonow–Reynolds rule (J.C.S., 1921, **119**, 466) that the interfacial tension between the mutually saturated phases is equal to the difference in their surface tensions. Coincidence in the values of the latter is, with a zero interfacial tension, not sufficient to cause complete miscibility; other properties must coincide at the same time, and the rates of change of all three tensions with concentration must be zero.

L. S. Theobald.

Work of adhesion between solid and liquid phases. F. E. Bartell and H. J. Osterhof (Z. physikal. Chem., 1927, **130**, 715—723).—A method is described for measuring contact angles at solid–liquid interfaces and for determining the adhesion constant K even when the contact angle is zero. From these data it is possible to evaluate the adhesion tension and the work of adhesion at the interface. Values are given for these quantities for a number of liquids in contact with carbon black and with silica.

H. F. Gillbe.

Adsorption of gases by solids with special reference to the adsorption of carbon dioxide by charcoal. H. H. Lowry and P. S. Olmstead (J. Physical Chem., 1927, **31**, 1601—1626).—Theoretical.

A physical interpretation of the theory of adsorption, based on the assumption that there is a force of attraction represented by a potential gradient between dissimilar molecules. The theory when tested by the data of Lowry and Morgan (A., 1925, ii, 1053) and other investigators, for the adsorption of carbon dioxide by charcoal, is satisfactory.

L. S. THEOBALD.

Adsorption of acids by coconut charcoal and acetylene carbon. D. NAMASIVAYAM (J. Indian Chem. Soc., 1927, **4**, 449—458).—The adsorption of formic, acetic, propionic, butyric, valeric, chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, dibromoacetic, glycollic, *iso*butyric, *iso*valeric, oxalic, hydrochloric, hydrobromic, nitric, sulphuric, and phosphoric acids by coconut charcoal shows that there is no simple relation between the degree of adsorption and the ionisation constants of the acids. For the range of dilution studied (0·2—0·05M), the adsorption of most of the acids follows the equation $m=\alpha C^{1/k}$. The values of k for formic acid and its homologues are nearly equal, and the values of α for hydrochloric, hydrobromic, and nitric acids are also nearly equal. Oxalic acid is not adsorbed so much as acetic acid (cf. Fromageot and Wurmser, A., 1925, ii, 384). With solutions of acetic and oxalic acids, and acetylene carbon, it is found that the solvent is preferentially adsorbed. H. BURTON.

Experimental contribution to the theory of equation of state for adsorbed substances. H. L. ROY (J. Indian Chem. Soc., 1927, **4**, 307—319). —The surface tensions of aqueous solutions of acetic, propionic, butyric, valeric, hexoic, heptoic, octoic, and nonoic acids, determined by Drucker (A., 1905, ii, 680), Rehbinder (A., 1924, ii, 662), Szyszkowski (A., 1908, ii, 1018), and the author, using a modified form of Sugden's method, are compared with values calculated from the equations $\pi=RTc/k+\beta c$ and $\pi=RT/2\beta\times ln(2\beta c/k+1)$, where β is twice the surface occupied by 1 g.-mol. of the dissolved substance. The calculated and observed values agree up to moderate concentrations. Molecular cross-sections (f), calculated for the dilute solutions from $f=\beta/2N$, are approximately independent of concentration, and do not increase with increasing mol. wt. Similar measurements and calculations have been made for solutions of methyl, *s*-dimethyl-, ethyl-, and *s*-diethyl-carbamides, and phenol. The results confirm those obtained for the acids. H. BURTON.

Adsorption by polar precipitates. IV. Further experiments with silver salts. J. N. MUKHERJEE, J. K. BASU, and A. MUKHERJEE (J. Indian Chem. Soc., 1927, **4**, 459—466; cf. Beekley and Taylor, A., 1925, ii, 855).—Silver chloride, bromide, and iodide have negative charges when in contact with water, but become positively charged after being in contact with dilute silver salts. For silver bromide and iodide, the order of adsorption of anions is benzoate > nitrite > acetate > nitrate, throughout the range of concentrations studied (0·001—0·00005N). Silver bromate is adsorbed more at lower dilutions. The above series corresponds with that in which the salts are arranged in the order of increasing solubility. Using sodium salts, the order of adsorption is thiocyanate > arsenite > salicylate > acetate > bromide, which again is the same as that given by the increasing solubility, the bromide being an exception. H. BURTON.

Adsorption and diffusion by metals of electrolytically evolved hydrogen and the influence of the electrolyte. A. COEHN and H. BAUMGARTEN (Z. physikal. Chem., 1927, **130**, 545—565).—The charge carried by the gas bubbles in solutions is of great influence on the adsorption and diffusion of hydrogen through palladium, palladium-silver alloys, and iron. The potential changes caused by the diffusion of hydrogen through these metals have been measured. The extent to which the adsorption and diffusion are dependent on the nature and concentration of the electrolyte from which the gas is evolved indicates whether the adsorbed hydrogen is nascent or in the ordinary gaseous state. With platinum the charge on the bubbles of gas has no influence on the diffusion, the reverse being true for the metals mentioned above and for tantalum; gaseous hydrogen is thus not adsorbed by platinum at the ordinary temperature.

H. F. GILLBE.

Surface tension of aqueous solutions of acids. L. ABONNENC (Compt. rend., 1927, **185**, 948—950).—Measurements by the author's method (Ann. Physique, 1925, [x], **3**, 184) of the surface tension of aqueous solutions of mono- and poly-basic strong acids at 21° indicate that the hydrogen ions (and possibly the hydroxyl ions) are the active constituents which lower the surface tension of water. This is in agreement with the selective adsorption exhibited by these ions, and is confirmed by the slopes of the curves where m is the relative change in surface tension and c the concentration. J. GRANT.

Effect of unimolecular films on the evaporation of ether solutions. I. LANGMUIR and D. B. LANGMUIR (J. Physical Chem., 1927, **31**, 1719—1731; cf. Rideal, A., 1926, 119).—The effect of unimolecular films of stearic and oleic acids, of cetyl palmitate, and cetyl and myricyl alcohols on the rate of evaporation of saturated solutions of ethyl ether in water has been measured. The rate of evaporation of ether is reduced to less than one tenth of its value when no film is present. It is of advantage to use the reciprocal of the usual quantity measured in g./cm.^{2} per sec., and to define it as the evaporation resistance, R, measured in cm.^{2} sec./g. Calculations based on Rideal's data for water (*loc. cit.*) then show that a unimolecular film of oleic acid produces a resistance of 800 units at 25°, compared with 3 units when no film is present. Cetyl alcohol opposes a resistance of 6×10^4 units to the evaporation of water. In the case of ether, the effect of the film is due, not to its resistance, but to the cessation of the surface currents which it causes. The evaporation resistance, R, equals h/CD, where h is the thickness of any film or layer through which diffusion occurs, D is the diffusion coefficient, and C is the concentration of the diffusing substance. The concentration of water in the film of cetyl alcohol is then 10^{-8} g./cm.^{3} A method is proposed for calculating the resistance due to the underlying liquid layer for any solution.

L. S. THEOBALD.

Physical chemistry of colour lake formation. II. Adsorption of typical dyes by basic mordants. H. B. WEISER and E. E. PORTER (J. Physical Chem., 1927, **31**, 1704—1715; cf. A., 1927, 1021; Marker and Gordon, B., 1924, 1010).—The adsorption of orange-II and metanil-yellow by the hydrous oxides of chromium and aluminium, and of methylene-blue by those of iron and chromium has been measured at various hydrogen-ion concentrations. In every case, lake formation consists of adsorption of the coloured ion by the hydrous oxide. There is no evidence of the formation of definite compounds at any p_H value. Lake formation is a typical adsorption phenomenon, dependent on the physical character of the mordant, the concentration of the dye, and the hydrogen-ion concentration of the bath. The conclusion of Marker and Gordon (*loc. cit.*) that at low p_H values ferric oxide and alumina form salts with orange-II is disproved. A high concentration of sulphuric acid prevents adsorption of the dye and precipitates the corresponding free acid, and the alleged compounds are mixtures of mordant and this acid. The effect of variation in hydrogen-ion concentration on the adsorption of the anion of the dye, in the case of acid dyes, is similar to the adsorption of sulphate or oxalate (A., 1927, 1021), provided that the dye remains soluble.

Precipitation of the dye in the presence of a mordant and adsorption by the mordant must be distinguished. With metanil-yellow, adsorption is normal up to a concentration of 0·001N-hydrochloric acid. Beyond this concentration, however, precipitation of the dye is proportional to the quantity of acid added, and there is probably adsorption as well as precipitation from the more acid mixtures.

Methylene-blue is adsorbed only when the dye bath is sufficiently alkaline to induce negative peptisation of the mordant, and the amount adsorbed measures the charge on the particles due to the adsorption of hydroxyl ions. L. S. THEOBALD.

Importance of ζ-potential in the electro-osmotic transport of water through collodion membranes. Theory of anomalous osmosis. P. J. JURISIC (Biochem. Z., 1927, **189**, 294—301).—The electro-osmotic transport of fluid through a collodion membrane takes place from regions of high to those of low electrokinetic (ζ-) potential, and there is no direct relationship between velocity of transport and membrane potential. P. W. CLUTTERBUCK.

Measurement of osmotic pressures. J. C. W. FRAZER and W. A. PATRICK (Z. physikal. Chem., 1927, **130**, 691—698).—A method has been evolved for measuring the osmotic pressure of any solution of a non-volatile solute. The solvent is submitted to a negative pressure until its vapour pressure becomes identical with that of the solution, with which it is in thermal equilibrium; this tension is obtained by allowing the solvent to evaporate through a porous disc made by sintering a mixture of powdered "pyrex" glass and clay. Preliminary measurements with 0·00836—0·00047M-solutions of potassium chloride indicate that the results given by this method are in fair agreement with the requirements of the Debye–Hückel theory. H. F. GILLBE.

Osmotic pressures of ideal solutions. W. D. BANCROFT and H. L. DAVIS (Z. physikal. Chem., 1927, **130**, 626—630).—Equations for the osmotic pressure of ideal solutions are discussed. Raoult's law is a special case of the equation $PV_s = RTN/n \, . \log p/p_1$. H. F. GILLBE.

Soret effect in dilute solutions. H. R. BRUINS (Z. physikal. Chem., 1927, **130**, 601—606).—For very dilute solutions of mannitol, the Soret coefficient does not approach zero as the dilution increases, but assumes a constant value which is independent of the concentration. H. F. GILLBE.

Optical properties of sulphonecyanine-5R in different saline solutions. F. VLÈS and (MLLE.) M. GEX (Compt. rend., 1927, **185**, 946—948).—The earlier experiments (A., 1927, 1023) have been extended to solutions of some of the chlorides and sulphates of the alkali and alkaline-earth metals. The curves for the function $\varphi = f(px)$, where px is the colog. of the molecular concentration of the salt, are of the same type as for solutions of potassium chloride, but vary in length and are displaced along the px axis, the position of the mid-point of the indicator range being specific for each salt. Irregularities at the ends of the curves indicate precipitation of the indicator or, in the case of very dilute solutions, a second equilibrium. The range of the indicator probably depends on the activity of the salt. J. GRANT.

Dielectric constants of solutions of electrolytes. IV. Investigation of acids, salts, and bases in water. V. Measurements with sucrose, carbamide, benzoic and sulphanilic acids, betaine, and alanine in aqueous solution. VI. [With H. ULICH.] **Test of the experimental basis of the method of measurement.** P. WALDEN and O. WERNER (Z. physikal. Chem., 1927, **129**, 389—404, 405—416, 417—426; cf. A., 1927, 307).—IV. The method employed previously has been improved, and results have been obtained for a number of bases and salts in aqueous solution.

V. New measurements with sucrose and with carbamide are in good agreement with Harrington's results, but Fürth's curves are not confirmed, the discrepancies being ascribed to slow hydrolysis. Results for sulphanilic and benzoic acids do not confirm Blüh's figures. Betaine and alanine produce an increase in the dielectric constant of the solvent which is in agreement with Pfeiffer's theory.

VI. A critical discussion of the experimental method and apparatus. H. F. GILLBE.

Extinction coefficients of mixtures of uranyl nitrate and organic acids in the ultra-violet as experimental evidence in favour of the formation of unstable intermediate compounds. J. C. GHOSH and B. N. MITTER (J. Indian Chem. Soc., 1927, **4**, 353—366).—The extinction coefficients of mixtures of uranyl nitrate and varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, and mandelic acids have been measured for different wave-lengths. The values obtained can be explained if it is assumed that 1 mol. of uranyl nitrate and 1 mol. of the acid form an unstable, intermediate complex, possessing a definite

molecular extinction coefficient. The dissociation constant of the intermediate complex diminishes with increase in the mol. wt. in homologous series; it increases about 12 times when the hydrogen atom in a methyl group is replaced by a carboxyl group; it increases 2·5 times when a hydroxyl group is substituted for a hydrogen atom in a monobasic acid.

H. BURTON.

F. p. of aqueous solutions of hydrochloric acid. H. M. CHADWELL (J. Amer. Chem. Soc., 1927, 49, 2795—2801).—Previously recorded results are extended to more concentrated regions (cf. Hovorka and Rodebush, A., 1925, ii, 772), the temperature being measured by a platinum thermometer. Assuming the activity coefficient 0·819 for 0·07M-acid (Scatchard, A., 1925, ii, 397), the coefficients up to 1M are in satisfactory agreement with the results of Scatchard and of Lewis and Randall.

S. K. TWEEDY.

Effect of electrolytes on the viscosity of solutions of sodium palmitate. J. W. McBAIN, H. J. WILLAVOYS, and H. HEIGHINGTON (J.C.S., 1927, 2689—2699).—By the falling-sphere method the changes in viscosity of sodium palmitate solutions, of concentrations 0·75, 1·0, and 1·5N_w, on the addition of varying quantities of electrolytes have been investigated. With increasing concentration of electrolyte, the viscosity rises rapidly to a maximum and then falls again until the salting-out concentration is reached. The maximum viscosity increases with the concentration of the palmitate, but the amount of salt required diminishes. The rise in viscosity is contrary to the behaviour to be expected from the Donnan equilibrium. The curves are similar in form to those obtained by Loeb for amphoteric colloids, but show a much greater increase in viscosity and have a different significance. The rise in viscosity is explained on the basis of McBain's general hypothesis of aggregation. The initial aggregation, due to dehydration by reduction of vapour pressure, probably takes place in such a way as to enclose and immobilise a large proportion of the liquid. Increased viscosity may also be due to peculiar surface effects resulting from the extension of chains of oriented molecules inwards from the surface of the aggregate. An explanation of the subsequent fall in viscosity is suggested on the basis of a combination of the principles of dehydration by lowering of vapour pressure, of orientation of like molecules, and of the principle underlying the Donnan equilibrium. The dependence of the phenomenon on the nature of the electrolyte is also discussed.

M. S. BURR.

Ultramicroscopic examination of starch sols. M. SAMEC (Arh. Hemiju, 1927, 1, 243—244).—Solutions of starch examined under an ultramicroscope exhibit thread-like aggregates of erythro-starch and granular aggregates of amylo-starch. Heating diminishes the Brownian movement of the particles of starch sols, thus accelerating aggregation. Peptisation is accompanied by diminution in the size of the ultramicrons, the number of which in unpeptised starch sols is therefore less than might be expected from osmotic pressure measurements.

R. TRUSZKOWSKI.

Dependence of viscosity of starch suspensions on the velocity [of flow]. R. KOHLER (Kolloid-Z., 1927, 43, 187—190).—A modification of the simple Ostwald viscosimeter is described in which low rates of flow are obtained even with a wide capillary tube. With this apparatus, the characteristic curves obtained by Hatschek with the Couette apparatus (cf. A., 1926, 1097) showing the relationship between viscosity and shear gradient are reproduced. Suspensions of starch (10, 15, 20, and 25% by vol.) in a mixture of carbon tetrachloride and paraffin were used. The viscosity, η, and the pressure of flow, p, are connected by the expression of Waele and Ostwald, $\eta \cdot p^{n-1}=k$, where n is always greater than 1.

O. J. WALKER.

Number of phases in colloidal systems. P. BARY (Rev. gén. Colloïd., 1927, 45, 617—623).—Theoretical. The correct definition of the term "phase" is discussed, and new arguments are brought to bear on the proposal, made previously ("Les Colloïdes," 1921, 418), that when two phases are in contact and at equilibrium, the system must be characterised by a positive interfacial tension. It follows from this that suspensions and gels must be considered as diphasic systems, whilst solutions and jellies contain only one phase. A suspension of gold, in the presence of a protective colloid, consists of two phases, one being the solution of the protective colloid, the other the gold.

L. L. BIRCUMSHAW.

Variation of the charge of colloidal particles. II. Effect of dilution and of non-electrolytes on the charge and its variation with concentration of electrolytes. J. N. MUKHERJEE, S. G. CHAUDHURY, and S. P. R. CHOUDHURI (J. Indian Chem. Soc., 1927, 4, 493—514; cf. A., 1926, 352).—Migration velocity measurements, at 35°, have been made with arsenious sulphide, gold, and copper ferrocyanide sols. Dilution with water causes a large decrease in the rate of migration (cm. sec./volt$\times 10^5$), falling from 60 to 12 for arsenious sulphide on twenty-fold dilution The initial fall is small when compared with the initial fall for gold and copper ferrocyanide. The effect of ethyl alcohol on colloidal arsenious sulphide containing varying amounts of hydrochloric acid is to diminish the rate of migration. Hydrochloric acid and potassium chloride cause a steady diminution in the rate of migration, sodium benzoate shows two maxima and then a decrease, whilst sodium citrate and potassium ferrocyanide show a decrease followed by an increase. The initial variations with the last three electrolytes are complex, probably because of interaction between the anions in the surface of the sol and those of the added electrolyte or of the hydroxyl ions formed by hydrolysis. With sodium and lithium chlorides there is an increase in the negative charge, at low concentrations, which is probably due to adsorption of chloride ions. The variation produced in the charge on colloidal arsenious sulphide on the addition of nine mixtures of electrolytes has been studied, and the results are discussed. There is no simple relationship between the charge and the coagulating concentration.

H. BURTON.

Modification of the electric sign of colloids at will. A. Boutaric (Rev. gén. Colloïd., 1927, **44**, 585—591; cf. A., 1927, 621; Boutaric and Dupin, *ibid.*, 309).—When positive colloids are treated with increasing quantities of electrolytes with multivalent anions, or negative colloids with increasing quantities of electrolytes with multivalent cations, two zones of flocculation are observed, with an intermediate zone of non-flocculation. This phenomenon is illustrated by experiments with gamboge and aluminium chloride, and with ferric hydroxide and sodium phosphate. The signs of the positive and negative colloids are reversed by the action of electrolytes with multivalent anions and cations, respectively, when the electrolyte concentration corresponds with that of the non-flocculating zone. By the successive addition of the two types of electrolytes, a series of alternately positive and negative colloids may be obtained.

L. L. Bircumshaw.

Law of mass action and colloids. H. H. Weber (Biochem. Z., 1927, **189**, 381—406).—The curve expressing the union of hydrogen and hydroxyl ions with multivalent acids and bases is interpreted as a "residual normality" (proportion of undissociated to total normality) curve. The residual normality curve is described as a function of the hydrogen-ion concentration and of the "true" (not mean) dissociation constants of the single ions determined from electrotitration curves. The effects of changes of ionic activity and of secondary changes of ionic concentrations of multivalent electrolytes by the formation of undissociated salts on the residual normality curve are analysed in relation to the mass law. The rule of Michaelis that the formation of undissociated salts by an ampholyte does not affect the isoelectric point is, in its general form, incorrect. A formula is given for determining the isoelectric point which shows the effect of such salt formation on the isoelectric point and permits its calculation from various dissociation constants. The frequently observed shifting of the isoelectric point of protein and protein systems (cells) by addition of neutral salts is thus explained in terms of the law of mass action.

P. W. Clutterbuck.

Influence of proteins on solubility of calcium phosphate. J. Csapo (J. Biol. Chem., 1927, **75**, 509—515).—Solutions of primary calcium phosphate were mixed with varying amounts of blood-serum, adjusted to different reactions by addition of sodium hydroxide, and, after keeping at 0° for 16 hrs., were centrifuged, the calcium and phosphorus content of the supernatant fluid being determined. The results indicate a decrease in the solubility of calcium phosphate from p_H 6·0 to 6·7, followed by increasing solubility up to p_H 7·3; thereafter the solubility decreases with increasing alkalinity, the rate of decrease being lower the greater the amount of serum present. For $p_H > 6·7$, the solutions are turbid owing to the presence of part of the calcium phosphate in stable suspension. The presence of larger amounts of serum shifts the minimum and maximum of the solubility curve towards the alkaline side, the reverse being true in the presence of excess of phosphate.

C. R. Harington.

Solubility, swelling, and adsorption of cellulose in alkali. W. von Neuenstein (Kolloid.-Z., 1927, **43**, 241—249).—The amount of cellulose dissolved in alkali depends on the amount of cellulose taken (cf. von Buzágh, this vol., 17), and it is probable that both adsorption and peptisation processes take place. The degree of swelling of cellulose in water and alkali is similarly affected, and it is suggested that the content of electrolytes or of decomposition products in the cellulose may have an influence on the swelling.

O. J. Walker.

Action of alkalis on clay. H. B. Oakley (J.C.S., 1927, 2819—2831).—Suspensions of purified clay were treated with alkali, the clay was removed by coagulation, the p_H of the clear liquid measured, and the total alkali in solution determined by titration. Equivalent quantities of bases were thus found to be taken up at p_H values below about 9. In more alkaline solutions the amounts removed are in the increasing order lithium, sodium, potassium, barium, and calcium. The amounts of sodium and potassium taken up are fairly constant above p_H 11, but barium and calcium show no such limit. The order is the same as that found for amorphous silica (Joseph and Oakley, A., 1926, 132). The amounts of base taken up by both silica and clay are increased by the presence of the neutral salts of the metals concerned. The proportion of neutralised sodium hydroxide which forms soluble compounds is negligible until the p_H is above 9, when it increases rapidly with the alkalinity. The general behaviour of the clay suggests that it is an insoluble or a colloidal weak acid, with a dissociation constant of approximately 10^{-8}, in direct equilibrium with bases in solution, the salts formed being equally insoluble. With alkali more concentrated than p_H 9, however, the clay begins to break down, giving silicates and aluminates which may be soluble, *e.g.*, sodium, or insoluble, *e.g.*, calcium. The viscosity and specific volume of suspensions of clay show pronounced maxima between p_H 8 and 10 with sodium hydroxide, and the viscosity maximum is enormously increased when the clay is coagulated by sodium chloride. Sodium carbonate does not produce the same effect. This behaviour is explained by supposing that, at certain concentrations, sodium hydroxide forms a comparatively non-viscous sol with clay. The addition of sodium chloride produces a very gelatinous sol which, at still higher concentrations, is dissolved by the hydroxide. Comparisons with reference to base absorption and imbibitional water are made between Gezira and Mongalla clays. kaolin, bentonite, ball clay, amorphous silica, and synthetic alumino-silicate. The last-mentioned, although comparatively coarse and only slightly clay-like to the touch, shows considerable analogy with clay.

M. S. Burr.

Gibbs on emulsification. W. D. Bancroft and C. W. Tucker (J. Physical Chem., 1927, **31**, 1681—1692).—The modern theory of emulsification was given implicitly by Gibbs, who recognised definitely that a film has two surfaces and therefore two surface tensions, which are not necessarily equal, if in contact with different phases. In all emulsions the dispersed liquid is on the side of the film having the higher

surface tension, and an experimental technique has now been developed to show that the surface tension of an emulsifying film is higher on the side of the emulsified liquid. Certain qualitative results are given. L. S. THEOBALD.

Theory of peptisation. II. A. VON BUZAGH (Kolloid-Z., 1927, **43**, 215—220; cf. A., 1927, 310).—Variations in the concentration of the colloidal solution with the proportion of solid phase are found in the peptisation of palmitic acid by alkali hydroxides and of sulphur gels. The time must be regarded as a variable in peptisation processes, since there may be either ageing of the sol or a slow change in the composition and state of the solid phase. In the peptisation of ferric hydroxide gel the concentration of the sol decreases with time if a large amount of the solid phase is present. The composition of the latter may change also owing to hydrolytic processes.

O. J. WALKER.

Theory of peptisation. III. Peptisation by means of hydrophilic sols. A. VON BUZÁGH (Kolloid-Z., 1927, **43**, 220—224).—When sols are used as peptising agents the curve connecting quantity of colloid dissolved and amount of solid taken exhibits a maximum as in the case of peptisation by electrolytes (cf. preceding abstract). The systems investigated were the peptisation of charcoal and of ferric hydroxide by various soap solutions, of kaolin by humic acid, and of aluminium hydroxide by alkaline alizarin solutions. O. J. WALKER.

Denaturation of proteins. W. C. M. LEWIS (Z. physikal. Chem., 1927, **130**, 345—352).—Recent views on the nature of denaturation and subsequent flocculation are considered, with special reference to the work of P. S. Lewis (A., 1926, 1204; 1927, 270). It is suggested that whilst flocculation involves the amino- and carboxyl groups of contiguous protein units, the process of denaturation cannot depend on the hydrolysis of the polypeptide linking and is not directly connected with the amino- and carboxyl groups of the protein. Various possibilities in regard to this process are considered, the hydrolysis of a grouping analogous to an ethylene oxide linking being favoured. It is suggested that the process involves the spatial separation (possibly by hydroxyl groups) of the carboxyl and amino-groups belonging to one and the same protein unit, which is thus opened up in a mechanical sense. The mutual affinities of the carboxyl and amino-groups in the same unit are now decreased, with increasing possibility of union with neighbouring units, and so of flocculation.

L. L. BIRCUMSHAW.

Gelatinisation of lyophilic sols and the structure of lyophilic gels. H. G. B. DE JONG (Z. physikal. Chem., 1927, **130**, 205—216).—Gelatinisation of agar sols has all the characteristics of a flocculation, but, in spite of this, the electric charge and the hydration of the particles remain almost unchanged. This can only be the case if, at the moment of gelatinisation, these two factors are not distributed uniformly over the particles, which must have unprotected as well as strongly protected regions. Gelatinisation results through these unprotected re[illegible] while the electric charge and the hydration remain free to line the inner sides of the spaces formed in the resulting spongy aggregates. Assuming this to be the nature of gel structure, syneresis during the change to a permanent deformation is to be expected, and this has been shown to be the case by submitting threads of a gel of viscose to a stress, when a decrease in volume is obtained. It is further shown that after a permanent deformation an originally isotropic gel shows an anisotropic swelling on suitable immersion, the change in dimension in the direction of the stress being always less than that in the transverse direction. This is reversed for a compression. The significance of the forces of adhesion at the points of contact and of the charge and hydration at the remaining free places is discussed in relation to the swelling equilibrium and to gelatinisation. L. S. THEOBALD.

Action of benzenesulphonic and naphthalenesulphonic acids on gelatin. C. MARIE and A. BUFFAT (Z. physikal. Chem., 1927, **130**, 233—236).—Benzenesulphonic acid dissolves gelatin rapidly, but naphthalenesulphonic acid precipitates it from solution in water. The sodium, potassium, and copper salts behave like the respective acids.

L. S. THEOBALD.

Pectin jellies. (MISS) G. SPENCER (Fourth Colloid Symposium Monograph, 1926, 302—303).—Pectin jellies may be acid or alkaline; the pectin is always positively charged. Excess of sugar crystallises out, and aids hydrolysis of the pectin.

CHEMICAL ABSTRACTS.

Organophilic colloids. G. S. WHITBY (Fourth Colloid Symposium Monograph, 1926, 203—223).—In any homologous series of compounds containing an active group (OH, CN, CHO, CO), imbibition by rubber increases as the series is ascended; the reverse is the case for cellulose nitrate and acetate. The behaviour of numerous solvents is described. The properties of colloids are discussed.

CHEMICAL ABSTRACTS.

Cataphoresis, electrical charge, critical potential, and stability of colloids. H. R. KRUYT, A. C. W. ROODVOETS, and P. C. VAN DER WILLIGEN (Fourth Colloid Symposium Monograph, 1926, 304—310).—Experiments with an arsenic trisulphide sol show that the rate of cataphoresis increases with addition of potassium chloride at all concentrations. There is no reason to reject the theory of critical potentials. CHEMICAL ABSTRACTS.

Influence of capillary activity on cataphoresis and coagulation. H. FREUNDLICH and G. V. SLOTTMAN (Z. physikal. Chem., 1927, **129**, 305—320).—The cataphoretic transference velocity of arsenious sulphide sols has been measured in presence of ammonium and mono-, di-, tri-, and tetra-ethylammonium chlorides at various concentrations; the concentrations necessary for coagulation have also been determined. Comparison of the concentrations required to bring about equal lowering of the charge on the particles shows good agreement with Traube's rule; the Traube coefficient is about 1·8, *i.e.*, the square root of the more usually observed value. Similar results are found for methyl-, trimethyl-, propyl-, and tripropylammonium chlorides. The tetra-alkylammonium salts

are peculiar in that the coagulating influence is less than would be expected as a result of introducing another methyl group into the next lower homologue, but is much greater than that of the corresponding trialkylammonium salt. Similar measurements have been made of the transference velocity and coagulating concentration of ferric hydroxide sols, prepared by oxidising iron pentacarbonyl with hydrogen peroxide, in presence of sodium benzenesulphonate, *p*-toluenesulphonate, and *p*-ethylbenzenesulphonate. The Traube coefficient is in these cases about 3.

The capillary activity of a substance is a deciding factor in its cataphoretic and coagulative influence.

H. F. GILLBE.

Cataphoresis and [electric] charge. H. R. KRUYT and P. C. VAN DER WILLIGEN (Z. physikal. Chem., 1927, **130**, 170—176).—The velocity of cataphoresis of sols of arsenious and mercury sulphides is increased by the addition of univalent cations and lowered by that of multivalent cations, effects which continue nearly to the precipitation concentration. The results are discussed in relation to Powis' theory of critical potential (A., 1916, ii, 521), which they do not necessarily contradict. L. S. THEOBALD.

Association in liquids. [EARL OF] BERKELEY (Nature, 1927, **120**, 840—841).—A device which might be applied to the investigation of association in liquids is described. If a liquid is contained in a tubular cell closed at the top by a semi-platinised plate and at the bottom by a mirror, the cell being mounted as a centrifuge, the system of interference rings centred about the vertical axis will, on rotation of the cell, move across the field of view. A knowledge of the number of rings and the rate at which they pass would give insight into the changes in the " optical density " of the liquid.

A. A. ELDRIDGE.

Equilibrium between the methoxide and hydroxyl ions in mixtures of methyl alcohol and water. I. (FRL.) A. UNMACK (Z. physikal. Chem., 1927, **129**, 349—369).—From conductivity, solubility, and reaction velocity measurements the equilibrium constant K' of the reaction $OH'+MeOH \rightleftharpoons OMe'+H_2O$ has been calculated from the equation $K'=[OH']a_1/[OMe']a_2$, in which a_1, the activity of the methyl alcohol, and a_2, the activity of the water, are obtained from vapour-pressure measurements. From the conductivity determinations $K'=0{\cdot}35$, and from solubility measurements, 0·20, the concentrations being in mol./litre. The constant is somewhat dependent on the ionic concentration and on the ratio of the concentrations of methyl alcohol and water. H. F. GILLBE.

Acid dissociation of aquo-ions. J. N. BRÖNSTED and C. V. KING (Z. physikal. Chem., 1927, **130**, 699—708).—The acidity of a positive aquo-ion such as the hexa-aquochromic ion is governed by a dissociation of the type $[Cr(H_2O)_6]^{+++} \rightleftharpoons \left[\begin{matrix} OH \\ Cr(H_2O)_5 \end{matrix}\right]^{++} + H^+$. The variation with concentration of the acid-base dissociation constant K_c is in agreement with the theoretical equation $\log K_c = \log$
where μ is the ionic strength, K_a the acid dissociation constant, and z the valency of the ion. K_c for the hexa-aquochromic ion, determined by measurement of the velocity of hydrolysis of ethyl diazoacetate in presence of hexa-aquochromic picrate and perchlorate, at 15° and infinite dilution, is $1{\cdot}26\times10^{-4}$.

H. F. GILLBE.

Activity of weak acids in aqueous sulphate solutions. M. RANDALL and C. F. FAILEY (J. Amer. Chem. Soc., 1927, **49**, 2678—2681).—From measurements of the distribution of mono- and di-chloroacetic acids between magnesium sulphate solutions and di-*n*-butyl ether at 25°, the " activity coefficient " of each acid, defined as the ratio of the molality in pure water to that in a salt solution of a given activity, is shown to diminish by an amount which is larger the greater the dissociation constant of the acid. This agrees with the assumption that the stronger acid forms the larger amount of hydrogen sulphate ion. Potassium sulphate lowers the " activity coefficient " to a greater extent than magnesium sulphate (cf. Randall and Langford, A., 1927, 729).

S. K. TWEEDY.

Hydrogen-ion concentration of saturated solutions of calcium carbonate and hydrogen carbonate in water. J. W. WILLIAMS and J. A. CHUCKA (J. Amer. Med. Assoc., 1927, **89**, 445—446). —The p_H value at 25° of calcium carbonate suspensions, determined with the hydrogen electrode, was 8·64—8·86 (average 8·78); that of calcium hydrogen carbonate solution, determined with the quinhydrone electrode, was 5·98 in presence of excess of carbon dioxide, and 6·19 otherwise.

CHEMICAL ABSTRACTS.

Application of Ghosh's theory to complex compounds. A. GRUNBERG (Ann. inst. platine [Russia], 1926, **4**, 276—298).—Conductivity measurements for many complex cobalt and platinum salts are in accord with Ghosh's theory, but the compounds $[Pt(NH_3)_4Cl_2](NO_3)_2$, $[Co(NH_3)_5NO_2]Br_2$, and $[Co(NH_3)_5NO_2](NO_3)_2$ give high values on account of hydrolysis. Sources of variation are discussed.

CHEMICAL ABSTRACTS.

Mol. wt. determination of saturated vapours from pure liquids and mixtures by the method of displacement by a current of air. M. S. VREVSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 593—597).—A method for determination of mol. wt. of saturated or dissociated vapours has been devised in which a current of air is passed through the volatile liquid instead of the vapours displacing air as in Victor Meyer's method. A. RATCLIFFE.

Dissociation of acetic acid vapour and the equilibrium between a solution of acetic acid and its vapour. M. S. VREVSKI, K. MISCHTSCHENKO, and B. MUROMCEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 598—607).—The pressure and density of the saturated vapour of acetic acid obtained by the method of displacement by a current of air agree with the equation of Gibbs at temperatures between 30° and 90°. This also applies to acetic acid solutions. The partial pressures of (AcOH) and $(AcOH)_2$ in the vapour have been calculated. A. RATCLIFFE.

Dissociation of the vapour of formic acid and the equilibrium between a solution of formic acid and its vapour. M. S. VREVSKI and A.

GLAGOLEVA (J. Russ. Phys. Chem. Soc., 1927, **59**, 608—616).—The saturated vapour of formic acid at temperatures between 25° and 80° and the vapour of formic acid solutions at 60° and 80° are found to obey Gibbs' law. The number of associated molecules in the vapour of a formic acid solution of a given concentration decreases with rise of temperature, but the percentage of water in the vapour phase is increased. A. RATCLIFFE.

Equilibrium between solutions of formic acid in benzene and the vapour phase. M. S. VREVSKI, N. HELD, and G. SCHUKAREV (J. Russ. Phys. Chem. Soc., **59**, 1927, 617—630).—By studying the composition of the vapour and vapour pressures of a solution of formic acid in benzene at temperatures below 73·2° at which two layers exist, it is shown that this system belongs to group IV according to the two-layer system classification of Rosenbum and Büchner ("Die Heterogenen Gleichgewichte," 1918). Further, at 71° the system changes from group IV to group III. The densities and partial pressures at 59·96° and 25° are in agreement with Gibbs' law. The proportion of double molecules in the vapour increases rapidly with rise of temperature. A. RATCLIFFE.

Distribution of a base (sodium hydroxide) between two acids (nitric and hydrochloric) in saturated aqueous solutions. V. I. NIKOLAEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 677—684).—Analyses of solutions saturated with respect to sodium nitrate and sodium chloride at temperatures between 15° and 210° show that with rise of temperature or with an excess of the base or the free acids in solution nitric acid takes up in every case more of the base than hydrochloric acid. It is possible that heats of dissolution of the base, acids, and products of the reaction as well as the presence of water have an influence on the distribution of the base between the acids in a saturated solution. A. RATCLIFFE.

Molecular volume of water in metal salt hydrates. E. MOLES and M. CRESPI (Z. physikal. Chem., 1927, **130**, 337—344; cf. Moles, A., 1926, 336).—A determination of the molecular volumes of the hydrates of manganous, ferrous, cobalt, nickel, copper, and zinc sulphates shows that the volume of the first water molecule lies between 10 and 11, whilst that of the remaining molecules is about 14·6. Nickel sulphate monohydrate forms an exception, the molecular volume being abnormally high. The results are in accord with the Werner co-ordination theory, but they lead to the conclusion that the first, not the seventh, water molecule is united with the anion. The molecular volumes of the following hexa-aquochromic salts have also been determined: potassium chrome alum, violet chromic sulphate, violet chromic tetrasulphate, violet chromic chloride, and violet chromic chlorosulphate. The same relations are found to hold as for the sulphates of bivalent metals. The hexa-aquosulphates are formulated as follows: $[Cr(H_2O)_6]_2(SO_4{\cdot}H_2O)_3,2H_2O$, $K[Cr(H_2O)_6](SO_4{\cdot}H_2O,SO_4),5H_2O$, and $H[Cr(H_2O)_6](SO_4{\cdot}H_2O)_2$. The values 52 and 51·6, calculated for the molecular volume of the monoaquosulphate anion from data for the two series of sulphates, are in good agreement with the value 54 calculated for H_2SO_4,H_2O at 0° Abs. L. L. BIRCUMSHAW.

System ethyl alcohol–carbon tetrachloride. S. F. CALHOUN and T. C. POULTER (Proc. Iowa Acad. Sci., 1926, **33**, 169).—The total and partial vapour pressures of the system ethyl alcohol–carbon tetrachloride were determined at 25° and 60°. An apparatus for the determination of vapour pressures of substances which do not readily react with mercury was designed. CHEMICAL ABSTRACTS.

System magnesium sulphate–water from 68° to 240°. H. L. ROBSON (J. Amer. Chem. Soc., 1927, **49**, 2772—2783).—The solubility of magnesium sulphate monohydrate, determined in a special solubility bomb, decreases rapidly as the temperature rises to 200°, and then slowly up to at least 238°. Étard's measurements probably fall on the supersaturation curve (A., 1894, ii, 442). The solubilities of the hexa-, penta-, and tetra-hydrates were measured at 85°, 95°, and 100°; optical and crystallographic properties of all the hydrates are recorded and the methods of preparation are discussed. It is suggested that the rate at which a salt approaches equilibrium with its aqueous solution is related to its degree of crystallographic perfection. S. K. TWEEDY.

Boundaries of the heterogeneous region of cadmium amalgams. A. L. T. MOESVELD and W. A. T. DE MEESTER (Z. physikal. Chem., 1927, **130**, 146—153).—The liquidus curve for the cadmium amalgams has been determined by measurements of the *E.M.F.* of homogeneous liquid amalgams at six temperatures in the range 0—41°. The change in composition (concentration) of the liquid with temperature can be represented by the equation $C=2{\cdot}855+0{\cdot}0954t+0{\cdot}00128t^2$. The solidus curve could not be determined in a similar manner. Exact data for the latter are unknown, and former determinations, which are only approximate, may be uncertain on account of the slowness with which equilibrium is established in solid amalgams. A 10% amalgam is recommended for use in the Weston cell. L. S. THEOBALD.

Thermal dissociation of strontium carbonate. E. O. JONES and M. L. BECKER (J.C.S., 1927, 2669—2676).—Two different forms of apparatus are described for the measurement of dissociation pressures. Between 650° and 1100°, the observed values for strontium carbonate lie on a curve of the same form as that found by others for calcium and barium carbonates, viz., $\log p_1-\log p_2=-K(1/T_1-1/T_2)$, K for strontium being taken as $1{\cdot}05\times10^4$ and the dissociation tension at 928° as 10 mm. The curve lies wholly between those of the other two carbonates. The temperature at which the dissociation pressure is 1 atm. is, by extrapolation, 1258°, approximately 100° higher than those given by Brill (A., 1905, ii, 522) and Hedvall (A., 1917, ii, 208). Except for the extrapolated values at high temperatures, the authors' results are not in good agreement with those of Pott (Diss., Freiburg, 1905). Confirmation of the validity of the curve, especially at low temperatures, has been obtained, however, by using the carbonate to control the carbon dioxide tension in a study of the

C–CO–CO_2 equilibrium. The equilibrium constants thus determined for the system at different temperatures lie closely on Tigerschiold's curve (Jernkontoret's Annaler, 1923, 67). No evidence of the existence of a basic carbonate has been obtained.

M. S. Burr.

Cause of formation of hair copper in copper mattes. (System: iron–copper–sulphur.) P. P. Fedotéev [with D. N. Nedrigailov] (Z. anorg. Chem., 1927, **167**, 329—340; cf. Tiedemann, B., 1926, 710).—The constitution of the system ferrous sulphide–cuprous sulphide has been investigated by thermal analysis and by microscopical examination, which latter leads to the conclusion that the two sulphides are only partly miscible in the solid state. The formation of hair copper in the system probably depends on the equilibrium $Cu_2S \rightleftharpoons Cu + CuS$, set up in solid solution.

R. Cuthill.

Phase diagram of sodium nitrate. N. S. Kurnakov and V. J. Nickolajev (Z. physikal. Chem., 1927, **130**, 193—204).—The ternary system Na_2O–N_2O_5–H_2O has been investigated by measurements of solubility and of the density of the saturated solutions at 25° and 65°.

L. S. Theobald.

Equilibrium in the system $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°. R. M. Caven and W. Johnston (J.C.S., 1927, 2902).—An error in a previous paper (cf. A., 1927, 1142) is corrected.

O. J. Walker.

System potassium carbonate–sodium carbonate–water at 40°; trihydrate of sodium carbonate. J. W. Bain (J. Amer. Chem. Soc., 1927, **49**, 2734—2738).—The existence of sodium carbonate trihydrate is demonstrated; it is converted into monohydrate with evolution of heat at 39·8°. The recorded data for the solubility of sodium carbonate at 40°, and for some unknown temperature range above this, refer to solutions in equilibrium with the metastable monohydrate and require revision (cf. Bain, A., 1925, ii, 577; Hill and Miller, A., 1927, 418).

S. K. Tweedy.

System mercuric iodide–potassium iodide–water. (Mlle.) M. Pernot (Compt. rend., 1927, **185**, 950—953).—Measurements at 20°, 34°, and 80° by the method of Schreinemakers indicate the existence of the compound HgI_2,KI,H_2O. The compounds described by other workers may be mixtures of the above with potassium iodide.

J. Grant.

System $FeCl_2$–$NiCl_2$–H_2O at 25°. Y. Osaka and T. Yaginuma (Z. physikal. Chem., 1927, **130**, 480—481).—Two series of solid solutions are formed. Ferrous chloride (with $4H_2O$) is saturated when 10·6% of the metal is replaced by nickel, and nickel chloride (with $6H_2O$) is saturated when 65·6% of the metal is replaced by iron. The liquid phase in equilibrium with the two saturated solid solutions has the composition $FeCl_2$ 21·60, $NiCl_2$ 19·36, H_2O 59·04%.

R. W. Lunt.

Ternary system manganous phosphate–phosphoric acid–water, and the manganodiphosphoric acids. G. Grube and M. Staesche (Z. physikal. Chem., 1927, **130**, 572—583).—Transport measurements indicate that solutions of manganous phosphate in concentrated phosphoric acid contain a complex manganese anion. The formula of the acid, as determined by observation of the isotherms of the system $Mn_3(PO_4)_2$–H_3PO_4–H_2O at 25° and 55°, is $H_4Mn(PO_4)_2,3H_2O$. Tripotassium hydrogen manganodiphosphate pentahydrate and sodium dihydrogen manganodiphosphate tetrahydrate are stable red crystalline salts. The free acid forms almost colourless crystals which on dissolution in water gradually precipitate the sparingly soluble manganous phosphate, $Mn_3(PO_4)_2,2H_2O$. Over concentrated sulphuric acid the trihydrate of the acid loses two molecules of water. The only stable compounds existing between 25° and 55° in presence of phosphoric acid at various concentrations are anhydrous manganous phosphate and manganous hydrogen phosphate, and $H_4Mn(PO_4)_2,3H_2O$.

H. F. Gillbe.

Reciprocal system: water, sodium chloride, magnesium sulphate, magnesium chloride, sodium sulphate. A. Küpper (Caliche, 1927, **8**, 467—487).—The isotherms of this system from 0° to 83° are described and figured, and solubility tables are given from 0° to 100° for each of the salts.

Chemical Abstracts.

Quaternary system: water, sodium nitrate, sodium chloride, sodium sulphate, between 100° and 0°. A. Chretien (Caliche, 1926, **8**, 390—408).—Graphs and tables are given. At 68·5° the solution is saturated with respect to chloride, nitrate, anhydrous sulphate, and darapskite, $Na_2SO_4,NaNO_3,H_2O$. Darapskite is not formed above 68·5° when the solution is saturated with sodium chloride. Above 78·5° the sulphate is anhydrous, and below 7·2° is present as decahydrate in contact with solutions saturated also with nitrate and chloride only. At 16° there are four solid phases: chloride, darapskite, anhydrous sulphate, and sulphate decahydrate.

Chemical Abstracts.

System $FeCl_3$–$AlCl_3$–H_2O at 25°. G. Malquori (Gazzetta, 1927, **57**, 665—665).—Neither double salts nor mixed crystals are formed.

R. W. Lunt.

System $AlCl_3$–KCl–HCl–H_2O at 25°. G. Malquori (Gazzetta, 1927, 57, 661—662).—Neither additive compounds nor mixed crystals are formed; the fractional crystallisation of aluminium and potassium chlorides is readily carried out in the presence of 10% of hydrogen chloride.

R. W. Lunt.

System $Al(NO_3)_3$–KNO_3–$Fe(NO_3)_3$–H_2O at 25°. G. Malquori (Gazzetta, 1927, **57**, 663—664).—This system shows neither double salt nor mixed crystal formation.

R. W. Lunt.

High-temperature equilibrium between thorium oxide and carbon. C. H. Prescott, jun., and W. B. Hincke (J. Amer. Chem. Soc., 1927, **49**, 2744—2753).—The equilibrium $ThO_2 + 4C$ (graphite) $= ThC_2 + 2CO$ was investigated between 2000° and 2500° Abs. in a graphite furnace. The equilibrium pressures are given by $\log_{10} p$ (atm.)$=8{\cdot}069-19{,}325/T$, from which $\Delta F=176{,}970-73{\cdot}89T$ and $\Delta H=176{,}970$ g.-cal./mol. at 1 atm. The heat of formation of thorum carbide is $\Delta H=-78{,}930$ g.-cal./mol.; its m. p. is very close to 2773° Abs.

S. K. Tweedy.

High-temperature equilibrium between aluminium oxide and carbon. C. H. PRESCOTT, jun., and W. B. HINCKE (J. Amer. Chem. Soc., 1927, **49**, 2753—2759).—The equilibrium pressures for the reaction $2Al_2O_3+9C=Al_4C_3+6CO$ between 2000° and 2300° Abs. are given by: $\log_{10}p$ (atm.) $=8\cdot21-18.480/T$, whence $\Delta F=507,760-225\cdot6T$ and $\Delta H=507,760$ g.-cal./mol. at 1 atm.; the heat of formation and free energy of formation of aluminium carbide at 25° are —60,260 g.-cal. and —53,240 g.-cal., respectively. Berthelot obtained —220,830 g.-cal. for the former figure. S. K. TWEEDY.

Saturation of sugar-lime solutions. II. A. H. W. ATEN, P. J. H. VAN GINNEKEN, and E. VERWEY (Z. physikal. Chem., 1927, **130**, 365—377; cf. A., 1912, i, 9).—Experiments on the saturation of sugar-lime solutions by carbon dioxide are recorded. The influence of time, temperature, and the composition of the original solution has been investigated, and curves are given showing the relation of R to N under different conditions, R being the degree of saturation of the solution (or the ratio of the absorbed carbon dioxide to the normality of the original solution), and N the ratio of the normality of the filtrate to that of the original solution. From dilute solutions (up to about 0·7 mol. of sugar $+N$CaO) a basic precipitate separates when R is $>0\cdot5$, which can be represented by the formula $3CaO,2C_{12}H_{22}O_{11},xCaCO_3$. The value of x increases with R, and for precipitates formed at the ordinary temperature is greater than 8. The precipitate changes slowly (more rapidly on shaking) with the formation of a hydrate of calcium carbonate, $CaCO_3,6H_2O$. From stronger sugar-lime solutions, *e.g.*, 0·7 mol. of sugar $+1\cdot7N$CaO, a second strongly basic precipitate is formed when $R=0\cdot1$—$0\cdot3$. The composition of this varies from $6CaO,3C_{12}H_{22}O_{11},CO_2$ to $6CaO,3C_{12}H_{22}O_{11},2CO_2$. The separation of each precipitate is a reversible process, that from more concentrated solutions passing into solution on warming and reappearing on cooling, whilst that from more dilute solutions is less soluble at higher temperatures than at the ordinary temperature. The conductivity of the saturated solution undergoes a marked decrease with time, and from a consideration of the data it appears that the solution contains complexes of the composition $xCaCO_3,yCa(OH)_2,zC_{12}H_{22}O_{11}$, where $x/y=0\cdot5$—2. The experimental results are discussed, with special reference to the probable influence of the sugar on the formation and composition of the precipitates. L. L. BIRCUMSHAW.

Hydrolysis of compounds which may occur in Portland cement. W. LERCH and R. H. BOGUE (J. Physical Chem., 1927, **31**, 1627—1646).—The hydrolysis of the compounds $3CaO,SiO_2$, $3CaO,Al_2O_3$, β-$2CaO,SiO_2$, $5CaO,3Al_2O_3$, γ-$2CaO,SiO_2$, and $2CaO,Fe_2O_3$ in the pure state has been investigated at the ordinary temperature but without reference to the conditions which obtain in cement mortars and concretes. In each case, the compound is hydrolysed and an equilibrium is reached. The order in which the compounds give up lime, in decreasing amount, is that given above, and the times required for equilibrium to be reached are, aluminates, 1 day, tricalcium silicate, 8 days, and the remaining compounds, 12 days. The hydroxyl-ion concentrations necessary to prevent hydrolysis are, respectively, in terms of p_H, —, 12·3, 13·7, 11·7, —, and 13·0 for the compounds in the above order. When the soluble products are removed from the system, the silicates, aluminates, and ferrite hydrolyse eventually to hydrous silica, hydrous alumina, and hydrous ferric oxide, respectively. When the soluble products are not removed, hydrolysis proceeds with the formation of calcium hydroxide and a silicate, aluminate, or ferrite, which is less basic, the composition of this component being dependent on the concentration of hydroxyl ion and the amount of available water. L. S. THEOBALD.

Equilibria in systems in which phases are separated by a semipermeable membrane. XXIII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 635—642).—A further discussion of the influence of temperature and pressure on osmotic equilibria (see A., 1927, 1142).

Reaction regions. XVI. $(NH_4)_2Cr_2O_7$–K_2SO_4–KCl and $(NH_4)_2Cr_2O_7$–Fe–S. W. P. JORISSEN and G. M. A. KAYSER (Z. physikal. Chem., 1927, **130**, 482—487).—Data are given, and expressed graphically, for the limits of composition within which reaction takes place when induced by a burning magnesium ribbon in the above systems. R. W. LUNT.

Heat of mixing of metals. M. KAWAKAMI (Z. anorg. Chem., 1927, **167**, 345—363).—The heat of mixing of a number of pairs of the following metals in the molten state and in various proportions has been measured: mercury, potassium, sodium, tin, cadmium, bismuth, zinc, lead, and antimony. Where no compound formation occurs, the heat of mixing is, in general, negative, but in cases where compounds are known to be formed the heat effect is positive. It therefore appears probable that intermetallic compounds which can exist in the solid state do not dissociate on fusion. R. CUTHILL.

Temperature effects of mixing non-aqueous liquids. W. M. MADGIN, J. B. PEEL, and H. V. A. BRISCOE (J.C.S., 1927, 2873—2877).—A consideration of the data previously obtained (A., 1927, 521), relating to the thermal effects occurring on mixing a number of pairs of non-aqueous liquids, makes it evident that these changes are not related to the polarity of the liquids as indicated by their dielectric constants. The effect of variation of initial temperature on the temperature change on mixing has been determined for a series of twelve mixtures in which the temperature change varies from a large positive to a large negative value. The variation of the change with the initial temperature is always in the same direction, *i.e.*, it becomes more positive or less negative the lower the initial temperature. The effect may be explained by assuming that the two liquids contain associated molecules which dissociate on mixing and combine with one another to form compound molecules, the first process being endothermic. Alteration of the initial temperature changes the thermal effect of the reactions, and also the positions of equilibria. M. S. BURR.

Heat of dissolution of potassium nitrate in water. W. A. ROTH (Z. physikal. Chem., 1927, **130**, 539—544).—Measurements of the solubility of potassium nitrate in water confirm the evidence for the existence of two modifications given by crystallographic and thermal data. The heat of dissolution in 350 mols. of water at 20·5° is −8·518, and in 460 mols., −8·367 kg.-cal. These values do not alter with time. Intermediate values gradually change with time, owing probably to the presence of two modifications. The heat of transition from one form to the other is 0·15 kg.-cal. H. F. GILLBE.

Heat of formation of zinc oxide. G. S. PARKS, C. E. HABLUTZEL, and L. E. WEBSTER (J. Amer. Chem. Soc., 1927, **49**, 2792—2795).—The molal heat of dissolution of zinc oxide in 2·633*N*-hydrochloric acid is −15,263 g.-cal. (15°) at 20°. Combination of this result with the heat of dissolution of zinc in acid of the same concentration (Richards and Burgess, A., 1910, ii, 391) gives 83,240 ± 200 g.-cal. for the heat of formation of zinc oxide at 20°.

S. K. TWEEDY.

Calculation of heats of combustion. J. E. SNYDER (J. Amer. Chem. Soc., 1927, **49**, 2806—2807; cf. Kharasch and Sher, A., 1925, ii, 636).—The heat of combustion, in kg.-cal./mol. at constant pressure, of aromatic compounds containing carbon and hydrogen with or without oxygen is given by $26{\cdot}05\lambda+24{\cdot}85\mu+y$, where μ and λ represent the number of μ and λ electrons in the compound (Pauling, A., 1926, 662) and y is a term represented by 13 for each ethylenic linking and 22·7, 19·5, 13, 13, 6·5, 3·2, and 3·2, respectively, for the ether, aldehyde, primary alcohol, ester, secondary alcohol, phenol, and tertiary alcohol groups. The carboxyl and ketone groups do not influence y. The average difference between the calculated and experimental values is 0·37%. S. K. TWEEDY.

Calorimetric method for determination of the coefficient of absorption of radium β-rays. D. K. YOVANOVITCH (Arh. Hemiju, 1927, **1**, 206—212).—The heat changes accompanying the absorption by aluminium, copper, or lead of the α- and β-radiation of radium are respectively 129·0 and 13·4 g.-cal./hr.; the coefficient of absorption of β-rays is 51·02.

R. TRUSZKOWSKI.

Transference numbers and degree of solvation of the ions of lithium chloride in certain alcohols. J. N. PEARCE and W. G. EVERSOLE (Proc. Iowa Acad. Sci., 1926, **33**, 151—164).—The true and ordinary transference numbers of lithium ions in solutions of lithium chloride in methyl, ethyl, and *n*-propyl alcohols have been determined with camphor as the reference substance. In a given solvent these values and the degree of solvation decrease as the concentration of the salt is increased; for a fixed concentration the degree of solvation decreases as the complexity of the solvent molecule increases.

CHEMICAL ABSTRACTS.

Correction of conductivity data for the conductivity of the solvent. W. F. K. WYNNE-JONES (J. Physical Chem., 1927, **31**, 1647—1662).—A solvent correction can be applied to conductivity data in water, methyl and ethyl alcohols, on the assumption that the impurity present is carbon dioxide, which is probably to be found even in the most highly purified solvents. The effect on conductivity data in any solvent will be determined by its solubility therein and by the type of compound formed. When the concentration and characteristics of the latter are known, the appropriate correction can be applied by the methods now described. When this is not the case, the correction can be applied if the law followed is known, although this method is less desirable than those mentioned above. In the case of aqueous solutions, the nature of the cell is of greater importance than the conductivity of the water, when strongly acid or alkaline solutions are employed at high dilutions. L. S. THEOBALD.

Molecular structure in solution. III. Electrical conductivities of aqueous solutions of cobalt chloride and hydrochloric acid. Prediction of crystal structure. O. R. HOWELL (J.C.S., 1927, 2843—2850).—The electrical conductivities of a series of solutions containing a constant amount of cobalt chloride with increasing concentrations of hydrochloric acid have been determined and compared with those of a similar series for hydrochloric acid alone. By plotting the differences in the values for corresponding solutions against concentration of acid, a curve is obtained which exhibits a pronounced minimum at the same concentration of acid as that which gives a maximum on the viscosity-difference curve previously obtained (A., 1927, 205). Its general form may be accounted for on the theory originally put forward (*loc. cit.*), viz., that, with increasing acid concentration, the hydrated cation, $Co(H_2O)_6^{\cdot\cdot}$, is progressively converted into the anion $CoCl_4''$. The conductivity-difference curve falls sharply to the minimum, whilst the viscosity-difference curve falls slightly before rising to the maximum. This is due to the initial depression of ionisation of cobalt chloride by addition of acid. The conductivity decrease is aided by reduction of ionisation, but the viscosity increase is checked, because of the decrease in the number of viscous $Co(H_2O)_6^{\cdot\cdot}$ ions. For the same reason there are similar resemblances and differences between the curve obtained by plotting concentration of acid against difference of specific resistance, instead of conductivity, and those showing differences of refractive index and density (A., 1927, 1136). The structure of zinc and magnesium orthosilicates, and of cobalt oxide and fluoride, originally predicted from the theory of the colour of cobaltous compounds (A., 1924, ii, 817), has since been confirmed by other methods. M. S. BURR.

Thickness of the Helmholtz double layer. J. F. MCCLENDON (Science, 1927, **66**, 200).—The thickness of the double electric layer around colloid particles is considered by Gouy to be of dimensions greater than molecular. The surface of a charged metallic electrode, immersed in a solution of an electrolyte, and the layer of excess ions of opposite sign act as the plates of a condenser, the capacity of which can be measured, whence the thickness of the Helmholtz double layer can be calculated. Using gold electrodes the values for 0·1*N*- and 0·001*N*-

solutions, respectively, were 0·194 and $0{\cdot}325 \times 10^{-6}$ cm. The former value is in fair agreement with Gouy's value, and the change, as for Gouy's values, is in the direction of increase of thickness with dilution of the electrolyte. A. A. ELDRIDGE.

Theory of the hydrogen electrode. F. LEUTHARDT (Helv. Chim. Acta, 1927, **10**, 888—896).—The importance of considering the solubility of hydrogen in the aqueous medium when making measurements with the hydrogen electrode is emphasised. If γ_0 is the solubility in a standard solution and γ that in the medium under examination, the correction to apply to the observed *E.M.F.* is $\Delta\pi = RT/2F \,.\, \log_e \gamma_0/\gamma$. Measurements with the cells H_2|HClc|HClc, aqueous solution of glycerol|H_2 yield values in good agreement with this expression. Further support is afforded by measurements of similar cells, with and without glycerol, in which one electrode was maintained at a constant temperature whilst the temperature of the other was varied. Values of $\Delta\pi$ for solutions of hydrochloric acid, potassium chloride, acetic acid, glycerol, and ethyl alcohol at various concentrations are tabulated. These values are fairly large; *e.g.*, for 1·0, 2·0, and 4·0*N*-solutions of potassium chloride the values of $\Delta\pi$ at 15° are 2·5, 5·4, and 10·3 millivolts, respectively. J. S. CARTER.

Effect of neutral salts on potential of hydrogen electrode. III. J. PRZEBOROVSKI and M. FLEISSNER [with T. POPOWA] (Z. anorg. Chem., 1927, **167**, 364—368; cf. A., 1924, ii, 87).—The potential of a hydrogen electrode in a solution of hydrogen bromide is increased by the presence of the chlorides or bromides of potassium, sodium, or lithium. In general, the bromides have a greater effect than the corresponding chlorides, the lithium salts have the greatest effect, and the potassium salts the least, the results as a whole pointing to a close connexion between the neutral salt effect and hydration. With addition of increasing amounts of ethyl alcohol to a solution of sulphuric acid, the potential of a hydrogen electrode immersed in the solution first decreases, then passes through a minimum, and finally rises again, and in presence of alcohol the neutral salt effect is less than it is in solutions containing no alcohol. R. CUTHILL.

Apparent potential of dextrose solutions. R. WURMSER (Compt. rend., 1927, **185**, 1038—1041).—Platinum or gold electrodes in a buffered 3% solution of dextrose at 40° attain potentials which are equal for the two metals, but the potential and the rate at which it is developed depend on the nature of the buffer and on the p_H value. The final value (E) is given (with respect to the normal hydrogen electrode), for a 0·1*M*-phosphate buffer mixture, by the relation, $E = 0{\cdot}489 - 0{\cdot}086 p_H \pm 0{\cdot}002$ volt. At 7·5 $-0{\cdot}147$ volt, which is near the value obtained for lævulose (A., 1927, 316). The presence of a dye (methylene-blue, phenosafranine, or Janus-green) lowers or raises the potential according as it is present in the oxidised or reduced state. For $p_H > 10$ the limiting potentials are not constant, owing to the partial utilisation in side reactions of the hydrogen liberated. J. GRANT.

Simple type of flowing junction. E. J. ROBERTS and F. FENWICK (J. Amer. Chem. Soc., 1927, **49**, 2787—2791).—The two streams of solution play on opposite sides of a vertical mica strip and flow down wax channels past a small hole in the strip. A constant *P.D.* is attained in a few seconds. The observed *P.D.* between 0·1*M*-hydrochloric acid and 0·1*M*-potassium chloride solutions agrees fairly well with that obtained by MacInnes and Yeh (A., 1922, ii, 252) and is in accord with the value calculated from Lewis and Sargent's equation. S. K. TWEEDY.

Cells with identical unchangeable electrodes. V. KARPEN (Compt. rend., 1927, **185**, 942—944).—The experiments previously described (A., 1927, 1144) have been extended to other types of unattackable electrodes and analogous results obtained. The *E.M.F.* is lower in an atmosphere of hydrogen, but is unaltered in oxygen. Cells with such electrodes (*e.g.*, carbon or platinum) in an aqueous solution of sodium hydroxide and in an immiscible liquid (*e.g.*, amyl alcohol) give potentials of the order of 0·5 volt, the electrode in the aqueous layer being negative. J. GRANT.

Contact resistance between electrodes and electrolytes. O. SCARPA and E. DENINA (Z. Physikal. Chem., 1927, **130**, 449—471).—Since the sum of all the potentials in a circuit comprising a source of *E.M.F.* and an electrolyte containing two electrodes is zero, the following expression obtains: $V - ir - E^+ - E^- - e^+ - e^- - i\rho^+ - i\rho^- = 0$, where V is the *E.M.F.* of the source, i the current, E^+ and E^- are the *E.M.F.* of polarisation at the electrodes, e^+ and e^- the contact potentials between the electrodes and the electrolyte, and ρ^+ and ρ^- the contact resistance between electrodes and electrolyte. The difficulties associated with the determination of E^+, E^-, e^+, and e^- have been avoided by the use of a double electrode which may be either cathode or anode. From measurements of the resistance of the electrolyte from one member of the double electrode to the other values have been obtained for the apparent contact resistance. These measurements have been carried out by an alternating-current bridge method, a small alternating current passing through the electrolyte between the two members of the double electrode, precautions being taken to ensure that these were at the same potential. Values of the apparent contact resistance per sq. cm. of electrode surface have thus been obtained for a wide range of continuous currents flowing through the electrolyte from the double-membered electrode to the other electrode. The data refer to the following: anodes and cathodes of nickel, copper, retort carbon, lead, gold, silver, soft and electrolytic iron, graphite, and platinised platinum in sodium hydroxide solution and in sulphuric acid solution. It is shown that the contact resistance so determined is a function of the degree of polarisation of the electrodes, of the nature of the electrodes and of the electrolyte, of the current density, of the duration of the polarisation, of the physical state of the electrode surface, and of the temperature. R. W. LUNT.

Effects of uneven distribution of current density over an electrode. E. S. HEDGES (J.C.S., 1927, 2710—2711).—In electrolysis the current tends

to concentrate at the edges and corners of a rectangular electrode, and all dependent phenomena follow the same course, *e.g.*, film formation, corrosion, or metallic deposition. Curious effects are observed with easily passivated metals. The inside of an anode may become passive and the outside active, the lower portion of the outside passive and the upper active near the liquid line, or only the corners and edges of an electrode may be passive. The inside of a cobalt electrode sometimes dissolves to give a solution of green cobaltic ions, whilst on the outside a pink cobaltous solution is formed. Periodic phenomena have been observed, but they do not consist of an alternation of the active and passive regions as required by Adler's theory (A., 1912, ii, 891). In fact they do not differ from those observed at higher current densities when the whole surface of the electrode becomes alternately active and passive. In addition, electrodes have been examined which, although differentiated into active and passive zones, do not dissolve periodically. M. S. Burr.

Flame and combustion. W. A. Bone and D. T. A. Townend (Nature, 1927, **120**, 880).—Polemical. A. A. Eldridge.

Ignition of natural gas–air mixtures by heated metal bars. H. F. Coward and P. G. Guest (J. Amer. Chem. Soc., 1927, **49**, 2479—2486).—Wide metal bars ignite mixtures of natural gas (93·2% of methane) and air more readily than narrow bars, and metals of greater catalytic effect must be much hotter than those of smaller catalytic effect. This temperature difference may attain several hundred degrees. For nickel, tungsten, and certain steels the ignition temperature rises regularly with increasing natural gas content, although for platinum the most violently explosive mixtures require the highest temperatures. Iron bars did not give reproducible results. Catalytically active solid surfaces tend to raise the ignition temperature of the mixture; nickel exhibits definite catalytic action as compared with silica. Moderate turbulence brings inflammable gas into the zone of burnt-out mixture and this raises its temperature (possibly to the ignition point) when it is near to, but not on, the heated surface. S. K. Tweedy.

Thermal decomposition of ozone. E. H. Riesenfeld and W. Bohnholtzer (Z. physikal. Chem., 1927, **130**, 241—276).—The thermal decomposition of ozone in the dark has been investigated using a Warburg differential manometer. The values of the concentration, c, and of the velocity of decomposition, $\Delta c/\Delta t$, in mol. per litre were derived by graphical means. The decomposition of ozone in pure ozone–oxygen mixtures can be resolved into two reactions, one unimolecular and the other bimolecular. At a pressure of 400 mm. and a temperature of 90°, the velocity coefficients k_1 and k_2 of these reactions have the mean values $0·488\times10^{-2}$ and 2·30, respectively, and at 99·5°, the values $0·673\times10^{-2}$ and 6·34. These are maximal values for the limiting velocity of decomposition, *i.e.*, the decomposition obtained when accelerators of the reaction are excluded. The bimolecular reaction is independent of pressure, but the unimolecular reaction is inversely proportional to the total pressure prevailing at a given time. The temperature coefficient between 90° and 100° for the unimolecular reaction is 1·8 and for the bimolecular reaction 2·94; near 90°, the velocity of decomposition can be expressed by the formula $\Delta c/\Delta t=(1·8c\,.\,P^{-1})1·8^{(t-90)/10}+(2·30c^2)2·93^{(t-90)/10}$, where P is the total pressure in mm. of mercury and c is the concentration in mol. per litre. The values for the limiting velocity of decomposition agree with those of previous workers, and since this velocity is independent of the size, shape, and material of the reaction vessel, it is assumed that both reactions are of the homogeneous type. Traces of catalysts have a marked effect, a hundredfold increase being not unusual. Two types of catalysis have been observed, the one, as produced by dust particles, for example, proceeding as a unimolecular reaction, and the other, which is produced by gaseous organic substances, showing a high and uncertain order of reaction, explicable on the assumption that the catalyst is destroyed during the course of the reaction. The addition of carbon dioxide, nitrogen, helium, or argon accelerates the decomposition of ozone. The bimolecular reaction increases whilst the unimolecular reaction, in consequence of the increase in pressure, decreases. Referred to the same pressure of ozonised oxygen, the unimolecular reaction is retarded, but referred to the same total pressure it is accelerated. L. S. Theobald.

Thermal decomposition of ozone. Computation of velocity coefficients determined by the manometric method. R. O. Griffith and A. McKeown (J. Amer. Chem. Soc., 1927, **49**, 2721—2729).—A reply to the criticism of Wulf and Tolman (A., 1927, 631). Velocity coefficients of the above reaction may be vitiated by incorrect interpretation of the observed pressure differences and by erroneous estimation of the pressure corresponding with total decomposition. Warburg's data (A., 1902, ii, 130) suffer slightly from the first error; Wulf and Tolman's data are vitiated more seriously by the second error, and Jahn's results (A., 1906, ii, 225) suffer very considerably from both errors. S. K. Tweedy.

Velocity of interaction of ions. F. G. Soper (J. Physical Chem., 1927, **31**, 1790—1797; cf. Bronsted and Livingston, A., 1927, 319).—Theoretical. The rate of interaction of ions can be represented by the equation $\log k=c+0·66z_Az_Bu^{\frac{1}{2}}$, where k is the classical velocity coefficient, z_A and z_B are the valencies of the ions, and u is the ionic strength. The potential energy possessed by the ions in virtue of their charges is regarded as contributing to the critical increment of the reaction, and is evaluated on the Debye–Hückel theory. The velocity equation has been tested by determining graphically the value of the constant of the last term, using the data of other investigators for the reactions between the following pairs of ions: iodide and persulphate, formate and silver, hydroxyl and dibromosuccinate, iodide and iodate, and ferric and stannous. The average value of the constant is $0·62\pm0·13$. L. S. Theobald.

Effect of shaking on the evolution of gases from supersaturated solutions and its importance for the measurement of the velocity of certain

chemical reactions. K. J. PEDERSEN (J. Amer. Chem. Soc., 1927, 49, 2681—2689).—The velocity of the unimolecular action of acid with sodium hydrogen carbonate (Faurholt, A., 1925, ii, 295) passes through a maximum as the number of horizontal shaking impulses given to the solution per minute is progressively increased; the length of each impulse also has an effect. The maximum is attributed to a kind of resonance effect on the motion of the liquid in the vessel. A mathematical expression for the velocity of evolution of gas during a reaction is derived and numerical examples illustrating its application are given. The importance of the results in avoiding the supersaturation error in certain reaction-velocity measurements is discussed (cf. Bronsted and King, A., 1925, ii, 1171). S. K. TWEEDY.

Determination of the kinetics of excessively rapid reactions by separation of the reactions. E. ABEL and R. SIEBENSCHEIN (Z. physikal. Chem., 1927, 130, 631—657).—Periodic acid does not react directly with iodides with the formation of free iodine, but is first reduced to iodic acid, which then reacts in the usual way with a further quantity of iodide. The kinetics of the reactions involved are discussed. H. F. GILLBE.

Kinetics of the addition of water to oxy-compounds. New hydrogen-ion catalysis. L. SMITH, G. WODE, and T. WIDHE (Z. physikal. Chem., 1927, 130, 154—166).—The catalytic activity of nitric and perchloric acids in the addition of water to epichlorohydrin and to ethylene oxide has been investigated. Catalysis by the hydrogen ion takes place, the nature of the anion being of little importance in the first case. In aqueous solution the elements of hydrochloric acid quickly unite with epichlorohydrin, the reaction being of the third order, but with the other acids addition of water is much slower. Catalytic activity of the hydrogen ion is also shown in the case of trimethylene oxide and sulphuric acid. In all cases the addition of water in neutral solution is extremely slow. L. S. THEOBALD.

Decomposition of triethylsulphonium bromide in mixed solvents. R. F. CORRAN (Trans. Faraday Soc., 1927, 23, 605—614).—The velocity coefficients of the unimolecular decomposition of triethylsulphonium bromide have been determined at 80° and 90° in mixtures of benzyl alcohol with toluene and glycerol, respectively. In general the reaction in organic solvents reaches practical completion, but in the mixtures containing glycerol an equilibrium was obtained and a correction for it applied to the velocity coefficients in these mixtures. The results show that the rate of decomposition is increased by toluene and decreased by glycerol. Both solvents, however, cause a fall in the apparent critical increments of activation as calculated from the temperature coefficients. This indicates anomalous behaviour on the part of the glycerol. The absorption spectra of the salt in various mixtures have been determined for the short infra-red region by the methods of Taylor and Lewis (J.C.S., 1922, 121, 665), the radiomicrometer being replaced by a thermopile and Moll galvanometer. With the benzyl alcohol–toluene mixtures there is a shift in the position of the band head which is in satisfactory agreement with the alteration in the observed critical increment. For the glycerol mixtures the head of the band shifts towards the shorter wave-lengths, which is opposite to that calculated from the critical increment, but in the direction to be expected from the effect of glycerol on the velocity coefficient. Therefore the band head probably gives the true critical increment. No explanation of the anomaly can be given. Investigations on the velocity of decomposition in practically dust-free propyl alcohol solutions indicate that the dust ordinarily present has no appreciable influence (cf. Rice, A., 1926, 917). M. S. BURR.

Oxidation of organic molecules. II. C. FROMAGEOT (J. Chim. phys., 1927, 24, 623—656; cf. A., 1926, 1124).—Acetaldehyde is slowly oxidised by ceric ions when the former is present in great excess. The oxidation may be attributed to a relatively small number of abnormally reactive molecules, consisting probably of hydrated vinyl alcohol, and the velocity of the reaction is conditioned by the speed of formation of these active molecules. Similar keto-enol tautomerism is indicated by a study of the ultraviolet absorption spectrum of pyruvic acid in aqueous solution at varying concentration and p_H. Ceric ions oxidise the ketone form instantaneously and the enol form more slowly but with the absorption of a larger amount of oxygen. There is no difference in the behaviour of the two forms towards thallic ions, the oxidation being much slower in this case. An approximate calculation of the proportions of the two forms present under various conditions has been made, and it is shown that the oxidation of the ketone form by ceric ions takes place in accordance with the equation $Ac\cdot CO_2H+0\cdot 5O_2 \longrightarrow AcOH+CO_2$. Evidence is given of the formation of an intermediate complex between the ceric ions and the pyruvic acid. G. A. ELLIOTT.

Mutarotation. III. Dextrose equilibria in methyl alcohol and mixtures of methyl alcohol and water. J. C. ANDREWS and F. P. WORLEY (J. Physical Chem., 1927, 31, 1880—1883).—The equilibrium optical rotation of dextrose in methyl alcohol and in mixtures of methyl alcohol and water has been measured. The proportion of α-glucose is increased as water is replaced by methyl alcohol. No change in the optical rotation could be detected after dissolving in methyl alcohol or water mixtures of α- and β-glucose in the calculated proportion for equilibrium. The results are considered not to eliminate the possibility of the formation of an intermediate substance, although none could be detected. L. S. THEOBALD.

Mutarotation and the reaction of the solution. H. COLIN and (MLLE.) A. CHAUDUN (Bull. Soc. chim., 1927, [iv], 41, 1461—1465).—The effect of lithium and calcium hydroxides on the rate of mutarotation of dextrose is similar to that of sodium hydroxide (A., 1927, 426) for concentrations below $N/500$. The accelerating influence of methylamine is greater than that of ammonia, and is even greater than would be expected from its conductivity, the active agent being assumed to be the hydroxyl ion. Carbamide at a concentration of 2%, and pyridine in

$0{\cdot}01N$-solution have no effect whatever. The rate of transformation of dextrose is accelerated by all acids, except at very high dilutions, whereas the mutarotation of lævulose is retarded by weak acids at all dilutions, and by strong acids in very dilute solution, but is promoted by concentrated strong acids.

R. CUTHILL.

Hydrolysis of the peptide (-CO·NH-) linking. A. I. ESCOLME and W. C. M. LEWIS (Trans. Faraday Soc., 1927, **23**, 651—660).—The rate of hydrolysis of acetylglycine at 60° and 70°, and of benzoylglycine at 80° and 90°, by hydrochloric acid of different concentrations, has been determined in aqueous solutions, and also in solvents consisting of mixtures of water with glycerol, propyl alcohol, and potassium chloride, respectively. In all cases the reaction is unimolecular. Under all conditions the same critical increment of activation has been obtained for both amino-acids, namely, 22,000 g.-cal. No quantitative statement of the mechanism of the process involved has been found possible, but the results suggest that the activity of the hydrogen ion and of the water are important factors, except where a strong electrolyte, such as potassium chloride, is present, when the activity theory becomes inapplicable. The results also suggest that the activity of the substituted amino-acid, which should logically enter into any "activity" theory of chemical change, cannot differ much from the ordinary volume concentration. With the object of getting further information on this point, solubility determinations of acetylglycine and benzoylglycine in mixtures of water, glycerol, and hydrochloric acid have been made. The addition of glycerol, however, diminishes the solubility of acetylglycine, whilst it increases that of benzoylglycine.

M. S. BURR.

Activity theory of reaction velocity. Interaction of *N*-chloroacetanilide and hydrochloric acid. F. G. SOPER and D. R. PRYDE (J.C.S., 1927, 2761—2770).—The velocity equation for those reactions which involve neutral molecules and are catalysed by acids is discussed. The classical velocity coefficients are not true constants, and the use of an equation of the type $v=kC_{\text{catalyst}}\,C_AC_B$ for determining the effective concentration of the catalyst is not justifiable. Defining the activity a_A of a substance in the usual way, the simplest type of the modified velocity equation is $v=ka_Aa_B$. This equation is supported by measurements of the rate of interaction of *N*-chloroacetanilide with hydrochloric acid. The speed of this transformation, which involves two successive stages (cf. Orton and Jones, Rep. Brit. Assoc., 1910, 85), is approximately equal to that of the first stage, viz., the formation of chlorine. The rate of formation of chlorine was measured in the presence of acetanilide, phenol, and *p*-cresol. Correction of this rate for the speed of hydrolysis of *N*-chloroacetanilide to hypochlorous acid gave that of the direct interaction of the chloroamine and hydrochloric acid. The activity of the chloroamine in presence of hydrochloric acid was deduced from solubility measurements, and the activity of the un-ionised hydrochloric acid was replaced by the activity product of the hydrogen and chlorine ions. The reaction velocity is also shown to be independent of viscosity.

O. J. WALKER.

Velocity of hydrolysis of phenylsuccinimide derivatives. A. SANNA (Gazzetta, 1927, **57**, 761—771).—The velocity of hydrolysis of the following phenylsuccinimides in alcohol by alcoholic sodium hydroxide solution has been determined at 25°: *o*-, *m*-, *p*-nitro-; *o*-, *m*-, *p*-chloro-; *o*-, *m*-, *p*-bromo-; *o*-, *m*-, *p*-iodo-phenylsuccinimide. The data indicate that the reaction is bimolecular.

R. W. LUNT.

Chemical reactivity of atoms and groups in organic compounds. J. F. NORRIS (Z. physikal. Chem., 1927, **130**, 662—672).—The velocity coefficients of the reaction between ethyl alcohol and substituted derivatives of benzoyl chloride (at 0°) and of diphenylchloromethane (at 25°) have been measured at about $0{\cdot}1M$-concentration. The influence of substituents is the reverse for the two series of compounds, and is much greater for the alkyl derivatives. The reactivity of the chlorine atom in the acyl compounds is influenced more by the position than by the nature of the substituent; the influence of position decreases in the order ortho, meta, para. Negative groups in all positions increase lability, but the tendency of positive groups to decrease reactivity is masked in the ortho-position. Diphenylchloromethane is considerably more labile than benzoyl chloride: the velocity coefficient for the acyl chloride increases 9 times between 0° and 25°, whereas for the alkyl chloride the constant increases 26 times.

The reactivity of the hydroxyl hydrogen atom in a number of alcohols has been studied by measuring the rate of reaction of the alcohol with *p*-nitrobenzoyl chloride at 25°. For the normal primary alcohol series the reactivity of the hydroxyl hydrogen atom decreases with the first three members, increases with the next three, and finally decreases. For secondary alcohols with the hydroxyl group in position 2 the reactivity decreases with the first three members and then increases. A similar periodicity in cycles of three is produced by the introduction of methyl groups. In a straight carbon chain the position of the hydroxyl group is of very great influence on the reactivity. In the aromatic alcohol series the reactivity alternates as the distance between the phenyl radical and the hydroxyl group increases.

Preliminary measurements have been made of the reactivity of the hydroxyl group in alcohols by study of the reaction between the alcohol and hydrogen bromide. Increase of chain length of both the primary and secondary alcohols causes alternation of the reactivity, which is also influenced considerably by the position of a methyl group as a side-chain.

H. F. GILLBE.

Relation between rate of stirring and velocity of reaction in heterogeneous systems. A. KLEINÓWNA (Rocz. Chem., 1927, **7**, 159—162).—Polemical, in reply to Bekier and Rodziewicz (A., 1927, 426).

R. TRUSZKOWSKI.

Effect of alkali on oxidation of sodium sulphite with air. S. MIYAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 40—45).—See A., 1927, 525.

Effect of alkali on oxidation of ferrous hydroxide with air. S. MIYAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 35—39).—See A., 1927, 425.

Heterogeneous thermal decomposition of ammonia in strong electric fields. R. E. BURK (Proc. Nat. Acad. Sci., 1927, **13**, 719—720).—Electric fields up to 150,000 volts per cm. have no effect on the rate of decomposition of ammonia on electrically heated wires. W. E. DOWNEY.

Dissolution velocity of zinc in a current of sulphuric acid. M. STRAUMANIS (Z. physikal. Chem., 1927, **129**, 370—388).—The rate of dissolution of the metal has been determined by a method in which the acid is allowed to flow at a constant rate on to a fixed horizontal plate of the metal, collected in a vessel below, and returned by means of a pump to its original position so as to maintain a continuous flow. The quantity of metal dissolved is measured in terms of the volume of hydrogen evolved. The variation of the dissolution velocity of zinc in 0·5*N*-sulphuric acid in presence of cupric, nickel, silver, bismuth, and cobaltous sulphates and auric chloride at various concentrations has been determined. The accelerating influence of these metals is not in the same order as their position in the electropositive series. The velocity during the induction period of the reaction, *i.e.*, before the catalysing metal has deposited on the zinc plate, is a linear function of the time. Change of the velocity of the acid stream has but little influence on the rate of dissolution. The rate of dissolution of zinc and of cadmium in dilute sulphuric or hydrochloric acid in presence of other metallic salts indicates that the whole process may be qualitatively explained on the theory of local currents, if due consideration be attached to the variation of the over-voltage and of the potential of the dissolving metal with the current strength and with the concentration and nature of the acid. H. F. GILLBE.

Corrosion of lead by mineral waters. P. KAJA.—See B., 1927, 911.

Effect of addition of some alkaloids on the rate of dissolution of iron in dilute hydrochloric acid. II. Effect of nicotine, narcotine, and gelatin, and the fall of *E.M.F.* produced in the iron in presence of brucine. M. B. RANE (J. Indian Chem. Soc., 1927, 4, 387—395; cf. A., 1925, ii, 410).—The increase in the rate of dissolution of iron wire in hydrochloric acid is not due to the catalytic influence of the iron salt formed during the reaction, but probably to the capillaries produced in the iron (cf. McCulloch, A., 1925, ii, 879). The inhibiting effect of alkaloids on the evolution of hydrogen has been observed with nicotine and narcotine. Gelatin has a similar effect, but no effect is observed with sucrose, dextrose, aniline hydrochloride, phenol, cresol, nitrobenzene, and phenylenediamine. The *E.M.F.* of iron in contact with *N*-hydrochloric acid and *N*-ferrous sulphate falls when small quantities of brucine are added. H. BURTON.

Silver-ion catalysis of persulphate oxidations. I. Salt effect on the velocity of oxidation of ammonia. II. Comparison of the velocity with various reducing agents. C. V. KING (J. Amer. Chem. Soc., 1927, **49**, 2689—2699).—The influence of hydroxides in the above oxidation reaction observed by Yost (A., 1926, 365) is a perfectly general salt effect conforming to Bronsted's theory (assuming the reaction course deduced by Yost), since the same results are obtained in the presence of added nitrates. The sodium ion has less effect than the potassium ion. The reaction is only pseudo-unimolecular in that range of salt concentration in which change of ionic concentration during the reaction counteracts the consumption of ammonia. The reaction $S_2O_8'' + C_2O_4'' \longrightarrow 2SO_4'' + 2CO_2$ in presence of silver ions is very much more rapid than would be expected, and it appears that the nature of the reducing agent may have some influence on the velocity. S. K. TWEEDY.

Effect of hydrochloric acid on the oxidation of stannous chloride with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1927, **2**, 259—269).—The catalytic effect of hydrochloric acid on the atmospheric oxidation of stannous chloride has been investigated. With hydrochloric acid concentrations of less than about 0·25*N*, the order of the reaction is between first and zero. Above that concentration the velocity is independent of the stannous chloride concentration. The temperature coefficient between 20° and 40° is small. C. W. GIBBY.

Application of the interference method to the determination of the surface area of metallic nickel films. F. H. CONSTABLE (Nature, 1927, **120**, 769—770).—A nickel film, electrolytically deposited on china clay coated with graphite, was activated by oxidation in air and reduction by hydrogen at 520°. The surface area per unit mass was calculated from the slope of the straight line obtained on plotting the conductivity against the equivalent air thickness corresponding with the colour shown by the partly oxidised rod. The results show that the surface of electrolytic nickel is 1·84 times the apparent area, and that the apparent surface may be considerably increased by reduction at 400°. A. A. ELDRIDGE.

Catalysis by nickel of the union of hydrogen and oxygen. D. R. HUGHES and R. C. BEVAN (Proc. Roy. Soc., 1927, **A**, **117**, 101—108).—Nickel wires were heated in hydrogen and mixtures of hydrogen with oxygen, the current and corresponding fall of potential of the wires being measured. The same current raised the temperature of the wire more when it was in hydrogen than when it was in the mixture, from which it is concluded that the surface of the wire was in a very different condition in the two experiments. The wire was (*a*) previously heated in hydrogen, (*b*) heated in a mixture of hydrogen and oxygen at a temperature well below that of combination, and (*c*) heated in oxygen until it had become visibly oxidised, and in each case subsequently heated in hydrogen at a pressure of 12910×10^{-6} mm. and the resistance determined. For a given current the temperature of the visibly oxidised wire was the same as that of the wire which had been heated in the mixture, whereas the nickel which had not been in contact with oxygen was at a much higher temperature. It is concluded that when nickel is heated in the mixture it becomes completely covered with a layer of oxide, and that a hydrogen molecule leaving the surface removes more energy than one leaving the metal surface at the same temperature.

The coefficient of radiation of the oxidised wires was found to depend on the thickness of the oxidised

sheath, in contrast with the average heat removed from the surface by an escaping molecule of hydrogen, which depends only on the nature of the surface. From determinations of the temperature coefficient of resistance of a nickel wire, the "accommodation" coefficient of hydrogen in contact with the respective surfaces was calculated, and found to be 0·25 for nickel, 0·48 for oxidised nickel, at a temperature of 164°. The value for oxygen in contact with oxidised nickel was 0·95. The rate of formation of water on thinly and visibly oxidised wires, respectively, was practically the same. From experiments on the rate at which a reduced wire is oxidised when brought into contact with a standard oxygen–hydrogen mixture at a temperature at which the gases will combine at a measurable rate, it is shown that the reduction of the oxidised wire does not start all over the outer surface of the oxide film, but that either the hydrogen penetrates the film, and the reduction occurs at the junction of the metal and the oxide, or the reduction starts at nuclei. Of the two alternatives, the former seems more probable when the film is thin.

L. L. BIRCUMSHAW.

Colloidal palladium as catalyst at the hydrogen electrode. E. BIILMANN and A. KLIT (Z. physikal. Chem., 1927, **130**, 566—571).—An investigation has been made of electrodes at which the reaction H_{gas} $H^{\cdot}$ is catalysed by colloidal palladium. At polished platinum and gold electrodes similar potentials are obtained to those at ordinary platinised electrodes under the usual conditions. The extent to which the electrodes become polarised is dependent on the concentration of the colloidal palladium; only with concentrations above 2 mg. of palladium per litre can a well-defined measurable potential be obtained.

H. F. GILLBE.

Catalyst for hydrogenation in the cold, and mechanism of this catalysis. M. BOURGUEL (Bull. Soc. chim., 1927, [iv], **41**, 1443—1450).—Experiments have been made on the reduction of hydrocarbons in the cold with a catalyst prepared by reducing sodium chloropalladite with hydrazine hydrate in the presence of starch as protective colloid. In the reduction of acetylenes and of acetylenic acids and alcohols, there is an abrupt change in the rate of reduction when the amount of hydrogen taken up is exactly equal to 2 atoms per mol. of the unsaturated compound, and at the same time, and not before, the substance ceases to react with cuprous chloride. In explanation of the results, Armstrong and Hilditch's theory is advocated, a palladium–hydrogen complex being formed first, then adding on the organic substance, and finally decomposing into the metal and reduced compound. As it is observed that in the reduction of a liquid immiscible with water the palladium is removed from its aqueous colloidal solution to form a film at the interface of the two liquids, the formation of an oriented layer of the palladium–hydrogen complex is suggested, the hydrogen atoms being directed towards the organic liquid and attracting molecules of the acetylene type in preference to those of the ethylene type.

R. CUTHILL.

Catalytic formation of methane from carbon monoxide and hydrogen. III. Study of various catalysts. K. CHAKRAVARTY and J. C. GHOSH (J. Indian Chem. Soc., 1927, **4**, 431—436).—The effects of various catalysts, mostly mixed metallic hydroxides, for the reaction $2CO+2H_2=CH_4+CO_2$ have been studied, and it is found that whilst some of them, *e.g.*, nickel hydroxide on aluminium hydroxide, were active at 300°, they were not steady, and the rate of fall of activity was rapid. The sugar charcoal–nickel catalyst on pumice (A., 1925, ii, 1175) is more active if 50% more nickel is used in its preparation and, in contradistinction to the others used, loses its activity very slowly.

H. BURTON.

Oxidation of ammonia in presence of contact catalysts. IV. J. ZAWADZKI and H. NARKIEWICZ (Rocz. Chem., 1927, **7**, 369—379).—The catalytic action of platinum gauze on ammonia and oxygen may be represented graphically by a series of closed curves, the co-ordinates of which are the temperature and the velocity of the current of gas mixture. By taking finer gauze and increasing the number of layers through which the gases pass, the optimum point of oxidation to nitric oxide is shifted towards the region of higher temperature and shorter contact, so that yields of more than 90% may be obtained above 1000°.

R. TRUSZKOWSKI.

[Catalytic] oxidation of ammonia. F. RASCHIG. —See B., 1927, 906.

[Catalytic] oxidation of ammonia. G. B. TAYLOR.—See B., 1927, 936.

Decomposition of carbon monoxide by reduced copper below 400°. A. STEOPOE (Bul. Chim. Soc. Romana Stiin., 1926, **29**, 79—82).—A reduced copper catalyst was prepared by passing a current of carbon monoxide over cupric oxide precipitated on asbestos. The cupric oxide had been dried below 120°, and reduction was carried out at 200°. On continued passage of carbon monoxide over this catalyst carbon dioxide was formed (*a*) by reduction of some residual cuprous oxide, and (*b*) by decomposition of the carbon monoxide. The extent of each reaction was determined by measuring the amount of carbon dioxide produced and the variation in weight of the catalyst. The yield of carbon dioxide due to reaction (*b*) increased from 0·46% at 200° to 1·43% at 350°. Similar results were obtained with a catalyst prepared in the same way from commercial copper sulphate.

A. B. MANNING.

Action of acetylene on metals yielding explosive acetylides. J. F. DURAND and M. BANOS (Bull. Soc. chim., 1927, [iv], **41**, 1294—1299). —When dry acetylene is passed over finely-divided silver, some reaction occurs at 400°, and at 600° a brilliant flame appears, moving against the gas current. During this phenomenon hydrogen is evolved, carbon is deposited on the silver, and silver is deposited on the tube in which the experiment is carried out. With gold, the phenomenon is observed at 480°. Using copper, preheated at 400° in a stream of carbon dioxide, the phenomenon is observed at 480°, the flame appearing and disappearing regularly to 620°, when it disappears. On cooling, the phenomenon reappears at 480°. Similar results are

obtained using mercury, the phenomenon appearing at 540°, continuing rhythmically to 680°, and then disappearing. In view of the results using mercury (vapour), it is concluded that the phenomenon is due to chemical catalysis, and not to adsorption on the metal. H. BURTON.

Catalytic oxidation of ethyl alcohol. G. FESTER and G. BERRAZ (Anal. Asoc. Quím. Argentina, 1927, **15**, 210—215).—The oxidation of ethyl alcohol by air when passed over heated catalysts has been studied. Vanadium pentoxide, silver vanadate, and copper vanadate deposited on silica, silver vanadate on fuller's earth, and zinc oxide were used as catalysts. Acetaldehyde, acetic acid, and carbon dioxide were determined in the products.

The principal product was always acetaldehyde (up to 23·8% with silver vanadate). The optimum temperature was about 360°. Above this, excessive formation of carbon dioxide took place. The optimum combination of high yield of acetaldehyde and low carbon dioxide formation was obtained with vanadium pentoxide (9—13% and 2—5%, respectively) and zinc oxide (10·7% and 4·8%). R. K. CALLOW.

Catalytic oxidation of gaseous cyanogen to nitric oxide, and the intermediate product. S. ABE and R. HARA (Tech. Repts. Tohoku Imp. Univ., 1927, **7**, 1—23).—Experiments in which gaseous cyanogen was oxidised with air in presence of various catalysts show that the first stable products are nitric oxide and carbon monoxide and that under the most favourable conditions more than 90% of the cyanogen is thus oxidised. With the most efficient catalyst, platinum net, production of nitric oxide begins rather abruptly at about 450—550° and is maximal at about 700—800°. At higher temperatures conversion of cyanogen into free nitrogen commences. At each temperature there appears to be an optimum velocity of gas flow. Maximum yields are obtained with a rapidly-flowing inlet gas containing 4% of cyanogen. Platinised asbestos, ferric oxide, nickel oxide, and copper oxide are also efficient catalysts. With ferric oxide and nickel oxide considerable quantities of carbon are deposited under certain special conditions, *e.g.*, high concentrations of cyanogen. Under certain conditions and with copper oxide as catalyst yellowish-vermilion solid deposits were found in the exit tube of the furnace. On heating, this substance yields a white sublimate and a residue containing copper. In presence of copper oxide, oxidation of cyanogen occurs at temperatures of the order 220—230°.

The walls of the tube eventually became coated with a minute quantity of a white *substance*, $C_3H_2ON_4$, produced by the action of moisture on a transparent yellow *compound*, C_2N_2O, thus: $2C_2N_2O+H_2O=C_3H_2ON_4+CO_2$. The catalytic oxidation of cyanogen is therefore represented by the equations: $2C_2N_2+O_2=2C_2N_2O$; $2C_2N_2O+3O_2=4CO+4NO$.

The isolation of an intermediate compound, together with the discovery that cyanic acid is formed at an intermediate stage in the oxidation of hydrogen cyanide (Hara and Sinozaki, A., 1925, ii, 983), suggests that in the catalytic oxidation of ammonia the first reaction is not the production of nascent or atomic nitrogen, but rather the formation of some intermediate compound containing oxygen.

J. S. CARTER.

Catalytic activity and adsorptive power of supported iron, cobalt, nickel, copper, and silver. R. N. PEASE and L. STEWART (J. Amer. Chem. Soc., 1927, **49**, 2783—2787).—The above metals deposited on diatomite brick were used as catalysts in the hydrogenation of ethylene. The catalysts were similarly prepared and are therefore comparable. Cobalt and nickel caused instantaneous action at $-20°$; iron was moderately active at 0°, copper at 50°, and silver at 100°. A support gives stability where it is needed, but it yields a catalyst of somewhat smaller surface. Supported copper is a poorer catalyst than the unsupported material. This metal can be reduced at comparatively low temperatures, and the use of a support, which obviates reduction at high temperatures and the accompanying sintering and deactivation, is of no particular advantage as it is in the case of the other metals. More hydrogen is adsorbed by nickel and cobalt than by the other metals, and more ethylene by iron. In the presence of silver at 100° the reaction rate is proportional to the hydrogen, and independent of the ethylene, concentration (Pease, A., 1923, ii, 862). In the presence of iron at 0° excess of hydrogen increases the rate, whilst excess of ethylene has little influence. Heats of activation are recorded. The highly active hydrogenation catalysts are those metals which in ionisation produce large numbers of stable complexes in solution. This is probably due to a capacity for electron sharing, and it may be that this associative property of the metal brings the reactants together and renders them both labile, so that a system of lower free energy is produced. S. K. TWEEDY.

Aluminium ovens for catalytic purposes. F. FISCHER and H. TROPSCH.—See B., 1927, 927.

Electrolytic deposits of cadmium for the protection of metals and alloys against corrosion. J. COURNOT and J. BARY.—See B., 1927, 910.

Electromotive behaviour of complex cyanides of manganese and the cyanide, $K_3Mn(CN)_4$. G. GRUBE and W. BRAUSE (Ber., 1927, **60**, [*B*], 2273—2278; cf. Bellucci and Corelli, A., 1914, i, 260; Grube, A., 1927, 119; Manchot and Gall., *ibid.*, 220).—Crystalline potassium manganocyanide is conveniently prepared by the action of aqueous potassium cyanide on manganese carbonate at 70—80° in an atmosphere of hydrogen. It is converted by prolonged oxidation in warm solution by air into potassium manganicyanide. The manganous salt is stable in aqueous solution only in the presence of an excess of potassium cyanide; it is quantitatively oxidised by potassium ferricyanide to manganicyanide, the end-point being readily determined potentiometrically. The normal potential of the process $Mn(CN)_6'''' + \oplus \rightleftharpoons Mn(CN)_6'''$ is $-0·225\pm0·004$ volt or $-0·223\pm0·004$ volt in 1·54N- or 2·3N-potassium cyanide solution. The *compound* $K_3Mn(CN)_4$ is prepared by electrolytic reduction of a solution of potassium mangano- and mangani-cyanide in aqueous potassium cyanide at 1—2° in a diaphragm cell from which air is excluded; the anolyte is 1·5N-potassium cyanide solution and

polished platinum foil electrodes are employed. It is an unstable, colourless compound which, even at a low temperature, readily decomposes water and passes back into the manganocyanide. H. WREN.

Relative stability of nitrous oxide and ammonia in the electric discharge. W. K. HUTCHISON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1927, A, **117**, 131—136).—The stabilities of nitrous oxide and of ammonia under electrical excitation were compared by measuring the effect of the same discharge passed simultaneously through the two gases in series, in parallel, and independently through each alone. The increase of pressure in the discharge tubes due to the decompositions was calculated for different initial pressures and with different times and strengths of discharge, using platinum, aluminium, and glass electrodes. When the discharge is feeble, the absolute amount of decomposition is independent of the initial pressure of the gas, but with increasing intensity of discharge the amount of decomposition becomes proportional to the initial pressure. All measurements were made with discharges sufficiently intense to bring the reaction into this " unimolecular " region, and in all cases the ammonia appeared to be 5—7 times as difficult to decompose as the nitrous oxide. The results agree in a general way with what might be expected from the known thermal reactions.

L. L. BIRCUMSHAW.

Electrochemical preparation of Scheele's green. B. P. BRUNS.—See B., 1927, 947.

Electrolytic oxidation of *p*-toluic acid in alkaline solution. A. J. ALLMAND and A. PUTTICK (Trans. Faraday Soc., 1927, **23**, 641—650).—An attempt has been made to increase the efficiency of the electrolytic process for the oxidation of *p*-toluic acid in alkaline solution to terephthalic acid by the superposition of an alternating current on the direct current. With direct current alone the highest current efficiency, 16%, is obtained at a platinum anode with a current density of 4 amp./sq.dm. in $2N$-potassium hydroxide containing $0{\cdot}25N$-potassium *p*-toluate. Discoloured solutions are obtained when the free alkali concentration is decreased, and the yield is lowered when either alkali or salt concentration is increased, or the current density is increased or decreased. With superposed alternating current, whether of frequency 50 or 500, or of high or low current density, no improvement in efficiency is effected, and with currents of low frequency, or with large currents of high frequency, the efficiency is definitely lowered. There are three anodic processes, (i) evolution of unutilised oxygen, (ii) oxidation of *p*-toluic acid to terephthalic acid, (iii) complete oxidation of *p*-toluic acid with formation of carbon monoxide and carbon dioxide. The action of the alternating current is to favour (i) and (iii) more than (ii). Anode potential measurements have been made, and it is impossible to trace any connexion between these and the different terephthalic acid yields.

M. S. BURR.

Electrolytic reduction and reactions in the glow discharge at the liquid-gas interface. A. KLEMENC (Z. physikal. Chem., 1927, **130**, 378—389). —The behaviour on electrolysis, using a Wehnelt gas electrode, of dilute and more concentrated sulphuric acid, of ferrous or ferric sulphate solution in sulphuric acid, and of potassium nitrate in potassium or sodium hydroxide solution has been examined with the object of determining whether or not the electrolytic processes at a hydrogen electrode are dependent on the presence of a solid electrode. The results with sulphuric acid confirm those previously found by Haber and Klemenc (A., 1915, ii, 212). A reduction of the ferric sulphate occurs, but it is not possible to decide whether the ferric ion is reduced by the slow electrons discharged from the gas cathode, or according to the equation $Fe^{\cdot\cdot\cdot}+H \longrightarrow Fe^{\cdot\cdot}+H^{\cdot}$. Potassium nitrate solutions undergo considerable reduction in the glow discharge, nitrous acid, nitric and nitrous oxides, and nitrogen being formed, but no ammonia. It follows that electrolytic reduction by means of hydrogen can take place when the gas is not in contact with a metal electrode. L. L. BIRCUMSHAW.

Primary decomposition of molecules in photochemical reactions. R. H. GERKE (J. Amer. Chem. Soc., 1927, **49**, 2671—2677).—Photochemical reactions are divided provisionally into three classes according as the absorption of light produces excited atoms (or molecules), causes a decomposition of molecules into atoms (" primary decomposition reactions "), or excites a catalyst or sensitiser. A given photochemical reaction may belong to the first class in one region of the spectrum and to the second class in another region. Many examples are considered. Reactions of the second class, but not of the first class, have a quantum efficiency independent of the pressure and of the wave-length of the light.

S. K. TWEEDY.

Photolytic formation of hydrogen peroxide. E. BAUR and C. NEUWEILER (Helv. Chim. Acta, 1927, **10**, 901—907).—Exposure of aqueous suspensions of zinc oxide in contact with air to sunlight results in the formation of hydrogen peroxide. According to the " molecular electrolysis " theory of photolysis (Baur, A., 1918, ii, 284) the process is represented by

$$ZnO\begin{cases}\oplus+OH'=\tfrac{1}{4}O_2+\tfrac{1}{2}H_2O\\ \ominus+H^{\cdot}+\tfrac{1}{2}O_2=\tfrac{1}{2}H_2O_2.\end{cases}$$

In presence of small amounts of glycerol, dextrose, or benzidine the yield of hydrogen peroxide is greatly increased. At the same time these added substances are themselves oxidised. Evidence has been obtained for the existence of dihydroxyacetone and possibly glycerose in exposed suspensions containing glycerol. Benzidine yields a brown, insoluble oxidation product. When zinc oxide is replaced by eosin or fluorescein formation of hydrogen peroxide is observed in presence of dextrose and benzidine, but not in presence of glycerol. J. S. CARTER.

Hydrogen peroxide formation photo-sensitised by mercury vapour. A. L. MARSHALL (J. Amer. Chem. Soc., 1927, **49**, 2763—2772).—The previous investigation (A., 1926, 252) was repeated with improved apparatus. The peroxide formed was removed practically undecomposed. The rate of hydrogen peroxide formation is proportional to the mol. fraction of hydrogen present and also to the arc current, and probably, therefore, to the light intensity. At high mercury vapour concentrations large quantities of

mercuric oxide are formed and the yield of peroxide is correspondingly low; the optimum vapour concentration is 0·005 mm. The optimum concentration of mercury vapour in the lamp for obtaining the maximum amount of resonance light (λ2536·7 Å.) is 0·01 mm. The temperature coefficient of the reaction is 1·04. S. K. TWEEDY.

Photochemical decomposition of hydrogen iodide. Mode of optical dissociation. B. LEWIS (Proc. Nat. Acad. Sci., 1927, **13**, 720—726).—The number of molecules of hydrogen iodide decomposed per quantum absorbed, using the lines 2080 and 2530 Å. of zinc, is 2·36 and 2·25, respectively.
W. E. DOWNEY.

Modified sulphide-nuclei theory of photographic sensitivity. J. SOUTHWORTH.—See B., 1927, 957.

Zinc oxide as a general sensitiser for photochemical reactions. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1927, 4, 299—306).—Exposure of solutions of 40 dyes to sunlight in presence of zinc oxide shows that the dyes absorbing light of long wave-length, *i.e.*, blue, green, violet, are bleached rapidly, then fluorescent dyes, and lastly red, orange, and yellow dyes. Alizarin-blue and methyl-orange show a slight increase in concentration, probably owing to evaporation of the solution, and no bleaching action. A list is given of 37 reactions which are sensitised by zinc oxide. The remainder of the paper is a criticism of work published by Baur (A., 1924, ii, 857; 1925, ii, 1082). H. BURTON.

Photochemical oxidation of leuco-malachite-green by uranyl nitrate in monochloroacetic acid solution. J. C. GHOSH and J. MUKHERJEE (J. Indian Chem. Soc., 1927, 4, 343—352).—The oxidation of leuco-malachite-green by uranyl nitrate is a photochemical reaction. The reaction rate varies directly as the intensity of the light and concentration of the uranyl nitrate. The life period of the excited molecules is calculated as being $4{\cdot}9\times10^{-11}$ sec. There is no temperature coefficient for the reaction. Application of Einstein's law of photochemical equivalence shows that more than one quantum of energy is necessary to transform 1 mol. of the leuco-compound. The region 478—410 μμ is most suitable for the reaction; all measurements were made within this region. Light absorbed by the malachite-green formed during the oxidation has no effect on the rate of change of the reaction. The reciprocal of the reaction rate when plotted against the reciprocal of the concentration of the leuco-compound gives a straight line.
H. BURTON.

Dehydration of hydrated salts. IV. M. A. RAZUKIN and D. A. BRODSKI.—See B., 1927, 875.

Distillation of alkali metals. R. J. CLARK (Proc. Camb. Phil. Soc., 1927, **23**, 953—955).—The metal is washed in dry ether containing 4 or 5% of alcohol, wiped with filter-paper, and dropped into a glass still of special design. The metal is melted in a vacuum, separated from the skin of oxide, and is then thrice distilled in a vacuum. The method has been used for the purification of certain halides.
W. E. DOWNEY.

Chemical nature of precipitated basic cupric carbonate. J. R. I. HEPBURN (J.C.S., 1927, 2883—2896).—The initial process which occurs on mixing equimolecular solutions of copper sulphate and sodium carbonate (cf. A., 1925, ii, 696) has been investigated, the concentration of the precipitants being varied from 1·0 to 0·00625*M*. The relationship between the carbon dioxide content of the precipitate and the concentration of carbon dioxide in the solution can be represented by a Freundlich adsorption isotherm, and the view is therefore advanced that the formation of basic cupric carbonate is due to adsorption of un-ionised carbonic acid by hydrated cupric oxide which is in a very active state. Other views regarding the nature of precipitated basic cupric carbonate are discussed. O. J. WALKER.

Basic mercurous nitrate. S. JAJTE (Rocz. Chem., 1927, 7, 156—158).—*Basic mercurous nitrate*, $3Hg_2O,N_2O_5$, crystallised from a solution containing mercurous nitrate, silver nitrate, and nitric acid after a year. R. TRUSZKOWSKI.

Separation of pure radium salts from isomorphous mixtures with barium salts. A. G. ELISEEV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 443—454).—In presence of hydrogen chloride in proportions increasing up to 11 g. per 100 g. of water, the solubility of barium chloride at 25° diminishes practically linearly; subsequently the solubility isotherm approaches the axis of abscissæ asymptotically, the whole of the salt being precipitated when 30 g. of hydrogen chloride are present per 100 g. of water. At 0°, 100 g. of water dissolve 30·7 g. of barium chloride (cf. Engel, Ann. Chim. Phys., 1888, [vi], **13**, 371). Investigation of the isotherm at 25° of the system $RaCl_2$–$BaCl_2$–HCl–H_2O shows that the solubility of radium choride is diminished by the presence of hydrogen chloride to a greater extent than that of barium chloride, and that radium chloride does not influence appreciably the solubility of the barium salt. The curves indicating the quantities of radium and barium chlorides in equilibrium with definite proportions of hydrogen chloride show that, by addition of the acid to a solution of the mixed chlorides saturated at 25° and by removing small fractions, values exceeding 2 are obtainable for the coefficient of enrichment.

These results form the basis of the industrial treatment of an ore of the composition CaO 32·01, BaO 4·63, Fe_2O_3 7·06, Al_2O_3 4·41, CuO 3·1, Bi_2O_3 trace, PbO 0·08, U_3O_8 1·49, V_2O_5 3·29, P_2O_5 0·12, As_2O_3 0·02, SO_3 2·4, CO_2 25·49%, rare earths traces. The ore was treated with hydrochloric acid and the insoluble residue boiled with 2·5 times its weight of sodium carbonate in saturated aqueous solution, the carbonates thus obtained being decomposed by hydrochloric acid. Saturation of the solution of the mixed chlorides with hydrogen chloride gave a precipitate containing all the barium and radium, most of the admixed metals, especially the vanadium, uranium, calcium, and lead, remaining dissolved. The mixed barium and radium chlorides were then subjected to fractional precipitation by means of hydrogen chloride. T. H. POPE.

Boric acids and alkali borates. IV. Solid alkali perborates. H. MENZEL [with J. MECKWITZ and W. KRETZSCHMAR] (Z. anorg. Chem., 1927, 167, 193—229; cf. A., 1927, 1043).—Addition of ethyl alcohol to a mixed solution of lithium monoborate and hydrogen peroxide precipitates *lithium perborate*, $LiBO_3,2H_2O$, or $LiBO_2,H_2O_2,H_2O$, from which, by recrystallisation from water, or by careful dehydration, the lower *hydrate*, $LiBO_3,H_2O$, or $LiBO_2,H_2O_2$, may be obtained. Further dehydration, *e.g.*, by heating at above 100° in a vacuum, leads to loss of active oxygen, and at the same time the substance acquires the property of reacting with water with liberation of oxygen, probably owing to the presence of some such substance as $(LiBO_2)_2,O_2$, and ultimately the monoborate remains. With entrance on this final stage, the crystal structure changes completely, which suggests that the perborate cannot be regarded merely as the monoborate with hydrogen peroxide of crystallisation. The perborates of potassium and ammonium apparently exist only in the form of the hemihydrates, *e.g.*, $KBO_3,0{\cdot}5H_2O$; other hydrates which have been reported are to be regarded as having been impure. Attempts to remove the water by heating lead to decomposition, as with the lithium salt, although in the case of the ammonium salt the changes are somewhat more complex, owing to oxidation and volatilisation of the cation. The structure of the alkali perborates has been considered in the light of Hermans' theory of the constitution of the borates (A., 1925, i, 500). It is considered that the only true alkali perborate is the anhydrous sodium salt (Le Blanc and Zellmann, A., 1923, ii, 415), this being a boryl derivative of sodyl hydroxide, NaO·OH, containing a boron atom with the co-ordination number 3. The other alkali perborates, on the other hand, are salts of dibasic acids containing two boron atoms with the co-ordination number 4, the lithium and hydrated sodium salts having the formula $M_2(B_2O_6,2H_2O)$ and the potassium and ammonium salts the formula $M_2(B_2O_6,H_2O)$. The division of the perborates into true and *pseudo*-salts on the basis of their reaction with potassium iodide, as suggested by Riesenfeld and Reinhold (A., 1910, ii, 33) for the percarbonates, must be rejected, as this test is influenced by purely physical factors such as solubility, and there are, moreover, all stages of transition between the two groups. R. CUTHILL.

Rare earths. P. B. SARKAR (Ann. chim., 1927, [x], 8, 207—262).—By a critical examination of the data available in the literature and by the preparation of a number of new simple and complex salts of scandium an attempt is made to determine the analogies which exist between the compounds of this element and those of other tervalent elements, the iron and the rare-earth groups, respectively. From the point of view of the solubility of its salts scandium resembles in general the elements of the rare earths, but it also exhibits many close analogies with the iron group in the crystalline form and composition of many of its complex salts. Thus the acetylacetonates of scandium are isomorphous with those of iron, and the double alkali sulphates with those of aluminium, whilst it forms a series of double alkali sulphates corresponding with the anhydrous alums which are quite unknown in the rare-earth series; its basic nitrates closely resemble those of chromium. Spectroscopic evidence obtained using a very pure sample purified by the sublimation of scandium acetylacetonate confirms its relationship with the aluminium family. No such intimate relationship is found, however, between the simple salts of scandium and those of either the rare-earth or iron group of elements, scandium occupying a transitional position between the two groups. The following new salts of scandium are described: double *thiocyanates* of the type $M_3Sc(SCN)_6,4H_2O$ of *ammonium*, *potassium*, *d* 1·8480, and *sodium*; double *sulphates* of the type $MSc(SO_4)_2$ of *potassium*, *ammonium*, *rubidium*, and *cæsium*; double *sulphates* of the type $M_3Sc(SO_4)_3$ of *sodium* $+6H_2O$, and of *thallium*: the electrolytic conductivity of scandium sulphate $Sc_2(SO_4)_3$ suggests that it is really scandium scandisulphate $Sc[Sc(SO_4)_3]$; *potassium scandium selenate* $KSc(SO_4)_2,2H_2O$; *basic nitrates* of composition $Sc(OH)(NO_3)_2,3H_2O$ [erroneously described by Crookes (A., 1909, ii, 44) as the anhydrous normal nitrate], $Sc_2O(NO_3)_4,0{\cdot}5H_2O$ (stable between 90° and 115°), and $Sc_4O_5(NO_3)_2$ (stable between 120° and 200°). Scandium hydroxide forms a crimson lake with ammonium aurintricarboxylate (Hammett and Sottery, A., 1925, ii, 601), which, unlike the corresponding aluminium lake, is very soluble in ammonium carbonate solution, the sensitivity of the test being of the order of $2{\cdot}4\times10^{-7}$ g.-atom of scandium per c.c. A similar study of various new salts of gadolinium and europium shows that these elements resemble both the cerium and yttrium groups of the rare-earth elements and form a transition between the two groups. The following new salts of gadolinium are described: *formate*; *hydrogen tartrate* $+2H_2O$; normal *tartrate* $+5H_2O$; *citrate* $+5H_2O$ and $+4H_2O$; *acetylacetonate* $+3H_2O$, m. p. 143·5—145°; nitrate $+6H_2O$, m. p. in sealed tube 91° (not $6{\cdot}5H_2O$, as described by Benedicks, A., 1900, ii, 209); *basic nitrate*, $3Gd_2O_3,4N_2O_5,3H_2O$; *antipyrine additive* compound of the nitrate $Gd(NO_3)_3,3C_{11}H_{12}ON_2$; *hexamethylenetetramine additive* compound of the nitrate $Gd(NO_3)_2,2C_6H_{12}N_4,10H_2O$; *bromate* $+9H_2O$, m. p. 80°; *thiocyanate* $+7H_2O$; double *salt* with mercuric cyanide, $Gd(SCN)_3,3HgCN_2,12H_2O$; *orthophosphate* $+5{\cdot}5H_2O$; *iodate* $+5{\cdot}5H_2O$; *perchlorate* $+8H_2O$; *periodate* $+4H_2O$; *chlorate* $+10H_2O$; *double potassium oxalate*, $K_2C_2O_4,KGd(C_2O_4)_2,4H_2O$; *double carbonates* of the type $M_2CO_3,Gd_2(CO_3)_3,nH_2O$ of *potassium* $+12H_2O$, *ammonium* $+4H_2O$, and *sodium* $+13H_2O$; salts with *potassium ferrocyanide*, $KGdFe(CN)_65H_2O$; *ferricyanide* $+4{\cdot}5H_2O$; *sulphite* $+12H_2O$ and $+11H_2O$; *double potassium chromates*, $K_2CrO_4,Gd_2(CrO_4)_3,7H_2O$ and $5K_2CrO_4,2Gd_4(CrO_4)_3,10H_2O$. The following new salts of europium are described: *oxalate* $+10H_2O$ and $+5H_2O$; *nitrate* $+6H_2O$, m. p. in sealed tube, 85°; *citrate* $+5H_2O$; *hydrogen tartrate* $+2H_2O$; normal *tartrate* $+5H_2O$; *acetylacetonate* $+3H_2O$, m. p. 136—137°; *acetate* $+4H_2O$ and $+3H_2O$; *iodate* $+5{\cdot}5H_2O$; *cyanoplatinates* $+21H_2O$, $+18H_2O$, and $+H_2O$; *carbonate* $+3H_2O$; *double potassium oxalate* $+2H_2O$; *orthophosphate* $+4H_2O$.

J. W. BAKER.

Double salt formation between thallous carbonate and carbonates of the rare earths. G. CANNERI (Gazzetta, 1927, **57**, 732—735).—The preparation of crystalline double carbonates of the general formula $R_2(CO_3)_2,2Tl_2CO_3$ (also $+6H_2O$; R being lanthanum, cerium, neodymium, praseodymium, and yttrium) is described. R. W. LUNT.

Silicic acids. IV. R. SCHWARZ and H. RICHTER (Ber., 1927, **60**, [*B*], 2263—2270; cf. A., 1925, ii, 222; A., 1927, 634).—Fused mixtures, corresponding in composition with the formulæ $Na_4Si_3O_8$ and $Na_2Si_3O_7$, become crystalline after long preservation at 500°, and then exhibit the radially arranged needles of a monotropic substance. They are, however, only mixtures of meta- and di-silicate or disilicate and silicon dioxide, since the so-called granatic acid gives an *X*-ray spectrum very closely similar to that of disilicic acid, and its vapour tension isotherms, like those of " trisilicic acid " (which appears to give an individual *X*-ray spectrum), do not give any indication of the presence of a hydrate of the required composition. Granatic and trisilicic acids cannot therefore be regarded as chemical individuals. The presence of definite hydrates is not shown by the vapour-tension isotherms of silicic acid gels obtained by cautious neutralisation of 5% solutions of sodium meta- and di-silicates with hydrochloric acid followed by thorough washing of the precipitates. Dehydration of the gels by acetone under varied conditions results in the removal of water to a content of about 13%, thus indicating the presence of disilicic acid. Its production from sodium metasilicate is explained by the displacement of the equilibrium, $2Na_2SiO_3+H_2O$ $Na_2Si_2O_5+2NaOH$, towards the right during neutralisation with hydrochloric acid. Addition of barium chloride to solutions of sodium meta- or di-silicate or sodium hydrogen silicate results in the precipitation of a mixture of barium meta- and di-silicates; if a large excess of sodium hydroxide is present, homogeneous barium metasilicate is precipitated. Barium meta- and di-silicates are obtained from solutions of lithium orthosilicate even in the presence of a large excess of lithium hydroxide. The SiO_3'' and Si_2O_5'' ions appear to be the only ones present in solutions of alkali silicates; they form an equilibrium which usually is largely in favour of the disilicate ion (cf. Hagg, A., 1926, 924). H. WREN.

Germanium. XXI. Germanium tetrafluoride. L. M. DENNIS and A. W. LAUBENGAYER (Z. physikal. Chem., 1927, **130**, 520—531).—The most satisfactory method of preparation of germanium tetrafluoride is by the thermal decomposition of pure barium fluogermanate, prepared by dissolving germanium oxide in 48% hydrofluoric acid solution and adding a saturated solution of the theoretical quantity of barium chloride; the granular precipitate, after drying at 120°, rapidly evolves gas when heated at 700°. The product, purified by fractional distillation at −104°, is a colourless, fuming gas, condensible at the temperature of liquid air to a mass of white crystals which sublime on allowing the temperature to rise. Liquid germanium tetrafluoride is produced at −15° under its own vapour pressure of 3032 mm. On passage of the gas through water a clear acid solution is at first obtained, from which, as the operation is continued, a gelatinous precipitate of hydrated germanium dioxide separates; addition of potassium hydroxide to the clear solution causes the precipitation of potassium fluogermanate. Glass in presence of moisture is rapidly etched, but quartz is not attacked below 700°. There is no indication of dissociation at 1000°. Some evidence has been obtained for the production of germanium difluoride when the tetrafluoride is passed over heated germanium. H. F. GILLBE.

Germanium. XXIII. Germanium monosulphide. L. M. DENNIS and S. M. JOSEPH (J. Physical Chem., 1927, **31**, 1716—1718; cf. A., 1927, 1156).—The optimum temperature for the preparation of germanium monosulphide by Winkler's method (A., 1886, 985) by the reduction of the disulphide in a current of hydrogen is approximately 480°. The product obtained consisted of very hard, black crystals, which were probably rhombic bi-pyramids having the faces 010, 1001, 001, 101, 110, together with thin tablets having a graphitic lustre and showing pleochroism in the thinnest flakes. The crystals are practically insoluble in mineral acids, but can be brought into solution by fusion with potassium hydroxide or by long digestion with an aqueous solution of the same reagent. L. S. THEOBALD.

Germanium. XXIV. Dihalides of germanium, tin, and lead. F. M. BREWER (J. Physical Chem., 1927, **31**, 1817—1823).—The properties of the halogen compounds of germanium, tin, and lead are compared. L. S. THEOBALD.

Production of zirconium oxide, and constitution of some zirconium salts. P. SCHMID (Z. anorg. Chem., 1927, **167**, 369—384).—Zirconium ores are most satisfactorily opened up by fusion with lime, the temperature of a gas furnace being sufficient for the process. By treating the product with an appropriate amount of hydrochloric acid, the calcium, iron, and aluminium may be brought into solution, and then by warming the residue, which contains the whole of the zirconium as calcium zirconate, with more hydrochloric acid zirconium oxychloride is obtained. Alternatively, the mass resulting from the fusion may be treated with sulphuric acid, when the calcium remains undissolved. By the action of hydrochloric acid on solutions of the oxychloride, the *compounds* $ZrOCl_2,HCl,5H_2O$, and $ZrOCl_2,HCl,6H_2O$ may be obtained. By the action of ammonia on the oxychloride, hydrogen chloride is removed, and on drying the product at 110° crystalline metazirconic acid results. This reaction shows that the chlorine atoms in the oxychloride are probably present as loosely attached hydrogen chloride. Since, further, the two molecules of water in the oxychloride dihydrate cannot be removed without decomposition occurring, this water is apparently an integral part of the structure of the molecule. These facts, and the existence of Endemann's oxychloride (A., 1875, 1162), may be explained by supposing that the oxychloride is derived from the hydroxide by two of the hydroxo-groups binding hydrogen chloride, and the other two

holding water molecules by their subsidiary valencies, the formula being $[(H_2O)_3(OH)_2Zr(OHH)_2]Cl_2,2H_2O$.
R. CUTHILL.

Zirconium. J. H. DE BOER.—See B., 1927, 941.

Compound of lead iodide with stannous iodide. N. A. TANANAEV and I. TANANAEV (Z. anorg. Chem., 1927, **167**, 341—344).—The reddish-orange compound obtained by the action of stannous chloride and potassium iodide on lead nitrate (A., 1925, ii, 324) appears to have the formula Pb_2SnI_6, although the exact composition varies somewhat with the conditions of formation. R. CUTHILL.

Constitution of nitrogen peroxide. M. BATTEGAY and W. KERN (Bull. Soc. chim., 1927, [iv], **41**, 1336—1341).—Nitrogen peroxide reacts with certain anilides in such a way as to suggest that its constitution should be represented by the formula $O:N\cdot O\cdot NO_2$; thus with *p*-toluenesulphonyl-*p*-toluidide it gives first a mononitro-, then a dinitro-derivative, and finally a nitrosoamine of the latter. With *p*-toluenesulphonylmesidide in carbon tetrachloride nitrogen peroxide yields solely the -*nitrosoamine*, $C_6H_2Me_3\cdot N(NO)\cdot SO_2\cdot C_6H_4Me$, pale brown crystals decomposed at 121—122°, and with the anilide, $CPh_3\cdot C_6H_2Me_2\cdot NH\cdot SO_2\cdot C_6H_4Me$, it yields the N-*nitrosoamine*, $CPh_3\cdot C_6H_2Me_2\cdot N(NO)\cdot SO_2\cdot C_6H_4Me$, pale yellow crystals decomposing at 110—120°. Other reactions of the peroxide, studied by Wieland and others, suggest the simple formula $O_2N\cdot NO_2$; it seems probable that the true explanation is that nitrogen peroxide in the liquid form exists in the above two tautomeric forms. A. R. POWELL.

Azido-carbon disulphide. III. Behaviour towards chlorine, bromine, and iodine. W. H. GARDNER and A. W. BROWNE (J. Amer. Chem. Soc., 1927, **49**, 2759—2763).—Solid azido-carbon disulphide reacts explosively with chlorine and bromine, but not at all with iodine. By carrying out the former reactions in cooled non-aqueous solutions *compounds* are formed, probably $ClSCSN_3$ and $BrSCSN_3$. The former is a viscous, yellow oil, formed from a white solid first produced. In ethereal solution, bromine reacts with silver azido-dithiocarbonate to form a *tribromo-azido-dithiocarbonate*, Br_3SCSN_3; in chloroform and carbon tetrachloride solutions a mixture of this with the monobromo-derivative is produced. The hydrolysis of non-aqueous solutions of the monobromo-derivative with aqueous potassium hydroxide solution probably proceeds as follows: $BrSCSN_3+2KOH=KBr+KOSCSN_3+H_2O$; $2KOSCSN_3+2KOH=K_2S_2O_3+2KCNS+2N_2+H_2O$; $K_2S_2O_3+2KOH+2KOSCSN_3=2K_2SO_3+2KSCSN_3+H_2O$. Addition of iodine to concentrated aqueous sodium azido-dithiocarbonate solution causes the immediate formation of a heavy black oil. S. K. TWEEDY.

Decomposition of the vanadyl sulphates at high temperatures. C. EICHNER (Compt. rend., 1927, **185**, 1200—1202).—In confirmation of previous results (A., 1921, ii, 554) it is shown that quadri- or quinque-valent vanadium, when heated in sulphuric acid solution, is oxidised or reduced, respectively, until a state of equilibrium is reached. Eventually most of the vanadium is precipitated as $VOSO_4$, and not as $V_2O_3(SO_4)_2$ as stated by Rosenheim and Mong (A., 1925, i, 1411). The remaining liquid contains a mixture of sulphates of quadri- and quinquevalent vanadium, tervalent vanadium (in the form of the compound $NH_4V(SO_4)_2$ of Rosenheim and Mong) being obtained only in the presence of ammonium sulphate at a temperature above 400°, when the latter decomposes and reduces the vanadium to the tervalent state. J. GRANT.

Thio-salts. III. Polyphenolic complexes. L. FERNANDES and F. PALAZZO (Gazzetta, 1927, **57**, 567—574; cf. A., 1927, 636).—Ammonium thiomolybdate gives with phenols no compound or coloration, and from the oxythiomolybdate coloured syrups only are obtained; ammonium dithiomolybdate yields, however, with pyrocatechol the *compound* $[MoO_2S(C_6H_4O_2)](NH_4)H,3H_2O$, or in presence of pyridine the corresponding *pyridine* salt. Pyrogallol yields the *compound* $[Mo_2O_3S_3(C_6H_4O_3)_2](C_5H_5N)_2H_2,3H_2O$ (if the oxythio-salt is used, ammonium thiomolybdate separates), and gallic acid the *barium* salt, $[Mo_2O_3S_3(C_6H_2O_3\cdot CO_2)_2]BaH_2,12H_2O$. Salicylic acid does not yield such compounds.

The absorption spectra of molybdosalicylic acids, of pyrocatechol molybdates, and of thiomolybdates are compared. Compounds from thiomolybdates differ from those from molybdates in that addition of a second molecule of a phenol does not intensify the colour, the co-ordination valency of the molybdenum being already partly satisfied by the sulphur atom. It is concluded that co-ordinating capacity in derivatives of gallic acid, pyrogallol, 2 : 3-dihydroxybenzoic acid, pyrocatechol, and salicylic acid diminishes in this order. E. W. WIGNALL.

Coloration anomalies of ferric and alkali thiocyanates. E. KAHANE (Bull. Soc. chim., 1927, [iv], **41**, 1403—1410).—The slow decolorisation of solutions of alkali thiocyanate containing small quantities of ferric salts is accelerated by boiling and is due to a reduction of the ferric salt to ferrous accompanied by the formation of perthiocyanic derivatives. Conversely, the pink colour that develops on exposing commercial preparations of alkali thiocyanates to ultra-violet light is due to oxidation of the small quantity of ferrous salt always present with the formation of ferric thiocyanate. This action is accelerated by the presence of oxidising agents and proceeds in the reverse direction when the coloured salt is kept in the dark. The removal of the traces of iron salts from preparations of thiocyanates is extremely difficult, but nearly pure preparations of the ammonium salt may be obtained by diluting alcoholic solutions with ether; the yield, however, is poor. Salts purified in this manner do not become coloured on exposure to direct sunlight.
A. R. POWELL.

Double compound of chromic and hydrogen chlorides. J. R. PARTINGTON and S. K. TWEEDY (J.C.S., 1927, 2899—2900).—By passing hydrogen chloride through a concentrated solution of green chromic chloride a heliotrope double *chloride*, $CrCl_3,HCl,xH_2O$ (where x is approximately 6), is precipitated. The substance is insoluble in ether

and in methyl and ethyl alcohols, and in water gives a pink solution which immediately turns green.

O. J. WALKER.

Basic chromic compounds. N. BJERRUM and C. FAURHOLT (Z. physikal. Chem., 1927, **130**, 584—591).—The hexaquochromic ion, $Cr(H_2O)_6^{\cdots}$, may be determined by adding to the solution cæsium sulphate solution and precipitating cæsium alum by the addition of alcohol. The precipitate, after washing with alcohol, is oxidised with hydrogen peroxide in alkaline solution, potassium iodide and hydrochloric acid are added, and the liberated iodine is titrated with standardised thiosulphate solution. By this method the percentage of hexaquochromic ion has been determined in chromic nitrate solutions of concentrations 0·1—0·01M which have been heated at 75° for several days with or without the addition of sodium hydroxide. Determinations have also been made of the quantity of latent basic chromium compounds formed in the solutions by precipitation with sulphuric acid and alcohol. The formation of non-colloidal substances of this nature reaches equilibrium in a few days, whereas the colloidal forms are still being produced after heating for several months.

H. F. GILLBE.

Transformation of sodium chromate into dichromate by means of carbon dioxide. N. F. YUSHKEVICH and J. N. SHOKIN.—See B., 1927, 936.

Oxide of fluorine or fluoride of oxygen? B. BRAUNER (Nature, 1927, **120**, 842).—The substance obtained by Lebeau and Damiens (A., 1927, 1044) is regarded as oxygen difluoride, OF_2, differing in constitution and properties from chlorine monoxide, Cl_2O.

A. A. ELDRIDGE.

Compounds of the halogens with each other, and with the halogen hydrides. K. H. BUTLER and D. MCINTOSH (Proc. Nova Scotian Inst. Sci., 1927, **17**, 23—25).—When bromine is dissolved in liquid chlorine the ebullioscopic constant is greater than for other solutes. To decide whether or not this is due to combination between solvent and solute, the f.-p. curve of the system chlorine–bromine has been determined. The curve is continuous and has no maximum.

M. S. BURR.

Behaviour of iron with other elements. G. TAMMANN and K. SCHAARWACHTER (Z. anorg. Chem., 1927, **167**, 401—410).—The heating and cooling curves of mixtures of iron with various other elements have been determined. Sulphur, selenium, tellurium, antimony, zinc, and aluminium do not react appreciably below their m. p., but with calcium, boron, silicon, and graphite reaction commences even below the m. p. of the eutectics. Red phosphorus and arsenic begin to react when their vapour pressure approaches 1 atm.

R. CUTHILL.

Univalent iron. W. MANCHOT (Annalen, 1927, **459**, 47—52).—Polemical against Reihlen and von Friedolsheim (A., 1927, 951).

J. W. BAKER.

Univalent iron, nickel, and cobalt. III. Reduction process in the case of iron. W. MANCHOT and H. GALL (Ber., 1927, **60**, [*B*], 2318—2322; cf. A., 1927, 1157).—Ferrous mercaptide is conveniently prepared by reducing ferric chloride in aqueous solution with ethyl mercaptan and subsequent addition of ammonia, ethyl mercaptan, and alcohol to the solution, all operations being conducted in the absence of air. The compound is very readily oxidised and, in presence of oxygen, transforms ethyl alcohol into acetaldehyde. It very rapidly absorbs nitric oxide, yielding the compound $Fe(NO)_2{\cdot}SEt$, m. p. 78°, and ethyl thionitrite. Reduction of the mercaptides of iron, nickel, and cobalt is attributed to the chemical affinity of sulphur for nitric oxide and occurs according to the scheme: $X(SR)_2+nNO=(NO)_{n-1}XSR+NO{\cdot}SR$. In the cases of Roussin's salts the change appears to be $Fe(SK)_2+3NO=(NO)_2Fe{\cdot}SK+NO{\cdot}SK$; in confirmation, it is observed that a red, oily substance apparently very closely analogous to ethyl thionitrite is obtained from potassium hydrogen sulphide and ethyl nitrite. The action of ferrous sulphate, potassium hydrogen sulphite, and potassium nitrite yields directly the black salt $(NO)_7Fe_4S_3K$, but this is a secondary compound from the red salt $(NO)_2Fe{\cdot}SK$ and $(NO)FeCl_2$.

H. WREN.

Thiosulphatocobalt complexes. II. Potassium thiosulphatocobaltipentacyanide. P. R. RAY (J. Indian Chem. Soc., 1927, **4**, 325—330).—Thiosulphatopentamminecobaltic chloride (A., 1927, 742) is decomposed by concentrated potassium cyanide solution, yielding *potassium thiosulphatocobaltipentacyanide*, $K_4[S_2O_3,Co(CN)_5]$. This complex salt is neutral, gives no reaction for cobalt ions, yields precipitates with most metallic salts, is slowly hydrolysed in aqueous solution to the aquo-salt, $K_2[H_2O,Co(CN)_5]$, and is diamagnetic. Mol. wt. determinations show that in 1·5—2% aqueous solution the salt is not completely dissociated. The coagulating power of its ion is greater than that of the ferrocyanide ion. The pentamminecobaltic chloride is decomposed by sodium nitrite, yielding *cobalt trinitrotriammine* $[(NO_2)_3,Co(NH_3)_3]$.

H. BURTON.

Complex compounds of tervalent iridium. V. V. LEBEDINSKI (Ann. inst. platine, 1926, No. 4, 235—242).—When sodium chloroiridate dodecahydrate (1 g.) is heated with ethylenediamine monohydrate (2 c.c.) and water (10 c.c.) in a sealed tube at 140°, and the product treated with potassium iodide, *triethylenediamine iodoiridite*, $[en_3\,Ir]I_3,H_2O$, rose-yellow, is obtained. *Precipitates* are obtained with: sodium chloroplatinite (yellow), ammonium chloroplatinate (pink), sodium cyanoplatinite (white), bromoplatinic acid (yellow), sodium chloro-osmate (yellowish-green), potassium ferrocyanide (yellow), potassium ferricyanide (orange-yellow), sodium picrate (canary-yellow), $[en_2\,Ir][C_6H_2(NO_2)_3O]_3$.

CHEMICAL ABSTRACTS.

Preparation of platinum. V. V. LEBEDINSKI and V. G. CHLOPIN (Ann. inst. platine, 1926, No. 4, 317—323).—1—1·2 Litres of a mixture of nitric acid (*d* 1·4), hydrochloric acid (*d* 1·19), and water (1 : 3 : 4 vols.) is added, first at 70—80°, then at the b. p., to the ore (100 g.), and evaporated at 30 mm. The residue, including osmium, iridium, etc., is heated on a water-bath for 2—2·5 hrs. and on a sand-bath at 140—142° with concentrated sulphuric acid until hydrogen chloride is removed. The diluted solution (500—600 c.c.), after heating for 30 min. on the water-

bath, yields ammonium chloroplatinate with ammonium chloride (150 g.), the precipitate being washed with saturated ammonium chloride solution, ice-water, and alcohol. CHEMICAL ABSTRACTS.

Use of electrolytic bridge for determining soluble salts. R. O. E. DAVIS (U.S. Dept. Agric. Circ. 423, 1927, 13 pp.).—The construction and use of a simple form of Wheatstone's bridge suitable for approximate determination of the conductivity of drainage waters and wet soils are described. Tables are provided to enable the amount of soluble matter to be calculated from the conductivity. If a large quantity of organic matter is present, the results are untrustworthy. R. CUTHILL.

Accuracy of titration of acids and alkalis. T. MIŁOBEDZKI (Rocz. Chem., 1927, 7, 295—308).—Sources of error in the titration of various acids and alkalis using various indicators are discussed. The accuracy of titration of $0·1N$-hydrochloric acid with $0·1N$-sodium hydroxide is from 0·01 to 0·03%, and the titre found is accurate to 99·8—99·9%. R. TRUSZKOWSKI.

Differential electrometric titration as a precision method. D. A. MACINNES (Z. physikal. Chem., 1927, 130, 217—221).—The method of differential electrometric titration (A., 1927, 35) is applicable to the determination of end-points in titrations of high precision, such as those of oxalic acid and potassium permanganate, hydrochloric acid and sodium hydroxide, and arsenious oxide and iodine. The curve obtained by this method for the reaction of a base with an acid in the presence of quinhydrone shows two maxima, indicating two points of inflexion in the curve obtained by the usual method, which, if not clearly recognised, may lead to error in its use. L. S. THEOBALD.

Colouring matters operating in the presence of neutral salts, and the construction of a scale of indicators with varying mass indices for the comparison of saline solutions. F. VLES, P. REISS, and (MLLE.) M. GEX (Compt. rend., 1927, 185, 1127—1130; cf. this vol., 14).—The behaviour of indicators of various types in a number of saline solutions has been investigated spectrophotometrically, and their mid-point values (mass indices) have been determined colorimetrically by means of the comparator with reference to potassium chloride. The indicators fall into groups which appear to correspond with their constitutions. The authors' concentration–absorption equation (*loc. cit.*) holds for the various indicators in potassium chloride solutions. J. GRANT.

Automatic apparatus for the determination of moisture [by distillation with benzene etc.]. H. ROSSLER.—See B., 1927, 895.

Determination of halogens by Volhard's method. G. LEIMBACH (Caliche, 1927, 8, 428—430).—After filtration, an aliquot part of the filtrate is titrated; much nitrate causes only slightly high results, and iodates do not interfere. CHEMICAL ABSTRACTS.

Micro-determination of iodine in potable waters. M. SETTIMJ.—See B., 1927, 958.

Determination of iodates in the presence of iodides, nitrates, nitrites, and chlorides. G. LEIMBACH (Caliche, 1927, 8, 409—411).—Sufficient silver nitrate is added to precipitate the iodide and part of the chloride, and the acidified filtrate is boiled with a slight excess of chlorine or sodium hypochlorite and phenol to remove the nitrite. Some of the iodate, however, becomes decomposed. CHEMICAL ABSTRACTS.

Determination of sulphur in ores. K. K. JARVINEN.—See B., 1927, 910.

Rapid determination of sulphur in iron ores. C. C. HAWES.—See B., 1927, 939.

Microtitration of sulphate ions and of barium ions by a centrifugal method. R. F. LE GUYON (Bull. Soc. chim., 1927, [iv], 41, 1387—1389).—Barium and sulphate ions may be determined by centrifugovolumetry, using sulphuric acid and barium chloride, respectively, in the way previously described (cf. A., 1926, 927). A determination takes 8—10 min. and the end-point may be observed within 0·05 c.c. A. R. POWELL.

Determination of sulphur trioxide in the presence of sulphur dioxide. J. R. ECKMAN.—See B., 1927, 876.

Determination of sulphuric acid in drinking water by the use of benzidine. F. RASCHIG.—See B., 1927, 894.

Determination of selenium and tellurium by means of titanous chloride. O. TOMIČEK (Bull. Soc. chim., 1927, [iv], 41, 1389—1399).—Tellurates and tellurites may be titrated potentiometrically with titanous chloride in the presence of hydrochloric acid, the end-point being marked by a sharp change of potential when all the tellurium is precipitated in the elementary form. In sulphuric acid solution two breaks are obtained in titrating telluric acid, the first corresponding with reduction to tellurous acid and the second with total reduction to tellurium. For the gravimetric determination of tellurium the reduction to the element is carried out in a solution containing 30 c.c. of 20% hydrochloric acid per 100 c.c., using 3 c.c. of a 20% titanous chloride solution for every 0·1 g. of tellurium present as tellurate. The precipitate is washed with dilute acid, then with water, dried at 105°, and weighed. Selenium may be determined potentiometrically in selenates in a similar manner to tellurium in tellurates, but only one potential change occurs in sulphuric acid solutions. A. R. POWELL.

Reaction of tellurium. O. TOMICEK (Bull. Soc. chim., 1927, [iv], 41, 1399—1403).—The reduction of tellurates and tellurites to tellurium by titanous chloride in hydrochloric acid solutions (cf. preceding abstract) is sufficiently delicate to serve as a test for tellurium in the absence of gold, copper, selenium, and the platinum metals; in 5 c.c. of concentrated hydrochloric acid 0·00005 g. of tellurium gives with 2 c.c. of 2% titanous chloride solution a grey cloud which slowly flocculates. In the presence of a large quantity of sodium or ammonium acetate and a little acetic acid titanous or chromous chloride reduces tellurium compounds to hydrogen telluride, which

may be detected by the production of a mirror when the gas is passed through a heated tube, as well as by its characteristic disagreeable odour. Selenium, phosphorus, arsenic, antimony, bismuth, tin, and lead give a similar reaction. A. R. POWELL.

Simplified apparatus for micro-Kjeldahl determinations. J. G. VAN DER SANDE (Chem. Weekblad, 1927, **24**, 558).—The apparatus is provided with a dropping funnel fused on to the tube connecting the steam flask with the Kjeldahl flask, so that the sodium hydroxide solution may be added to the latter in position. The condenser is arranged vertically, with its end drawn out to a capillary, and dipping below the surface of the standard acid solution.

S. I. LEVY.

Improved micro-Kjeldahl ammonia distillation apparatus. G. KEMMERER and L. T. HALLETT.—See B., 1927, 958.

Spectrophotometric detection of boron. W. C. HOLMES.—See B., 1927, 936.

Determination of small quantities of carbon monoxide in air. N. KOMAR.—See B., 1927, 936.

Colorimetric method for the field determination of the carbon dioxide tension and free carbon dioxide, hydrogen carbonates, and carbonates in natural waters. I. Theoretical. E. B. POWERS.—See B., 1927, 958.

Determination of carbon disulphide in its emulsions. H. J. FISHER.—See B., 1927, 876.

Systematic qualitative analysis of cations without the use of hydrogen sulphide or its derivatives. O. MACCHIA (Z. anal. Chem., 1927, **72**, 180—185).—The substance is heated with nitric acid to destroy iodides and organic substances, the solution is evaporated to dryness, the residue gently heated to carbonise organic matter, and the resulting mass (or the original substance if free from organic substances) digested with aqua regia. Irrespective of whether the substance is completely dissolved or not, nitric acid is added and the mixture evaporated nearly to dryness. After slight dilution, ammonia to alkalinity, ammonium carbonate, hydrogen peroxide, and ammonium phosphate are added, the solution is boiled and filtered, and the precipitate, *A*, digested with aqua regia whilst the filtrate, *B*, is acidified with nitric acid whereby silver is precipitated as chloride and removed by filtration. The solution of *A* is concentrated and digested hot with sodium hydroxide, peroxide, and carbonate, giving precipitate *C* and filtrate *D*. The former is washed with saturated sodium carbonate solution and dissolved in a mixture of formic and nitric acids, part of the solution being tested for manganese by boiling with lead peroxide and the remainder being treated with ammonia, ammonium chloride, and hydrogen peroxide, giving precipitate *E* and filtrate *F*. The latter is tested for the alkaline-earths and magnesium in the usual way, whilst *E* is dissolved in sulphuric acid and hydrogen peroxide and the iron and bismuth are separated from the manganese by means of ammonia and dextrose, and from one another by reduction of the iron with sulphur dioxide and precipitation with ferricyanide, followed by precipitation of bismuth with sodium hydroxide. Filtrate *D* is treated with sulphuric acid, which removes lead, then with sodium carbonate to precipitate antimony, tin, and aluminium, leaving chromate in solution. Tin and aluminium are extracted from the precipitate by treatment with formic acid, and tin alone is precipitated by addition of citric acid followed by ammonia. Filtrate *B* is divided, a small portion being tested for mercury with a clean piece of copper foil and a second small portion for arsenic by heating with aluminium and sodium hydroxide and allowing the hydrogen to impinge on silver nitrate test paper; the main portion is evaporated to dryness and the residue ignited to expel ammonium, mercury, and arsenic compounds, and extracted with bromine water to dissolve alkali metal salts. The insoluble material is collected and dissolved in nitric acid, and the solution digested with sodium hydroxide and bromine and filtered. The filtrate, if yellow, contains chromate, which is confirmed by the hydrogen peroxide test, and zinc, which is confirmed by addition of ferrocyanide to the acidified solution. The precipitate is dissolved in hydrochloric acid, copper removed by treatment with sulphur dioxide and thiocyanate, nickel with dimethylglyoxime in ammoniacal solution, cadmium as a white precipitate of hydroxide on adding sodium hydroxide and hydrogen peroxide to the cold filtrate from the nickel, and cobalt by boiling the filtrate from the cadmium to precipitate black cobaltic hydroxide.

A. R. POWELL.

Determination of potassium in mixtures of salts, especially in Chile saltpetre, by the perchlorate method. G. LEIMBACH.—See B., 1927, 874.

Microchemical detection of rubidium. E. BURKSER and S. RUBLOF (Mikrochem., 1927, **5**, 137—145).—A solution of a rubidium salt in concentrated hydriodic acid yields with equal volumes of a 14% solution of silver iodide in the same acid and of a 4·5% solution of gold in iodine and hydriodic acid black, hexagonal crystals of the *compound* $3AuI,AuI_3,4RbI,AgI$ when the rubidium is in excess, and of the *compound* $3AuI,AuI_3,3RbI,2AgI$ when an excess of the reagents is used. The formation of these black crystals forms a delicate test for rubidium in the presence of potassium or ammonium salts, as little as $1—3\times10^{-8}$ g. of rubidium in one drop of a solution on a microscope slide giving a detectable reaction; cæsium interferes, as it gives a similar reaction, but the crystals have a pronounced tendency to collect into stellar aggregates. The method is far more delicate than the corresponding tests using chlorides or bromides of gold and silver. The gold iodide solution is made by allowing fine filings of gold to remain for 1 week in contact with iodine, hydriodic acid (*d* 1·5), and a little ether, and the silver solution by dissolving freshly precipitated and washed silver iodide in hydriodic acid.

A. R. POWELL.

Rapid potentiometric determination of silver and zinc in the same solution. E. MÜLLER and H. HENTSCHEL (Z. anal. Chem., 1927, **72**, 188—195).—The neutral nitrate solution of the two metals is titrated at 75° with 0·1*N*-potassium bromide solution,

using a silver indicator electrode and a normal calomel electrode with an opposing potential of +0·176 volt. Without filtering the silver bromide the solution is then titrated with ferricyanide for zinc, using a platinum indicator electrode and an opposing potential of +0·31 volt, until the galvanometer registers zero.

A. R. Powell.

Influence of ammonia on the results of the determination of magnesium by Schmitz' method. J. Majdel (Arh. Hemiju, 1927, **1**, 216—217; cf. Technic List., 1925, **6**, 16).—The completeness of precipitation of magnesium as pyrophosphate depends on the concentration of ammonium salts present, the best results being given by the addition of one fifth of the volume of 10% ammonia.

R. Truszkowski.

Determination of traces of impurities in lead. B. S. Evans.—See B., 1927, 911.

Rapid potentiometric determination of lead and cadmium in the same solution. E. Muller and W. Pree (Z. anal. Chem., 1927, **72**, 195—200).—The neutral nitrate solution of the two metals is divided and one portion is titrated at 75° with 0·1*N*-sodium ferrocyanide solution, using a platinum indicator electrode and an opposing potential of +0·18 volt, until the galvanometer registers zero. The sum of the lead and cadmium is thus obtained; cadmium alone is determined in the second portion by a similar titration at 60°, using an opposing potential of +0·2 volt, after precipitating the lead by addition of sodium sulphate and alcohol. A. R. Powell.

Determination of cuprous oxide and copper in mixtures containing both. W. D. Bonner and B. D. Kaura.—See B., 1927, 940.

Volumetric determination of cerium. G. Autie (Bull. Soc. chim., 1927, [iv], **41**, 1535—1546).—The accuracy of the various methods which have been proposed from time to time for the volumetric determination of cerium has been examined. The only satisfactory methods are those involving oxidation of a cerous salt with alkaline permanganate (Meyer and Schweitzer, A., 1907, ii, 581), or with a persulphate (von Knorre, A., 1900, ii, 576), and the potentiometric method (Tomiček, A., 1925, ii, 716). In using von Knorre's method, the ceric salt formed by oxidation should, when the excess of persulphate has been destroyed by boiling, be determined with hydrogen peroxide in concentrated nitric acid solution, as otherwise errors arise owing to the precipitation of what appears to be a form of ceric hydroxide.

R. Cuthill.

Volumetric determination of aluminium. A. Wohlk (Dansk Tidsskr. Farm., 1927, **1**, 525—536).—The method depends on the formation of the complex salt, $Al(C_2O_4)_3K_3$, which is neutral in solution. The dilute solution of the aluminium salt is heated to boiling and precipitated with approximately *N*-ammonia, methyl-red being used as indicator. The precipitate is collected, washed back into the beaker with boiling water, and stirred thoroughly until all lumps are broken up. A little ammonium chloride and two drops of methyl-red are added, and ammonia solution is added drop by drop until the colour of the solution changes to yellow. The liquid is heated to boiling, the aluminium hydroxide collected on the original paper and washed, first with ammonium nitrate containing a few drops of ammonia, and finally with neutral ammonium nitrate. The paper and precipitate are returned to the beaker, and the precipitate is dissolved by warming with a measured volume of a standardised solution of oxalic acid. After cooling and diluting to 100 c.c., 1—2 g. of neutral potassium or sodium oxalate are added, and the excess of oxalic acid is titrated with 0·5*N*- or *N*-sodium hydroxide, using methyl-red as indicator.

A solution of borax may be used in place of sodium hydroxide for titrating the oxalic acid, or, if only small amounts of aluminium are to be determined, a solution of potassium iodide and iodate may be added, and the liberated iodine determined by titration with thiosulphate solution.

H. F. Harwood.

Analytical consequences of the region of stability of cryolite. A. Travers (Compt. rend., 1927, **185**, 1043—1046; cf. A., 1927, 1141).—The liberation of hydroxyl ions in the equilibrium $Al(OH)_3+6F'$ AlF_6+3OH' may be used to demonstrate the dissociation of heated kaolin into free silica and alumina, and to detect free hydrated alumina in certain clays. For the separation of silica and fluorine (*e.g.*, in rock analysis) the method of Berzelius and that involving the formation of potassium fluosilicate are incorrect in the presence of alumina. If the ratio Al_2O_3/SiO_2 is less than $\frac{1}{3}$, and if the rock is attacked by fused alkali carbonates alone, the alumina may be removed as an insoluble permutite, and the fluorine may be determined accurately in the water extract. When the p_H value of the water extract is higher (*e.g.*, with mica or topaz), the permutite decomposes and the alumina passes into solution as aluminate, and is subsequently precipitated after neutralisation as a complex fluoride. J. Grant.

Potentiometric determination of indium. U. B. Bray and H. D. Kirschman (J. Amer. Chem. Soc., 1927, **49**, 2739—2744).—Acidified indium chloride solution, 0·05*N* or less with respect to hydrochloric acid, is titrated with potassium ferrocyanide, the end-point being determined potentiometrically. An insoluble *compound*, presumably $KIn_5[Fe(CN)_6]_4$, is formed. Since the composition of the analogous zinc compound is known (Treadwell and Chervet, A., 1923, i, 764) the ferrocyanide solutions may be standardised with respect to indium by means of pure metallic zinc. S. K. Tweedy.

"Potassium chlorate" method for determining manganese. IV, V, and VI. M. Marqueyrol and L. Toquet (Ann. Chim. analyt., 1927, [ii], **9**, 324—330; cf. A., 1927, 1162).—By using nitric acid (*d* 1·332) and carrying out the precipitation on a water-bath, manganese in any concentration can be determined accurately. The advantages of the method are that large quantities of the metal can be used, that no empirical constant is involved, and that the completeness of the precipitation can always be verified. C. W. Gibby.

Separation of manganese in rock analysis. E. V. Holt and H. F. Harwood (Min. Mag., 1927,

21, 318—323).—The manganese present in small amount (usually less than 1%) in rocks interferes with the separation of alumina, lime, and magnesia. The various methods of separation are mentioned and preference is given to that in which the manganese is precipitated with the alumina and ferric oxide by ammonia in the presence of an oxidising agent. As oxidising agents trials were made with ammonium persulphate, hydrogen peroxide, chlorine, and bromine. The last of these—bromine water added gradually to the boiling alkaline solution—gave the best results.

L. J. SPENCER.

Rapid determination of manganese in steels. A. QUARTAROLI.—See B., 1927, 910.

Analysis of nickel-chromium and nickel-chromium-iron alloys. D. HARVEY.—See B., 1927, 879.

Detection of uranium by a photo-luminescence test. J. PAPISH and L. E. HOAG (Proc. Nat. Acad. Sci., 1927, **13**, 726—728).—Uraniferous material is fused with potassium fluoride and the resulting mass examined by near ultra-violet light. An orange-yellow luminescence is characteristic of uranium. Sodium fluoride gives a similar result, but niobic acid also produces fluorescence in this case.

W. E. DOWNEY.

Gravimetric and volumetric micro-determination of bismuth. R. STREBINGER and W. ZINS (Mikrochem., 1927, **5**, 166—192).—The nitrate solution is evaporated to dryness, the residue dissolved in 0·1—0·15 c.c. of 3*N*-nitric acid and 2—2·5 c.c. of water, and the solution treated with potassium iodide, added a small crystal at a time until the liquid above the black precipitate of bismuth tri-iodide appears yellow. A further 2·5 c.c. of water are added and the mixture is heated slowly on the water-bath until the black precipitate is converted into copper-coloured, glistening crystals of bismuth oxy-iodide. Another 5 c.c. of water are added and heating is continued until the precipitate settles and the supernatant liquid is colourless; the solution is treated with 2—2·5 c.c. of 1% sodium acetate solution, cooled, and filtered, and the precipitate is washed with cold water, then with alcohol, dried at 105°, and weighed as BiOI. Alternatively, the dried precipitate may be heated in a current of air or oxygen and the liberated iodine collected in potassium iodide and titrated with thiosulphate.

A. R. POWELL.

Volumetric determination of bismuth. H. KUBINA and J. PLICHTA (Z. anal. Chem., 1927, **72**, 201—207).—The cold bismuth solution is treated with 0·1 g. of aluminium dust and 40 c.c. of 3*N*-potassium hydroxide solution. After gently shaking for 20 min. the mixture is heated to boiling until the precipitated bismuth flocculates and the aluminium is completely dissolved. The precipitate is washed by decantation and dissolved in 15 c.c. of a solution containing 200 g. of ferric chloride and 250 c.c. of concentrated hydrochloric acid per litre. The resulting ferrous chloride is titrated with permanganate after addition of the usual solution containing manganese sulphate and phosphoric acid. Good results are also obtained by precipitation of the bismuth in acid solution with copper in an atmosphere of carbon dioxide followed by titration of the cuprous chloride with potassium bromate; in this method lead does not interfere (cf. Reissaus, A., 1927, 334).

A. R. POWELL.

Separation and determination of metals by means of 8-hydroxyquinoline. VI. Determination of bismuth. R. BERG (Z. anal. Chem., 1927, **72**, 177—179; cf. A., 1927, 848).—In acetic acid or in ammoniacal tartrate solutions containing bismuth, 8-hydroxyquinoline produces an orange-yellow, crystalline precipitate of $Bi(C_9H_6ON)_3,H_2O$, stable at 105°, but becoming anhydrous after prolonged heating at 130—140°. The limit of sensitivity of the test is 1 part of bismuth in 300,000 parts of a dilute acetic acid or in 270,000 parts of an ammoniacal tartrate solution. For quantitative work the solution of bismuth salt must be free from halides; it is heated at 60—70° and treated with an excess of a cold saturated solution of the reagent in alcohol or acetone. The precipitate is collected, washed with hot water, dried at 100° or at 140°, and weighed as the monohydrate or anhydrous compound. Alternatively, the precipitate may be dissolved in hydrochloric acid and titrated with bromide-bromate solution.

A. R. POWELL.

Analytical chemistry of tantalum, niobium, and their mineral associates. IX. Separation of titanium from tantalum and niobium. W. R. SCHOELLER and E. C. DEERING.—See B., 1927, 940.

Refractometer for determining the refractive indices of gem-stones, crystals, and liquids. B. J. TULLY (Min. Mag., 1927, **21**, 324—328).—A convenient box-form of instrument contains a hemisphere of dense glass and a system of lenses and reflecting prisms. The shadow-edge of total reflexion is thrown on to a scale, giving in the eyepiece a direct reading of the refractive index.

L. J. SPENCER.

Silvering of glass plates for optical instruments. J. J. MANLEY (Phil. Mag., 1927, [vii], **4**, 1322—1323).—A film of silver which will endure polishing may be obtained by carrying out the whole of the deposition from the usual solutions at 0°. An equally satisfactory deposit, which does not require polishing, is produced by allowing the silvering solutions to act for 10—15 min. at the ordinary temperature, then stopping the deposition by passing a current of water through the silvering bath.

R. CUTHILL.

Explosions in the coating of mirrors. W. MEYER.—See B., 1927, 913.

Sodium flame for polarimetric work. T. McLACHLAN and A. W. MIDDLETON (Analyst, 1927, **52**, 639).—A brilliant sodium flame may be maintained by using a pencil obtained by mixing 33% of sodium chloride, 33% of sodium bromide, and 14% of magnesium oxide with sufficient water to obtain a damp mass, kneading it into 20% of sodium silicate, rolling out, and drying.

D. G. HEWER.

Composite yellow. J. PAPISH and F. E. AGEL (J. Physical Chem., 1927, **31**, 1746—1747; cf. Rayleigh, Nature, 1871, **3**, 234).—Difficulties were encountered in preparing composite yellow by Ray-

leigh's method (*loc. cit.*), but it can readily be obtained by placing together cells containing a saturated solution of potassium chromate, and a solution of neodymium chloride containing the equivalent of 4 g. of the sesquioxide per 100 c.c.

L. S. THEOBALD.

Monochromatic colour filters. F. WEIGERT and H. STAUDE (Z. physikal. Chem., 1927, **130**, 607—615).—The preparation is described of practically monochromatic colour filters, based, not on selective absorption, but on selective refraction. Although very simple to make, much greater intensity of light may be obtained than is given by expensive monochromators. H. F. GILLBE.

Transmission properties of some filters. E. PETTIT (Astrophys. J., 1927, **66**, 43—58).—Transmission curves of 44 filters are given from 0·23 to 2·3 μ, and in some cases to longer wave-lengths. The effect of sunlight on green celluloid, glass, silver, and gold films was observed. A. A. ELDRIDGE.

Simple form of automatic siphon. D. C. HARRISON (J.C.S., 1927, 2896—2897).—A glass siphon of diameter not greater than 5 mm. contains inside the bend about eight capillaries of diameters from 0·25 to 1 mm., projecting about 7 cm. into the shorter limb. The longer limb extends well below the capillaries and is coated with paraffin wax on the inside to within about 4 cm. of the ends of the capillaries. A rapid flow of liquid through the siphon is possible. O. J. WALKER.

Laboratory evaporation and filtration. J. H. LINSCHOTEN (Chem. Weekblad, 1927, **24**, 558—559).—Simple apparatus is described for the automatic continuous feeding of large quantities of liquids for evaporation or filtration. S. I. LEVY.

Differential ebulliscope. W. SWIENTOSLAWSKI (Z. physikal. Chem., 1927, **130**, 286—288).—A differential ebullioscope is described which overcomes variations in atmospheric pressure and avoids the use of two sets of b.-p. apparatus. The apparatus can also be used for the measurement of the coefficient dp/dt, and for the comparison of Beckmann thermometers. A diagram is given. L. S. THEOBALD.

Rapid mercury still. R. J. CLARK (Proc. Camb. Phil. Soc., 1927, **23**, 956—958).—A modification of Hulett's still (Physical Rev., 1905, [i], **21**, 288). A second air inlet admits air above the mercury surface. A boiler of 500 c.c. capacity can distil 1500 g. of mercury per hr. W. E. DOWNEY.

Adhesion phenomenon of mercury, and a new manometer. C. HAGEN (Physikal. Z., 1927, **28**, 735—737).—A piece of wide tubing is connected at one end to a vacuum and at the other to a movable mercury container. A side arm is connected to two similar vertical capillary tubes, one of which is closed and the other connected to a second side arm, restoring connexion with the main tube. When the vacuum is high the level of mercury can be raised so as to fill the closed capillary, and on lowering the container slowly the mercury adheres in the closed capillary but descends in the open one. The resultant difference in level varies with the pressure; *e.g.*, at 1×10^{-5} mm. it is 6 mm., at 3×10^{-5} about 1 mm., and at 9×10^{-5} mm. it is zero. The sealed end of the capillary must not be conical with a sharp angle, or adhesion will not occur.

The phenomenon has been utilised in devising a modified McLeod gauge sensitive to low pressures.

R. A. MORTON.

Specific heats at low temperatures. Apparatus for the rapid determination of specific heats of solids at low temperatures. F. SIMON and M. RUHEMANN (Z. physikal. Chem., 1927, **129**, 321—338).—A method is described for determining by a rapid series of measurements the mean specific heat of a substance over a very small temperature interval, and results are given for a number of metals at temperatures between 71° and 83° Abs. The following characteristic temperatures have been determined from the atomic heat at constant volume: tantalum 243·5°, chromium 486°, cobalt 383°, nickel 368°, and beryllium 1035°. H. F. GILLBE.

Sucrose solution for the calibration of viscosimeters. E. VON MUHLENDAHL (Z. angew. Chem., 1927, **40**, 1318—1320).—Paraffin or castor oil is not entirely suitable for calibration purposes owing to their variable chemical characteristics, and glycerol, although a well-defined compound, is hygroscopic. Sucrose is therefore used to calibrate an Ostwald capillary viscosimeter. Tables are given for water and sucrose solutions (60, 62, 64, 66%) at temperatures of 16—30°. The logarithm of the viscosity is proportional to the concentration and inversely proportional to the temperature. W. G. CAREY.

Chinese alchemy. B. E. READ (Nature, 1927, **120**, 877—878).—Evidence supporting the view that Chinese alchemy originated independently of, and antedated, the Egyptian school is adduced.

A. A. ELDRIDGE.

Geochemistry.

Theory of the upper atmosphere and meteors. H. B. MARIS (Nature, 1927, **120**, 839).

Rôle of ozone in the atmosphere. J. LÉVINE (Compt. rend., 1927, **185**, 962—963).—Dobson's conclusion (Proc. Roy. Soc., 1924, **A**, **114**, 521) that the ozone content of the atmosphere depends on the distribution of the atmospheric pressure, being higher during depressions than during anticyclones, is in agreement with that of the author (Compt. rend., 1923, **176**, 705). J. GRANT.

Natural mineral waters in the light of modern research. O. BAUDISCH and D. DAVIDSON (Arch. Int. Med., 1927, **40**, 496—520).—The catalase and peroxidase activities of Saratoga mineral waters disappear when the water is irradiated by ultraviolet light in the presence but not in the absence of

oxygen. These waters give no blue coloration with potassium ferricyanide but give a green coloration with nitrosophenol, apparently dependent on the presence of ferrous iron in a combined condition. After irradiation in presence of oxygen the waters no longer give a green colour with nitrosophenol and therefore the catalytic activity appears to be dependent on the presence of ferrous iron. Simple solutions of ferrous salts such as ferrous hydrogen carbonate do not, however, behave similarly to the mineral waters. W. O. KERMACK.

Chemical composition of the interior of the earth and the moon. S. MOHOROVICIC (Arh. Hemiju, 1927, **1**, 95—104).—From seismological, petrological, and astronomical-geodetic considerations it is concluded that the earth consists mainly of iron, magnesium, silicon, and oxygen, whilst the moon contains in addition relatively more aluminium and calcium. The rigidity of the earth is a little more than three times as great as that of the moon. Venus and Mercury probably possess a similar composition to the earth, whilst that of Mars is closer to that of the moon. The planetoids are of similar composition to meteorites, whilst the planets more distant from the sun probably resemble the fixed stars in composition, this being unknown. R. TRUSZKOWSKI.

Radioactivity and the temperature of the interior of the earth and the moon. S. MOHOROVIĆIĆ (Arh. Hemiju, 1927, **1**, 226—236).—From a consideration of the thickness of the Sial granite substratum and its radioactivity, thermal conductivity, and elasticity, it is concluded that at a depth of 50 km. the rocks of the moon exist only in the liquid state, whilst at 70 km. only the gaseous phase can exist. In the earth, a temperature high enough to liquefy rocks (2500°) is attained at a depth of 50 to 60 km. below high mountains.
R. TRUSZKOWSKI.

Case of pseudopolychroism in calcite. B. DIMITRIEVITCH (Compt. rend., 1927, **185**, 1143—1144).—Pseudopolychroism has been detected in a colourless calcite (from Avala, Serbia), found in the form of plates in the fissures of rocks and associated with non-polychroic calcite or with felspars. The calcite behaves as a rectilinear polariser, but the action of hydrochloric acid (5%) removes the active agent and leaves an opaque non-pseudopolychroic residue of isotropic corpuscles. Since the calcite is derived from felspars, these corpuscles are probably composed of kaolin or gelatinous silica contained in the calcite in the form of a mechanical mixture.
J. GRANT.

Exploitation of the magnesian lakes of the Crimean peninsula. S. F. SHEMTSCHUSHNI (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 370—378).—Figures are given showing the compositions of the saline contents of five lakes of the Perekopski group at different times. The salts contain predominating proportions of magnesium chloride and their use as sources of magnesium compounds is discussed. T. H. POPE.

Chemical nature of natural hydrates of ferric oxide. N. S. KURNAKOV and E. J. RODE (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 305—332).—Investigation of the heating and dehydration curves of natural hydrates of ferric oxide indicates that the only existing hydrate of definite composition is the monohydrate, Fe_2O_3,H_2O, which probably corresponds with natural gothite and lepidokrotite. The natural hydrated forms of ferric oxide may be separated into three classes: (1) Hydrohæmatites, constituting the α-phase of variable composition. The water present varies within wide limits up to about 8% and is of zeolitic type, forming solid solutions with hæmatite. The heating curves exhibit a break at about 129—150°, corresponding with commencement of the dehydration of the solid solutions. (2) Gothites, lepidokrotites, limonites, bog iron ores, representing the β-phase of variable composition and containing 9·9—13·2% of water, probably contain the definite hydrate, Fe_2O_3,H_2O (10·1% H_2O) with any excess of water in the form of a solid solution. The heating curve shows clearly the gothite halt, corresponding with a change in the properties of the substance, and also, when the water-content is sufficiently high, a change in direction at 125—135°, indicative of decomposition of the gothite or β-solid solution. The dehydration curves change direction at 200—250°, at which temperature equilibrium between the two solid α- and β-phases is established; the lower branch corresponds with the solid solution of water and gothite and the upper with that of water and hæmatite. (3) Xanthosiderites, limonites, which form the γ-phase, with water-content 13·8% or more. With these, the heating curves exhibit, in addition to the gothite halt, a second break in the continuity at 120—150°, sometimes accompanied by reheating. At this point there probably exists a mixture of the β- and γ-solid solutions. T. H. POPE.

Structure of felspars and of mica. M. DOMINIKIEWICZ (Rocz. Chem., 1927, **7**, 345—356).—The kaolin nucleus is an integral part of the molecule of felspar and of mica, anorthite being normal calcium kaolinate and orthoclase a silicate of potassium kaolinate. In the process of kaolinisation of felspar the potassium silicate split off combines with the aluminate, but not with the silicate fragment of the molecule. Kaolinisation takes place, not only under the influence of atmospheric agencies, but also by the action of volatile acids, steam, etc. The conversion of alkaline felspar into mica is explicable on the basis of hydrolytic or pneumalytic elimination of 8 alkali silicate nuclei, the silicate molecules of which are replaced by hydrogen atoms. Acid micas possessing various alumina and silica contents are products of the progressive disintegration of the kaolin nuclei. The existence of mixtures of these various disintegration compounds is quite possible. The simplest micas may be considered as being built up of natrolite nuclei, whence the space formula of lepidolite is derived. By substitution of the free —SiO— radicals of the natrolite nucleus by magnesia the simplest biotites and phlogopite are obtained. Other biotites may be regarded as substitution products of the natrolite or kaolin nuclei by magnesium silicate, silicate molecules combining with the aluminate portion of these nuclei. R. TRUSZKOWSKI.

Action of dilute acid and of sodium carbonate solution on mica. A. Fioletova (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 426—433).—A sample of black mica (biotite) was decomposed when treated with 10% hydrochloric acid for 10 hrs., whereas more than one half remained undecomposed after three successive treatments, each of 2 hrs.' duration, with 2% hydrochloric acid. Preliminary heating of the biotite to dull redness renders the decomposition more difficult. With clay containing a large proportion of biotite, a certain but not a complete separation is possible by means of 2% hydrochloric acid, if the material is previously heated to dull redness for not more than 2—3 hrs.; when the clay contains the usual small proportion of mica in thin pieces, it is probable that this treatment effects dissolution of the whole of the mica. A suggested structure for mica is given. T. H. Pope.

Formation of radioactive manganiferous deposits from Tanokami, and the source of manganese in the deep-sea nodules. S. Iimori (Bull. Chem. Soc. Japan, 1927, **2**, 270—273; cf. A., 1926, 380, 494).—Analyses of manganiferous deposits from Tanokami and of deep-sea nodules are compared and discussed. C. W. Gibby.

Green kaolin from Tanokami. S. Iimori (Bull. Chem. Soc. Japan, 1927, **2**, 274—278).—An analysis of green kaolin from Tanokami has been made. The elements present in the chromosphere are also the universal minor constituents of igneous rocks. C. W. Gibby.

Temperature-range of formation for tourmaline, rutile, brookite, and anatase in the Dartmoor granite. A. Brammall and H. F. Harwood (Min. Mag., 1927, **21**, 205—220).—The association of tourmaline with both α-quartz and β-quartz (transition at 575°) proves that some of the tourmaline was formed below 575° and some above that temperature, possibly up to 800°. The stability range of rutile corresponds with that of tourmaline, and is higher than that of anatase and still higher than that of brookite. L. J. Spencer.

Chemical classification of the mica group. III. Molecular volumes. A. F. Hallimond (Min. Mag., 1927, **21**, 195—204).—The molecular volumes of a number of analysed micas belonging to different groups (A., 1925, ii, 819; 1926, 815) are tabulated and plotted against the RO-content. A good agreement is shown with the volumes calculated as an additive property of the constituent oxides. L. J. Spencer.

Study of bituminous rocks. G. Testi and G. Inardi (Annali Chim. Appl., 1927, **17**, 446).—Many substances which do not exhibit fluorescence when exposed to ultra-violet rays show marked fluorescence if dissolved in a suitable solvent. The presence of hydrocarbons in rocks may be detected by this means. Two or three g. of the powdered rock are shaken with 20—30 c.c. of a solvent for petroleum in either a flat-bottomed glass dish or a quartz test-tube. In presence of hydrocarbons, the liquid gradually develops increasing fluorescence on exposure to ultra-violet rays, the phenomenon being observed more readily if the solution is absorbed by filter-paper. In absence of hydrocarbons, either no fluorescence or one of different character appears. A sample of ichthyolic shale gave, however, no fluorescence, possibly owing to the presence of sulphur. T. H. Pope.

Occurrence of the platinum metals. J. L. Howe (Science, 1927, **66**, 220—221).—It is probable that all meteorites contain the platinum metals. An attempt is made to calculate the relative amounts of the metals of the eighth periodic group in the earth. A. A. Eldridge.

Organic Chemistry.

Chemical reactivity of atoms and groups in organic compounds. J. F. Norris.—See this vol., 26.

Future development of organic chemistry. C. F. van Duin (Z. physikal. Chem., 1927, **130**, 353—364).—A large number of otherwise inexplicable reactions may be interpreted by means of the principle of induced alternate polarity, which is held to be of great importance for the future development of organic chemistry. The following problems, among others, are considered from the point of view of the theory: substitution in the benzene nucleus; the heat of combustion of isomeric benzene derivatives; the activation of halogen atoms; the acidity of acids and the basicity of amines; the elimination of halogen hydrides, *e.g.*, hydrogen chloride from 3 : 4′-dinitrostilbene dichloride (cf. Harrison and Wood, A., 1926, 604); various additive reactions, including the addition of bromine to *m*- and *p*-sulphocinnamic acid, the addition of nitric acid to αα-diphenylethylene, the addition of water to 3 : 4′-dinitro- and -diamino-tolanes. L. L. Bircumshaw.

Atmospheric oxidation of hydrocarbons. A. Kailan and L. Olbrich (Monatsh., 1927, **48**, 537—541).—The oxidation of paraffin wax at 183—184° and of toluene at 99·4° by a current of purified air passed at the rate of 6 litres/hr. has been studied for varying periods and the amount of oxidation determined by investigations of the acid values, oxygen content, hydrolysis and acetylation, and densities of the products. Oxidation of paraffin wax proceeds more rapidly in the second period of 25 hrs. than in the first, and after 100 hrs. 8% of the residue is hydrolysable, whilst a distillate containing fatty acids, alcohols, and aldehydes is obtained. The amount of carbon dioxide produced increases proportionately to the duration of the oxidation. Naphthalene is less readily oxidised than paraffin wax by atmospheric oxygen under the same conditions, although double the amount of carbon dioxide is

produced in this case. Increase of the velocity at which the air is passed to 60 litres/hr. decreases the amount of oxidation produced by a given volume of air. In this case oxidation is most rapid in the earlier stages and mercury acts only as a very feeble catalyst. In spite of the lower temperature the velocity of oxidation of toluene is greater than that of naphthalene, and here again the velocity of oxidation is greater during the second period of 25 hrs. than during the first. No increase in the velocity of oxidation was observed in the presence of manganese dioxide.

J. W. Baker.

Action of acetylene on metals yielding explosive acetylides. J. F. Durand and M. Banos.—See this vol., 28.

Action of acetylene on the oxides of carbon. C. Sandonnini (Gazzetta, 1927, **57**, 781—792).—A dry mixture of acetylene and carbon dioxide passed through a glass tube at 400° remained unchanged in the absence of a catalyst. On the surface of copper some water, carbon monoxide, and saturated hydrocarbons were formed in small quantity. Nickel-copper and cobalt-copper catalysts were only slightly more effective. A nickel catalyst caused 20% reaction at 175°, and 60% at 300°; at the latter temperature, a mixture of 630 c.c. of acetylene with 370 c.c. of carbon dioxide gave 140 c.c. of carbon dioxide unchanged, 10 c.c. of unsaturated hydrocarbons, 15 c.c. of hydrogen, and 65 c.c. of saturated hydrocarbons. Cobalt gave similar results; iron was inefficient, as were catalysts containing aluminium.

For acetylene–carbon monoxide mixtures, nickel and cobalt were the most efficient catalysts. The products contained water, carbon dioxide, formaldehyde, acetaldehyde, acraldehyde, and a mixture of unsaturated hydrocarbons, b. p. 135—150°. The carbonaceous mass remaining on the catalyst had Ni 15·2%, H 1·32%, C 78·4%, O 5·18%, or Co 21·55%, H 2·83%, C 65·92%, O 9·70%. It is assumed that oxygen is adsorbed by the carbon.

E. W. Wignall.

[Action of cyanogen bromide on dimagnesium acetylene dibromide.] H. Biltz (Ber., 1927, **60**, [*B*], 2413).—The dibromoacetylidene, reported as obtained by Nekrassov (A., 1927, 1051), has been shown to be dibromoacetylene (cf. Biltz, A., 1913, i, 241).

H. Wren.

Action of polyhalogenated compounds of methane and of ethane on magnesyl derivatives. IV. R. Binaghi (Gazzetta, 1927, **57**, 669—675).—An attempt to prepare hexaphenylethane from hexachloroethane by the action of magnesium phenyl bromide was unsuccessful; of *s*-di- and tetra-chloroethylene and *s*-tetrachloroethane, only the last reacts with magnesium phenyl bromide on heating, yielding a product decomposed by water to give *s*-tetraphenylethane.

With magnesium ethyl bromide hexachloroethane yields equal volumes of ethylene and ethane and a product decomposed by water to give equal volumes of ethylene and acetylene, some ethyl bromide and ethyl chloride being also formed (as in most of the following reactions). *s*-Tetrachloroethane yields ethane, and a product decomposed to give equal volumes of ethylene and acetylene. Tetrachloroethylene yields equal volumes of ethylene and ethane, and a product decomposed to give equal volumes of ethylene and acetylene. *s*-Dichloroethylene yields ethane, and a product decomposed to acetylene and ethylene; it is supposed that in the initial reaction acetylene is formed, and that this reacts with magnesium ethyl bromide to give ethane and the compound MgBr·C:C·MgBr.

E. W. Wignall.

Synthesis of αζ-dibromo-*n*-hexane and its action on *p*-toluenesulphonamide. A. Müller and A. Sauerwald (Monatsh., 1927, **48**, 521—527).—Hexane-αζ-diol is prepared in 55% yield by the vigorous reduction of methyl adipate with sodium in boiling absolute alcohol, the reaction being completed by heating in an oil-bath at 110—120°. On steam distillation of the product the diol passes over completely with the aqueous-alcoholic distillate, from which it is obtained by distillation in a vacuum, the diol boiling at 136—138°/11 mm. When hydrogen bromide is passed for 3·5 hrs. into the diol at 120—130° αζ-dibromo-*n*-hexane is obtained in 70% yield. When the dibromohexane is treated with *p*-toluenesulphonamide in the presence of alcoholic potassium hydroxide (cf. Müller and Sauerwald, A., 1927, 884) the products are *NN'-bis-*p*-toluenesulphonyl-αζ-diamino-*n*-hexane*, $(C_6H_4Me{\cdot}SO_2{\cdot}NH)_2(CH_2)_6$, m. p. 151·4°, which, when heated with hydrochloric acid (*d* 1·19) for 5 hrs. in a sealed tube at 170°, is hydrolysed to the hydrochloride of αζ-diamino-*n*-hexane (Curtius and Clemm, A., 1901, i, 68) and a *substance*, m. p. 72°, which on hydrolysis with hydrochloric acid (*d* 1·19) for 6·5 hrs. at 160° yields a *hydrochloride*, m. p. 234° [*chloroplatinate*, m. p. 196—197° (decomp.); *methiodide*, m. p. 265°], isomeric but not identical with the corresponding salts of α-pipecolin [hydrochloride, m. p. 210°; methiodide, m. p. 320—321° (uncorr.) (von Braun, A., 1910, i, 821, describes the product as 1-methyl-2-pipecolin methiodide, m. p. 255°)]. The original condensation product, m. p. 72°, is therefore isomeric but not identical with *N-*p*-toluenesulphonyl-α-pipecolin*, m. p. 54·5—55°, which was synthesised by the action of *p*-toluenesulphonyl chloride on α-pipecolin. All m. p. are corrected.

J. W. Baker.

Symmetrical dichlorodimethyl sulphate, chloromethoxysulphonyl chloride, and similar derivatives of formaldehyde. K. Fuchs and E. Katscher (Ber., 1927, **60**, [*B*], 2288—2296; cf. A., 1924, i, 1164).—The action of 1 mol. of paraformaldehyde on 1¼ mols. of chlorosulphonic acid at a temperature not exceeding 70° leads to the production of *chloromethoxysulphonyl chloride*, b. p. 49—50°/14 mm., 153—155°/750 mm. (slight decomp.), *d* 1·63, and methylene sulphate, m. p. 153°; with 2¼ mols. of chlorosulphonic acid the quantity of formaldehyde corresponding with the methylene sulphate is transformed into methoxysulphonyl chloride. If the products obtained from 1 mol. of paraformaldehyde and 1¼ mols. of chlorosulphonic acid are poured on to ice previous to distillation, a mixture of dichloromethyl ether, b. p. 101·5—102°, polymeric formaldehyde, hydrogen chloride, and *chloromethyl sulphate*, $(CH_2Cl)_2SO_4$, b. p. 96—97°/

14 mm., is obtained; in contrast with methyl sulphate, the latter substance is completely non-poisonous, strongly antibactericidal, almost odourless, and sweet in taste. Removal of unchanged chlorosulphonic acid and sulphuric acid may advantageously be accomplished by the use of sodium chloride in place of ice if the temperature is not allowed to exceed 70—80°. After similar use of anhydrous potassium sulphate the main isolable product is chloromethoxysulphonyl chloride with smaller amounts of dichloromethyl ether and chloromethyl sulphate. As expected, mixtures of chloromethyl sulphate and chlorosulphonic acid are converted by distillation in a vacuum either into chloromethoxysulphonyl chloride and methylene sulphate or entirely into chloromethoxysulphonyl chloride according to their relative proportion in the mixture. Under similar conditions, methylene sulphate is converted by chlorosulphonic acid into chloromethoxysulphonyl chloride. Dichloromethyl ether is transformed by chlorosulphonic acid at 60—70° and subsequent distillation exclusively into chloromethoxysulphonyl chloride; if, however, the product is treated with ice, a mixture of chloromethyl sulphate and chloromethoxysulphonyl chloride is produced. If attempts are made to distil a solution of small amounts of methylene sulphate in chloromethoxysulphonyl chloride or non-homogeneous chloromethyl sulphate, carbonisation occurs at a temperature not exceeding 70° although pure methylene sulphate does not char at 155°; similar effects are produced by a large number of organic compounds (ether, acetone, ethyl acetate, benzene, etc.) at 80—100°.

The reactions are adequately explained by the hypothesis that formaldehyde and chlorosulphonic acid yield primarily chloromethyl hydrogen sulphate and chloromethyl alcohol, in support of which it is observed that polymeric formaldehydes dissolve slowly in chlorosulphonic acid at 0°, yielding products which are almost completely soluble in water. Further, an equilibrium appears to exist between chloromethyl hydrogen sulphate and chloromethyl alcohol, since the maximum yield of products insoluble in water is only 70% of that calculated on the formaldehyde and distillation of the residue obtained after decomposition of excess of chlorosulphonic acid by ice gives the fission products of chloromethyl alcohol (polyoxymethylenes and hydrogen chloride). H. WREN.

Synthesis of partly acylated glycerides. B. HELFERICH and H. SIEBER (Z. physiol. Chem., 1927, **170**, 31—37).—The rapid hydrolysis of triphenylmethyl (=trityl) ethers of glycerol by hydrobromic–acetic acid at 0° provides a means of obtaining partly acylated glycerides. Glycerol α-monotrityl ether (Helferich, Speidel, and Toeldte, A., 1923, i, 331) gives, when treated with benzoyl chloride in pyridine, the *dibenzoate*, m. p. 90—92° which by hydrolysis with hydrobromic–acetic acid at 0° is converted into glyceryl αβ-dibenzoate, m. p. 59·5—60°. From glycerol αγ-ditrityl ether are obtained the *benzoate*, m. p. 108° ($+1·5H_2O$) or 130—132° (anhyd.; corr.), and glyceryl β-benzoate, the latter being identified by conversion into glyceryl β-benzoate αγ-di-*p*-nitrobenzoate, m. p. 152—152·5°. Glycerol αγ-ditrityl ether forms a p-*toluenesulphonate*, m. p. 163°. C. HOLLINS.

Autocatalytic oxidation of sulphydryl compounds. D. C. HARRISON (Biochem. J., 1927, **21**, 1404—1415).—Both the aerobic and anaerobic oxidation of sulphydryl compounds are catalysed by pure metal-free dithiodiglycollic acid, and this catalysis is not inhibited by cyanide. On the other hand, when the –S·S– linking of dithiodiglycollic acid is destroyed the catalytic action of the compound disappears. A mechanism is suggested by which the catalysis may take place. S. S. ZILVA.

Varying valency of platinum with respect to mercaptanic radicals. VI. (SIR) P. C. RAY, K. C. BOSE-RAY, and N. B. ADHIKARI (J. Indian Chem. Soc., 1927, **4**, 467—475).—Ammonia decomposes the complex compound, $PtCl_3,(C_2H_4)_3S_2$ (Ray, J.C.S., 1922, **121**, 1283), forming tetrammineplatinous dichloride. Benzylamine reacts yielding *tetrabenzylammineplatinous dichloride*, $[(CH_2Ph·NH_2)_4Pt]Cl_2$, m. p. 195°, whilst with ethylenediamine there are formed three *compounds*, $Pt_2Cl_6,3C_2H_4(NH_2)_2,(C_2H_4)_3S_3$, $PtCl_2,(C_2H_4)_2S_2$, and $PtCl_2,2C_2H_4(NH_2)_2$. Pyridine converts the original substance into tetrapyridineplatinous dichloride, dipyridineplatinous chloride (cf. A., 1926, 1023), and the *compound* $(C_5H_5N)_4Pt_2Cl_7$. Dimethylaniline yields the *compound* $NPhMe_2,PtCl_2$, piperidine gives the *compound* $3C_5H_{11}N,PtCl_2$, tripropylamine affords the *substance* $(C_2H_4)_2S_2,PtCl_2$, diethylamine furnishes the *compound* $2NHEt_2,PtCl_2$, which on crystallisation from acetone passes into the complex *compound*, $NHEt_2,PtCl_2,Me_2CO$, and *p*-phenylenediamine yields the *compound* $4C_6H_4(NH_2)_2,PtCl_3$. From these results it is concluded that the original complex is best represented by the formula $[(C_2H_4)_3S_2PtCl_2]Cl$. H. BURTON.

Mechanism of the hydrolysis of organic compounds. S. C. J. OLIVER and G. BERGER (Rec. trav. chim., 1927, **46**, 861—865).—In cases of hydrolysis of esters, ethers, and acid anhydrides where the reaction is catalysed by hydrogen ions, it is suggested that the reaction takes place through the addition of the ion to the oxygen atom of the group C·O·C. When this oxygen atom becomes induced positive by the presence of negative substituents, the reaction velocity depends on the concentration of water and no longer on that of the ion (A., 1927, 835). The very rapid addition of water to the doubly-linked oxygen atom in acetic anhydride prevents the detection of the influence of hydrogen ions, whereas it is detectable in the case of benzoic anhydride. G. A. C. GOUGH.

Strength of the linkings between hydrocarbon radicals and oxygen in simple and mixed ethers; mechanism of esterification and hydrolysis of esters. B. V. TRONOV, L. N. DIAKONOVA-SCHULIC, O. J. GULAEVA, and N. S. NIKIFOROVA (J. Russ. Phys. Chem. Soc., 1927, **59**, 545—562).—A *résume* of earlier work on the stability of carbon–oxygen linkings in ethers, acetals, and esters. The decomposition of these compounds at the ordinary temperature by hydrogen bromide in glacial acetic acid

solution under constant conditions was investigated, in order to determine the effect of different hydrocarbon radicals on the carbon–oxygen linking. The time required for the decomposition of a definite fraction of the compound was taken as a measure of the stability of the linking.

For ethers and esters the ease of elimination of hydrocarbon radicals is in the order: $CH_2Ph>Me>Et>C_5H_{11}>Ph$. The behaviour of the esters of inorganic acids is similar. The ease of decomposition of the esters of the same alcohol was in the order: H_2SO_4 and $HNO_3>H{\cdot}CO_2H>Et{\cdot}CO_2H>H_2CO_3>Me{\cdot}CO_2H>Ph{\cdot}CO_2H>CH_2Cl{\cdot}CO_2H>(CO_2H)_2>(CH_2{\cdot}CO_2H)_2$. The mineral acid esters are much more reactive than the others.

Different members of the ether and acetal series did not vary much in reactivity, with the exception of some methyl compounds.

The hydrolysis of esters by alkalis was also investigated, in order to elucidate the nature of the reaction, and various theories of its mechanism are discussed.

M. ZVEGINTZOV.

Decomposition of fatty acids by sulphuric acid. J. B. SENDERENS and J. ABOULENC (Compt. rend., 1927, **185**, 1087—1090).—Acetic acid and some of its homologues were decomposed by heating with five times their volume of sulphuric acid. Carbon monoxide was the first gas to be evolved, with increasing proportions of carbon dioxide and sulphur dioxide as the temperature was raised, and, finally, separation of carbon. The temperatures at which gas was first evolved were: with acetic, butyric, valeric, and hexoic acids, about 200°; *iso*butyric and *iso*valeric acids, 140°; *iso*hexoic acid, 150°; α-ethylbutyric acid, 130—140°. Thus the proximity of a side-chain to the carboxyl group facilitates decomposition.

B. W. ANDERSON.

Rate of reaction between bromine and unsaturated fatty acids as evidence of stereoisomerism. C. A. KNAUSS and J. G. SMULL (J. Amer. Chem. Soc., 1927, **49**, 2808—2815).—The rates of bromination, in carbon tetrachloride at the ordinary temperature, of oleic, linoleic, and linolenic acids decrease in this order, *i.e.*, the rate decreases with increase in unsaturation. The rates of bromination of the mixed fatty acids of poppy-seed, soya-bean, linseed, and perilla oils is in direct relation to the acid constituents. Under the influence of ultra-violet light, the bromination of both pure and mixed fatty acids proceeds beyond the bromination in the dark, indicating apparently the presence of unsaturated isomerides (10—15%) which are less readily brominated.

F. G. WILLSON.

Acetylated sulphates of sesquioxides. A. RECOURA (Compt. rend., 1927, **185**, 992—994).—After prolonged treatment with powdered acetic anhydride, white ferric sulphate forms a *compound*, $(Fe_2O_3,3H_2SO_4)_6,3SO_3,3Ac_2O$, which loses its 3 mols. of acetic anhydride in dry air, but recovers them in an atmosphere of acetic anhydride, in which it is stable. Ferric alum similarly forms a *compound*, $Fe_2(SO_4)_3,(NH_4)_2SO_4.H_2O,3Ac_2O$; in a dry atmosphere 2 mols. of the anhydride are lost rapidly, the third very slowly. The *compound*, $Al_2(SO_4)_3.2H_2O,3Ac_2O$, formed by ammonium alum, behaves similarly. Aluminium sulphate, $Al_2(SO_4)_3,15H_2O$, gives the *substance* $2Al_2(SO_4)_3,6H_2O,3Ac_2O$, which in dry air loses 1 mol. of anhydride rapidly, the second slowly, the third still remaining after 3 years' preservation.

B. W. ANDERSON.

Di-*n*-hexoyl peroxide and per-*n*-hexoic acid, and the detection of peroxides by electrolysis of potassium hexoate. F. FICHTER and R. ZUMBRUNN (Helv. Chim. Acta, 1927, **10**, 869—885: cf. A., 1926, 807).—Treatment of *n*-hexoic anhydride with freshly-prepared barium peroxide in moist ether yields, in addition to barium hexoate, some *di*-n-*hexoyl peroxide*, a colourless oil which does not solidify on cooling. The peroxide when heated evolves gas at 64—65° and explodes at 84—85°. It is soluble in organic solvents and forms a red dye with *p*-toluidine. With phenylhydrazine there is formed *n*-hexoylphenylhydrazide, m. p. 95·6—96·5° (cf. Autenrieth, A., 1888, i, 250). Treatment of an ice-cold mixture of *n*-hexoic anhydride and 100% sulphuric acid with 93% hydrogen peroxide (cf. D'Ans and Frey, A., 1912, i, 601) yields *per*-n-*hexoic acid*, b. p. 62—63°/13 mm., 41—42°/0·5 mm., m. p. 15°, which on heating evolves gas at 75°, and afterwards explodes. Explosive decomposition of the peroxide furnishes carbon dioxide, -decane, *n*-amyl alcohol, and hexoic acid, whilst slow decomposition at 65—70° yields pentene, *n*-amyl alcohol, and hexoic acid. The rate of hydrolysis of the peroxide is increased by borax or sodium hydrogen carbonate (cf. Boeseken and Gelissen, A., 1926, 166). Explosive decomposition of perhexoic acid at 240° gives carbon dioxide, pentene, and *n*-amyl hexoate, whilst slow decomposition at 75° affords small quantities of carbon dioxide and *n*-amyl hexoate, the main products being hexoic acid and oxygen. Electrolysis of potassium hexoate–hexoic acid solution, with platinum and graphite electrodes, shows that the reaction proceeds through the peroxide. This intermediate either decomposes at the anode yielding *n*-decane and carbon dioxide, or is hydrolysed to hexoic and perhexoic acids, followed by decomposition of the latter to *n*-amyl alcohol (cf. Petersen, A., 1898, i, 352) and carbon dioxide. The amyl alcohol furnishes pentene and *n*-amyl hexoate. The main product of electrolysis with a platinum anode is *n*-decane. H. BURTON.

Derivatives of trichloroacrylic acid. IV. Pentachloropropionic acid. V. Electrolytic dissociation constant. Salts. J. BOESEKEN (Rec. trav. chim., 1927, **46**, 841—843, 844—846).—IV. *Pentachloropropionic acid*, m. p. 210—215° (on heated mercury), prepared by passing chlorine through a carbon tetrachloride solution of trichloroacrylic acid in sunlight, gives *barium, calcium, potassium*, and *sodium* salts which are decomposed rapidly in aqueous solution with the formation of tetrachloroethane, carbon dioxide, and the metallic chloride. The acid decomposes in a similar manner in aqueous solution and possesses a strength comparable with the mineral acids.

V. Trichloroacrylic acid has κ_{25} 0·07. The normal *barium* ($+3\frac{1}{2}H_2O$), *calcium* ($+3\frac{1}{2}H_2O$), *strontium* ($+5H_2O$), *magnesium* ($+3\frac{1}{2}H_2O$), *zinc* ($+6H_2O$ and

$+3\frac{1}{2}H_2O$), *cadmium* ($+2H_2O$), and *mercury* salts (anhydrous) are described. G. A. C. GOUGH.

*iso*Erucic acid. T. J. MARCHANDANI and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **10A**, 57—63).—See A., 1927, 339.

Configurational relationships of α-hydroxybutyric and lactic acids. G. W. CLOUGH (J. Biol. Chem., 1927, **75**, 489—490).—A question of nomenclature (cf. Clough, J.C.S., 1918, **113**, 533, and Levene and Haller, A., 1927, 1053).

C. R. HARINGTON.

Preparation of β-hydroxybutyric acid. A. WACKER, GES. F. ELEKTROCHEM. IND., G. BASEL, and F. KAUFLER.—See B., 1927, 924.

Sulphomethylsuccinic acids. I. H. J. BACKER and J. BUINING (Rec. trav. chim., 1927, **46**, 847—854).—α-Sulphopropane-βγ-dicarboxylic acid ($+H_2O$), m. p. 89° (decomp.), may be obtained either by the interaction of potassium pyrosulphite and ammonium hydrogen itaconate in aqueous solution at 108° or by the interaction of ammonium α-bromopropane-βγ-dicarboxylate and ammonium sulphite. The acid is best isolated by means of the *barium* salt ($+6H_2O$). The *calcium* ($+7H_2O$), *lead* ($+6H_2O$), *copper* ($+6H_2O$), *nickel* ($+7H_2O$), and *cobalt* ($+6H_2O$) salts are described. Crystallisation of the *strychnine* salt ($+3H_2O$) followed by decomposition to the sodium salt gives a partly active product.

G. A. C. GOUGH.

Specific action of the oxime group on metallic salts. I. Reactions of cobalt, nickel, and copper salts with aldoximes. II. Reactions of ketoximes with metallic salts. W. HIEBER and F. LEUTERT (Ber., 1927, **60**, [*B*], 2296—2310, 2310—2317).—I. The behaviour of metals towards oximes appears to depend on the nature of the metallic salt and the constitution and configuration of the organic component. The oximes offer two centres for addition, but the oxygen and nitrogen atoms have a mutually weakening effect and hence only metallic salts which have a relatively pronounced specific affinity towards nitrogenous addenda and not too great lattice energy may be expected to yield additive compounds with oximes. In general, aldoximes unite readily with the halides of cobalt, nickel, and copper in the presence of alcohol, acetone, or chloroform. The compounds thus produced are immediately decomposed by water or ammonia. They are unchanged by attempted electrolysis in chloroform or acetone. Determinations of mol. wt. in ethylene dibromide do not give very definite results, since the compounds appear to be decomposed with liberation of the oxime but without precipitation of the metallic salts, thus indicating that additive compounds exist in solution which contain less than 4 mols. of oxime. The substances appear therefore to have the structure $[Hal_2X(\cdots N(OH){:}CHR)_{2\text{ or }4}]$. Among stereoisomeric aldoximes, only the labile β-varieties react immediately with metallic salts; since the α- and β-forms ultimately yield the same additive compounds, the reaction of the former is preceded by isomerisation to the β-derivatives. This behaviour of the oximes is in harmony with Meisenheimer's views on their constitution. Corresponding with the pronounced basicity of the nitrogen atom, only a feeble tendency towards salt formation is to be expected. This is observed only with the salts of heavy metals with weak acids or in alkaline solution. Copper acetate and α-benzaldoxime yield a substance which, however, is not a copper salt in the usual sense, the acetic acid residue being only partly replaced by the oxime groups. Acetaldehyde affords the *compounds* $4CHMe{:}N{\cdot}OH,CoCl_2$, $4CHMe{:}N{\cdot}OH,CoBr_2$, $4CHMe{:}N{\cdot}OH,NiCl_2$, $4CHMe{:}N{\cdot}OH,NiBr_2$, and $2CHMe{:}N{\cdot}OH,CuCl_2$. The *substances* $4CHPr^{\beta}{:}N{\cdot}OH,CoCl_2$, $4CHPr^{\beta}{:}N{\cdot}OH,NiCl_2$, and $4CHPr^{\beta}{:}N{\cdot}OH,CuCl_2$ are derived from *iso*butaldoxime. Benzaldoxime gives the additive *compounds*, $4CHPh{:}N{\cdot}OH,CoCl_2$, $4CHPh{:}N{\cdot}OH,CoBr_2$, $4CHPh{:}N{\cdot}OH,NiCl_2$, $4CHPh{:}N{\cdot}OH,NiBr_2$, $2CHPh{:}N{\cdot}OH,CuCl_2$. The *substances* $4CHPh{:}CH{\cdot}CH{:}N{\cdot}OH,CoCl_2$ and $2CHPh{:}CH{\cdot}CH{:}N{\cdot}OH,CuCl_2$ are derived from β-cinnamaldoxime. The sodium derivative of benzaldoxime and copper chloride in alcoholic solution yield a *substance* containing oxime and copper in the ratio 1 : 1; similarly β-cinnamaldoxime and copper acetate give the *compound* $(CHPh{:}CH{\cdot}CH{:}NO)_2Cu$. If a methyl-alcoholic solution of sodium hydroxide is treated with a little acetaldoxime, *iso*butaldoxime, β-benzaldoxime, or β-cinnamaldoxime and a trace of cobalt chloride or copper chloride is added, a characteristic colour is developed which usually passes into the organic medium after addition of chloroform and water. Complex metal–oxime anions appear to be produced. α-Benzildioxime and cupric chloride yield the *substance* $C_{14}H_{12}O_2N_2,CuCl_2,2H_2O$.

II. The ability of ketoximes to form additive compounds with metallic salts is notably less than that of aldoximes, and the peculiarities of the metallic salt are therefore more obvious. The formation of additive compounds is immediately observed when cobalt chloride or bromide is covered with a solution of acetoxime in chloroform; the appearance of the blue colour is specific and the reaction is very sensitive. Homogeneous products cannot, however, be isolated. Quantitative differences in the additive power of metallic salts to acetoxime are investigated by observing the changes of f. p. caused by the addition of the metallic bromide to a solution of the oxime in ethylene bromide. If addition with more than 1 mol. of oxime occurs the molecular concentration is lowered and the f. p. rises. The tendency to form compounds is found to increase in the series, cobalt, nickel, copper, which harmonises with the preparation of the *compounds* $CMe_2{:}N{\cdot}OH,CuCl_2$ and $CMe_2{:}NOH,(AcO)_2Cu$. Acetoxime adds bromides more readily than chlorides; with iodides, the isolation of the *compounds* $CoI_2,2CMe_2{:}N{\cdot}OH,0{\cdot}5Me_2CO$ and $NiI_2,2(?\beta)CMe_2{:}N{\cdot}OH$ has been effected. In harmony, the more or less complete replacement of iodine by the oxime residue is observed when acetoxime reacts with cobalt iodide in alcoholic solution whereby crystalline substances of the type $Co(I,CMe_2{:}N{\cdot}OH)_2$ are obtained. Methyl butyl ketoxime resembles acetoxime in giving a very sensitive colour reaction with cobalt chloride and chloroform. Fatty aromatic ketoximes have markedly less additive power. Acetophenoneoxime does

not react with cobalt or nickel halides, but with copper chloride in chloroform gives compounds, $CuCl_2$,1—2CMePh:N·OH. Feigl's "copper salt" of acetophenoneoxime is an additive compound. Benzophenone gives only a faint reaction with copper acetate, whereas with cupric chloride it affords the *compound* CPh_2:N·OH,$CuCl_2$. H. Wren.

Dioximes. XLIII. G. Ponzio and I. de Paolini (Gazzetta, 1927, **57**, 633—648).—The action of bromine on α-hydroxy-β-methylglyoxime yields a *compound* (I), decomp. 122—135°, regarded as

CMe(:NO·H)·C(OH)···N(OH)·CO·CMe:N·OH
O··········H

The substance is converted by sodium hydroxide solution into α-oximinopropionic acid and hydroxymethylglyoxime, and by hydrogen chloride in alcohol into the latter, with ethyl α-oximinopropionate; the action of nitrogen tetroxide yields ethylnitrolic acid (benzoyl derivative, new m. p. 131°); that of hydroxylamine, hydroxymethylglyoxime. The colour reactions of (I) with copper solutions under varying conditions are in harmony with the above formula; the compound has one hydrogen atom replaceable by metals, giving a *silver* salt, unchanged in boiling water, a *copper* salt regarded as co-ordinated with the α-oximino-nitrogen atom, soluble in ammonia solution to a violet-blue solution which changes to reddish-brown on adding hydroxylamine, ammonium dimethylhydroxyglyoxime cuprate being formed.

When heated with aniline, (I) gives *α-oximinopropionanilide*, (II), m. p. 144—145°, also obtained from pyruvanilide and hydroxylamine; the position of the oximino-group is found by treatment with bromine to give *α-oximinopropion-p-bromoanilide*, m. p. 206—208°, hydrolysed by sodium hydroxide solution to *p*-bromoaniline and α-oximinopropionic acid. The anilide (II) yields an *acetyl* derivative, m. p. 95° (+H_2O), 77—78° (anhyd.), and a *benzoyl* derivative, m. p. 105—107° (+H_2O), 98—100° (anhyd.).

Benzoyl chloride converts (I) into a *dibenzoyl* derivative, CMe(:N·OBz)·$C_2H_3O_4N$·CMe:N·OBz, m. p. 151° (decomp.) or, after washing with alcohol, 162° (decomp.). This with aniline at 50—60° yields benzanilide and α-oximinopropionanilide; in the cold, however, α-benzoyloximinopropionanilide and *α-oximino-β-benzoyloximinopropyl alcohol*, (III), m. p. 122—123° (decomp.), are formed, and it is suggested that the dibenzoyl derivative yields first the monobenzoyl derivatives of α-oximinopropionic acid and α-hydroxy-β-methylglyoxime. The compound (III) gives an intense cherry-red colour with ferric chloride, unchanged by hydrochloric acid, forms a copper derivative, is hydrolysed by sodium hydroxide solution to benzoic acid and hydroxymethylglyoxime, with benzoyl chloride gives α-hydroxydi-*N*-benzoyl-β-methylglyoxime, CMe(:N·OBz)·C(:N·OBz)·OH, and with acetic anhydride gives *α-acetyloximino-β-benzoyloximinopropyl alcohol*, m. p. 104—105°.

The product formulated by Ponzio (A., 1927, 134) as CMe(:N·OBz)·C(:N·OH)·OH, m. p. 146—147° (decomp.), is now regarded as the "*l*-derivative," *i.e.*, as α-benzoyloximino-β-oximinopropyl alcohol. It forms a *copper* derivative containing 2 mols. of the organic compound; acetic anhydride yields *α-benzoyloximino-β-acetyloximinopropyl acetate*, m. p. 86—87°.

α-Hydroxy-β-phenylglyoxime yields a molecular *compound* (IV), analogous to (I), decomp. at 125—135° to give 5-hydroxy-3-phenylazoxime, m. p. 200—202°; (IV) yields *ammonium* (m. p. 107—108°, decomp.), *silver*, and nickel salts; it is hydrolysed by sodium hydroxide to give hydroxyphenylglyoxime and *phenyloximinoacetic acid*, m. p. 135° (decomp.). With aniline in the cold, (IV) yields oximinophenylacetanilide, m. p. 154—155°, with hydroxyphenylglyoxime. E. W. Wignall.

Dioximes. XLIV. (Signa.) M. Aymaretto (Gazzetta, 1927, **57**, 648—655).—Oximinoacetic acid forms copper, *nickel*, and *cobalt* salts, [CH(:N·OH)CO_2]$_2$M,2H_2O. α Oximinopropionic acid yields similar *copper*, *nickel*, and *cobalt* (−3H_2O) salts, and a basic *copper* salt; the *sodium* salt is prepared by the action of sodium ethoxide on an alcoholic solution of the acid. α-Oximinobutyric acid yields an *ammonium* salt, m. p. 158° (decomp.), and *sodium*, *potassium* (+H_2O), *copper* (+H_2O), *cobalt* (+2H_2O), and *nickel* (+2H_2O) salts; the last-named also gives two *complexes*, in which the water is replaced by 2 mols. of ammonia and of pyridine, respectively. Oximinophenylacetic acid yields a *nickel* salt (+0·5H_2O, replaceable by 3C_5H_5N), a *cobalt* salt (+2H_2O), and a *copper* salt. These salts are considered to be co-ordinated, thus: M=[-CO_2·CR:N(OH)···]$_2$. E. W. Wignall.

Mutarotation. VIII. Mutarotation of mannose. C. N. Riiber and J. Minsaas (Ber., 1927, 60, [*B*], 2402—2412; cf. A., 1926, 1228).—The possibility of the existence of more than two modifications of a given sugar in its aqueous solution cannot be satisfactorily examined by observations based on a single physical constant; for this purpose it is necessary to determine more than one additive property when, if only two forms are present, the ratio $k_1/k_2=K$ must be constant for each property. Thus for mannose the value K is 0·50 and 0·47 as deduced from observations on specific rotation and molecular solution volume, whereas determination of the index of refraction leads to the value K=0·64. Hence more than two modifications of mannose are present in the aqueous solution in which, however, the known α- and β-varieties predominate. Hudson's classification of sugars into α- and β-varieties in accordance with optical activity alone is open to criticism, since contradictory results are obtained when other physical constants are made the basis of division. Precise directions for the preparation of crystalline α- and β-mannose are given. H. Wren.

Constitution of the disaccharides. XVI. Cellobiose. W. N. Haworth, C. W. Long, and J. H. G. Plant (J.C.S., 1927, 2809—2814).—*Methyl octamethylcellobionate*, b. p. 169—171°/0·05 mm., n_D^{l} 1·4609, furnishes on hydrolysis with hydrochloric acid 2 : 3 : 4 : 6-tetramethylglucose, m. p. 93—94° (92·7% yield), and 2 : 3 : 5 : 6-tetramethylglucono-lactone, m. p. 26—27° (Haworth and Long, A., 1927, 450), in 80% yield. The phenylhydrazide of 2 : 3 : 5 : 6-tetramethylgluconic acid, prepared from

the above lactone, is identical with that obtained from methyl octamethylmaltobionate and 2 : 3 : 5 : 6-tetramethyl-(γ)-glucose.

These results confirm the structure of cellobiose as a glucose β-glucoside previously advocated (Charlton, Haworth, and Peat, A., 1926, 273) and removes the need for any reservation in favour of an alternative formulation as a γ-glucose β-glucoside. S. COFFEY.

Production of cellobiose from cellobiose octa-acetate. F. C. PETERSON and C. C. SPENCER (J. Amer. Chem. Soc., 1927, **49**, 2822—2825).—Finely-powdered cellobiose octa-acetate (10 g.) is incorporated during 1 hr., with stirring, with 85 c.c. of 10% sodium ethoxide in 95% alcohol. The precipitated sodium salt is collected, washed with absolute alcohol, dissolved in the minimum of water, and the filtered aqueous solution acidified with glacial acetic acid, whereon the cellobiose separates, in crystalline form, in 95% yield. It is purified by dissolving in the minimum of water, filtration, and reprecipitation with acetone. The yield of purified product, m. p. 225°, is 85%. F. G. WILLSON.

Glucosides of *Fatsia japonica*, Dcne. et Planc. I. *Fatsia* sapotoxin. II. Fatsin. III. Biological. K. OHTA (Kitasato Arch. Exp. Med., 1926, **7**, 301—313).—The *sapotoxin*, $C_{37}H_{62}O_{10}$, was obtained by extracting the powdered, air-dried leaves with warm alcohol, purifying the extract with lead acetate, and treating the alcoholic residue with 98% methyl alcohol. When heated with 1% sulphuric acid in 50% alcohol, a clear yellow solution and an insoluble *sapogenin*-I, $C_{32}H_{54}O_4$, were obtained. Fatsin, $C_{31}H_{53}O_{20}$, when heated with excess of 2% sulphuric acid, is hydrolysed to sugar, a volatile organic acid, ether-soluble *α-sapogenin*, $C_{18}H_{30}O_3$, and ether-insoluble *β-sapogenin*, $C_{16}H_{25}O_3$. Neither *Fatsia* sapotoxin nor fatsin eliminates sugar under the action of taka-diastase. CHEMICAL ABSTRACTS.

Cellulose space lattice of plant fibres. O. L. SPONSLER (Nature, 1927, **120**, 767).—The two different types of *X*-ray diffraction patterns obtained respectively by Herzog and the author from cellulose fibres are discussed. Their lack of agreement is considered, and it appears that the values used for the *a* axis and the *b* axis of the elementary cell proposed by Herzog were both produced by the same set of planes. When the value 4·30 Å. is discarded, Herzog's axial dimensions must also be discarded, together with the conclusions (*a*) that four anhydro-glucose units are contained in the elementary cell, and (*b*) that certain interference maxima are produced by impurities in the fibre, or that there are two types of carbohydrates embodied in the cellulose of the fibre. The correspondence between the value 4·30 and a certain interference maximum obtained from mercerised cellulose likewise has no significance. A. A. ELDRIDGE.

Characteristics of celluloses, oxycelluloses, and hydrocelluloses. L. CAMILLERI (Anal. Fís. Quím., 1927, **25**, 434—439).—Cotton cellulose and α-cellulose from rice-straw (*a*) and the oxycelluloses (*b*) and hydrocelluloses (*c*) derived from them, were examined. The following measurements are recorded: Cotton cellulose; *d* (by three methods): (*a*) 1·5945—1·6017, (*b*) 1·5805—1·5847, (*c*) 1·6051—1·6109; calorific value: (*a*) 4789·6, (*b*) 4865, (*c*) 4783·8. α-Cellulose; *d*: (*a*) 1·5847—1·5947, (*b*) 1·5766—1·5804, (*c*) 1·6064—1·6101; calorific value: (*a*) 4779·4, (*b*) 4868·6, (*c*) 4783·4. The products of distillation were analysed. The gaseous products showed distinct differences in amount, about 7% being obtained from the hydrocelluloses and 14% from the celluloses and oxycelluloses. Slightly less liquid was obtained from the celluloses. R. K. CALLOW.

***X*-Ray investigation of cellulose nitrate.** R. O. HERZOG and S. VON NARAY-SZABÓ (Z. physikal. Chem., 1927, **130**, 616—625).—The Debye–Scherrer diagrams given by specimens of cellulose nitrate prepared in different ways and of different nitrogen content all exhibit the same interference. It is therefore concluded that the various cellulose nitrates are in reality mixtures of cellulose trinitrate and unchanged cellulose. Consideration of the kinetics of the nitration and of nitration in general favours the theory of the exclusive production of cellulose trinitrate. The latter belongs to the quadratic system, the lattice constants being a=14·75, b=7·88, and c—10·30 Å.; the elementary cell contains four molecules. H. F. GILLBE.

Cryoscopic behaviour of cellulose acetate. A correction. K. HESS (Annalen, 1927, **457**, 307—308; cf. Hess and Schultze, A., 1927, 753).—Certain errors in values for rotatory power are corrected. C. HOLLINS.

Lignin. II. W. KUSTER and E. SCHODER [with A. BAHL, R. DAUR, W. SCHAIRER, and K. MASSONG] (Z. physiol. Chem., 1927, **170**, 44—59; cf. Kuster and Schnitzler, B., 1926, 151).—"Merolignin," isolated from the product of heating lignin with β-naphthol and a trace of hydrochloric acid (*loc. cit.*), is now found to be dinaphthapyran, $C_{21}H_{14}O$, a molecule of formaldehyde being supplied by the lignin (cf. Freudenberg, A., 1926, 935). Under similar conditions merolignin is also formed from β-naphthol and formaldehyde–resorcinol resin (but not formaldehyde–phenol resin, in which pyran rings are absent). Merolignin from primary lignin prepared by Friedrich's method (A., 1926, 824) is free from fluorescent compounds, but resinified pine sawdust, freed from wood gum by treatment with 5% sodium hydroxide, yields in addition to merolignin a fluorescent hydrocarbon, m. p. 249—250°, which is probably chrysene. This is also obtained from lignin prepared by Willstatter and Zechmeister's method.

Dinaphthapyran, m. p. 201° [picrate, m. p. 181—183° (lit. 172°)], best synthesised by Wolff's method (A., 1893, i, 222), gives a *perbromide*, $C_{21}H_{13}Br_3$, which is converted by alcoholic potassium hydroxide into a *compound*, m. p. 271° (decomp.).

Starch and sucrose both yield, when heated with β-naphthol and a little hydrochloric acid, no merolignin but a yellow, crystalline *compound*, $C_{14}H_{10}O$, m. p. 337 (sublimes). C. HOLLINS.

Amino-derivatives of isoprene and of ethyl butyl ether. J. SUPNIEWSKI (Rocz. Chem., 1927, **7**, 176—182).—The following dimethylallyl deriv-

atives are prepared: *γ-methyl-Δ^{β}-butenylamine* ($(CMe_2\!:\!CH\cdot CH_2\cdot NH_2)_3$, b. p. 80—90°/35 mm.: *n-butyl-di-γ-methyl-Δ^{β}-butenylamine*, b. p. 70—100°/25 mm.; *γ-methyl-Δ^{β}-butenyl cyanamide*, b. p. 142—145°/20 mm.; *methyl γ-methyl-Δ^{β}-butenyl ether*, b. p. 85—90°; *γ-methyl-Δ^{β}-butenyl thiocyanate*, b. p. 65—70°/35 mm.; *ethoxybutylamine*, b. p. 142—145°, and *dibutylethoxybutylamine*, b. p. 203—208°. R. TRUSZKOWSKI.

Triacetonamine hydrate. F. FRANCIS (J.C.S., 1927, 2897—2898).—A satisfactory method for the preparation of the above (yield 20—26%) is described. Nitrosotriacetonamine is decomposed catalytically by alkalis, giving a quantitative yield of phorone. S. COFFEY.

Stereoisomerism and anæsthetic action. Separation of methylethyldimethylaminomethylcarbinol into its two enantiomorphs and preparation of the two optically active stovaines. E. FOURNEAU and I. RIBAS (Anal. Fís. Quím., 1927, **25**, 401—408).—Optically active forms of "stovaine" (hydrochloride of methylethyldimethylaminomethylcarbinol benzoate) have been prepared from the active carbinols, separated with the aid of α-(2-naphthoxy)propionic acid (Fourneau and Balaceano, A., 1926, 288).

d-*Methylethyldimethylaminomethylcarbinol* l-α-(2-*naphthoxy*)*propionate* and the l-*base*-d-*acid* salt, m. p. 125—126°, $[\alpha]_D^{20}$ −57·3° and +57·7° in alcohol, were obtained in turn by crystallisation from a solution of the *r*-carbinol salt of the *l*-acid followed by conversion of the residue into the salt of the *d*-acid. Hydrolysis yielded d- and l-*methylethyldimethylaminomethylcarbinols*, b. p. 55°/15 mm., $[\alpha]_D^{20}$ +7·7° and −7·6° in water, which yielded, respectively, d- and l-*stovaines*, m. p. 186—187°, $[\alpha]_D$ ±8·5° in water. These separated with alcohol of crystallisation and effloresced rapidly. Inactive stovaine (m. p. 174—175°), which crystallises without alcohol, is probably pseudo-racemic. Physiological tests show that *d*-stovaine is a more powerful anæsthetic than *l*-stovaine. R. K. CALLOW.

Decomposition of amino-acids and aminopurines by methylglyoxal and related substances. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, **188**, 197—210).—Data are given for the amounts of carbon dioxide, ammonia, and aldehyde (or ketone) formed when a solution of methylglyoxal is boiled for varying periods with certain amino-acids in an atmosphere of nitrogen. The following amino-acids were used and the following aldehydes (or ketones) formed: *dl*-alanine (acetaldehyde), *dl*-amino*iso*butyric acid (acetone), *dl*-leucine (*iso*valeraldehyde), phenylglycine (benzaldehyde), cystine (acetaldehyde), aspartic acid (acetaldehyde), asparagine (acetaldehyde), glutamic acid (propaldehyde and acetaldehyde), glycine (formaldehyde). Data are also given for the deamination effected by methylglyoxal on guanidine, creatine, creatinine, adenine, guanine, and guanidine. E. A. LUNT.

Reaction of chloroacetic acid with ammonia, and the preparation of glycine. G. R. ROBERTSON (J. Amer. Chem. Soc., 1927, **49**, 2889—2894).—Glycine is obtained in 50% yield from chloroacetic acid by dissolving 1 mol. of the latter in 4 litres of ammonia solution (*d* 0·90), and keeping the solution for 24 hrs. at 30° or at least 2 days at 20°. The solution is then evaporated to 500 c.c. to recover ammonia, and the flocculent silver oxide obtained from 170 g. of silver nitrate by means of aqueous sodium hydroxide is added. After removal of the precipitated silver chloride, the filtrate is again evaporated, with stirring, to about 200 c.c., to decompose silver-ammonia complexes. The filtered residue should then give no turbidity with hydrobromic acid, any traces of silver remaining being precipitated by adding water and re-evaporating. The silver-free solution is finally decolorised with charcoal, and the glycine precipitated by adding an equal volume of 95% alcohol. To remove ammonia, the product is dissolved in water (200 c.c.), shaken with 10 g. of granular permutite, and reprecipitated with 250 c.c. of 95% alcohol. The silver is conveniently recovered by suspending the chloride in 400 c.c. of boiling aqueous 25% sodium hydroxide and adding dextrose gradually until precipitation of the metal is complete. F. G. WILLSON.

Synthesis of local anæsthetics of the novocaine group. J. SUPNIEWSKI (Rocz. Chem., 1927, 7, 163—171).—The following substances are prepared: *ethyl* n-*butylaminoacetate*, b. p. 174—176°/20 mm.; *ethyl* n-*butylallylaminoacetate*, b. p. 150—160°/7 mm.; n-*butylallylaminoethyl alcohol*, b. p. 214—215°/745 mm.; *pyrrolidinoethyl* p-*nitrobenzoate hydrochloride*, m. p. 188—189°, and *pyrrolidinoethyl* p-*aminobenzoate hydrochloride*, m. p. 199—200°. R. TRUSZKOWSKI.

Preparation of taurine in considerable quantity. W. O. KERMACK and R. H. SLATER (Biochem. J., 1927, **21**, 1065—1067).—Sodium tauroglycocholate is boiled with hydrochloric acid, the whole filtered, concentrated, and then precipitated with alcohol; 5 kg. of the sodium salt yielded 173 g. of taurine. S. S. ZILVA.

Nitrile esters of dicarboxyglutaconic acid. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 278—287).—The condensation of diethyl ethoxymethylenemalonate with sodiomalononitrile yielded *diethyl sodio-αα-dicyano-α-carboxyglutaconate*, m. p. 238—239°, from which *diethyl αα-dicarbamyl-α-carboxyglutaconate*, m. p. 139—140°, was obtained. These products are identical with the corresponding compounds obtained by condensing diethyl sodiomalonate with ethoxymethylenemalononitrile. Similarly, the condensation of ethyl ethoxymethylenecyanoacetate with sodiomalononitrile, and of ethyl sodiocyanoacetate with ethoxymethylenemalononitrile yielded in each case *ethyl sodio-ααγ-tricyanoglutaconate monohydrate*, m. p. 190°, from which *ethyl ααγ-tricyanoglutaconate*, m. p. 241—242°, was obtained. By similar reactions *triethyl sodio-γ-cyano-α-carboxyglutaconate*, *triethyl γ-cyano-α-carboxyglutaconate*, *sodio-ααγγ-tetracyanopropylene*, and *tetracyanopropylene* were obtained. This last compound is strongly acidic and soluble in water, and as the reaction of its sodio-derivative with hydrochloric acid is reversible, the compound was obtainable only by extraction with ether of the acid solution. In the preparation of tetracyanopropylene a *compound*, $C_7H_2N_4$,EtOH, m. p. 211—212°, was formed incidentally. B. W. ANDERSON.

Active component of the Bertram root [*Radix pyrethri*]. E. Ott and A. Behr (Ber., 1927, 60, [*B*], 2284—2287).—The powdered root is extracted with alcohol and the residue left after removal of the solvent is treated with ether. The ethereal solution is shaken with sodium hydroxide and, after evaporation, affords crude pyrethrine, which is divided by light petroleum into insoluble pyrethrine and a portion rendered soluble by the presence of fats. Mild hydrolysis removes the latter, which are derived to a considerable extent from stearic acid. Pyrethrine cannot be purified by means of tin tetrabromide (cf. A., 1924, i, 418). The non-homogeneous material, which contains hydrocarotin, $C_{18}H_{30}O$, m. p. 137°, is hydrolysed to *iso*butylamine and undecadienoic acid and hence is the *iso*butylamide and not the piperidide of the latter acid. The term "pyrethrine" has been applied to the active component of *Radix pyrethri* since the first examination of the drug; its application by Staudinger and Ruzicka (cf. A., 1924, i, 758) to two dissimilarly constituted components of another plant is therefore criticised. H. Wren.

Action of organo-magnesium derivatives on tetraethyloxamide. R. Barré (Compt. rend., 1927, 185, 1051—1052; cf. A., 1927, 447).—The condensation of ethyl oxalate with magnesium diethylamine bromide gives a 70—75% yield of *tetraethyloxamide*, m. p. 35—36°, b. p. 142°/4 mm. In the cold, magnesium ethyl bromide reacts with this amide to form 70% of propionylformdiethylamide and 20% of *α-diethylaminobutyrdiethylamide*, b. p. 98—99°/3 mm. (*picrate*, m. p. 114°), with traces of dipropionyl and evolution of ethylene. At 90°, in toluene, a greater proportion of the second compound is formed and perceptible amounts of dipropionyl. The sole product of the reaction between magnesium phenyl bromide and tetraethyloxamide is *α-diethylaminodiphenylacetdiethylamide*, b. p. 182—184°/3 mm. (*perchlorate*, m. p. 177°), which, on hydrolysis, forms hydroxydiphenylacetdiethylamide. B. W. Anderson.

M. p. of the chloroplatinates of monomethyl- and *as*-dimethyl-guanidine. M. Schenck and H. Kirchhof (Ber., 1927, 60, [*B*], 2412—2413; cf. Werner and Bell, J.C.S., 1922, 121, 1790; Philippi and Morsch, A., 1927, 1175).—Methylguanidine chloroplatinate and *as*-dimethylguanidine chloroplatinate have m. p. 190—192° and decomp. 225° respectively. H. Wren.

Magnesylurethane. I. R. Binaghi (Gazzetta, 1927, 57, 676—689).—The action of magnesium ethyl bromide on urethane yields ethane and the "*magnesylurethane*" MgBr·NH·CO_2Et (*urethanomagnesium bromide*). This forms *compounds* with ether and with pyridine; it is decomposed completely by water, is converted by acetyl chloride into acetylurethane, by benzoyl chloride into benzoylurethane, and is decomposed by acetaldehyde and by benzaldehyde, additive compounds having probably been formed. Acetophenone, benzophenone, ethyl acetate, and benzyl acetate have a similar action. "*Magnesylphenylurethane*" (*phenylurethanomagnesium bromide*) gives stable crystalline products. E. W. Wignall.

Organoberyllium halides. H. Gilman and F. Schulze (J. Amer. Chem. Soc., 1927, 49, 2904—2908).—Beryllium methyl iodide could not be obtained by the method of Durand (A., 1926, 718), but is obtained by heating beryllium with ethereal methyl iodide in presence of mercuric chloride at 80—90° for 15 hrs. *Beryllium ethyl* and n-*butyl iodides* are obtained similarly, and *beryllium phenyl iodide* is obtained by heating beryllium with ethereal iodobenzene and mercuric or beryllium chloride at 150—175°. *Beryllium ethyl bromide* was prepared analogously at 80—90°. The beryllium alkyl halides are decomposed by water with formation of the corresponding hydrocarbons. Carbon dioxide does not appear to react with beryllium methyl iodide, but the latter yields some beryllium dimethyl when heated, so that the equilibrium 2BeRX $\rightleftharpoons$ BeR_2+ BeX_2 appears to be set up under certain conditions (cf. Gilman and Schulze, following abstract). Beryllium methyl iodide and phenylcarbimide yield acetanilide. The beryllium alkyl halides are generally less reactive than the beryllium dialkyls and Grignard compounds. F. G. Willson.

Beryllium dialkyls. H. Gilman and F. Schulze (J.C.S., 1927, 2663—2669).—Beryllium dialkyls were not obtained by heating beryllium with mercury alkyls although this method succeeds with mercury aryls. The alkyls are obtained in good yield (90%) by allowing anhydrous beryllium chloride to react with magnesium alkyl halides in ether, air and oxygen being rigidly excluded. After removing most of the solvent the mixture is distilled for a long period at 150—200°. A concentrated ethereal solution of the dialkyl distils over, from which the latter may be obtained by sublimation in ether. *Beryllium dimethyl*, a solid, subliming at about 200°, and *beryllium diethyl*, m. p. −13° to −11°, b. p. 93—95°/4 mm., 110°/15 mm., are spontaneously inflammable in air, but *beryllium di*-n-*butyl*, b. p. 170°/25 mm., is rapidly oxidised to beryllium *n*-butyl oxide. The alkyls react violently with water, forming the corresponding hydrocarbon and beryllium oxide. With carbon dioxide in ethereal solution beryllium dimethyl gives acetic acid, whilst the diethyl affords triethylcarbinol. Beryllium dialkyls with phenylcarbimide or α-naphthylcarbimide form the corresponding anilides or naphthalides, and show an immediate positive colour reaction with Michler's ketone (cf. A., 1925, ii, 1011). Beryllium dimethyl reacts with benzophenone, giving diphenylmethylcarbinol (identified as αα-diphenylethylene), and with benzoyl chloride, giving phenyldimethylcarbinol, whilst the corresponding diethyl reduces benzophenone to benzhydrol. Beryllium alkyls afford beryllium alkyl iodides with iodine and when treated with anhydrous beryllium chloride, beryllium diethyl furnishes beryllium ethyl chloride. Hence the equilibrium BeR_2+BeX_2 $\rightleftharpoons$ 2BeRX probably exists under certain conditions. S. Coffey.

Action of vanadium salts on Grignard's reagents. J. Supniewski (Rocz. Chem., 1927, 7, 172—175).—The addition of vanadium salts to Grignard's reagents leads to the formation of hydrocarbons, no organic vanadyl derivatives being produced. R. Truszkowski.

Mechanism of reactions accompanying the formation of Cadet's oil. A. Valeur and P.

GAILLIOT (Compt. rend., 1927, **185**, 956—958; cf. A., 1927, 1176).—When arsenious acid and potassium acetate are heated to form Cadet's oil, methyl arsenide, AsMe, b. p. 190°/5 mm., is formed, probably by a reaction between potassium acetate and arsenic suboxide. The decomposition of this compound gives rise to the cacodyl, cacodyl oxide, trimethylarsine, and hepta- and penta-methyltriarsine which are found in Cadet's oil. A red polymeride of methyl arsenide has been isolated. B. W. ANDERSON.

Dehydrogenation by selenium. II. O. DIELS and A. KARSTENS (Ber., 1927, **60**, [*B*], 2323—2325).—Sulphur may frequently be replaced by selenium as dehydrogenating agent with great advantage since hydroaromatic systems are frequently converted into uniform dehydrogenated products by the latter substance, whereas they are completely decomposed by the former; the yields of the products are also greatly improved. The examples cited include abietic acid to retene, dodecahydro-9 : 10-benzophenanthrene to 9 : 10-benzophenanthrene and cadinene to cadaline (cf. Ruzicka and Meyer, A., 1921, i, 573). H. WREN.

Oxidation of cyclic hydrocarbons by an acetic acid solution of hydrogen peroxide. G. CHARRIER and A. MOGGI [with C. FERRI] (Gazzetta, 1927, **57**, 736—741).—Hydrogen peroxide in acetic acid solution attacks benzene with difficulty, but on prolonged boiling oxidises it to carbon dioxide (oxalic acid is unstable under the conditions employed) and a yellow, resinous substance. Naphthalene is oxidised fairly quickly to resinous products and phthalic acid; acenaphthene yields acenaphthenequinone and naphthalic acid. Phenanthrene yields phenanthraquinone, followed by diphenic acid and much resin; similarly, 2-phenyl-αβ-naphtho-1 : 2 : 3-triazole yields 4-*o*-carboxyphenyl-2-phenyl-1 : 2 : 3-triazole-5-carboxylic acid; anthracene gives anthraquinone. E. W. WIGNALL.

Spectroscopic determination of very small amounts of benzene. H. LEY and F. VANHEIDEN (Ber., 1927, **60**, [*B*], 2341—2344).—Solutions of benzene in ethyl alcohol obey Beer's law within the concentration 0·089 and 0·0044%. The presence of less than 0·001% of benzene can be determined spectroscopically, the measurements being preferably made with reference to the second and third long wave-length benzene bands. Benzene was found to the extent of 0·0074% and more in samples of ethyl alcohol dehydrated by Young's method. H. WREN.

Halogenation. III. Bromination. P. S. VARMA and B. NARAYAN (J. Indian Chem. Soc., 1927, **4**, 283—289; cf. A., 1927, 452).—Moderately good yields of bromobenzene can be obtained by brominating benzene in presence of fuming nitric–nitrosulphonic acids (50%). Brominations in presence of concentrated and fuming sulphuric acids, concentrated and fuming nitric acids, concentrated and fuming nitric–sulphuric acids, and sodium nitrite and concentrated or fuming sulphuric acid have been studied, and the results are given. The presence of acetic acid has no appreciable effect on the reactions. H. BURTON.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. III. Nitration of *m*-nitrophenylbenzylsulphone. B. CHATTERJEE and R. ROBINSON (J.C.S., 1927, 2780—2784).—The nitration of this compound has been studied in connexion with the theory of electrostriction of the sulphonium ions (see this vol., 71). The double dipole $-\overset{+}{S}\overset{-\,-}{O_2}$ may be compared with the single dipole $-\overset{+}{N}O_2$, and *m*-nitrophenylbenzylsulphone is selected because the group $-C_6H_4{\cdot}NO_2(m)$ should be almost neutral; the results are to be ascribed, therefore, to the influence of the sulphone group. The following sulphones are prepared from the corresponding benzyl chlorides and sodium *m*-nitrobenzenesulphinate: m-*nitrophenylbenzylsulphone*, m. p. 101—102°; m-*nitrophenyl*-o-*nitrobenzylsulphone*, m. p. 192—193°; m-*nitrophenyl*-m-*nitrobenzylsulphone*, m. p. 194—195°; m-*nitrophenyl*-p-*nitrobenzylsulphone*, m. p. 180—181°. The nitration of *m*-nitrophenylbenzylsulphone with nitric acid (*d* 1·5) furnishes approximately 25, 28, and 40%, respectively, of the above *o*-, *m*-, and *p*-nitrobenzylsulphones. The three isomerides are so sparingly soluble in most organic solvents that the proportions had to be determined colorimetrically by the following reactions. An alcoholic solution of the *p*-isomeride gives a carmine coloration with 10% aqueous sodium hydroxide. The *o*-isomeride gives an intense violet coloration with concentrated alkalis in alcoholic acetone, whilst the *m*-compound develops a brownish-red tint only on keeping. All three isomerides develop characteristic colorations when solid potassium hydroxide is added to cold acetone solutions, but when water is added the colours due to the *o*- and *p*-derivatives are discharged, whilst that due to the *m*-isomeride persists. The views expressed by Ingold, Ingold, and Shaw (A., 1927, 550) regarding the effect of the sulphone group on substitution are criticised. S. COFFEY.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. IV. Nitration of toluene-ω-sulphonic acid and toluene-ω-sulphonyl chloride. A. C. BOTTOMLEY and R. ROBINSON (J.C.S., 1927, 2785—2790; cf. preceding abstract and A., 1927, 550).—Sodium toluene-ω-sulphonate, when treated at 0° with nitric acid (*d* 1·5), affords an 88% yield of sodium nitrotoluene-ω-sulphonates (minimum yield, *m*-isomeride 9·2%), whilst the free ω-sulphonic acid furnishes 63·6% of mixed sodium nitrotoluene-ω-sulphonates (minimum yield, *m*-isomeride 8·9%). In the nitration of toluene-ω-sulphonyl chloride the proportion of *m*-isomeride obtained varies with the efficiency of the method of salting out the sodium nitrotoluene-ω-sulphonates, the results being: yields of mixed isomerides 63 and 73·5%, minimum yields of *m*-isomeride 28 and 39%. *o*- and *m*-Nitrotoluene-ω-sulphonates, either separately or when mixed, develop no coloration when heated with concentrated aqueous potassium hydroxide solution, whereas the *p*-isomeride gives a yellowish-orange solution, which is more intense in the presence of *o*-isomeride and still more intense

in the presence of *m*-isomeride. A colorimetric examination based on this reaction showed that the nitration product from toluene-ω-sulphonyl chloride contains less than 5% of *o*-isomeride and approximately 55% of *m*- and 45% of *p*-isomerides. The nitration products from toluene-ω-sulphonic acid and its sodium salt are identical in composition and equivalent to 10% of *m*-, 48% of *p*-, and 42% of *o*-nitrotoluene-ω-sulphonate. Dinitrotoluene-ω-sulphonates were absent.

From these results it is concluded that the sulphonic ion group, $^-SO_3$, although negatively charged, still retains a higher electron affinity than a hydrogen atom, hence its *m*-directive effect is due to a general electric effect. S. COFFEY.

Some derivatives of diphenylmethane. K. N. MENON (J. Indian Chem. Soc., 1927, **4**, 437—439).—4 : 4′-Dibromodiphenylmethane is nitrated in acetic anhydride to *4 : 4′-dibromo-3 : 3′-dinitrodiphenylmethane*, m. p. 238—240°. Attempts to obtain ring closure from this compound and from *4 : 4′-di-iododiphenylmethane*, m. p. 93—93·5°, were unsuccessful. H. BURTON.

Structure of the hydrocarbon $C_{17}H_{18}$ obtained by the dehydration of diphenyl-*tert*.-butylcarbinol. D. E. BATEMAN and C. S. MARVEL (J. Amer. Chem. Soc., 1927, **49**, 2914—2919).—α-Diphenylpropaldehyde was oxidised with alkaline permanganate to α-diphenylpropionic acid, and the latter converted, through the acid chloride, into the *methyl* ester, b. p. 149—152°/3 mm., d_4^{20} 1·1206, n_D^{20} 1·5691. When treated with ethereal magnesium methyl iodide, this yields *γγ-diphenyl-β-methyl-Δ^α-butene*, b. p. 132—133°/4·5 mm., d_4^{20} 1·0060, n_D^{20} 1·5757, identical with the hydrocarbon obtained by the dehydration of diphenyl-*tert*.-butylcarbinol (cf. Ramart-Lucas, A., 1913, i, 1325), which is conveniently prepared by heating the latter with a small proportion of *p*-toluenesulphonic acid for 2 hrs. on the steam-bath. *s*-Tetraphenyldi-*tert*.-butylethane could not be obtained by the usual methods from diphenyl-*tert*.-butylmethyl chloride. F. G. WILLSON.

2-Methylnaphthalene. II. Synthesis of hydrocarbons of the benzanthracene group. K. DZIEWOŃSKI and E. RITT (Bull. Inter. Acad. Polonaise, 1927, **3 A**, 181—192).—The pyrogenic transformation of 2-methylnaphthalene derivatives results in the formation of 1 : 2-benzanthracene and its methyl derivatives. When 1-benzyl-2-methylnaphthalene, b. p. 221°/17 mm., obtained by the interaction of benzyl chloride and 2-methylnaphthalene in the presence of anhydrous zinc chloride, is distilled over zinc dust, the principal product is 1 : 2-benzanthracene, m. p. 158—159°, whilst 2 : 3-benzanthracene, m. p. 335—336°, is obtained in small amount. If, however, 1-benzoyl-2-methylnaphthalene is subjected to the same process in the presence of a current of hydrogen, 1 : 2-benzanthracene alone is formed. This pyrogenic transformation is applicable to the preparation of similar hydrocarbons; *e.g.*, from 2-methylnaphthalene and *o*- or *p*-toluoyl chloride in the presence of aluminium chloride, 1-*o*-toluoyl-2-methylnaphthalene and 1-*p*-toluoyl-2-methylnaphthalene can be prepared and converted into the corresponding 6- or 8-methyl derivative of 1 : 2-benzanthracene. These compounds may be converted into the corresponding methyl-1 : 2-benzanthraquinone derivatives by means of chromic acid. The following substances are described: *1 : 2-Benz-9 : 10-anthraquinone*, m. p. 168°; *1-benzoyl-2-methylnaphthalene*, b. p. 233°/13 mm., m. p. 74°; *3-benzoyl-4-methylphthalic acid*, m. p. 184°; *1-p-toluoyl-2-methylnaphthalene*, m. p. 106—107°; *6-methyl-1 : 2-benzanthracene*, m. p. 127°; *6-methyl-1 : 2-benz-9 : 10-anthraquinone*, m. p. 174°; *1-o-toluoyl-2-methylnaphthalene*, b. p. 238°/14 mm.; *8-methyl-1 : 2-benzanthracene*, m. p. 145°. R. A. MORTON.

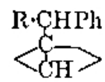
Action of hydrogen peroxide and of hypochlorous acid on anthracene. G. CHARRIER and G. B. CRIPPA [with E. SARAGA] (Gazzetta, 1927, **57**, 741—748).—When anthracene is suspended in water and heated with hydrogen peroxide, anthraquinone is formed, with another product, m. p. 250—270°, which when treated with zinc and sodium hydroxide gives dianthrone, m. p. 235—245°, also obtained when a similar suspension is exposed to sunlight and extracted with zinc and sodium hydroxide.

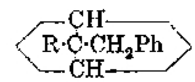
Anthracene suspended in water and treated with hypochlorous acid yields a product, m. p. 180—185°, decomp. from 150°, which contains chlorine and dissolves in organic solvents to strongly fluorescent solutions, from which a substance, m. p. 230—250°, free from chlorine, crystallises; the latter when prepared by long boiling of the reaction product with alcohol has m. p. 235—250°, and is considered to be dianthranolyl ether, $(HO{\cdot}C_{14}H_8)_2O$ (Liebermann and Mamlock, A., 1905, i, 521). E. W. WIGNALL.

Alkylanthracenes and "transannular tautomerism." III. 1 : 5-Dichloro-9-benzylanthracene. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (Ber., 1927, **60**, [*B*], 2353—2366; cf. A., 1926, 1030; 1927, 140).—1 : 5-Dichloroanthrone is converted by magnesium benzyl chloride into *1 : 5-dichloro-9-hydroxy-9-benzyl-9 : 10-dihydroanthracene*, m. p. 154°, transformed by hydrochloric and glacial acetic acids into *1 : 5-dichloro-9-benzylanthracene*, m. p. 127°. The latter substance reacts with bromine to form a colourless *dibromide*, which readily loses hydrogen bromide, giving the pale yellow *compound*, $C_{21}H_{13}Cl_2Br$, m. p. 184°, to which the endocyclic constitution $C_6H_3Cl{<}\begin{matrix}CH\\CPh{:}Br\\CH\end{matrix}{>}C_6H_3Cl$ is ascribed by Barnett and Matthews (contrast Cook, following abstract). The bromine atom of this compound is unusually reactive (wherefore it is regarded as impossible that the compound should be 1 : 5-dichloro-10-bromo-9-benzylanthracene) and is readily replaced by OH, OMe, OEt, or OAc by boiling with aqueous acetone, alcohols, or sodium acetate, respectively; if the solution is kept neutral by addition of calcium carbonate the following colourless *compounds* are obtained: $C_{21}H_{14}OCl_2$, m. p. 205—207°, unchanged by diazomethane, hydroxylamine, or zinc dust and ammonia, converted by phenylcarbimide into the *phenylurethane*, m. p. 104—106° (decomp.); $C_{22}H_{16}OCl_2$, m. p. 167°; $C_{23}H_{18}OCl_2$, m. p. 190°;

$C_{23}H_{16}O_2Cl_2$, m. p. 247—248°. To these an endocyclic structure is also ascribed. If precautions are not taken to maintain the solution neutral, the following yellow compounds are obtained in place of the colourless series. They are regarded (Barnett and Matthews) as ω-substituted 1 : 5-dichloro-9-benzylanthracenes on account of their colour, fluorescence, and absorption spectrum, and the conversion of the methoxy-compound into an unstable *dibromide* which decomposes into benzaldehyde and 1 : 5-*dichloro-9-bromoanthracene*, m. p. 158—159°. *Substances*, $C_{21}H_{13}Cl_2{\cdot}OH$, m. p. 155° (obtained also by boiling the colourless hydroxy-compound with acetone and sulphuric acid), which does not react with phenylcarbimide or diazomethane but, like the colourless isomeride, is converted by hydrogen bromide in toluene into the original bromide; $C_{21}H_{13}Cl_2{\cdot}OAc$, m. p. 187—188°, also obtained from the colourless or yellow hydroxy-compound and glacial acetic acid or by isomerisation of the colourless acetate; $C_{21}H_{13}Cl_2{\cdot}OMe$, m. p. 156—157°, also derived from the colourless methoxy-compound or the yellow hydroxy-derivative by treatment with methyl alcohol and hydrochloric acid; $C_{21}H_{13}Cl_2{\cdot}OEt$, m. p. 113°, also obtained from the colourless or yellow hydroxy-compounds and ethyl alcohol and sulphuric acid. The bromo-compound is converted by the following bases into colourless *compounds* probably constituted similarly to the colourless series: by diethylamine in chloroform into the *substance*, $C_{25}H_{23}NCl_2$, m. p. 125°; by piperidine into the *compound*, $C_{26}H_{23}NCl_2$, m. p. 171—172°; by aniline into the *derivative*, $C_{27}H_{19}NCl_2$, m. p. 162°; by dimethylaniline into the *substance*, $C_{29}H_{23}NCl_2$, m. p. 237—238°. The bromo-compound gives a *pyridinium* salt, $C_{26}H_{18}NCl_2Br,EtOH$, m. p. 190—193° (decomp.), which loses the pyridine residue when heated with aqueous acetone, methyl or ethyl alcohol giving the colourless derivatives obtained from the bromide. The following transformations are suffered by the respective substances when suspended or dissolved in chloroform and treated with an excess of nitrogen peroxide followed by addition of light petroleum: 1 : 5-dichloro-9-benzylanthracene to a *dinitro*-compound, $C_{21}H_{14}O_4N_2Cl_2$, m. p. 177° (decomp.), converted by pyridine into a *mononitro*-derivative, $C_{21}H_{13}O_2NCl_2$, m. p. 176°; monobromo- and colourless ethoxy-compound into a *trinitro*-derivative, $C_{21}H_{13}O_6N_3Cl_2$, m. p. 168° (decomp.), transformed by cold pyridine into a *dinitro*-compound, $C_{21}H_{12}O_4N_2Cl_2$, m. p. 157° (decomp.); yellow methoxy-compound to a *dinitro*-derivative, $C_{22}H_{16}O_5N_2Cl_2$, m. p. 170° (decomp.), converted by warm pyridine into the *mononitro*-compound, $C_{22}H_{15}O_3NCl_2$, m. p. 145°. H. WREN.

Isomeric derivatives of 1 : 5-dichloro-9-benzylanthracene. J. W. COOK (Ber., 1927, **60**, [*B*], 2366—2369; cf. A., 1926, 838, 953, 1131).—The author does not agree with Barnett and Matthews in assigning to the series of colourless compounds (preceding abstract) the endocyclic structure but regards them as having the constitution  (I), for the following reasons. The substituents in the colourless series have the great reactivity characteristic of groups in the position 10 in 9 : 10-derivatives of dichloroanthracene; the hydroxy-compound (R=OH) is methylated by short treatment with methyl-alcoholic hydrogen chloride and easily acetylated by glacial acetic acid; the pyridinium group of the salt ($R{=}NC_5H_5{\cdot}Br$) is unusually labile. The distribution of affinity of the carbon atom in compounds of the types (II) and (III) is such that weakened activity must be expected from the colourless forms if they actually have the endocyclic constitution, whereas the reverse is the case.


(II.)


(III.)

The endocyclic structure of the colourless series is not in harmony with the observation that the colourless hydroxy-compound readily yields a phenylurethane, whereas the yellow isomeride is indifferent towards phenylcarbimide. The behaviour is explained if the colourless compound has the structure I (R=OH) and steric hindrance is assumed to be operative with the yellow variety. The ready transformation of the colourless into the yellow isomerides is assumed to occur through dissociation into the free radicals, ·CHPh:C<>CH·+R, isomerisation of the complex radical into its more stable form, CH<>C·CHPh·, and union of R with the new radical. H. WREN.

Rubrene: ψ-rubrene. C. MOREU, C. DUFRAISSE, and G. BERCHET (Compt. rend., 1927, **185**, 1085—1087).—When rubrene in benzene solution is treated with gaseous hydrogen iodide it is completely transformed into a colourless isomeride, *ψ-rubrene*, m. p. 278°. Iodine is liberated during the transformation, but in amounts bearing no relation to the simple hydrogenation of rubrene, and the end-product does not contain added hydrogen or iodine. ψ-Rubrene evolves violet vapours when heated, and gives an intense green solution in hot sulphuric acid. When crystallised from benzene it contains 1 mol. of solvent, which it loses at 210°. Rubrene remains unattacked by the usual methods of hydrogenation, but ψ-rubrene, when heated in a sealed tube with hydrogen iodide at 200°, forms an uncrystallisable oil.

B. W. ANDERSON.

Dissociation of rubrene peroxide. C. MOUREU and C. DUFRAISSE (Z. physikal. Chem., 1927, **130**, 472—479).—Rubrene in solution is readily oxidised to a stable, colourless peroxide, which in the solid state or in solution at 100—150° readily dissociates into rubrene and oxygen. The light absorption of rubrene, examined in the range 5610—4100 Å., is characterised by maxima at 5300, 4920, and 4700 Å. In benzene solution cryoscopic measurements lead to values of $M=485$ (theory 532), in ethylene bromide $M=364$. It is therefore thought to exhibit dissociation in solution similar to that of hexaphenylethane. R. W. LUNT.

Urethanes. IV. Acyldiurethanes and their reactions with ammonia and amines. S. BASTERFIELD, E. L. WOODS, and M. S. WHELEN (J. Amer. Chem. Soc., 1927, **49**, 2942—2948; cf. A., 1926, 1132).—Treatment of oxalyldiurethane with cold, concentrated, aqueous ammonia affords oxamide and urethane, together with a small proportion of carb-

amide. Dry ammonia at 90—100° affords similarly urethane. Ethylamine and oxalyldiurethane afford diethyloxamide in 70% yield, together with urethane, whilst aniline at 150—190° yields similarly mainly oxanilide, with some carbanilide. At 100°, a 60% yield of oxanilide is produced, together with, apparently, *α-carbethoxy-β-phenyloxamide*, m. p. 224°, and phenylcarbamide and urethane. Dry ammonia at 100° is without action on malonyldiurethane, but the latter and concentrated aqueous ammonia yield malonamide, ammonium barbiturate, and urethane. Ethylamine and malonyldiurethane afford malondiethylamide in 92% yield. Aniline at 190° yields malonanilide and carbanilide; at 150°, the foregoing products are obtained, together with, apparently, *α-phenyl-β-phenylcarbamylmalonamide*, m. p. 234—235°; at 120°, the latter compound is produced in larger proportion, with malonanilide and phenylcarbamide, carbanilide not being produced, whilst at 100° no reaction takes place in several hours. Aqueous ammonia and phthalyldiurethane afford urethane and phthalamide. Aniline at 190° affords carbanilide and phthalanil, whilst at 100° (8 min.) the main product is, apparently, *α-phenyl-β-carbethoxyphthalamide*, m. p. 225°. Carbonyldiurethane and aqueous ammonia afford mainly urethane, which is subsequently converted to a large extent into carbamide, biuret, and cyanuric acid. Ethylamine and carbonyldiurethane yield ethylurethane, carbamide, and a *substance*, m. p. 155°, together with a 75% yield of ethyl allophanate The courses of the above reactions appear to be connected with a tendency to the formation of the amides of acids stronger than carbonic, rather than to the formation of carbamides.

F. G. WILLSON.

Preparation of monohalogenophenylimides of dichloromaleic, tetrachlorosuccinic, and dibromosuccinic acids, and their molecular stability. A. SANNA and E. MACCIOTTA (Gazzetta, 1927, **57**, 772—776; cf. this vol., 26).—*p*-Bromophenyl- (m. p. 130°) and *m*-bromophenyl- (m. p. 125°) αβ-dibromosuccinamic acids give on treatment with acetic anhydride the corresponding *imides*, m. p. 155° and 74—75°, respectively. *o*-, *m*-, and *p*-Chlorophenylsuccinimides are converted by phosphorus pentachloride first into the o-, m-, and p-*chlorophenyldichloromaleinimides*, m. p. 120°, 172—173°, and 212°, respectively, and the latter into the o-, m-, and p-*chlorophenyltetrachlorosuccinimides*, m. p. 132—133°, 185°, and 205°, respectively.

Solubility considerations prevent a study of the stability of these compounds; the introduction of halogen is, however, seen to stabilise the heterocyclic ring.

E. W. WIGNALL.

Preparation of halogenodiphenylsuccinamides. A. SANNA and (SIGNA.) G. REPETTO (Gazzetta, 1927, **57**, 777—780).—Succinic acid reacts with *o*-, *m*-, and *p*-chloroaniline to give oo'-, mm'-, and pp'-*dichloro*-s-*diphenylsuccinamides*, m. p. 202° (decomp.), 232°, and 246°, respectively; mm'- and pp'-*dibromo*-s-*diphenylsuccinimides*, m. p. 222° and 271°, respectively, are similarly prepared.

E. W. WIGNALL.

Dimorphism of 2-chloroaceto-*p*-toluidide. M. SCHOFIELD (J.C.S., 1927, 2903; cf. A., 1912, i, 1027).—2-Chloroaceto-*p*-toluidide, m. p. 83°, crystallises from benzene, alcohol, and many other solvents in needles. When crystallised from light petroleum it is converted into a second form, m. p. 104° (plates), which may be transformed into the lower-melting, more soluble form by crystallisation from benzene.

G. A. C. GOUGH.

***p*-Cymene. IX. Nitration of 2-amino-*p*-cymene.** A. S. WHEELER and F. P. BROOKES (J. Amer. Chem. Soc., 1927, **49**, 2832—2834; cf. this vol., 55).—Treatment of 2-acetamido-*p*-cymene in sulphuric acid with nitric acid at 0° affords 5-*nitro*-2-*acetamido*-p-*cymene*, yellow, m. p. 148°, which, on hydrolysis with hydrochloric acid, yields 2-*amino*-5-*nitro*-p-*cymene*, b. p. above 250° (*hydrochloride*). Reduction of the *benzoyl* derivative, m. p. 215—218°, of the latter with tin and hydrochloric acid in alcohol affords 5-*amino*-2-*benzamido*-p-*cymene*, m. p. 115° [*hydrochloride*, m. p. above 200° (decomp.); *acetyl* derivative, m. p. 120°]. 1-(o-*Nitrocarvacrylazo*)-2-*naphthol*, red, m. p. 245°, and *sodium* 2-(5-*nitrocarvacrylazo*)-1-*naphthol*-4-*sulphonate*, red, were prepared.

F. G. WILLSON.

Preparation and base strengths of some amines. W. H. CAROTHERS, C. F. BICKFORD, and G. J. HURWITZ (J. Amer. Chem. Soc., 1927, **49**, 2908—2914).—The hydrolysis constants ($K_{hyd} \times 10^{10}$), and dissociation constants ($K_B \times 10^5$) of the following amines have been determined by measuring the p_H of solutions of the bases in water in presence of definite added fractional equivalents of hydrochloric acid, and are quoted below in the above order: benzylamine, 4·26, 2·35; β-phenylethylamine, 1·48, 6·78; γ-phenylpropylamine, 0·63, 15·9; δ-phenylbutylamine, 0·40, 24·8; ε-phenylamylamine, 0·33, 30·6; *o*-methylbenzylamine, 5·89, 1·70; *m*-methylbenzylamine, 4·24, 2·40; *p*-methylbenzylamine, 3·98, 2·55; *o*-methoxybenzylamine, 1·81, 5·56; *m*-methoxybenzylamine, 6·46, 1·56; *p*-methoxybenzylamine, 3·10, 3·22; benzylmethylamine, 2·63, 3·80; benzylethylamine, 2·10, 4·75; benzyl-*n*-propylamine, 2·40, 4·18; and β-phenylethylmethylamine, 0·75, 13·9. In amines of the type $Ph\cdot[CH_2]_x\cdot NH_2$, the continuous decrease of   with increase in *x* is not quite regular, and the results do not accord with Derick's rule (A., 1911, ii, 713) or Simms' equation (A., 1926, 681). In the methoxy- and methyl-benzylamines the effects of the ring substituents are slight and vary irregularly with change of position. It is concluded that Bourgeaud and Dondelinger's values of K_B for benzylmethylamine and benzylethylamine are erroneous (A., 1925, ii, 117).

m-*Methoxybenzylacetamide*, m. p. 58·5—59°, b. p. 191—198°/11 mm., was prepared by catalytic reduction of *m*-anisonitrile in acetic anhydride, and hydrolysed by heating with methyl-alcoholic sodium hydroxide at 140—150° to m-*methoxybenzylamine*, b. p. 131°/26 mm., 140°/37 mm. The following *NN'*-*p*-toluenesulphonamides are described: *benzylmethyl*-, m. p. 94·4—94·8°; *benzylethyl*-, m. p. 49—50°; *benzylpropyl*-, m. p. 46—47°; β-*phenylethylmethyl*-, m. p. 44—45°; *dibenzyl*-, m. p. 161°, and *di*-β-*phenylethyl*-p-*toluenesulphonamide*, m. p. 101°. The *N*-monosubstituted *p*-toluenesulphonamides are not soluble in aqueous alkali, but dissolve in aqueous-alcoholic

(1 : 2) sodium hydroxide, by means of which they can be separated from the corresponding disubstituted derivatives. F. G. WILLSON.

Crystalline compounds obtained by the action of aromatic amines on semicarbazide and its derivatives. J. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1927, 59, 579—592).—See A., 1927, 1061. M. ZVEGINTZOV.

Investigation by means of thermal analysis of the reaction for obtaining naphthylamines from naphthols. B. N. MENSCHUTKIN and N. A. BUTKOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 405—420).—Thermal analysis of the binary systems involved in the reaction $C_{10}H_7{\cdot}OH+NH_3\longrightarrow C_{10}H_7{\cdot}NH_2+H_2O$ in presence of zinc chloride or calcium chloride is complicated by the difficulty of obtaining the naphthylamines and naphthols pure and by their proneness to resinification. Hence aniline and mono- and di-methylaniline have been used in addition to the naphthylamines, and zinc bromide, which is more readily dehydrated than the chloride, has also been used.

The solubility curve of the system zinc bromide–aniline shows a maximum corresponding with the compound $ZnBr_2,2NH_2Ph$, m. p. 270°, which is readily obtained, with considerable development of heat, when the components are mixed. The eutectic point between this compound and zinc bromide is at 172° and corresponds with 81·6% of zinc bromide. With mono- and di-methylanilines, zinc bromide forms the compounds $ZnBr_2,2NHMePh$, decomp. 285°, and $ZnBr_2,2NMe_2Ph$, decomp. above 280°. With the system zinc bromide–α-naphthylamine, the maximum solubility corresponds with the compound $ZnBr_2,4C_{10}H_7{\cdot}NH_2$, m. p. 241°; the eutectic point between this compound and zinc bromide is at about 225° and about 35% of the bromide, the other eutectic point, about 47°, corresponding with about 0·5% of zinc bromide. For the system zinc bromide–β-naphthylamine, the maximum of the solubility curve is at 261° and the composition that of the compound $ZnBr_2,2C_{10}H_7{\cdot}NH_2$, m. p. 261°; the eutectic point on the zinc bromide side, about 200°, corresponds with about 60% of the bromide. For the system zinc chloride–α-naphthylamine, the maximum of the solubility curve corresponds with the compound $ZnCl_2,4C_{10}H_7{\cdot}NH_2$, m. p. 253°, the eutectic points being 220° and about 47° (38% and about 0·1% of zinc chloride). The system zinc chloride–β-naphthylamine forms the compound $ZnCl_2,2C_{10}H_7{\cdot}NH_2$, m. p. 275°; the eutectic points are about 205° (about 62% of zinc chloride) and about 111° (very little zinc chloride). β-Naphthol and β-naphthylamine form the compound $2C_{10}H_7{\cdot}OH,C_{10}H_7{\cdot}NH_2$, m. p. 120°, the eutectic points of the system being 116° and 101° with 5% and 84% of the amine (cf. Kremann and Strohschneider, A., 1919, ii, 54).

Recent work increases the probability that, with organic reactions proceeding catalytically, the formation of molecular compounds of the catalyst with the reacting substances or with the products of the reaction retards the reaction, and this is undoubtedly the case in the formation of naphthylamines from naphthols. T. H. POPE.

p-Cymene. VIII. p-Cymylene-2 : 5-diamine. Dyes derived from 2-amino- and 5-bromo-2-amino-p-cymene. A. S. WHEELER and L. F. P. CUTLAR (J. Amer. Chem. Soc., 1927, 49, 2819—2822; cf. A., 1927, 352).—*2-Amino-p-cymene nitrate*, m. p. 140° (decomp.), *hydrobromide*, m. p. 169° (decomp.), and *trichloroacetate*, m. p. 162° (decomp.), are described. Treatment of diazotised sulphanilic acid with 2-amino-p-cymene affords *5-(4′-sulphobenzeneazo)carvacrylamine hydrochloride*, red, m. p. 282°, which, on reduction with stannous chloride, yields p-cymylene-2 : 5-diamine. When boiled with methyl-alcoholic p-nitrosodimethylaniline, 2-amino-p-cymene yields *dimethylaminocymylphenazine*, blue, m. p. 48° (decomp.). The following *dyes*, prepared by coupling diazotised 5-bromo-2-amino-p-cymene (*sulphate*, m. p. 123°, decomp.) with the substances mentioned, are described: o-cresol, brown, m. p. 112°; pyrocatechol, brown, m. p. 235°; phloroglucinol, red, m. p. 280°; carvacrol, brown, m. p. 192°, and p-toluidine (*hydrochloride*, brown, m. p. 188°). *Dyes* were also prepared from 5-bromo-2-amino-p-cymene and diazotised sulphanilic acid [*hydrochloride*, deep chrome, m. p. above 300° (decomp.)] and anthranilic acid (*hydrochloride*, brown, m. p. 189°). F. G. WILLSON.

Interaction of chloral and arylhydrazines. F. D. CHATTAWAY and R. BENNETT (J.C.S., 1927, 2850—2853).—2 : 4-Dihalogen-substituted phenylhydrazines react smoothly with chloral in alcoholic solution to afford the 2 : 4-dihalogen-substituted phenylhydrazone of the corresponding alkyl glyoxylate, $C_6H_3X_2{\cdot}NH{\cdot}N{:}CH{\cdot}CO_2R$ (I). If, however, the reaction takes place in aqueous or acetic acid solution one molecule of water and one molecule of hydrogen chloride are eliminated and αα-dichloro-β-2 : 4-dihalogenobenzeneazoethylenes, $C_6H_3X_2{\cdot}N{:}N{\cdot}CH{:}CCl_2$, are formed which yield β-bromo-substitution compounds on bromination and 2 : 4-dihalogenoanilines on reduction. With alcohols they afford compounds of the type I. In this way the following are prepared: *ethyl glyoxylate 2 : 4-dichlorophenylhydrazone*, m. p. 121·5° (hydrolysis gives ethyl alcohol and glyoxylic acid 2 : 4-dichlorophenylhydrazone); *2 : 4-dichlorophenylhydrazones* of *methyl*, m. p. 136·5, *n-propyl*, m. p. 65°, and *n-butyl glyoxylate*, m. p. 59°; *2 : 4-dibromophenylhydrazones* of *methyl*, m. p. 136°, *ethyl*, m. p. 119°, and *n-propyl glyoxylate*, m. p. 75°; *ethyl glyoxylate 2-chloro-4-bromophenylhydrazone*, m. p. 120°; *ethyl glyoxylate 4-chloro-2-bromophenylhydrazone*, m. p. 115°; *αα-dichlorobenzeneazoethylene*, m. p. 84·5° (scarlet); *αα-dichloro-β-bromo-β-2 : 4-dichlorobenzeneazoethylene*, m. p. 90° (red); *αα-dichloro-β-2 : 4-dibromo-*, m. p. 96·5, *αα-dichloro-β-2-chloro-4-bromo-*, m. p. 84°, and *αα-dichloro-β-4-chloro-2-bromo-benzeneazoethylene*, m. p. 81°. Glyoxylic acid reacts with 2 : 4-dichloro- and 2 : 4-dibromo-phenylhydrazine to give *glyoxylic acid 2 : 4-dichlorophenylhydrazone*, decomp. about 150°, and *2 : 4-dibromophenylhydrazone*, decomp. about 150°, respectively. Several alkyl glyoxylate dihalogenophenylhydrazones prepared from bromal were identical with the corresponding compounds prepared from chloral. G. A. C. GOUGH.

Manufacture of carbazides and thiocarbazides of the naphthalene series. BRIT. DYE-

STUFFS CORP., LTD., G. M. DYSON, F. A. MASON, and A. RENSHAW.—See B., 1927, 902.

Di-*p*-xylylguanidine. W. SCOTT, ASSR. TO E. I. DU PONT DE NEMOURS & CO.—See B., 1927, 924.

Halogenation of phenols. II. Iodination. F. G. SOPER and G. F. SMITH (J.C.S., 1927, 2757—2761; cf. A., 1926, 831).—Examination of the kinetics of the iodination of phenol over the hydrogen-ion concentration range $0{\cdot}5\times10^{-7}$ to 4×10^{-7} shows that no iodination is effected by iodine, although the ionisation constant of the iodine into positive iodine ions is 30 times that of hypoiodous acid. Interaction probably occurs between both the phenoxide ion and un-ionised phenol and the hypoiodous acid; the former reaction is 180 times as rapid as the latter.

G. A. C. GOUGH.

Action of nitric acid and mercury on aromatic hydrocarbons and a few of their derivatives. F. BLECHTA and K. PATEK (Z. ges. Schiess- u. Sprengstoffw., 1927, 22, 314—317; cf. Holdermann, A., 1906, i, 439).—When toluene is nitrated at 95° with 50% nitric acid containing 2% of mercury, nitrotoluene is produced together with *p*-nitrobenzoic acid, m. p. 237—238° (corr.), in 10% yield and trinitro-*m*-cresol, m. p. 105—106°. Neither trinitro-*o*- or -*p*-cresol nor nitrosalicylic acid is formed under these conditions (cf. Wolffenstein and Boters, A., 1913, i, 353). Benzoic acid on nitration in presence of mercury yields chiefly *m*-nitrobenzoic acid together with a small amount of 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid (cf. Wolffenstein and Paar, A., 1913, i, 363), whilst benzene itself yields nitrobenzene, dinitrophenol, and trinitrophenol. The use of mixed acid instead of nitric acid alone in the nitration of benzene or toluene in presence of mercury has no effect on the course of the reaction. The further nitration of aromatic nitrohydrocarbons is facilitated by the presence of mercury. In the nitration of nitrobenzene with 85% nitric acid the yield of dinitrobenzene is increased from 48·8% to 71·8% under comparable conditions on addition of 2% of mercury to the acid, no nitrophenol being formed. The rate of nitration is also increased, and the improvement is still more marked if 5% of mercury is used. Similarly, the yield of dinitrotoluene obtained by the nitration of *o*-nitrotoluene with 75% nitric acid is with mercury 70·8%, and without mercury 50·3%, a small amount (about 1%) of *o*-nitrobenzoic acid being produced. With *p*-nitrotoluene, the yield of dinitrotoluene is increased from 30·1% to 58·4%, and about 2% of *p*-nitrobenzoic acid is formed. The accelerating action of mercury in the nitration and oxidation of aromatic hydrocarbons is probably due to the intermediate formation of mercury aryl nitrates (cf. Dimroth, A., 1899, i, 428; 1902, i, 656). Mercury tolyl nitrate, which may be prepared as a brown viscous mass by heating together toluene and mercuric nitrate, regenerates toluene when heated with dilute sulphuric acid, but with 30% nitric acid nitrotoluene and nitrocresol are produced. The suggestion is made that in the latter case the mercury tolyl nitrate first decomposes, yielding toluene in the nascent state which is more readily nitrated and oxidised by dilute nitric acid than the normal product. Mercury aryl nitrates or acetates are liable to cause painful skin blisters and should be handled with care.

W. J. POWELL.

Halogenation of *p*-hydroxydiphenylamine. II. A. E. BRADFIELD, L. H. N. COOPER, and K. J. P. ORTON (J.C.S., 1927, 2854—2864).—The reaction of chlorine or bromine on *p*-hydroxydiphenylamine may result in substitution or in oxidation to the quinoneanil (benzoquinonephenylimine) if the hydrogen bromide is removed (cf. Orton and Smith, *ibid.*, 1908, 93, 314). The chlorine-substitution products are prepared from the *O*-acyl derivatives by the chloroamine method (Orton and King, *ibid.*, 1911, 99, 1185; A., 1927, 645) and their constitutions are determined by oxidation to the quinoneanils followed by oxidation of these compounds to chlorobenzoquinones and chloroanilines. Thus *p*-benzoyloxydiphenylamine (p-*toluenesulphonyloxy*-derivative, m. p. 126·5°) affords 4'-*chloro*-4-*benzoyloxydiphenylamine*, m. p. 148·5°, which on hydrolysis with aqueous potassium hydroxide gives 4'-*chloro*-4-*hydroxydiphenylamine*, m. p. 91° (p-*toluenesulphonyloxy*-derivative, m. p. 93—94°). The latter on oxidation gives 4-*chlorobenzoquinoneanil*, m. p. 83·5°. 2 : 2' : 4'-*Trichloro*-4-*benzoyloxydiphenylamine*, m. p. 114°, and 2 : 2' : 4'-*trichloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 130·5° (*hydroxy*-compound, m. p. 128°), are prepared from the 4-acyloxy-compounds or from their monochloro-derivatives; the latter compound yields on further chlorination 2 : 6 : 2' : 4'-*tetrachloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 126° (tetrachlorohydroxy-compound, m. p. 113°; *benzoyloxy*-compound, m. p. 114·5°), and 2 : 6 : 2' : 4' : 6'-*pentachloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 156·5° (also prepared by passing chlorine through an acetic acid solution of 4-*p*-toluenesulphonyl oxydiphenylamine; *pentachlorohydroxy*-compound, m. p. 156°; *monoacetyl* derivative, m. p. 126°; *benzoyloxy*-derivative, m. p. 133—134°). 2 : 2' : 4'-Trichlorobenzoquinoneanil, m. p. 72·5°, bronzy-red, 2 : 6 : 2' : 4'-*tetrachlorobenzoquinoneanil*, m. p. 143°, violet, and 2 : 6 : 2' : 4' : 6'-*pentachlorobenzoquinoneanil*, m. p. 163°, bronze coloured, are described. 2 : 3 : 6 : 2' : 4' : 6'-*Hexachloro*-4-*hydroxydiphenylamine*, m. p. 114° (*benzoyloxy*-derivative, m. p. 125°; p-*toluenesulphonyloxy*-derivative, m. p. 141°), and *heptachloro*-4-*hydroxydiphenylamine*, m. p. 158—159° (*benzoyloxy*-derivative, m. p. 164°), are described. 2 : 3 : 6 : 2' : 4' : 6'-*Hexachlorobenzoquinoneanil*, m. p. 141°, which gives trichlorobenzoquinone and *s*-trichloroaniline on hydrolysis with 1% sulphuric acid, and *heptachlorobenzoquinoneanil*, m. p. 114°, which gives tetrachlorobenzoquinone and *s*-trichloroaniline, are prepared in the usual ways. The pentachlorobenzoquinoneanil, when treated with a glacial acetic acid solution of concentrated hydrochloric acid, affords hexachlorohydroxydiphenylamine; the hexachlorobenzoquinoneanil gives similarly pentachlorohydroxydiphenylamine. 4'-*Bromo*-4-*benzoyloxydiphenylamine*, m. p. 150·5° (*hydroxy*-compound, m. p. 108°, and 4-*bromobenzoquinoneanil*, m. p. 100—104°, scarlet, probably dimorphous, described), is prepared by the interaction of bromine in glacial acetic acid with a solution of *p*-benzoyloxydiphenylamine and sodium acetate in the same solvent. 2 : 2' : 4'-*Tri*-

bromo-4-p-*toluenesulphonyloxydiphenylamine* is prepared similarly by bromination at 50°, whilst the corresponding tribromobenzoyloxy-compound (Smith and Orton, J.C.S., 1908, **93**, 314) is best prepared by the Schotten–Baumann method or by bromination of 4-benzoyloxydiphenylamine. 2 : 6 : 2′ : 4′ : 6′-*Pentabromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 210° (*hydroxy*-compound, m. p. 206—207°; *benzoyloxy*-compound, m. p. 141—142°; *benzoquinoneanil*, m. p. 184—185°), is prepared from the tribromo-compound by exposure to bromine vapour in the presence of sodium phosphate or borate. An attempt to sulphonylate the heptabromo-compound (Smith and Orton, *loc. cit.*) yielded a *substance*, m. p. 188°. All attempts to sulphonylate the 2 : 5 : 2′ : 4′-tetrabromo- and the 2 : 3 : 5 : 2′ : 4′-pentabromohydroxy-compounds failed.

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 185° (*hydroxy*-compound, m. p. 166°; *benzoquinoneanil*, m. p. 150°), and the corresponding *benzoyl* compound, m. p. 153°, are prepared from the tribromo-compounds by chlorination by the chloroamine method in acetic acid suspension. 2 : 2′ : 4′-*Trichloro*-6 : 6′-*dibromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 174° (*hydroxy*-compound, m. p. 180°; *benzoquinoneanil*, m. p. 170°), and the corresponding *benzoyloxy*-compound, m. p. 134°, are prepared by bromination of the trichloro-derivatives by the borate method. 2 : 2′ : 4′-*Trichloro*-5-*bromo*-4-*hydroxydiphenylamine*, m. p. 127—128° (*benzoyloxy*-compound. m. p. 186°; *sulphonyloxy*-compound, m. p. 114°; *benzoquinoneanil*, m. p. 115°), and 2 : 2′ : 4′-*trichloro*-5 : 6′-*dibromo*-4-*hydroxydiphenylamine*, m. p. 189° (*benzoquinoneanil*, m. p. 133°), which could not be sulphonylated or benzoylated, are obtained by bromination of the trichloro-compound in boiling chloroform solution. 2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromo*-4-*hydroxydiphenylamine*, m. p. 160° (*benzoyloxy*-compound, m. p. 163°), is obtained from the trichloro-compound by bromination in chloroform solution in sunlight and yields on oxidation 2 : 2′ : 4′-*trichloro*-3 : 5 : 6 : 6′-*tetrabromobenzoquinoneanil*, m. p. 136°, which is converted by hydrolysis into 2 : 4-dichloro-6-bromoaniline and chlorotribromobenzoquinone, m. p. 294°. The following corrected m. p. are given for substances described in previous papers: 3 : 5 : 2′ : 4′ : 6′-pentabromo-4-hydroxydiphenylamine, m. p. 157°; 3 : 5 : 2′ : 4′ : 6′-pentabromobenzoquinoneanil, m. p. 150·5°; 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromo-4-hydroxydiphenylamine, m. p. 216°; 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromobenzoquinoneanil, m. p. 171°.

G. A. C. Gough.

Polarity of the carbon–halogen linking. I. Determination of relative rates for the acid hydrolysis of positive halogens. II. Kinetics of the acid hydrolysis of halogenophenols and halogenonaphthols. J. R. Sampey (J. Amer. Chem. Soc., 1927, **49**, 2849—2852, 2855—2858).—I. The rates of dehalogenation of a number of bromo- and iodo-substituted phenols and naphthols were determined by heating known weights of these derivatives for varying periods with aqueous-alcoholic stannous chloride of known concentration at 70° in an atmosphere of nitrogen, and titrating the unused stannous chloride (cf. Nicolet, A., 1927, 869). The results obtained show the markedly positive nature of the halogens in the halogenonaphthols, but halogens in the 6- and 7-positions are not removed under the conditions applied. The latter observation supports the suggestion of Nicolet (*loc. cit.*) that quinones are formed intermediately in the removal of halogens by this method, especially in view of Vesely and Jakes' observation (A., 1923, i, 911) that the two most readily formed naphthaquinones possess one benzene nucleus intact.

II. The rate of dehalogenation of halogenophenols and halogenonaphthols under the conditions previously outlined increases markedly with increase in acidity of the system, but is independent of the concentration of the stannous chloride.

F. G. Willson.

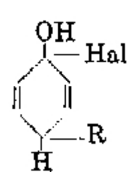
Reaction of phenol with propyl alcohol at high temperatures and pressures. V. N. Ipatiev, N. Orlov, and A. Petrov (J. Russ. Phys. Chem. Soc., 1927, **59**, 541—544).—The reaction between phenol and propyl alcohol in the presence of a catalyst at high temperatures and pressures was investigated for comparison with the behaviour of methyl alcohol under similar conditions. Heating for 12 hrs. at 380—400° and 125—130 atm. gave a liquid mixture of phenyl propyl ether, propyl ether, alkylphenols (among them *o*-propylphenol) and their propyl ethers, and polymethylene hydrocarbons, together with a gas consisting of unsaturated and saturated hydrocarbons. At normal pressure, only a small quantity of phenyl propyl ether, together with propylene, was obtained. M. Zvegintzov.

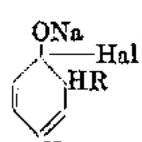
Migration of diphenylmethyl and benzyl groups in phenol. J. van Alphen (Rec. trav. chim., 1927, **46**, 799—812).—Diphenylchloromethane reacts with phenol at 110° either alone or in the presence of zinc chloride to give hydrogen chloride, 4-*hydroxytriphenylmethane*, m. p. 111°, 2 : 4-*dibenzhydrylphenol* (?), m. p. 128—129°, 2 : 4 : 6-*tribenzhydryl)phenol*, m. p. 168°, and *s*-tetraphenylethane, m. p. 211°. 4-Hydroxytriphenylmethane was also prepared by the action of zinc dust and acetic acid on 4-*hydroxytriphenylcarbinol*, m. p. 143°, which in turn was prepared from magnesium phenyl bromide and ethyl *p*-hydroxybenzoate. Similarly 2-hydroxytriphenylcarbinol, m. p. 143°, and 2-hydroxytriphenylmethane, m. p. 122° (cf. Baeyer, A., 1907, i, 759), were prepared; the latter compound, however, could not be found in the products of the reaction. Evidence of substitution in the 2 : 4 : 6-positions is found in the inert nature of that compound towards bromine, whilst 4-hydroxytriphenylmethane reacts with bromine in acetic acid to give 2 : 6-dibromo-4-hydroxytriphenylmethane, m. p. 130°. Moreover, only two diphenylmethyl groups can be introduced into *p*-hydroxybenzoic acid by heating it at 180° with diphenylchloromethane to give 4-*hydroxy*-3 : 5-*dibenzhydrylbenzoic acid*, m. p. 252° (Maquenne block), whilst *m*-chlorophenol reacts under similar conditions to give 3-*chloro*-2 : 4 : 6-*tribenzhydrylphenol*, m. p. 88—90°.

The suggestion that the first-mentioned reaction is preceded by the formation of diphenylmethyl ethers

and their consequent isomerisation through an intermediate oxonium salt to the substituted ring compound is confirmed by the isolation of 2 : 4 : 6-tri- and 2 : 4-dibenzhydrylphenol from the product obtained by heating benzhydryl methyl ether at 160° in the presence of hydrogen chloride. In a similar way 4-hydroxydiphenylmethane may be obtained from phenyl benzyl ether or from benzyl chloride and phenol by heating at 100° and 160°, respectively, in the presence of zinc chloride. The hypothesis is extended to other substitution reactions of phenols and amines, *e.g.*, the production of 2 : 6-dinitrophenol from the nitration of *o*-nitrosalicylic acid and of 2-bromo-4 : 6-dinitrophenol by the bromination of 4-bromo-2 : 6-dinitrophenol. G. A. C. GOUGH.

Alkylation of phenols. Introduction of diphenylmethyl. M. BUSCH and R. KNOLL [with A. LEUZE and A. RUPPERT] (Ber., 1927, **60**, [*B*], 2243—2257; cf. Busch, Z. angew. Chem., 1925, **35**, 1145; Schorigin, A., 1927, 54).—Diphenylmethyl bromide and phenol in the presence or absence of solvent yield *p*-hydroxytriphenylmethane, whereas sodium phenoxide affords the corresponding *ortho*-compound. Benzhydryl aryl ethers are obtained by means of diphenyldiazomethane. Schorigin's observation that benzhydryl phenyl ether is formed by the action of diphenylmethyl bromide on sodium phenoxide dissolved in an excess of phenol (*p*-hydroxytriphenylmethane is also produced in almost equal yield) is explained by Claisen's generalisation that alkylation of phenols in dissociating media yields mainly ethers, whereas *C*-alkylation takes place in non-dissociating media. Nuclear alkylation is observed with a large number of phenols and their sodium compounds, whereas only the strongly acidic nitrophenols afford ethers. The presence of negative groups in the phenolic nucleus facilitates the entry of benzhydryl groups. If the *p*- and both *o*-positions are occupied, *C*-alkylation is rendered difficult, but the slight tendency towards *O*-alkylation is established by the observation that reaction occurs at most to a very limited extent and the effect cannot be attributed to steric hindrance. Reaction occurs with the formation of intermediate products some of which have been isolated, substances of the types I, II, and III being postulated in the alkylation of phenols (I), phenoxides (II), and phenoxides in dissociating media (II and III). The action of phenols on diphenyldiazo-

(I.) 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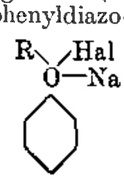

(III.)

methane appears to afford a certain method for the preparation of ethers accompanied by only minute proportions of phenols (contrast Schorigin, *loc. cit.*); tetraphenylketazine is invariably produced also. Introduction of negative groups into the phenolic nucleus facilitates the production of *O*-compounds, the yields of which reach 95% under favourable conditions. Accumulation of alkyl groups hinders the reaction. Dihydric phenols do not yield ethers, but appear to accelerate the formation of ketazine, which may become almost explosive. Polyhydric phenols appear to behave in the tautomeric ketonic form.

The following compounds are described: *p*-hydroxytriphenylmethane, m. p. 112° (also $+C_6H_6$, m. p. 81—82°); 2-*hydroxy*-5-*diphenylmethylazobenzene*, m. p. 148; 4-*nitro*-2′-*hydroxy*-5′-*diphenylmethylazobenzene*, m. p. 188—189°; *o*-hydroxytriphenylmethane, m. p. 125° (also $+C_6H_6$, m. p. 77·5°, and +EtOH, m. p. 76—80°); phenyl benzhydryl ether, m. p. 55°; 3-3-*benzhydryl*-p-*cresol*, m. p. 135°; 2-*hydroxy*-5-*methyl*-3-*diphenylmethylazobenzene*, m. p. 155°; 4-*nitro*-2′-*hydroxy*-5′-*methyl*-3′-*diphenylmethylazobenzene*, m. p. 252°; 3 : 5-*dibenzhydryl*-p-*cresol*, m. p. 190°, which does not couple with diazonium salts; 4-*nitro*-2 : 6-*dibenzhydrylphenol*, m. p. 256°; p-*nitrophenyl benzhydryl ether*, m. p. 156°; o-*nitrophenyl benzhydryl ether*, m. p. 107°; 4-*hydroxy*-3 : 5-*dibenzhydrylbenzaldehyde*, m. p. 230° [also $+C_6H_6$, m. p. (indef.) 200—205°], and the additive *compounds*, $C_{20}H_{16}O_2,CHPh_2Br$, m. p. 140° (decomp.); and $C_{20}H_{16}O_2,CHPh_2Cl$, m. p. (indef.) 180° (decomp.) after softening at 165°; unstable *phenylhydrazone* and p-*bromophenylhydrazone*, m. p. 184° (decomp.), of 4-hydroxy-3 : 5-dibenzhydrylbenzaldehyde; phenyl triphenylmethyl ether, m. p. 103°; *p*-hydroxytetraphenylmethane, m. p. 282°; p-*tolyl benzhydryl ether*, m. p. 77·5°, and the corresponding non-crystalline m-*tolyl* and o-*tolyl* compounds; 6-*chloro*-m-*tolyl benzhydryl ether*, m. p. 73°; 4 : 6-*dichloro*-m-*tolyl benzhydryl ether*, m. p. 106°; 3 : 4-*dimethylphenyl benzhydryl ether*, m. p. 87°, and the corresponding, non-crystalline compounds from *p*- and *m*-xylenol; 2 : 5-*dimethyl*-4-*benzhydrylphenyl benzhydryl ether*, m. p. 135°; m-*nitrophenyl benzhydryl ether*, m. p. 115°; *guaiacyl benzhydryl ether*, m. p. 86°; *thymyl benzhydryl ether*, m. p. 87°; β-*naphthyl benzhydryl ether*, m. p. 106°, and the non-crystalline α-*naphthyl benzhydryl ether*. H. WREN.

Direct introduction of substituents in aromatic mercaptans. T. VAN HOVE (Bull. Soc. chim. Belg., 1927, **36**, 548—558).—See A., 1927, 555.

Measurement of the basicity of carbinols. K. ZIEGLER and E. BOYE (Annalen, 1927, **458**, 229—247).—Previous measurements by the "titration method" (cf. Baeyer and Villiger, A., 1902, i, 769) have frequently been vitiated by (*a*) the difficulty of accurately observing the end-point, (*b*) the occurrence of "pseudo-halochromy," (*c*) differences in absolute colour-intensity of carbonium ions. Thus, under comparable conditions, the dilutions at which the colours of tri-*p*-diphenylyl-, phenyldi-*p*-diphenylyl-, and triphenyl-carbinol in acetic acid containing 5% of sulphuric acid become just imperceptible are in the ratio 100 : 10 : 1. "Pseudo-halochromy" is due to the presence of impurities which also yield coloured products with acids. For example, the titration basicity of diphenyl-α-naphthylcarbinol is approximately 1, the value 8·83 obtained by Skraup and Freundlich (A., 1922, i, 539) being due to the persistence of a yellow coloration after the disappearance of the true greenish-red halochromy. A rough measure of the basicity of a carbinol is afforded by the ease

with which it is precipitated as perchlorate by adding a solution of perchloric acid in acetic anhydride to its ethereal solution. In this way it is shown that *p*-nitrotriphenylcarbinol is much less basic than triphenylcarbinol, the value 17·74 previously obtained (A., 1923, i, 667) being again due to pseudohalochromy. The concentration (*c*) of carbonium salt in solutions of carbinols in acetic acid containing 5% of sulphuric acid and 0—12% of water has been determined colorimetrically by a method similar to that of Lund (A., 1927, 661). Under these conditions the carbinol–carbonium salt equilibrium does not obey the simple dilution law, but the relative order of basicity of the carbinols is correctly given by the order of the " basicity curves " obtained by plotting *c* against the concentration of water. The following increasingly basic series of carbinols differs considerably from that obtained by the titration method: triphenyl-, diphenyldiphenylyl-, phenylbisdiphenylyl-, diphenyl-*p*-tolyl-, trisdiphenylyl-, diphenyl-*p*-anisyl-, phenyldi-*p*-anisyl-, tri-*p*-tolyl-, tri-*p*-anisyl-. The method is not applicable to very weakly basic carbinols, nor to those which form mono- and di-acid salts of different colours. In discussing the results it is pointed out (cf. Brand, A., 1925, i, 397) that Baeyer's law of powers (*loc. cit.*) is not applicable to phenylated triphenylcarbinols and that no simple relation exists between the basicity of a carbinol and either (*a*) the ability to ionise of the corresponding triarylmethyl chloride (cf. A., 1910, i, 236; 1922, i, 148), or (*b*) the tendency to association of the corresponding triarylmethyl. Determinations of the relative valency-demands of aryl radicals by the carbinol method (Skraup and Freundlich, *loc. cit.*) are, therefore, of no value. H. E. F. NOTTON.

Formation of triphenylmethyl peroxide from carbon dioxide and magnesium phenyl bromide. F. F. BLICKE (J. Amer. Chem. Soc., 1927, **49**, 2843—2849).—When carbon dioxide is passed through a warm ethereal solution of magnesium phenyl bromide, the solution becomes deep orange. The colour is partly discharged by shaking the solution with air, and at the same time triphenylmethyl peroxide is precipitated, thus indicating the formation of triphenylmethyl in the Grignard solution (cf. Meyer and Togel, A., 1906, i, 757). Improved methods for the preparation of α-bromonaphthalene, α-naphthoic acid, di-α-naphthyl ketone, and di-α-naphthylcarbinol are described. F. G. WILLSON.

" Tervalent " carbon. VI. *pp'p''*-Trinitrotriphenylmethyl. K. ZIEGLER and E. BOYE (Annalen, 1927, **458**, 248—256).—The crystalline *aci*-sodium salt of *pp'p''*-trinitrotriphenylmethane (cf. Hantzsch and Hein, A., 1919, ii, 254) is less reactive than sodiotriphenylmethane, and is stable in absence of oxygen. With excess of bromine it gives pp'p''-*trinitrotriphenylmethyl bromide*, decomp. 191°, which reacts in pyridine with the above sodium salt, forming green pp'p''-*trinitrotriphenylmethyl* (cf. Gomberg, A., 1904, i, 489). This cannot be an *aci*-ester of trinitrotriphenylmethane, since the above sodium salt does not yield similar compounds with simple alkyl and aralkyl halides, whilst with triphenylmethyl bromide it gives a mixture of triphenylmethyl and the new radical. The latter is also formed together with metallic silver from the sodium salt and silver nitrate in pyridine. It combines slowly with bromine and affords a second example (cf. A., 1926, 57) of a radical which shows very little tendency to associate, being derived from a weakly basic carbinol. H. E. F. NOTTON.

Tolyl ethers and their reactions with metallic sodium. P. SCHORIGIN (Ber., 1927, **60**, [*B*], 2369—2372; cf. A., 1927, 54).—p-*Tolyl triphenylmethyl ether*, m. p. 114°, prepared by the action of triphenylmethyl chloride on sodium *p*-tolyloxide, is decomposed by sodium in the presence of toluene at 100° into triphenylmethane and *p*-cresol. Similarly, m-*tolyl triphenylmethyl ether*, m. p. 101°, gives triphenylmethane and *m*-cresol. Phenolic transformation is not observed in either case. Phenyl allyl ether, b. p. 93—94°/26 mm., d_4^{15} 0·9832, and *o*-tolyl allyl ether, b. p. 104°/26 mm., d_4^{15} 0·9698, are decomposed by sodium with production of phenol and *o*-cresol, respectively. The compound described by van Alphen as *p*-tolyl triphenylmethyl ether is identified as triphenylmethyl ethyl ether, m. p. 82°. H. WREN.

Action of triphenylcarbinol on cresols. P. SCHORIGIN (Ber., 1927, **60**, [*B*], 2373—2378).—Triphenylcarbinol is converted by *o*-cresol in the presence of glacial acetic and concentrated sulphuric acids at the atmospheric temperature into ααα-triphenyl-β-*o*-hydroxyphenylethane, m. p. 186°, in about 34% yield. Similarly, *m*-cresol gives 2-*hydroxy*-4-*methyltetraphenylmethane*, m. p. 213—214°, obtained also from triphenylmethyl chloride and sodium *m*-tolyloxide in xylene. Unexpectedly, *p*-cresol and triphenylcarbinol under like conditions give triphenylmethane in almost theoretical yield. Reaction does not occur in the absence of sulphuric acid and triphenylcarbinol does not yield triphenylmethane under the influence of sulphuric and acetic acids; the presence of *as*-*o*-xylenol but not of quinol causes production of triphenylmethane. At 100°, reaction occurs in the same manner as at the ordinary temperature. If the carbinol and cresol are used in the molecular proportion 1 : 0·5, a poorer yield of triphenylmethane is obtained. It appears therefore justifiable to assume that *p*-cresol acts as oxygen acceptor (ratio 1 : 1) in the reduction of triphenylcarbinol; it is probably converted into polymerised *p*-benzoquinonemethide. Triphenylcarbinol in the absence of *p*-cresol is converted by glacial acetic and sulphuric acids at 100° into triphenylmethane to a small extent, but mainly converted into products of higher m. p. which have not been closely examined. Triphenylmethyl chloride and sodium *p*-tolyloxide give ααα-*triphenyl*-β-p-*hydroxyphenylethane*, m. p. 182°. H. WREN.

Quinonoid and quinolide structure. A. RÉCSEI (Ber., 1927, 60, [*B*], 2378—2388).—The similarity of the absorption spectra of *p*-benzoquinonediethylsulphone, $O{:}C_6H_4(SO_2Et)_2$ (cf. A., 1927, 1079), and the salts of triphenylmethane and azobenzene establishes the quinolide structure for the latter substances. The absorption curves of quinonoid and quinolide compounds differ from one another in that the latter is displaced more towards the region of greater wave-

length. In consequence of the greater absorption of quinolide compounds the first half period is deeper than that of the quinonoids. The quinolide curve slopes more steeply than the quinonoid, which resembles more closely the sine curve. The second, steeply rising period of the quinolide compounds always reaches a greater height than that of quinonoids. The differences may be regarded as characteristic of the curves of the two classes. Quinonoid compounds are usually yellow or colourless and auxochromes have not a bathochromic action. Quinolides, in the absence of auxochromes, are yellow or brown, whilst auxochromes have a strongly bathochromic effect. Transitions are observed between the quinonoid and quinolide structures. Thus dimethylaminofuchsone exhibits colours and absorption spectra differing with the solvent which can be arranged in a continuous series. Such a transition cannot be represented by fixed formulæ. H. WREN.

Colour and constitution. W. DILTHEY (Helv. Chim. Acta, 1927, **10**, 866—868).—Polemical against Kehrmann (A., 1927, 1184). H. BURTON.

Purification of abietic acid from rosin, and preparation of some of its derivatives. C. C. KESLER, A. LOWY, and W. F. FARAGHER (J. Amer. Chem. Soc., 1927, **49**, 2898—2903).—Pure abietic acid is obtained in 80% yield from "G" grade rosin (91% abietic acid) by the following procedure: the rosin is first isomerised, either by passing a current of dry hydrogen chloride through the molten material for 20 min., or by boiling the rosin with 3 parts of alcohol containing 1% of hydrogen chloride for 15 min. Aqueous or alcoholic sodium hydroxide is then added in amount sufficient to neutralise the hydrochloric acid and to neutralise also one fourth of the abietic acid present, when the *acid sodium* salt, $C_{19}H_{29}\cdot CO_2Na,3C_{20}H_{30}O_2$, m. p. 177°, separates in crystalline form, the rescue being removed with filtrate and washings. Acidification of this salt with the calculated amount of mineral or acetic acid affords abietic acid, m. p. 166°. Treatment of (neutral) sodium abietate with ethyl sulphate at 100° affords *ethyl abietate*, b. p. 204—207°/4 mm., d_4^{15} 1·032, n 1·5265. The following esters were prepared similarly from the sodium salt and the appropriate alkyl *p*-toluenesulphonates: n-*propyl*, b. p. 237—240°/4 mm., d 1·015, n 1·5229; iso*propyl*, b. p. 214—217°/4 mm., d 1·010, n 1·5200; n-*butyl*, b. p. 247—250°/3 mm., d_4^{15} 1·014, n 1·5192; iso*butyl*, b. p. 222—225°/4 mm., d_4^{15} 1·008, n 1·5171; iso*amyl*, b. p. 254—257°/4 mm., d_4^{15} 1·001, n 5165; *allyl*, b. p. 282—285°/5 mm., d_4^{15} 1·024, n 1·5242; and *menthyl*, m. p. 77—83°. The following esters were obtained by treating equimolecular mixtures of dry, powdered sodium abietate and the sodium salt of the appropriate hydroxylic derivative with carbonyl chloride at the ordinary temperature: *phenyl*, b. p. 330—333°/4 mm., d_4^{15} 1·056, n 1·5354; cyclo*hexyl*, b. p. 299—302°/4 mm., d_4^{15} 1·061, n 1·535; m-*tolyl*, b. p. 310—313°/5 mm., d_4^{15} 1·039; *α-naphthyl*, b. p. 290°/2 mm. (decomp.), d_4^{15} 1·116; *terpineol*, b. p. 310°/2 mm. (decomp.), d_4^{15} 1·082, and *bornyl abietate*, m. p. 75—80°. *Benzyl abietate*, b. p. 294—297°/4 mm., d_4^{15} 1·036, n 1·551, is obtained by adding aqueous 40% sodium hydroxide (25 c.c.) and then water (25 c.c.) to abietic acid and benzyl chloride (0·25 mol. each) in carbon tetrachloride, and refluxing for 3 hrs. *Cholesteryl abietate*, m. p. 122—125°, is obtained by heating equivalents of cholesterol and abietic acid at 200° for 2 hrs. in presence of zinc, with subsequent dissolution in benzene, washing, and removal of solvent. *Cetyl abietate*, m. p. 42°, was prepared by heating cetyl iodide with sodium abietate at 150° for 6 hrs. Certain of the above esters can be used as plasticisers in cellulose nitrate lacquers.
F. G. WILLSON.

Bile acids. L. RUZICKA and E. A. RUDOLPH (Helv. Chim. Acta, 1927, **10**, 920—925).—Distillation of barium choloidanate with soda-lime at 300°/12 mm. gives a mixture of unsaturated hydrocarbons, b. p. 100°/720 mm. to 150—160°/1 mm. The fraction of b. p. 170—180°/720 mm., d_4^{20} 0·8792, n_D^{20} 1·4968, contains a *hydrocarbon*, probably $C_{11}H_{16}$, having either two or three double linkings. The fraction of b. p. 125—135°/12 mm., d_4^{21} 0·9441, n_D^{21} 1·5373, contains a dicyclic *hydrocarbon*, $C_{15}H_{20}$, having four double linkings, whilst the fraction of b p. 170—180°/12 mm., d_4^{22} 0·9707, n_D^{22} 1·5558, contains a dicyclic *hydrocarbon*, $C_{19}H_{26}$, having four or five double linkings. The results do not yield information as to the structure of the bile acids.
H. BURTON.

Calculation of general, alternating, and *ortho*-effects of substituents. C. F. VAN DUIN (Rec. trav. chim., 1927, **46**, 770—774).—Theoretical. A reply to Berger (A., 1927, 873). It is pointed out that in comparing the observed effect of the introduction of a *m*-methyl group into the benzoic acid molecule on the dissociation constant with the entry of that group into the hexahydrobenzoic acid molecule, the ratio of the differences from unity of each individual dissociation constant ratio should be taken and not, as Berger has done, the ratios themselves. When calculated thus a figure 3·75 [calculated from Højendahl's theory (A., 1924, ii, 122), 3·3] is obtained. G. A. C. GOUGH.

Calculation of general, alternating, and *ortho*-effects of substituents. G. BERGER (Rec. trav. chim., 1927, **46**, 855—857).—The assumption of van Duin that the general effect is entirely due to a direct influence of the substituents on the key-atom leads to the prediction that chlorine substitution in the δ-position of *n*-valeric acid should have a greater effect than substitution in the β- or the γ-position (owing to the stereo-proximity of the carboxyl group). Examination of the recorded data on dissociation constants, however, shows that δ-substitution actually has less effect. Unpublished data are quoted showing that the velocities of the reactions of the three toluoyl chlorides at 25° with an excess of *n*-butyl alcohol, with excess of benzyl alcohol, and with an equimolecular amount of benzyl alcohol in benzene are in the orders *o*->*m*->*p*-; *o*->*p*->*m*-; *o*->*m*->*p*-, respectively. The assumption of the additive nature of the effects gives a negative reaction velocity for the introduction of a *m*-nitro-group into some of the compounds studied by Olivier (A., 1923, i, 908).
G. A. C. GOUGH.

Calculation of general, alternating, and *ortho*-effects of substituents. C. F. van Duin (Rec. trav. chim., 1927, 46, 858—860).—In reply to Berger (preceding abstract) the work of Ruzicka and his co-workers (A., 1926, 727) is quoted to show that the ease of ring formation is not connected directly with the distance between the terminal carbon atoms and hence the application of this argument to substitution and dissociation constants is probably not justified. It is pointed out that neither the additive nor the multiplicative method of determining the total effect of substituents will predict the stability of *trans*-2 : 4-dimethoxycinnamic acid to bromine.

G. A. C. Gough.

Reaction of *para*-substituted benzyl chlorides with sodium hydrogen sulphide. C. Barkenbus, E. B. Friedman, and R. K. Flege (J. Amer. Chem. Soc., 1927, 49, 2549—2553).—Treatment of the sodium salt of 6-hydroxy-2-thio-4-methylpyrimidine with *p*-cyanobenzyl chloride in absolute alcohol affords 6-*hydroxy*-2-p-*cyanobenzylthiol*-4-*methylpyrimidine*, m. p. 240—241°, which on hydrolysis with hydrochloric acid yields p-*cyanobenzylmercaptan*, m. p. 37°, b. p. 135—138°/7 mm. Treatment of the sodium salt of the latter with *p*-cyanobenzyl chloride in absolute alcohol affords p-*cyanobenzyl sulphide*, m. p. 115°, whilst p-*cyanobenzyl disulphide*, yellow, m. p. 148°, is obtained by atmospheric oxidation of the mercaptan in aqueous-alcoholic ammonia. Treatment of *p*-cyanobenzyl chloride with alcoholic sodium hydrogen sulphide in a current of hydrogen sulphide affords *p*-cyanobenzyl sulphide (78·2%) and *p*-cyanobenzylmercaptan (10·2%). If the reaction is carried out with access of air, the sulphide and disulphide are the sole products. Treatment of ethyl ω-chlorotoluate with alcoholic sodium hydrogen sulphide affords *ethyl benzylmercaptan*-p-*carboxylate*, b. p. 140—141°/6 mm., together with the corresponding *sulphide*, m. p. 78°. The latter was also prepared from ethyl ω-chlorotoluate and alcoholic sodium sulphide. Hydrolysis of *p*-cyanobenzylmercaptan with hydrochloric acid yields *benzylmercaptan*-p-*carboxylic acid*, m. p. 176°.

F. G. Willson.

Derivatives of δ-benzamidovaleric acid, and the synthesis of putrescine. S. J. Kanevskaia (J. Russ. Phys. Chem. Soc., 1927, 59, 639—647).—Benzoylputrescine was synthesised by Hofmann's method from δ-benzamidovaleramide. The free acid and thionyl chloride gave δ-*benzamidovaleryl chloride*, an oil which decomposed on distillation in a vacuum. Reduction by Rosenmund's method (hydrogen in presence of palladium catalyst) gave, instead of the expected aldehyde, *N*-benzoylpiperidone, m. p. 112°. The same reaction takes place in a boiling inert solvent by the elimination of hydrochloric acid. The chloride gives an *anilide*, m. p. 170—171°, and an *amide*, m. p. 180—181°, which by the action of bromine and alkali yields *benzoylputrescine*, an oil which decomposes on distillation in a vacuum and forms a *hydrochloride*, m. p. 169—170°. By means of the Schotten–Baumann reaction, a characteristic *dibenzoyl* compound, m. p. 175—176°, is obtained, whilst prolonged boiling with concentrated hydrochloric acid gives putrescine hydrochloride. M. Zvegintzov.

Synthesis of benzoylcadaverine. S. J. Kanevskaia (J. Russ. Phys. Chem. Soc., 1927, 59, 649—652; cf. preceding abstract).—Benzamidohexoamide, m. p. 140—141°, obtained by Gabriel's method from benzoylpiperidine *via* benzoylchloroamylamine by the action of phosphorus pentachloride, was treated with bromine in an excess of potassium hydroxide. *Benzoylcadaverine*, a strongly basic oil, which decomposed on distillation in a vacuum, was obtained. When treated with an alcoholic solution of hydrochloric acid it gave the *hydrochloride*, m. p. 159—160°, and on benzoylation, *dibenzoylcadaverine*, m. p. 135—135·5°.

M. Zvegintzov.

Synthesis of *o*-nitrocinnamic acid and its photochemical behaviour. I. Tanasescu (Bull. Soc. chim., 1927, [iv], 41, 1074—1077).—Thin layers of finely-powdered *o*-nitrocinnamic acid (improved method of preparation given) are exposed to sunlight, when a red substance, m. p. 120°, is produced (cf. Friedländer and Ostermayer, A., 1882, 201; Sachs and Hilpert, A., 1904, i, 876), which is probably hydroxyisatogenic acid, $C_6H_4<\begin{matrix}CH\cdot OH\\ NO\end{matrix}>C\cdot CO_2H$. Prolonged exposure to sunlight does not increase the amount of coloured substance. H. Burton.

The two *o*-cyanocinnamic acids. W. Davies and H. G. Poole (J.C.S., 1927, 2661—2663).—Both *o*-cyanocinnamic acid, m. p. 256°, obtained in 36% yield by heating the sodium salt of 1-nitroso-β-naphthol in nitrobenzene, and *o*-cyano*allo*cinnamic acid, m. p. 137°, give on hydrolysis the same *o*-carboxycinnamic acid, m. p. 184°, which does not form a normal anhydride. Acetophenone-*o*-carboxylic acid (*oxime*, m. p. 156—157°; p-*nitrophenylhydrazone*, m. p. 211°; *phenylhydrazone*) was obtained as a by-product during a large-scale preparation of *o*-cyano*allo*cinnamic acid from nitroso-β-naphthol. The *allo*-acid, which is partly converted into its isomeride, m. p. 256°, on distillation, furnishes o-*cyano*allo-*cinnamoyl chloride*, m. p. 50°. S. Coffey.

Action of acetic anhydride and acetone in presence of pyridine on tyrosine and on phenylglycine. P. A. Levene and R. E. Steiger (J. Biol. Chem., 1927, 74, 689—693).—Attempted acetylation of tyrosine with commercial acetic anhydride and pyridine gave a *substance*, $C_{14}H_{17}O_4N$, m. p. 122—123°, which, when boiled with dilute sodium hydroxide, lost an acetyl group to give a *compound*, $C_{12}H_{15}O_3N$, m. p. 163—166°; the compound $C_{14}H_{17}O_4N$ was formed more readily on addition of acetone to the reaction mixture, and is regarded as a condensation product of acetyltyrosine with acetone. Similar treatment of phenylglycine yielded carbon dioxide and a *substance*, $C_{14}H_{13}O_2N$, m. p. 100—101°.

C. R. Harington.

Δ²-*cyclo*Pentenylalkylacetic acids and their action towards *B. lepræ*. IX. J. A. Arvin and R. Adams (J. Amer. Chem. Soc., 1927, 49, 2940—2942; cf. following abstract).—The following di-substituted malonic esters and acetic acids were prepared by methods analogous to those previously described (*loc. cit.*): *Ethyl* Δ²-cyclo*pentenyl-alkylmalonates*: -n-*amyl*-, b. p. 133—136°/3 mm., d_4^{20}

0·9981, n_D^{20} 1·4580; -n-*hexyl*-, b. p. 150—155°/4 mm., d_4^{20} 0·9867, n_D^{20} 1·4572; -n-*heptyl*,- b. p. 159—164°/3 mm., d_4^{20} 0·9791, n_D^{20} 1·4582; -n-*octyl*-, b. p. 169—174°/4 mm., d_4^{20} 0·9765, n_D^{20} 1·4591; and -n-*nonyl*-, b. p. 183—187°/5 mm., d_4^{20} 0·9756, n_D^{20} 1·4595. Δ²-cyclo*Pentenyl-alkyl-acetic acids*: -n-*amyl*-, b. p. 142—145°/5 mm., d_4^{20} 0·9629, n_D^{20} 1·4659; -n-*hexyl*-, b. p. 150—155°/5 mm., d_4^{20} 0·9573, n_D^{20} 1·4671; -n-*heptyl*-, b. p. 162—165°/4 mm., d_4^{20} 0·9499, n_D^{20} 1·4683; -n-*octyl*-, b. p. 170—173°/4 mm., d_4^{20} 0·9452, n_D^{20} 1·4687; and -n-*nonyl*-, b. p. 173—176°/3 mm., d_4^{20} 0·9436, n_D^{20} 1·4690 (cf. Perkins and Cruz, A., 1927, 359). Amongst the substituted acetic acids, the bactericidal effect increases with increasing mol. wt., and the sodium salt of the nonyl derivative is fatal to *B. lepræ* at a dilution of 1 : 150,000.

F. G. WILLSON.

ω-*cyclo*Hexylalkylalkylacetic acids and their action towards *B. lepræ*. VIII. R. ADAMS, W. M. STANLEY, S. G. FORD, and W. R. PETERSON (J. Amer. Chem. Soc., 1927, **49**, 2934—2940; cf. A., 1926, 1137).—The following compounds were prepared by condensing the appropriate ω-*cyclo*-hexylalkyl bromides with ethyl sodioalkylmalonates, hydrolysing the resulting substituted ethyl malonates, and eliminating carbon dioxide in the usual manner: *Ethyl* β-cyclo*hexylethyl-alkyl-malonates*: -*ethyl*-, b. p. 146—148°/2 mm., d_4^{25} 0·9907, n_D^{25} 1·4502; -n-*propyl*-, b. p. 153—156°/6 mm., d_4^{25} 0·9813, n_D^{25} 1·4518; -n-*butyl*-, b. p. 144—147°/4 mm., d_4^{25} 0·9714, n_D^{25} 1·4531; -n-*amyl*-, b. p. 174—176°/5 mm., d_4^{25} 0·9644, n_D^{25} 1·4537; -n-*hexyl*-, b. p. 188—191°/5 mm., d_4^{25} 0·9569, n_D^{25} 1·4539; -n-*heptyl*-, b. p. 171—173°/3 mm., d_4^{25} 0·9527, n_D^{25} 1·4545; -n-*octyl*-, b. p. 213—216°/7 mm., d_4^{25} 0·9449, n_D^{25} 1·4550; and -*allyl*-, b. p. 142—145°/2 mm., d_4^{25} 0·9915, n_D^{25} 1·4563. *Ethyl* γ-cyclo*hexylpropyl-alkyl-malonates*: -*ethyl*-, b. p. 149—151°/4 mm., d_4^{25} 0·9797, n_D^{25} 1·4528; -n-*propyl*-, b. p. 155—156°/4 mm., d_4^{25} 0·9743, n_D^{25} 1·4531; -n-*butyl*-, b. p. 160—161°/4 mm., d_4^{25} 0·9620, n_D^{25} 1·4534; -n-*amyl*-, b. p. 178—180°/4 mm., d_4^{25} 0·9603, n_D^{25} 1·4549; -n-*hexyl*-, b. p. 180—191°/4 mm., d_4^{25} 0·9501, n_D^{25} 1·4551; -n-*heptyl*-, b. p. 209—210°/5 mm., d_4^{25} 0·9471, n_D^{25} 1·4554, and -*allyl*-, b. p. 170—172°/5 mm., d_4^{25} 0·9837, n_D^{25} 1·4569. *Ethyl* δ-cyclo*hexylbutyl-alkyl-malonates*: -*ethyl*-, b. p. 165—167°/4 mm., d_4^{25} 0·9704, n_D^{25} 1·4536; -n-*propyl*-, b. p. 173—175°/4 mm., d_4^{25} 0·9695, n_D^{25} 1·4538; -n-*butyl*-, b. p. 175—177°/4 mm., d_4^{25} 0·9563, n_D^{25} 1·4546; -n-*amyl*-, b. p. 191—193°/5 mm., d_4^{25} 0·9530, n_D^{25} 1·4559; -n-*hexyl*-, b. p. 194—196°/4 mm., d_4^{25} 0·9514, n_D^{25} 1·4572; and -*allyl*-, b. p. 168—170°/4 mm., d_4^{25} 0·9742, n_D^{25} 1·4565. β-cyclo-*Hexylethyl-alkyl-malonic acids*: -*ethyl*-, m. p. 114—115°; -n-*propyl*-, m. p. 132—133°; -n-*butyl*-, m. p. 135—136°; -n-*amyl*-, m. p. 125—126°; -n-*octyl*-, m. p. 108—109°; and -*allyl*-, m. p. 95—96°. γ-cyclo*Hexylpropyl-alkyl-malonic acids*: -*ethyl*-, m. p. 143°; -n-*propyl*-, m. p. 130°; -n-*butyl*-, m. p. 138°; -n-*amyl*-, m. p. 148°; -n-*hexyl*-, m. p. 134°; and -n-*heptyl*-, m. p. 99°. δ-cyclo*Hexylbutyl-alkyl-malonic acids*: -*ethyl*-, m. p. 136°; -n-*propyl*-, m. p. 140°; -n-*butyl*-, m. p. 113°; -n-*amyl*-, m. p. 64°; and -*allyl*-, m. p. 143° β-cyclo*Hexylethyl-alkyl-acetic acids*: -*ethyl*-, b. p. 121—124°/3 mm., d_4^{25} 0·9619, n_D^{25} 1·4613; -n-*propyl*-, b. p. 122—125°/2 mm., d_4^{25} 0·9486, n_D^{25} 1·4623; -n-*butyl*-, b. p. 139—142°/4 mm., d_4^{25} 0·9410, n_D^{25} 1·4624; -n-*amyl*-, b. p. 182—185°/5 mm., d_4^{25} 0·9350, n_D^{25} 1·4626; -n-*hexyl*-, b. p. 174—177°/2 mm., d_4^{25} 0·9283, n_D^{25} 1·4628; -n-*heptyl*-, b. p. 162—185°/2 mm., d_4^{25} 0·9222, n_D^{25} 1·4631; -n-*octyl*-, b. p. 193—196°/4 mm., d_4^{25} 0·9193, n_D^{25} 1·4640; and -*allyl*-, b. p. 125—128°/2 mm., d_4^{25} 0·9714, n_D^{25} 1·4672. γ-cyclo*Hexylpropyl-alkyl-acetic acids*: -*ethyl*-, b. p. 146—147°/2 mm., d_4^{25} 0·9509, n_D^{25} 1·4622; -n-*propyl*-, b. p. 148—150°/2 mm., d_4^{25} 0·9419, n_D^{25} 1·4627; -n-*butyl*-, b. p. 153—154°/2 mm., d_4^{25} 0·9317, n_D^{25} 1·4630; -n-*amyl*-, b. p. 188—192°/5 mm., d_4^{25} 0·9266, n_D^{25} 1·4634; -n-*hexyl*-, b. p. 208—211°/8 mm., d_4^{25} 0·9221, n_D^{25} 1·4638; -n-*heptyl*-, b. p. 199—203°/2 mm., d_4^{25} 0·9137, n_D^{25} 1·4642; and -*allyl*-, b. p. 147—150°/2 mm., d_4^{25} 0·9552, n_D^{25} 1·4708. δ-cyclo*Hexylbutyl-alkyl-acetic acids*: -*ethyl*-, b. p. 173—175°/3 mm., d_4^{25} 0·9447, n_D^{25} 1·4622; -n-*propyl*-, b. p. 156—158°/1 mm., d_4^{25} 0·9408, n_D^{25} 1·4627; -n-*butyl*-, b. p. 178—180°/4 mm., d_4^{25} 0·9300, n_D^{25} 1·4631; -n-*amyl*-, b. p. 207—209°/8 mm., d_4^{25} 0·9254, n_D^{25} 1·4633; -n-*hexyl*-, b. p. 187—189°/1 mm., d_4^{25} 0·9191, n_D^{25} 1·4638; and -*allyl*-, b. p. 174—176°/6 mm., d_4^{25} 0·9531, n_D^{25} 1·4687. Amongst the above substituted acetic acids, increase in mol. wt. is accompanied by increasing toxicity to acid-fast bacteria, sodium salts of the acids of highest mol. wt. being much more effective against *B. lepræ* than those of chaulmoogric or hydnocarpic acids, or of any of the mixed acids from natural oils containing these.

F. G. WILLSON.

Complex salts of *o*-dinitriles with copper and pyridine. H. DE DIESBACH and E. VON DER WEID (Helv. Chim. Acta, 1927, **10**, 886—888).—*o*-Dibromobenzene when heated with a mixture of cuprous cyanide and pyridine for 8 hrs. at 200° in a sealed tube yields a small amount of phthalimide and a blue *compound*, $[C_6H_4(CN)_2,C_5H_5N]_2Cu$, also formed by the action of cuprous bromide and pyridine on *o*-phthalonitrile. From 4 : 5-dibromo-*o*-xylene are obtained similarly a blue *compound*, $[C_6H_2Me_2(CN)_2,C_5H_5N]_2Cu$, together with 4 : 5-*dimethylphthalimide*, m. p. 240—241°, hydrolysed by potassium hydroxide solution to 4 : 5-dimethylphthalic acid, m. p. 201° (cf. Korczynski, A., 1902, i, 274). 1 : 2-Dibromonaphthalene furnishes a dark green *compound*, $[C_{10}H_6(CN)_2,C_5H_5N]_2Cu$ (10%), together with naphthalene-1 : 2-dicarboximide (65%). These complex compounds are unaffected by warm, concentrated sulphuric acid and by concentrated alkalis, but are decomposed by hot, moderately concentrated nitric acid.

H. BURTON.

Action of organo-magnesium compounds on *o*-phthalonitrile. II. R. WEISS and G. SCHLESINGER (Monatsh., 1927, **48**, 451—457; cf. A., 1925, i, 139).—The action of magnesium phenyl bromide on *o*-phthalonitrile yields *phenyl*iso*indoloneanil*, $\begin{matrix}CPh{=}N\\ C_6H_4{\cdot}C{:}NPh\end{matrix}$, m. p. 234—236° (*perchlorate*; unstable *hydrochloride*), *o*-benzoylbenzamide, and a *compound*, $C_{14}H_{16}N_2O_3$, m. p. 169° (decomp.). Hydrolysis and simultaneous reduction of the anil by heating with hydriodic acid and red phosphorus under reflux for 0·75 hr. yields the lactam, $\begin{matrix}CHPh{\cdot}NH\\ C_6H_4{-}CO\end{matrix}$, identical with a

synthetic specimen prepared by the method of Rose (A., 1911, i, 372), the reduction occurring thus: $C_{20}H_{14}N_2-H_2O+H_2=C_{14}H_{11}ON+NH_2Ph$.

J. W. BAKER.

Substituted diaryl ethers. II. Friedel–Crafts reaction applied to di-*p*-tolyl ether. J. REILLY and P. J. DRUMM (J.C.S., 1927, 2814—2819).—2-*o-Carboxybenzoyldi*-p-*tolyl ether* (I), m. p. 155° (*silver* salt described), obtained by the condensation of phthalic anhydride and di-*p*-tolyl ether by the Friedel–Crafts method, yields di-*p*-tolyl ether and potassium phthalate on fusion with potassium hydroxide. The constitution is confirmed by the alternative preparation from *p*-bromotoluene and the dipotassium derivative of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid in the presence of copper powder and alcohol at 200°. The substance (I) does not combine with hydroxylamine hydrochloride and yields with difficulty the *phenylhydrazone*, m. p. 156°. When heated at 100° with concentrated sulphuric acid, or when boiled with benzene, phosphorus pentachloride, and aluminium chloride, it affords 2 : 7-dimethylfluoran, m. p. 254°. Since 2-*o*-carboxybenzoyl-di-*p*-tolyl ether may also be prepared by condensation of *p*-cresol with 2-chloro-4-methylbenzophenone-2′-carboxylic acid, the last-named substance must have the constitution here assigned and not the 3-chloro-6-methyl constitution as indicated by Heller and Schülke (A., 1908, i, 994), who prepared it from *p*-chlorotoluene and phthalic anhydride.

2-*Benzoyldi*-p-*tolyl ether*, m. p. 185—186°, prepared from benzoyl chloride, di-*p*-tolyl ether, and aluminium chloride, is converted into 9-phenyl-2 : 7-dimethylxanthen by boiling with acetic acid or by heating with phenylhydrazine at 160°. 2-Hydroxy-5-methylbenzophenone, m. p. 84·5°, and 2-*p*-tolyl-5-methylacetophenone, m. p. 168°, are best prepared by the Friedel–Crafts reaction, using *s*-tetrachloroethane as the medium.

G. A. C. GOUGH.

Dehydrogenation with sulphur and dehydrogenating disruption with manganese dioxide and sulphuric acid. L. RUZICKA and E. A. RUDOLPH (Helv. Chim. Acta, 1927, **10**, 915—920).—Irone (Tiemann and Krüger, A., 1894, i, 81) when heated with sulphur at 180—250° yields 1 : 6-dimethylnaphthalene (10%) (*picrate*, m. p. 109°), a methyl group being eliminated during the dehydrogenation. Oxidation of 1 : 6-dimethylnaphthalene with alkaline potassium ferricyanide at 80° yields *naphthalene*-1 : 6-*dicarboxylic acid*, m. p. 305° (decomp.) after sintering at 290° (cf. A., 1927, 60). Tetrahydronaphthalene is dehydrogenated by heating with sulphur to naphthalene (70%). Oxidation of menthene with manganese dioxide and sulphuric acid (cf. A., 1924, i, 171), and conversion of the resulting acids into their methyl esters, gives methyl benzenepentacarboxylate, m. p. 147—148°, and methyl terephthalate, m. p. 140°. Similar oxidation of ethyl 2-methyl-5-*iso*propylphenylacetate yields trimellitic acid, m. p. 224—225°.

H. BURTON.

Stereochemistry of aromatic compounds. V. Racemisation of optically active diphenic acids. R. KUHN and O. ALBRECHT (Annalen, 1927, **458**, 221—229).—Contrary to the statement of Christie and Kenner (J.C.S., 1922, **121**, 614), it has not been found possible to racemise *d*-4 : 6 : 4′ : 6′-tetranitrodiphenic acid, m. p. 258—259°, sintering (decomp.) from 220°, $[\alpha]^{22}$ +100·7° in 2*N*-sodium hydroxide, prepared from the brucine salt, $[\alpha]^{20}$ +9° in 10·4*N*-acetic acid. The optical activity of the acid is not changed by heating it in xylene vapour at 125°, with aluminium chloride at 160—170°, or with 2*N*-sodium hydroxide at 100°. 4 : 6 : 4′-Trinitrodiphenic acid has been resolved through its brucine salt into a *l*-form, m. p. 281—282° (decomp.), $[\alpha]^{22}$ −37·8° in 2*N*-sodium hydroxide, and a *d*-form, m. p. 279—280°, $[\alpha]^{20}_{\mathrm{D}}$ +33·3° (cf. J.C.S., 1923, **123**, 779). The velocities of racemisation of the *l*-acid at 74·6° and 98·6° in 2*N*-sodium hydroxide are lower than the corresponding values for *l*-4 : 6′-dinitrodiphenic acid (A., 1927, 876). The reaction is unimolecular and the heat of activation of the free anion calculated from the temperature coefficient, $(k_{t+10})/k_t=3{\cdot}4$, is 22,400 g.-cal./mol. These results further illustrate the stabilising effect of introducing 6-nitro-groups into optically active diphenic acids.

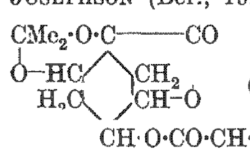
H. E. F. NOTTON.

Manufacture of dinaphthyldicarboxylic acids. I. G. FARBENIND. A.-G.—See B., 1927, 902.

Synthesis of hydrastic acid. T. S. STEVENS and M. C. ROBERTSON (J.C.S., 1927, 2790—2792).—The lactone of 6-hydroxymethylhomopiperonylic acid (A., 1927, 265) condenses with benzaldehyde at 120° in the presence of piperidine to give α-(6-*hydroxymethylpiperonyl*)*cinnamolactone*, m. p. 190—192°, which on oxidation with potassium permanganate in acetone solution affords 4 : 5-methylenedioxyphthalide, m. p. 188—189° [6-*hydroxymethylpiperonylic acid*, m. p. 140—150° (indef.; solidifying and remelting as the lactone; *silver* salt described)]. Oxidation of the phthalide with alkaline potassium permanganate gives hydrastic acid, m. p. 228°.

G. A. C. GOUGH.

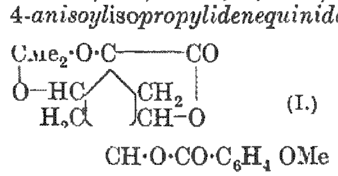
Monoacyl derivatives of quinic acid. K. JOSEPHSON (Ber., 1927, **60**, [*B*], 2270—2272).—The *iso*propylidene ether of quinic acid lactone (cf. Freudenberg, A., 1920, i, 322) is converted by cinnamoyl chloride in the presence of pyridine into *cinnamoyl*iso*propylidenequinide* (I), m. p. 189° (corr.), [α] +10·6° in chloroform.



(I)

H. WREN.

Acyl derivatives of quinic acid. P. KARRER and K. P. LINK (Helv. Chim. Acta, 1927, **10**, 794—799; cf. A., 1925, i, 673).—*iso*Propylidenequinide (cf. Fischer, A., 1921, i, 419) on anisoylation yields 4-*anisoyl*iso*propylidenequinide* (I), m. p. 126·5—127°, $[\alpha]_{\mathrm{D}}$ 3·1 in acetone, which is hydrolysed by dilute sulphuric acid to 4-*anisoylquinide*, m. p. 155°, $[\alpha]^{15}_{\mathrm{D}}$ −2·65° in acetone.



(I.)

This last compound when treated with sodium hydroxide solution yields 4-*anisoylquinic acid*, m. p. 193°, $[\alpha]^{18}_{\mathrm{D}}$ +1·7° in acetone, which when treated with acetone containing 2% of hydrogen chloride regenerates

(I). 4-p-*Hydroxybenzoyl*iso*propylidenequinide*, m. p. 179—180°, is obtained by hydrolysis of its *acetyl* derivative, m. p. 165—166°. H. BURTON.

Reduction of acid chlorides under reduced pressure. Preparation of aldehydes. V. GRIGNARD and G. MINGASSON (Compt. rend., 1927, **185**, 1173—1176).—Working at 200—225°/140—400 mm., with platinum oxide as catalyst, benzoyl chloride (60%), phenylacetyl chloride (50%), and phenylpropionyl chloride (20%) were hydrogenated to the corresponding aldehydes with the yields indicated, without any formation of the by-products which occur under normal pressure. In the aliphatic series, also, reduction to the aldehyde only takes place, but the aldehydes were carried away with the hydrogen chloride evolved. Under reduced pressure at 300°, using nickel as a catalyst, 60% of benzaldehyde was obtained from benzoyl chloride, but poor results were obtained with aliphatic acid chlorides. B. W. ANDERSON.

Constitution of *o*-nitrobenzaldehyde and the interference of nitro- and nitroso-groups on the Zerewitinoff method for the determination of active hydrogen. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1927, **49**, 2815—2818).—Nitrobenzene, *s*-trinitrobenzene, nitrosobenzene, *o*- and *p*-nitrotoluenes, and *p*-nitrosodimethylaniline all evolve gas when treated with magnesium alkyl halides of low mol. wt., thereby indicating the presence of "active hydrogen" (cf. Zerewitinoff, B., 1926, 720). The evolution of gas under similar conditions from *o*-nitrobenzaldehyde does not therefore support the cyclic formula suggested for this substance by Tanasescu (A., 1926, 726). F. G. WILLSON.

Hydroxymethylene-aldehydes. II. Condensations with hydroxymethylenephenylacetaldehyde. H. RUPE and A. HUBER (Helv. Chim. Acta, 1927, **10**, 846—858; cf. Rupe and Knup, A., 1927, 564).—Hydroxymethylenephenylacetaldehyde [*benzoyl* derivative, m. p. 72° (Rupe and Knup, *loc. cit.*, describe another benzoyl derivative, m. p. 115°); *methyl ether*, obtained by the action of diazomethane], reacts with hydrazine to form 4-phenylpyrazole, m. p. 230° (*silver* salt; *picrate*, m. p. 155°); with *o*-nitrophenylhydrazine, to yield 1-o-*nitrophenyl*-4-*phenylpyrazole*, m. p. 170°, and a *compound*,

$NO_2\cdot C_6H_4\cdot NH\cdot N:CH\cdot CPh:CH\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$,

m. p. 194°, formed by interaction with 2 mols. of the phenylhydrazine. The aldehyde condenses with *o*-phenylenediamine in alcohol solution to form the *compound* $C_6H_4<\begin{array}{l}N:CH\cdot CPh\\ \quad\quad\quad\;\,\Vert\\ NH—CH\end{array}$ vermilion, m. p. 250° (dark blue and yellow *hydrochlorides*). With *o*-nitroaniline there is formed o-*nitroanilinomethylenephenylacetaldehyde*, m. p. 112—130° (*oxime*, m. p. 154°), which on reduction forms the above seven-membered ring compound. The m-*nitroanilino*-derivative, m. p. 152° and 165—166° (*semicarbazone*, m. p. 194°), and the p-*nitroanilino*-derivative, m. p. 180° and 195°, are described. When the *p*-nitroanilino-derivative is treated with ammoniacal silver nitrate solution, a dark blue *compound*, $C_{15}H_{14}O_3N_3Ag$, m. p. 154° (decomp.), is formed. To this is assigned the structure $[O\cdot NO:C_6H_4:N\cdot CH:CPh\cdot CHO]AgNH_3$. *aci*-Quinonoid structures are allocated to the *o*- and *p*-nitroanilino-derivatives, since they give dark red colours with alcoholic potassium hydroxide. Reduction of the *p*-nitroanilino-compound with tin and acetic–hydrochloric acids furnishes p-*aminoanilinomethylenephenylacetaldehyde*, m. p. 95° [*hydrochloride*, m. p. 240° (decomp.)]. Methoxymethylenephenylacetaldehyde reacts with 2 mols. of aniline and *m*- and *p*-nitroanilines, yielding *anilinomethylenephenylacetaldehydeanil*, m. p. 137—139°, m-*nitroanilinomethylenephenylacetaldehyde*-m-*nitroanil*, m. p. 174°, and p-*nitroanilinomethylenephenylacetaldehyde*-p-*nitroanil*, m. p. 258—260°; with semicarbazide, to form 4-*phenylpyrazole*-2-*carboxylamide*, m. p. 166°, and with guanidine, to yield 2-*amino*-5-*phenylpyrimidine*, m. p. 162°. In all these reactions the methyl group is eliminated. Magnesium ethyl bromide reacts with the benzoyl derivative or the methyl ether of the hydroxy-aldehyde, eliminating benzoic acid or methyl alcohol, to form the *oxide*, $\begin{array}{r}CHEt\\ |\;\;\;\\ CH—O\;\;\;\;\,\end{array}$, b. p. 98—100°/11 mm. H. BURTON.

Isomerisation of hydroxy-aldehydes. I. Transformation of diphenylglycollaldehyde into benzoin. S. DANILOV (Ber., 1927, **60**, [*B*], 2390—2401).—The transformation of diphenylglycollaldehyde into benzoin is due to the conversion of the hydroxy-aldehydic to the hydroxy-ketonic arrangement and to rearrangement of the skeleton with disappearance of tertiary carbon atoms. The second condition excludes change in the reverse direction. The transformation is effected by boiling an alcoholic solution of the hydroxy-aldehyde with a few drops of sulphuric acid; ethylbenzoin and possibly benzophenone are obtained as by-products. Isomerisation cannot be effected in pyridine even in the presence of mineral acid. Oxidation of diphenylglycollaldehyde by copper sulphate in the presence of potassium hydroxide affords considerable amounts of benzil, reaction occurring also in this direction when the alcoholic solution of the aldehyde is heated with mercuric chloride.

Hydrobenzoin is obtained in 70% yield by reduction of an alcoholic solution of benzaldehyde by zinc and hydrochloric acid under definite conditions; the glycol is transformed into diphenylacetaldehyde, b. p. 157·5°/7 mm., when heated with crystalline oxalic acid. Cautious bromination of the aldehyde dissolved in carbon disulphide affords the non-crystalline *bromodiphenylacetaldehyde*, converted by freshly-precipitated barium carbonate at 100° into *diphenylglycollaldehyde*, which appears to exist in a liquid form and a solid variety, m. p. (indef.) 162° (also $+C_6H_6$). The relationship of the two forms is not definitely established. Either variety is readily converted into *diphenylglycollaldoxime*, m. p. 124°, which is unimolecular in boiling benzene and *diphenylglycollaldehydesemicarbazone*, m. p. 243° (decomp.). Reduction of the aldehyde by magnesium *tert.*-butyl chloride affords *as*-diphenylethylene glycol, m. p. 122°. Oxidation with silver oxide converts it into benzophenone, whereas with permanganate in pyridine it yields benzilic acid. H. WREN.

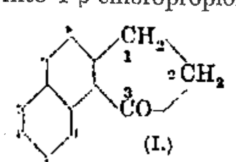
Constitution of the monomethyl ether of phloroglucylaldehyde. P. Karrer and A. Helfenstein (Helv. Chim. Acta, 1927, **10**, 789—794; cf. A., 1927, 564).—*p*-Toluenesulphonylation of phloroglucylaldehyde monomethyl ether (2 : 4-dihydroxy-6-methoxybenzaldehyde), m. p. 203° (Herzig and Wenzel, A., 1904, i, 251; 4-*benzoyl* derivative, m. p. 85°; *dibenzoyl* derivative, m. p. 131°), yields 2-*hydroxy*-4-p-*toluenesulphonyloxy*-6-*methoxybenzaldehyde*, m. p. 104°. Methylation of this compound yields 4-p-*toluenesulphonyloxy*-2 : 6-*dimethoxybenzaldehyde*, m. p. 137° after sintering at 118°, which is hydrolysed by alcoholic sodium hydroxide to 4-4-*hydroxy*-2 : 6-*dimethoxybenzaldehyde*, m. p. 224° after previous sintering. 6-p-*Toluenesulphonyloxy*-2 : 4-*dimethoxybenzaldehyde* has m. p. 144°. The dihydroxymethoxybenzaldehyde of m. p. 139° (A., 1927, 564) is 2 : 6-dihydroxy-4-methoxybenzaldehyde.

H. Burton.

Derivatives in the *cyclo*-octane series. M. Godchot and (Mlle.) Cauquil (Compt. rend., 1927, **185**, 1202—1203).—*cyclo*-Octanone when oxidised by chromic acid forms suberic acid. In ethereal solution the ketone is reduced by sodium in presence of a saturated solution of sodium hydrogen carbonate, yielding cyclo-*octanol*, m. p. 14—15°, b. p. 106—108°/22 mm., d^{17} 0·9663, n_D^{17} 1·4844 (*phenylurethane*, m. p. 62°), and a little "*azelaylpinacone*," $C_{16}H_{30}O_2$, m. p. 84—85°. By the dehydration of *cyclo*-octanol with boiling phthalic anhydride, *cyclo*-octene and a small quantity of a polymeride, $(C_8H_{14})_n$, are obtained. Magnesium methyl bromide reacts with *cyclo*-octanone, but the tertiary alcohol thus formed loses 1 mol. of water during distillation, giving Δ^1-*methyl*cyclo-*octene*, b. p. 158—160°, d^{15} 0·8515, n_D^{15} 1·4673 (*nitrosochloride*, m. p. 107—108°).

B. W. Anderson.

Synthesis of α-indanones. F. Mayer and P. Müller (Ber., 1927, **60**, [*B*], 2278—2283; cf. van Zütphen, Diss., Frankfurt, 1923).—1-Methylnaphthalene is converted by β-chloropropionyl chloride into 4-β-chloropropionyl-1-methylnaphthalene, transformed by concentrated sulphuric acid into 8-methyl-2-naphthindan-3-one (I). 1-Methylnaphthalene can be replaced by naphthalene or its 1-chloro-, 1-bromo-, or 2 : 6-dimethyl derivatives and β-chloropropionyl chloride by β-chloro-*n*-butyryl chloride.



Ring closure could not be effected with the ketones from 1-methoxynaphthalene, acenaphthene, or tetrahydronaphthalene or from 4-chloroacetyl-1-methylnaphthalene. The presence of two substituents in the nucleus appears necessary for ring closure of benzenoid ketones prepared with β-chloropropionyl chloride, whereas those derived from β-chloro-*n*-butyryl chloride give unsaturated compounds in place of the expected indanones. The course of the change therefore consists in initial loss of hydrogen chloride exclusively in the side-chain followed by transformation of the unsaturated ketone into the indanone. This view is supported by the direct production of indanones from crotonyl chloride and hydrocarbons and the inability of α-ketones from chloroacetyl chloride and naphthalene derivatives to pass into acenaphthenones. The following ketones are derived from naphthalene: 1-β-*chloropropionyl*- (whence 1-*phenyl*-3-α-*naphthylpyrazoline*, m. p. 167—168°); 1-β-*chloro*-n-*butyryl*-; 4-β-*chloropropionyl*-1-*methyl*-, m. p. 60°; 4-β-*chloro*-n-*butyryl*-1-*methyl*-, m. p. 48—49°; 4-*chloro*-1-β-*chloropropionyl*-, m. p. 47°; 4-*chloro*-1-β-*chloro*-n-*butyryl*-, 4-*bromo*-1-β-*chloropropionyl*-, m. p. 63°; 4-*bromo*-1-β-*chloro*-n-*butyryl*-; 1 : 6-dimethyl-4-β-chloropropionyl-, m. p. 58°; 4-*methoxy*-1-β-*chloropropionyl*-, m. p. 77—78°; 4-*chloroacetyl*-1-*methylnaphthalene*, b. p. 182—184°/15 mm. p-β-*Chloropropionyldiphenyl*, m. p. 120°, o-β-*chloropropionyldiphenylene oxide*, m. p. 158°, 5-β-chloropropionylacenaphthene, m. p. 81°, β-*bromo*-p-*methylpropiophenone*, m. p. 90°, 6-*chloro*-3-β-*chloropropionyltoluene*, m. p. 46°, 5-*chloro*-2-β-*chloropropionyltoluene*, o-*chloro*-2-β-*chloro*-n-*butyryltoluene*, 4-*chloro*-3-β-*chloropropionyltoluene* (1-*phenyl*-3 : 2'-*chloro*-m-*tolylpyrazoline*, m. p. 123°), 2-β-*chloropropionyl*-p-*xylene* (1-phenyl-3-p-xylylpyrazoline, m. p. 117°), and 2-β-*chloro*-n-*butyryl*-p-*xylene* are described. The following unsaturated ketones are derived from naphthalene: 4-*crotonyl*-1-*methyl*-, b. p. 205—206°/14 mm. (*dibromide*, m. p. 109°); 4-*acrylyl*-1-*methyl*-, b. p. 180—190°/14 mm. (*dibromide*, m. p. 89°); 4-*chloro*-1-*acrylyl*-, b. p. 180—192°/12 mm., (*dibromide*, m. p. 89°); 4-*chloro*-1-*crotonyl*-, b. p. 105—206° (*sic*)/14 mm. (*dibromide*, m. p. 135°); 4-*bromo*-1-*acrylyl*-, b. p. 210—215°/15 mm. (*dibromide*, m. p. 106°); 4-*bromo*-1-*crotonyl*-, b. p. 210—212°/14 mm. (dibromide, m. p. 137°); 1-*crotonylnaphthalene*, b. p. 194—196°/14 mm. (dibromide, m. p. 99°). 5-*Chloro*-2-*crotonyltoluene*, b. p. 151—153°/22 mm. and 2-*crotonyl*-p-*xylene*, b. p. 152—153°/22 mm., have been prepared. The following α-naphthindan-3-ones are described: 1 : 8-*dimethyl*-, m. p. 70°; 8-*methyl*-, m. p. 133°; 8-*chloro*-, m. p. 143°; 8-*chloro*-1-*methyl*-, m. p. 81°; 8-*bromo*-, m. p. 138°; 8-*bromo*-1-*methyl*-, m. p. 94°; 1-*methyl*-, m. p. 99°; 5 : 8-*dimethyl*-, m. p. 91°; the parent *substance* has m. p. 103°. The following indan-3-ones have been prepared: 6-*chloro*-5(7)-*methyl*-, b. p. 188—190°/14 mm.; 6-*chloro*-4-*methyl*-, m. p. 71°; 4-*chloro*-7-*methyl*-, m. p. 128°; 4 : 7-*dimethyl*-, m. p. 78°.

H. Wren.

Distyryl ketone and triphenylmethane. XIII. Coloured compounds of unsaturated ketones with acids. F. Strauss [with W. Heyn] (Annalen, 1927, **458**, 256—310).—Further evidence in favour of analogous general formulæ of the types (I)

[CR′R″·OMe]Cl,$HgCl_2$ and (II) [CR′R″·OH]Cl,$HgCl_2$ for the complex salts of the methochlorides and hydrochlorides, respectively, of unsaturated ketones is furnished (*a*) by the preparation from distyryl ketones of compounds of type (I) which closely resemble the corresponding compounds of type (II), and (*b*) by the conversion of (II) into (I) by methylation. *pp′*-Dimethoxycinnamylideneacetophenone [(*c*) cf. A., 1925, i, 1430], prepared from *p*-methoxycinnamaldehyde and *p*-methoxyacetophenone, yields a *dihydrochloride* and *mercurichloride* (type II), m. p. 144—146° (decomp.), which resemble the *hydrochloride*, decomp. 64—70°, and *mercurichloride* (type I), m. p. 138—142° (decomp.), of its methochloride.

γ-Chloro-α-methoxy-αε-di-*p*-anisyl-$\Delta^{\beta\delta}$-pentadiene (III), m. p. 86—88° (cf. A., 1910, i, 563), is converted by hydrogen chloride into αγ-dichloro-αε-dianisyl-$\Delta^{\beta\delta}$-pentadiene, but in presence of methyl alcohol it gives the methochloride (IV) of *pp'*-dimethoxydistyryl ketone (γ-chloro-γ-methoxy-αε-di-*p*-anisyl-$\Delta^{\alpha\delta}$-pentadiene). This cannot be isolated, but its *hydrochloride*, decomp. 75—80°, and *mercurichloride* (I), decomp. 175—178°, closely resemble the dihydrochloride and *mercurichloride* (II), decomp. 177—178°, of *pp'*-dimethoxydistyryl ketone. The transformation (III)⟶(IV), which takes place less readily in the distyryl than in the phenyl styryl ketones (*c*), must therefore consist in the migration of a methoxyl group. It is shown that hydrogen chloride probably combines with this group, forming an active polar molecule, which then yields mainly one or the other of the above products according to the conditions. The ketone methochloride is an intermediate product in the conversion of the abnormal ketone chlorides into the ketones in methyl alcohol. This reaction (A., 1906, i, 859) does not take place in anhydrous methyl alcohol; instead, αγ-dichloro-αε-diphenyl-$\Delta^{\beta\delta}$-pentadiene yields mainly a bimolecular chlorine-free *substance* of high m. p., which is also formed directly from the ketone and methyl-alcoholic hydrogen chloride. The coloured by-product obtained in the decomposition of γγ-chloromethoxy-αγ-dianisylpropylene (*c*) is 2 : 4 : 6-trianisylpyrylium chloride. The methochloride (IV) is converted by sodium methoxide into the dimethylacetal of *pp'*-dimethoxydistyryl ketone (*γγ-dimethoxy-αε-dianisyl-$\Delta^{\alpha\delta}$-pentadiene*), b. p. 222—224°/0·2—0·4 mm. (decomp.). When the abnormal ketonic chloride of distyryl ketone is warmed in ether with methyl alcohol and mercuric chloride it gives first γ-chloro-α-methoxy-αε-diphenyl-$\Delta^{\beta\delta}$-pentadiene (*c*), and then the *mercurichloride* (I), m. p. 134—136°, of distyryl ketone methochloride (*hydrochloride*). This last is converted by sodium methoxide into *γγ-dimethoxy-αε-diphenyl-$\Delta^{\alpha\delta}$-pentadiene*, m. p. 56—57°, b. p. 178—179°/0·4 mm., identified by hydrogenation to γγ-dimethoxy-αε-diphenylpentane. The complex salts of cinnamylideneacetophenone (*mercurichloride*) and of its methochloride (*hydrochloride*) are very soluble and much less stable than those of the isomeric distyryl ketone derivatives. Such weakly basic ketones tend to form complex salts with more than 1 mol. of mercuric chloride.

The above ketone methochloride derivatives are more simply prepared by treating a suitable complex salt (*e.g.*, the dihydrochloride of *pp'*-dimethoxydistyryl ketone and the ferrichloride of distyryl ketone or cinnamylideneacetophenone) of the ketone in ether with 5—8 mols. of anhydrous methyl alcohol. The isolation of the complex salt is not necessary and the product may be directly converted into the ketone dimethylacetal. The yield of the latter depends on the solubility of the intermediate methochloride complex and on the degree to which it is hydrolysed by the water formed in the reaction. Since the ketones do not appear to unite directly with methyl halides the reversible formation from the highly coloured ketone methochlorides and their complex salts of nearly or quite colourless ethereal solutions indicates that they are in equilibrium with non-ionised ψ-forms, CR'R''Cl·OMe.

Comparison of the absorption spectrum of the halochromic solution of distyryl or phenyl styryl ketone in 100% sulphuric acid with that of an equivalent solution of the corresponding abnormal ketochloride indicates that, contrary to the statement of Hantzsch (*loc. cit.*), the two solutions cannot contain the same complex salt. Further, the ketochlorides are rapidly changed under these conditions into water-soluble products, whilst the ketones are quantitatively regenerated from their solutions by water even when the sulphuric acid contains hydrogen chloride. By analogy with the ketone methochlorides it is suggested that the carbonium atom in the complex salts derived from the ketochlorides is that to which the methoxyl group becomes attached on methoxylation, *i.e.*, the α-carbon atom, and salts from the abnormal chloride of distyryl ketone are formulated,

[CHPh:CH·CCl:CH·CHPh]X. Wizinger's classification of chlorine as a negative auxochrome (A., 1927, 764) is not in accordance with results obtained with abnormal ketochlorides and triphenylmethyl chloride derivatives (cf. A., 1922, i, 148). H. E. F. NOTTON.

Substitution products of 4-hydroxybenzophenone and its methyl ether. W. BLAKEY, W. I. JONES, and H. A. SCARBOROUGH (J.C.S., 1927, 2865—2872).—Halogeno- and nitro-substituents enter first the positions adjacent to the hydroxyl group of 4-hydroxybenzophenone and further substitution takes place in the opposite nucleus. Conversion of the hydroxyl group into methoxyl lessens its directive power and generally only one of the adjacent positions is substituted, the second substituent entering the opposite nucleus and the third the nucleus containing the methoxyl group. 3-*Chloro-4-methoxybenzophenone*, m. p. 98°, obtained by chlorination of the methoxy-compound in glacial acetic acid, yields on further chlorination 3 : 5-*dichloro-4-methoxybenzophenone*, m. p. 74° (also prepared by chlorination of the methoxy-compound in acetic acid containing sodium acetate). The latter gives an *α-oxime*, m. p. 146°, which is transformed into 3 : 5-*dichloro-4-methoxybenzanilide*, m. p. 154°. 3 : 5-*Dichloroanisic acid*, m. p. 202°, may be obtained by hydrolysis of the anilide or by direct chlorination of the acid. 3 : 5-*Dichloro-4-hydroxybenzophenone*, m. p. 148°, is obtained by hydrolysis of the methoxy-compound or by chlorination of 4-hydroxybenzophenone. 3-*Bromo-4-methoxybenzophenone*, m. p. 94°, gives an *α-oxime*, m. p. 164°, which is transformed into 3-*bromo-4-methoxybenzanilide*, m. p. 170°, and a *β-oxime*, m. p. 111·5°, which is transformed into *benz-3-bromo-4-methoxyanilide*, m. p. 156°. 3-*Chloro-5-bromo-4-methoxybenzophenone*, m. p. 92°, is obtained by chlorination of the corresponding bromo-compound. 3-*Iodo-4-methoxybenzophenone*, m. p. 81°, prepared by the action of an acetic acid solution of iodine monochloride on the hydroxy-compound, yields an *α-oxime*, m. p. 182°, giving 3-*iodo-4-methoxybenzanilide*, m. p. 206°. The *β-oxime*, m. p. 135°, is transformed into *benz-3-iodo-4-methoxyanilide*, m. p. 164°. 3-*Iodo-4-hydroxybenzophenone*, m. p. 184°, is obtained by hydrolysis of the corresponding methoxy-compound

or by iodination of the hydroxy-compound with a 5% solution of iodine in potassium iodide. 3 : 5-*Di-iodo-4-hydroxybenzophenone*, m. p. 145°, is obtained by iodination of the hydroxy-compound with an acetic acid solution of iodine monochloride containing sodium acetate. 3-*Nitro-4-methoxybenzophenone*, m. p. 105°, prepared by the action of an excess of nitric acid (*d* 1·5), yields an *α-oxime*, m. p. 179°, giving 3-*nitro-4-methoxybenzanilide*, m. p. 163°. 3 : 5-*Dinitro-4-methoxybenzophenone*, m. p. 105°, is obtained by the action of a methyl-alcoholic solution of sodium methoxide on 4-chloro-3 : 5-dinitrobenzophenone (Ullmann, A., 1909, i, 473). Nitration of 4-hydroxybenzophenone with an excess of nitric acid (*d* 1·4) gives 3 : 5-*dinitro-4-hydroxybenzophenone*, m. p. 138° (cf. Ullmann, *loc. cit.*), together with unidentified substances. 3′-*Nitro-4-methoxybenzophenone*, m. p. 95°, is prepared by the interaction of *m*-nitrobenzoyl chloride, anisole, and aluminium chloride in carbon disulphide. 3 : 3′-*Dinitro-4-methoxybenzophenone*, m. p. 143° (*hydroxy*-compound, m. p. 165°), is prepared by the action of a solution of nitric acid (*d* 1·5) in glacial acetic and sulphuric acids at —10°; some 2′(?) : 3-*dinitro-4-methoxybenzophenone*, m. p. 125°, is concurrently formed. Nitration of 4′-nitro-4-methoxybenzophenone with nitric acid (*d* 1·5) alone yields 3 : 4′-*dinitro-4-methoxybenzophenone*, m. p. 174°. Nitration of 4-methoxybenzophenone yields 3 : 3′ : 5-*trinitro-4-methoxybenzophenone*, m. p. 184°, which is also obtained by nitration of the 3 : 3′- or the 3 : 5-dinitro-compounds. The structure follows from the fact that it gives some *m*-nitrobenzoic acid on oxidation and that no isomerides are formed in the second method of preparation. 2′(?) : 3 : 5-*Trinitro-4-methoxybenzophenone*, m. p. 142°, was separated from the nitration products of 4-methoxybenzophenone and of 3 : 5-dinitro-4-methoxybenzophenone.

G. A. C. Gough.

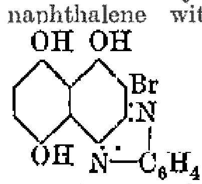
Organic compounds of sulphur. VIII. Action of Mg+MgI$_2$ on aromatic thioketones. A. Schonberg and O. Schutz [with W. Marschner] (Ber., 1927, 60, [*B*], 2351—2353).—4 : 4′-Dimethoxythiobenzophenone is converted by magnesium subiodide into tetra-amylethylene sulphide (cf. A., 1927, 667) and tetra-anisylethylene. In reactions of this type it is probable that additive compounds [MgI·S·CAr$_2$]$_2$ are intermediately produced and that they are also formed when thioketones react with Grignard reagents.

H. Wren.

Parachor and chemical constitution. VI. Cases of supposed ring–chain tautomerism. F. B. Garner and S. Sugden (J.C.S., 1927, 2877—2883).—Determinations of the parachor have been made to obtain evidence as to the structure of quinones, dibasic acid chlorides, and diketones. The parachors of quinones and diketones show that little or none of the peroxide form exists in them, whilst the parachors of the symmetrical and the unsymmetrical forms of phthalyl chloride are in agreement with the deductions made from purely chemical evidence. The following determinations are made: *p*-benzoquinone, 236·8 (calc. for the diketone, 236·1; for peroxide, 219·0); toluquinone, 272·0 (calc. for diketone, 275·1; for peroxide, 258·0); phthalyl chloride, m. p. 13°, 373·9; m. p. 88·5°, 367·8 (calc. for the *s*-form, 377·5; for the *as*-, 362·8); succinyl chloride, m. p. 18·5° (corr.), 282·6 (calc. for *s*-form, 282·6; for *as*-, 267·9); benzil, 480·8 (calc. for diketone, 476·0; for peroxide, 464·4); 2 : 2′-dimethoxybenzil, 596·8 (calc., for the diketone, 594·0; for the peroxide, 582·4). The high value for the parachor of the phthalyl chloride of m. p. 88·5° is probably due to partial conversion into the lower-melting form at the temperature at which the density determinations were made.

G. A. C. Gough.

Hydroxynaphthaquinone. VII. Bromination of naphthazarin. A. S. Wheeler and B. G. Carson (J. Amer. Chem. Soc., 1927, 49, 2825—2829; cf. A., 1923, i, 1020).—Bromination of naphthazarin (5 : 8-dihydroxy-1 : 4-naphthaquinone; cf. Dimroth and Ruck, A., 1926, 297) in boiling glacial acetic acid affords 2 : 3 : 6 : 7-*tetrabromonaphthazarin*, bronze-coloured, m. p. 300° (*diacetate*, yellow, m. p. 262°), which when boiled with alcoholic aniline yields a *dibromodianilinonaphthazarin*, bronze-coloured, m. p. 251°. Prolonged treatment of naphthazarin with bromine in acetic acid at the ordinary temperature affords 2 : 3 : 6 : 7-*tetrabromo*-1 : 4 : 5 : 8-*naphthadiquinone*, yellow, subliming at 275—280°, which is converted, as above, into a *dibromodianilino*-derivative, brown, subliming at 220—225°. 2 : 3-Naphthazarin dichloride (cf. Zincke and Schmidt, A., 1895, i, 613) is obtained by treating 1 : 4 : 5 : 8-tetrahydroxynaphthalene with chlorine in chloroform. 2 : 3-Dibromonaphthazarin, obtained by treating naphthazarin in glacial acetic acid with 1·5 mols. of bromine (cf. Wheeler and Edwards, A., 1918, i, 75), condenses with *o*-phenylenediamine in alcohol, with formation of a purplish-blue *compound*, decomp. about 225°, presumably of the annexed formula.



F. G. Willson.

Anthraquinonylisatogen and other condensation products of anthraquinone-2-aldehyde. P. Ruggli and A. Disler (Helv. Chim. Acta, 1927, 10, 938—947; cf. A., 1921, i, 811; 1925, i, 561).—Anthraquinone-2-aldehyde condenses with 2 : 4-dinitrotoluene in nitrobenzene–piperidine solution to form β-(2 : 4-*dinitrophenyl*)-α-(2-*anthraquinonyl*)-*ethylene*, m. p. 281° (*dichloride*, m. p. 250°; *dibromide*, m. p. 252°). The dibromide when treated with pyridine or alcoholic potassium hydroxide regenerates the stilbene derivative, whilst the dichloride is converted by pyridine into α-*chloro*-β-(2 : 4-*dinitrophenyl*)-α-(2-*anthraquinonyl*)*ethylene*, (I), m. p. 218°. Treatment of this last substance with pyridine–alcoholic potassium hydroxide furnishes β-(2 : 4-*dinitrophenyl*)-α-(2-*anthraquinonyl*)*acetylene* (II) (10—15% yield), m. p. 272—273° (*dichloride*, m. p. 246°; *dibromide*, m. p. 238°). When a solution of (I) or (II) in pyridine is exposed to sunlight there is produced 6-*nitro*-2-(2-*anthraquinonyl*)*isatogen*,

$NO_2\cdot C_6H_3<\substack{CO\\NO}>C\cdot C_6H_3<\substack{CO\\CO}>C_6H_4$, m. p. 282°,

converted by phenylhydrazine into 6-*nitro*-2-(2-*anthraquinonyl*)*indoxyl*,

$NO_2\cdot C_6H_3<\substack{C(OH)\\NH}>C\cdot C_{14}H_7O_2$, m. p. 328—334°

(*acetyl* derivative, m. p. 295° with previous decomp.).

Anthraquinone-2-aldehyde (1-*phenyl*-3-*methylpyrazolone* derivative, m. p. 243°; α-*ketodihydrothionaphthen* derivative, m. p. 334—336°) condenses with ethyl malonate, ethyl acetoacetate, benzoylacetone, α-picoline, and 2-methylquinoline, in presence of piperidine, to give the following derivatives of α-(2-anthraquinonyl)ethylene: ββ-*dicarbethoxy*-, m. p. 223°; β-*acetyl*-β-*carbethoxy*-, m. p. 180°; β-*benzoyl*-β-*acetyl*-, m. p. 243°; β-α-*pyridyl*-, m. p. 175°, and β-α-*quinolyl*-, m. p. 174°, respectively.

H. BURTON.

Anthraquinone derivatives (diurethano-1 : 1′-dianthraquinonyls). W. SMITH, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1927, 902.

Manufacture of dibenzanthronyls. I. G. FARBENIND. A.-G.—See B., 1927, 903.

Saponins and related substances. XVIII. Sugar-beet sapogenin. XIX. Identity of beet saponin with oleanol, the phytosterol-like substance from olive leaves, and with caryophyllin from cloves. A. W. VAN DER HAAR (Rec. trav. chim., 1927, **46**, 775—792, 793—798).—XVIII. By the addition of ether and light petroleum to an alcoholic solution of the alkali-soluble portion of the scum obtained when beet-sugar liquors are treated with lime, a saponin (*A*), blackening at 214—216°, is obtained. From the mother-liquors two other fractions are obtained: *B*, m. p. 214—216°, and *C*, m. p. 206°. Saponin *B*, on hydrolysis with dilute sulphuric acid, affords a sapogenin, m. p. 307°, together with pentoses and methylpentoses. Saponin *C* similarly gives pentoses, small amounts of methylpentoses, and the same sapogenin. This sapogenin, which was also obtained directly from beet (yield 0·0025%), was prepared in quantity from the scum by Kobert's method. It is concluded that the formula is actually $C_{31}H_{50}O_3$ (see also below) and not $C_{22}H_{36}O_2$ (Andrlík and Votoček, A., 1899, i, 157). The sapogenin gives Liebermann's cholesterol reaction and Kahlenberg's reaction with a chloroform solution of antimony pentachloride. The *potassium* salt, $OH{\cdot}C_{30}H_{48}{\cdot}CO_2K$, the *methyl* ester, m. p. 199—200° (*acetyl* derivative, m. p. 223°), and the *diphenylcarbamide*, m. p. 137—138°, are described. Acetic anhydride converts the sapogenin into *diacetylsapogenin anhydride*, m. p. 315°. When crystallising with a molecule of acetic anhydride it has m. p. 215° (solidifying and re-melting at 315°) and is evidently identical with diacetyloleanol (Power and Tutin, J.C.S., 1908, **93**, 897) and with diacetylcaryophyllin (Dodge, A., 1919, i, 91). *Monoacetylsapogenin*, m. p. 260° (corresponding with analogous derivatives obtained by the above authors), is prepared by the action of ethyl or methyl alcohol on the diacetyl anhydride.

XIX. The identity of these substances and their corresponding derivatives is deduced from a comparison of their recorded physical and chemical properties. Caryophyllin has +79·7° in chloroform (Dodge gives +54·5°) and yields a *methyl* ester, m. p. 198°. The following derivatives are compared and found to possess similar properties: methyl esters, acetyl derivatives of the methyl esters, diacetyl anhydrides, monoacetyl derivatives, and diphenylcarbamides. A table giving the colours obtained by Kahlenberg's reagent with various sterols and sapogenin derivatives is also included.

G. A. C. GOUGH.

Chemical nature of glycyrrhizin. M. GALASSI (Arch. Farm. sperim., 1927, **26**, 231—240).—In the pure crystalline form, neither glycyrrhizin nor glycyrrhizic acid reduces Fehling's solution, and the acid contains no nitrogen. Hydrolysis of the acid yields, not glycuronic acid, as stated by Tschirch and Gauchmann (A., 1908, i, 898), but gluconic acid (2 mols.) and glycyrrhetic acid (1 mol.), so that glycyrrhizic acid is a gluconic ester of glycyrrhetic acid.

T. H. POPE.

Action of cold concentrated sulphuric acid on pernitrosoketocineole. A. D'AMBROSIO (Gazzetta, 1927, **57**, 717—726).—When pernitrosoketocineole is treated with cold concentrated sulphuric acid under the conditions employed for the conversion of pernitrosocamphor into *iso*pinolone, nitrous oxide is evolved and 1-*acetyl*-3-iso*propylidene*-Δ^1-cyclo*pentene* (I), m. p. 90—91°, d^{27} 1·0857, n_D^{27} 1·59329, is obtained. The ketone forms an *oxime*, m. p. 167°, and a *semicarbazone*, m. p. 240° (decomp.); on catalytic hydrogenation, six atoms of hydrogen are taken up simultaneously (indicating the presence of a conjugated system) to give 1-β-*ethanol*-3-iso*propyl*cyclo*pentane*, b. p. 214—215°, which with alkaline potassium permanganate gives inactive dihydropinolone (1-acetyl-3-*iso*propyl*cyclo*pentane) (*semicarbazone*, m. p. 158°). The ketone (I) is oxidised by hydrogen peroxide to acetone and succinic acid. It is considered that in the formation of the ketone, water is added first to the pernitroso-group, then to the ether linking; ring closure then giving the compound

$$HO{\cdot}CMe_2{\cdot}CH\begin{array}{l} \diagup CH_2{\cdot}CH{\cdot}CMe{\cdot}OH \\ \diagdown CH_2{\cdot}C{-}N_2O_2H \end{array}$$

, there would be obtained on loss of nitrous oxide and opening of the *cyclo*propane ring the trihydrated form of the ketone (I).

E. W. WIGNALL.

Action of diazonium salts on α-terpineolhydroxylamineoxime. A. D'AMBROSIO (Gazzetta, 1927, **57**, 726—731).—α-Terpineolhydroxylamineoxime, prepared by the method of Cusmano (A., 1912, i, 272), reacts with benzenediazonium chloride to give a *benzeneazo*-compound, m. p. 199—200°, in which the ·NH·OH group has been replaced by ·N(OH)·N:NPh. The product forms a *copper* salt, m. p. 163°, and is decomposed by hydrochloric acid with evolution of nitrogen. Of the toluenediazonium chlorides, the *ortho*-compound gives an unstable product, the *meta*- does not react, and the *para*- gives a p-*tolueneazo*-compound, m. p. 71° (*copper* salt, m. p. 135°); the p-*phenetoleazo*-compound, m. p. 160°, forms a *copper* salt, m. p. 163°. The benzeneazo-compound is reduced to a *hydrazo*-compound, m. p. 201° (decomp.) (*copper* salt, m. p. 151° decomp.).

E. W. WIGNALL.

Catalytic dehydrogenation of hydroaromatic compounds. W. TREIBS and H. SCHMIDT (Ber., 1927, **60**, [*B*], 2335—2341).—Hydroaromatic hydroxy-

and keto-compounds can be dehydrogenated in the presence of a copper or nickel catalyst at temperatures (about 200°) below the b. p. of the liquids. Since the catalysts possess hydrogenating powers at this temperature the products are mixed with varying amounts of hydrogenated substances, the proportion of which can be diminished by dilution or removal of hydrogen by admixture with an indifferent gas. Dehydrogenation occurs more readily with unsaturated than with saturated compounds. The nickel catalyst is prepared by passing hydrogen over a mixture of pumice with nickel formate or freshly-precipitated nickel carbonate at 200—280° until water ceases to be formed; the copper catalyst is obtained by precipitating copper acetate with an excess of hot, concentrated sodium hydroxide and reducing the washed copper hydroxide deposited on copper gauze, pumice, or asbestos by hydrogen at 280°. The vapours of the substance are passed over the catalyst heated in glass tubes in a Heraeus furnace or, in some cases, the liquid is simply heated at its b. p. with the catalyst. The following examples are cited: piperitone and pulegone to thymol and menthone at 200°, whereas menthone and thujone are almost unaffected at this temperature; menthol and *neo*menthol at 280° mainly to menthone and thymol, the proportion of ketone increasing with decreasing temperature; fenchyl alcohol exclusively to fenchone; sabinol to thujone; pinocarveol to pinocamphone; carveol and dihydrocarveol to tetrahydrocarvone and carvacrol; *iso*pulegol to menthone and thymol; geraniol to citronellal; citronellol to citronellal; limonene and phellandrene to cymene and menthane; pinene to cymene and pinane.

H. WREN.

Hydration of nopinene. IV. Comparison of terpene alcohols obtained by hydration of nopinene and pinene. G. AUSTERWEIL (Bull. Soc. chim., 1927, [iv], 41, 1507—1511; cf. A., 1927, 60).—Pure nopinene is converted by 2 mols. of benzoic acid at 138—143° into a mixture of 16·2% of *iso*borneol and 83·8% of borneol. Under similar conditions pure *l*-pinene affords practically pure borneol. With salicylic acid similar results are obtained, but in each case the rotatory power of the terpene alcohol is lower than with the stronger benzoic acid. From these results it is inferred that nopinene is the source of camphene found in a specimen of turpentine or in the products of the action of an organic acid on the pinene fraction of a terpene. R. BRIGHTMAN.

Formation of camphene from pinene hydrochloride [bornyl chloride]. T. IKEDA (Sci. Papers Inst. Phys. Chem Res. Tokyo, 1927, 7, 62—73).—The formation of camphene when bornyl chloride vapour is passed over heated metallic oxides has been investigated. Of the oxides examined, lead oxide and barium oxide gave the best yield, the optimum temperatures being 250° and 300°, respectively. The oxides of zinc, magnesium, calcium, iron, and manganese gave relatively poor yields, other terpenes and polyterpenes also being formed. Ferric and zinc chlorides apparently effect the removal of hydrogen chloride catalytically, with production of a mixture of hydrocarbons. R. CUTHILL.

Dehydration of borneol. T. IKEDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 47—61).—By heating borneol with zinc chloride, an *ether*, $(C_{10}H_{17})_2O$, m. p. 43—44°, b. p. 317°/753 mm., was obtained. When an excess of zinc chloride was used, and the time of heating prolonged, a mixture of hydrocarbons was formed, the principal product being a *diterpene*, $C_{20}H_{32}$, b. p. 168—169°/10 mm., of uncertain structure. On reduction, this substance yielded a mixture of $C_{20}H_{51}$ hydrocarbons, one having m. p. 80—84°. A hydrocarbon $C_{20}H_{54}$, m. p. 88—89°, was also obtained by the action of magnesium on bornyl chloride in ethereal solution.

R. CUTHILL.

6-Methylbornylene. L. J. BRIUSOVA (J. Russ. Phys. Chem. Soc., 1927, 59, 653—657).—The dehydration of 6-methylborneol and the behaviour of the product towards perbenzoic acid were investigated. Unlike other dicyclic alcohols, 6-methylborneol gives on dehydration only one hydrocarbon, viz., 6-*methylbornylene*, m. p. 118·5—119°, oxidised by potassium permanganate to 6-methylcamphoric acid, and completely oxidised by perbenzoic acid.

M. ZVEGINTZOV.

Action of hydrogen iodide on nitroso-compounds. J. C. EARL and J. KENNER (J.C.S., 1927, 2139—2145).—The action of hydrogen iodide on a variety of nitroso-compounds takes place with elimination of iodine and reduction of the nitroso- to the corresponding hydroxylamino-derivative (cf. Thiele, A., 1894, i, 217; Baeyer, A., 1894, i, 252). Baeyer's conclusion that the nitrosochloride of tetramethylethylene reacts in a different way with hydrogen bromide in acetic acid is shown to be incorrect, although the hydroxylamino-derivative first formed loses the elements of hydrogen chloride when liberated in the presence of alkali, and the product isolated is β-*hydroxylamino*-βγ-*dimethyl*-Δ^{γ}-*butene hydrochloride*, which reduces Fehling's solution in the cold and with salicylaldehyde yields the *substance* $CH_2{:}CMe{\cdot}CMe_2{\cdot}\underset{\diagdown O \diagup}{N{-}CH}{\cdot}C_6H_4{\cdot}OH$, m p 53°. In the reactions between hydrogen iodide and the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate, the amount of iodine liberated corresponds approximately with the decrease of halogen ion present; hence in these instances the nitroso-group does not induce sufficient positive polarity in the chlorine atom to render it liable to displacement by hydrogen in the presence of hydrogen iodide. With *m*- and *p*-chloronitrosobenzene and hydrogen iodide reduction is immediately followed by the condensation of the hydroxylamino- with the nitroso-derivative, and, in presence of red phosphorus to remove the iodine as formed, 3 : 3′-dichloroazoxybenzene (m. p. 154°) or 4 : 4′-dichloroazoxybenzene (m. p. 96°) is produced in excellent yield. In neither case is there any evidence of the removal of chlorine by hydrolysis.

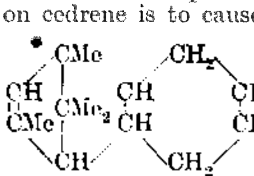
δ-Nitroso-δ-methylpentan-β-one (Harries and Jablonski, A., 1898, i, 400) yields in acetone a colourless solution which reacts but slowly with hydrogen iodide in the cold; on heating, however, the solution develops a blue colour, and on re-cooling is much more reactive. 8-Nitrosomenthone (Harries and Roeder, A., 1900, i, 182), although blue when pre-

pared, tends to polymerise and therefore reacts comparatively slowly, whilst with 4-nitrosomenthone (Baeyer, A., 1895, i, 549), which is known to be a bis-compound, iodine is slowly liberated when a cold solution in acetone is treated with hydrogen iodide. The primary product of the reaction between nitrous acid itself and hydriodic acid is probably dihydroxyammonia, which reacts further with nitrous acid, forming nitric oxide and water. Ethyl ether reacts slowly with hydrogen iodide at the ordinary temperature. W. J. Powell.

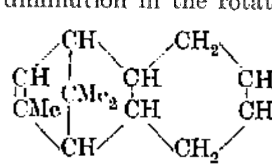
Mono- and sesqui-terpenes. [Caryophyllene, cedrene, and cadinene.] E. Deussen [with F. Weiss, P. Hacker, and P. Hille] (J. pr. Chem., 1927, [ii], **117**, 273—304; cf. A., 1926, 1252).—Treatment of caryophyllene dihydrochloride (1 mol.) with magnesium (2 atoms) in ether containing a small amount of ethyl bromide or bromobenzene yields an unsaturated *hydrocarbon*, $C_{15}H_{26}$, b. p. 131°/10 mm., d_4^{15} 0·8965, n_D^{18} 1·496, α −4·97°, R_L 66·9, which with aqueous mercuric acetate at 0°, and subsequent treatment with potassium iodide, furnishes a *compound*, $C_{15}H_{26}HgI{\cdot}OH$, m. p. 131—133°. γ-Caryophyllene condenses with ethyl diazoacetate in presence of copper powder at 165° to form *ethyl* γ-*caryophyllene*-cyclo*propanecarboxylate*, $C_{15}H_{24}{>}CH{\cdot}CO_2Et$, $[\alpha]_D^{18}$ +38·12°, R_L 86·44, which is reduced catalytically to a *dihydro*-derivative, $[\alpha]^{20}$ +13·43° in alcohol. This last compound on hydrolysis followed by oxidation with potassium permanganate yields *as*-dimethylsuccinic acid. By catalytic reduction of γ-caryophyllene there is obtained γ-dihydrocaryophyllene, b. p. 129—130°/14 mm., $[\alpha]_D^{19}$ −32·7° (cf. K. Meyer, Diss., Leipzig, 1912), which does not give a mercuric acetate additive compound. Ozonisation of γ-caryophyllene in chloroform solution yields an *ozonide*, $C_{15}H_{24}O_6$, $[\alpha]_D^{18}$ +23·4° in chloroform, which when decomposed with steam yields a volatile portion containing formaldehyde, formic acid, and a ketone, $C_8H_{14}O$, characterised as its *semicarbazone*, decomp. 207°, and a non-volatile fraction consisting of succinic acid and a ketone, $C_{10}H_{16}O_2$ (*semicarbazone*, decomp. 120°).

Magnesium phenyl bromide reacts with blue β-caryophyllene nitrosite (A., 1915, i, 274) to form a *base*, $C_{15}H_{26}O_2N{\cdot}NH_2$ (*sulphate*, m. p. 117°), also obtained from the nitrosite by treatment with hydrogen sulphide.

Reduction of cedrene with sodium and amyl alcohol gives a *dihydrocedrene*, $C_{15}H_{26}$, b. p. 118—124°/12 mm., d^{20} 0·9041, n_D^{20} 1·48719, α +33·1°, differing in physical constants from other described dihydrocedrenes (cf. Semmler and Mayer, A., 1912, i, 480). The effect of sulphuric acid of varying concentration on cedrene is to cause a diminution in the rotatory



(I.)



(II.)

power. Cedrene is not dehydrogenated smoothly by sulphur at 260°, but oxidation with manganese dioxide and 50% sulphuric acid furnishes acetic acid, together with small quantities of cedreneketonic acid (A., 1907, i, 946) and phthalic acid. Cedrene is probably (I) or (II). The effect of oxygen in presence of various catalysts on the higher-boiling fraction of cedar-wood oil is to cause thickening, owing to the formation of a resin-like substance.

Magnesium reacts with *l*-cadinene dihydrochloride, m. p. 118—118·5° (cf. Deussen, A., 1912, ii, 510), to form a *hydrocarbon*, $C_{15}H_{26}$ (10%), together with a *terpene*, $C_{15}H_{24}$ (90%), which with hydrogen chloride affords about 20% of *l*-cadinene dihydrochloride. H. Burton.

7-Hydroxy-3-phenylcoumarin. W. Baker (J.C.S., 1927, 2898—2899).—Jacobson and Ghosh (A., 1915, i, 832; 1916, i, 281) describe the preparation of a compound, m. p. 131°, from ethyl α-formylphenylacetate and resorcinol, which they claim to be 7-hydroxy-3-phenylchromone. Since such condensations are known to give coumarins (cf. Baker and Robinson, A., 1925, i, 1299; Baker, A., 1926, 74; Bargellini, A., 1925, i, 1299) the original experiments have been repeated. 7-Hydroxy-3-phenylcoumarin, m. p. 207—208°, is always produced and no trace of *iso*flavone can be detected. Ethyl α-formylphenylacetate and phloroglucinol when condensed in the presence of phosphoric anhydride afford the *acetyl* derivative, m. p. 255—256°, of a phenolic *compound*, m. p. 308—310°, which is not identical with 5 : 7-dihydroxy-3-phenylcoumarin. S. Coffey.

Methysticin. W. Lampe, J. Zielinska, and J. Majewska (Rocz. Chem., 1927, 7, 139—149).—The structural formula for methysticin proposed by Pomeranz (Monatsh., 1888, 9, 863) is in reality that of ψ-methysticin, as is shown by the following synthesis. *Methyl* α-*piperoylacetoacetate*, m. p. 166—167°, prepared from piperic acid, is converted into *piperoylacetone*, m. p. 119—120°, by heating with water under pressure, or into *methyl piperoylacetate*, m. p. 132—134°, identical with ψ-methysticin, by boiling with 75% acetic acid.

ψ-Methysticin yields 3 : 4-methylenedioxycinnamylideneacetone on hydrolysis with 10% sulphuric acid; with soduim hydroxide methysticinic acid is produced, from which ψ-methysticin may be prepared by methylation. *Methysticin dibromide*, m. p. 156°, is produced by the action of bromine on methysticin, whilst ψ-methysticin yields a *monobromo*-derivative (*methyl* α-*bromopiperoylacetate*), m. p. 98°. The following compounds are described: α-*bromo*-α-*cinnamoylacetone*, m. p. 91—93°, *ethyl* α-*piperoylacetoacetate*, m. p. 92—94°, and *ethyl piperoylacetate*, m. p. 73—75°. The reactions given by methysticin indicate that it is a condensation product of ψ-methysticin, and is 2-(3′ : 4′-methylenedioxystyryl)-6-methoxy-2 : 3-dihydro-γ-pyrone. R. Truszkowski.

Condensation of pyruvic acid with aromatic amines and aldehydes. S. Weil and S. Auerbachowna (Rocz. Chem., 1927, 7, 357—361).—Ethyl *p*-aminobenzoate, benzaldehyde, and pyruvic acid condense with the production of 4 : 5-*diketo*-2-*phenyl*-1-p-*carbethoxyphenylpyrrolidine*, m. p. 154—155°. Under similar conditions pyruvic acid does not react with methyl 4-amino-2-hydroxybenzoate and piper-

onal, but the *piperonylidene* derivative of the amino-acid, m. p. 174—175°, is formed. *o*-Nitro-*p*-toluidine and *m*-nitroarsanilic acid do not condense with piperonal and pyruvic acid. The presence of nitro- or hydroxy-groups *ortho* to the amino-group appears to inhibit condensation. R. TRUSZKOWSKI.

Catalytic reduction of nitriles. H. RUPE and L. STERN (Helv. Chim. Acta, 1927, **10**, 859—866).—An improved method of obtaining α-camphomethylamine [*oxalate*; *benzoyl* derivative, m. p. 82°; *acetyl* derivative, m. p. 84°, and *dimethylamino*-derivative (*hydrochloride*, m. p. 165° after browning at 150°) described] from α-camphomethylaminomethylene-camphor (A., 1925, i, 275) is described. *α-Camphomethylcarbamide* has m. p. 145°.

Reduction of the two stereoisomeric γ-cyano-βγ-diphenylbutyrophenones (αβ-diphenyl-β-phenacyl-propionitriles), m. p. 109° and 118° (Kohler and Allen, A., 1924, i, 855), under the same conditions (see A., 1923, i, 1199) shows that 75% of the form of higher m. p. is reduced, as is 75% of that of lower m. p. In the latter case, however, the remaining 25% of the nitrile rearranges to the less fusible form. The reduction product is 2 : 4 : 5-*triphenylpiperidine*, m. p. 72° (*hydrochloride*; *phenylthiocarbamide*, m. p. 165°; *nitroso*-derivative, m. p. 153°; *benzoyl* derivative, m. p. 155°). 2 : 4 : 5-*Triphenyl-1-ethylpiperidine* (*picrate*, m. p. 181°) has m. p. 121°, whilst 2 : 4 : 5-*triphenyl-1-methylpiperidine* (*methiodide*) has m. p. 141°. These results indicate that the nitrile of higher m. p. is $\begin{array}{l} Ph\cdot CH\cdot CH_2Bz \\ Ph\cdot CH\cdot CN \end{array}$ and that of lower m. p. $\begin{array}{l} Ph\cdot CH\cdot CH_2Bz \\ CN\cdot CHPh \end{array}$. H. BURTON.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. II. Nitration of 1-benzylpiperidine and some related substances. A. POLLARD and R. ROBINSON (J.C.S., 1927, 2770—2780).—Comparatively simple considerations of electron displacement towards the nitrogen atom to explain substitution in benzylammonium salts (cf. A., 1926, 397, 1132) cannot be extended to benzylpiperidine, which furnishes a higher yield of *m*-nitro-derivative than the closely related open-chain tertiary bases (A., 1926, 946). New determinations, using the bromination method of Francis and Hill (A., 1925, ii, 163), prove that the reaction product contains 72% of *m*-nitrobenzylpiperidine. 1-β-*Phenylethylpiperidine*, b. p. 262—264°/760 mm. (*picrate*, m. p. 144—145°), prepared from magnesium benzyl chloride and 1-*iso*butoxymethylpiperidine, gives 22% of *m*-nitro-derivative under similar conditions, whilst *γ-phenylpropylpiperidine*, b. p. 150°/15 mm. (*picrate*, m. p. 99—100°), affords 6% of the *m*-nitro-derivative.

The proportion of *m*-nitrobenzylpiperidine is reduced by the addition of ammonium nitrate (to 56%), or the more soluble trimethylammonium nitrate (to 16%), or carbamide. The effect caused by the latter is due to Flürscheim's effect (cf. A., 1926, 830) and not to the removal of nitrous acid. This effect is attributed to the progressive electrostriction of the cations by nitrate ions. The proportion of the *m*-isomeride is related to the existence of constitutive factors that hinder or assist the electrostriction of the cations, which will be influenced as follows: The degree of electrostriction should be greater (1) the smaller the number of atoms directly attached to the central charged atom. Thus *benzylmethylpiperidinium nitrate*, from the corresponding *iodide*, m. p. 147°, furnishes more than 90% of *m*-nitro-isomeride, whilst benzylpyridinium perchlorate affords only 67%; (2) the greater the volume of the central charged atom. This involves the probability of diminishing *m*-substitution in ascending a group of the periodic table; (3) the smaller the space occupied by atoms or groups attached to the central charged atom, and (4) the greater the mobility of the groups surrounding the central charged atom. The latter affords an explanation of the nitration of benzylpiperidine. The nitration of benzylpiperidine is unaffected by the addition of nitromethane or ethyl malonate and addition of nitrobenzene lowers the proportion of *m*-isomeride to only 58%.

The following compounds are also described: o-*nitrobenzylmethylpiperidinium iodide*, m. p. 183—184°; m-*nitrobenzylmethylpiperidinium iodide*, m. p. 204° after blackening at 198°; p-*nitrobenzylmethylpiperidinium iodide*, m. p. 188° (decomp.). The above *o*- and *p*-compounds, unlike the *m*-compound, develop a brownish-yellow colour in boiling methyl-alcoholic potassium hydroxide, whilst with acetone and solid potassium hydroxide only the *m*-derivative gives an intense violet colour. o-, m-, and p-*Nitrobenzylpiperidinium perchlorates* have m. p. 155—156°, 176—177°, and 181—182°, respectively. The *o*- and *p*-compounds afford *o*- and *p*-nitrotoluenes when boiled with sodium hydroxide solution. S. COFFEY.

Piperidine derivatives. IV. Substituted piperidinoalkyl benzoates and *p*-aminobenzoates. S. M. McELVAIN (J. Amer. Chem. Soc., 1927, 49, 2835—2840; cf. A., 1926, 1044).—The following piperidinoalkyl benzoate hydrochlorides were prepared by condensing substituted piperidines with the appropriate ω-chloroalkyl benzoates: *γ-piperidinopropyl*, m. p. 186—188°; *γ-2-methylpiperidinopropyl*, m. p. 167—169°; *γ-2-propylpiperidinopropyl*, m. p. 184—186°; *γ-3-methylpiperidinopropyl*, m. p. 178—180°; *β-3-methylpiperidinoethyl*, m. p. 134—136°, and *γ-3-carbethoxypiperidinopropyl benzoate hydrochloride*, m. p. 161—163°. The following were prepared by condensing piperidines with trimethylene chlorohydrin, esterifying the resulting γ-piperidinopropyl alcohols with *p*-nitrobenzoic acid, and finally reducing the nitro-group catalytically: *γ-piperidinopropyl* p-*nitrobenzoate*, m. p. 201—203°, and p-*aminobenzoate hydrochloride*, m. p. 214—216°; *γ-3-methylpiperidinopropyl* p-*nitrobenzoate*, m. p. 190—192°, and p-*aminobenzoate hydrochloride*, m. p. 158—160°; *γ-3-carbethoxypiperidinopropyl* p-*nitrobenzoate*, m. p. 177—179°, and p-*aminobenzoate hydrochloride*, m. p. 113—115°. Of the above derivatives, only those containing the alkyl-substituted piperidine nucleus exhibit anæsthetic action towards mucous membranes, and then only when the benzoyl group is separated from the piperidine nucleus by three methylene groups. In general, the substituted piperidino-derivatives are less toxic than those unsubstituted. F. G. WILLSON.

Piperidine derivatives. V. Preparation and reduction of phenyl-substituted 3-carbethoxy-4-piperidones. 1-*cyclo*Hexyl- and 1-phenylethyl-3-carbethoxy-4-piperidyl *p*-aminobenzoates. J. R. Thayer and S. M. McElvain (J. Amer. Chem. Soc., 1927, 49, 2862—2869; cf. preceding abstract).—β-Carbethoxyethylaniline, obtained from aniline and ethyl β-bromopropionate, has b. p. 133—135°/2 mm., n_D^{20} 1·5315, 1·0709 (*hydrochloride*, m. p. 98—99°) (cf. Harries and Loth, A., 1896, i, 321). Benzylamine affords similarly β-*carbethoxyethylbenzylamine*, b. p. 132—134°/2 mm., n_D^{20} 1·5059, d_{20}^{20} 1·9126 (*hydrochloride*, m. p. 147—149°). β-*Phenylethyl*-β-*carbethoxyethylamine*, b. p. 145—147°/2 mm., n_D^{20} 1·5040, d_{20}^{20} 1·0098 (*hydrochloride*, m. p. 161—163°), *phenyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 182—184°/2 mm., n_D^{20} 1·5176, d_{20}^{20} 1·0948, *benzyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 181—183°/2 mm., n_D^{20} 1·4942, d^{20} 1·0598, and β-*phenylethyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 190—193°/2 mm., n^{20} 1·4990, d_{20}^{20} 1·0598, are obtained analogously. Treatment of the above dicarbethoxy-tertiary amines with sodium in boiling xylene (cf. A., 1926, 1044) affords, respectively, 1-*phenyl*- (I), m. p. 144—145°, 1-*benzyl*- (II), m. p. 170—172°, and 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidone hydrochloride* (III), m. p. 165—167°). Reduction of (I) with hydrogen in presence of platinum oxide in alcohol, with subsequent treatment of the product with *p*-nitrobenzoyl chloride, yields 1-cyclo*hexyl*-3-*carbethoxy*-4-*piperidyl* p-*nitrobenzoate hydrochloride*, m. p. 188—190°. Similarly (III) affords 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidyl* p-*nitrobenzoate hydrochloride*, m. p. 195—197°, but reduction of (II) could not be controlled to yield a crystalline product. Catalytic reduction of the nitrobenzoates yields, respectively, 1-cyclo*hexyl*- (IV), m. p. 220—222°, and 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidyl* p-*aminobenzoate dihydrochloride*, (V), m. p. 215—218°. The anæsthetic effect of (V) on the rabbit's cornea, and its toxicity to white mice, are both slightly greater than that of cocaine, whilst (V) is more than twice as effective an anæsthetic as cocaine under similar conditions, with approximately only one fifth of the toxicity of the latter. F. G. Willson.

Phenylhydroxylamine derivative of isatin-7-carboxylic acid. H. Rupe and G. A. Guggenbuhl (Helv. Chim. Acta, 1927, 10, 926—937).—Isatin-7-carboxylic acid (Sandmeyer, A., 1919, i, 318) (β-*phenylhydrazone*, decomp. 267°; α-*oxime*, decomp. 254°; β-*semicarbazone*, decomp. 261°) is difficult to esterify. The *methyl*, m. p. 192° (α-*oxime*, decomp. 228—229°; β-*phenylhydrazone*, m. p. 202°), and *ethyl* esters, m. p. 189—190°, are described. The acid and esters react with phenylhydroxylamine, yielding *isatin-7-carboxylic acid phenylhydroxylamine* (I), decomp. 221·5°, represented by either the lactim or pseudo-acid structure, $CO_2H\cdot C_6H_3<\frac{CO}{-N}\geqslant C\cdot NPh\cdot OH$

$$CO_2H\cdot C_6H_3<\frac{CO}{NH}>C:NPh:O,$$ *methyl isatin-7-carboxylate phenylhydroxylamine* (II), decomp. 187·5° (*methyl ether*, decomp. 181·5°), and *ethyl isatin-7-carboxylate phenylhydroxylamine*, decomp. 176·5°, respectively. Reduction of (I) with zinc dust and acetic acid furnishes *isatin-7-carboxylic acid-α-anil* (III), $CO_2H\cdot C_6H_3<\frac{CO}{-N}\geqslant C\cdot NHPh$ (*zinc* salt; *hydrochloride*, m. p. 173°; *methyl ester hydrochloride*, decomp. 141—143°), which is oxidised by ferric chloride to isatin-7-carboxylic acid and aniline. Treatment of (I) and (III) with phenylhydrazine and hydroxylamine furnishes respectively isatin-7-carboxylic acid-β-phenylhydrazone, and -α-oxime. Similarly (II) yields the β-phenylhydrazone and α-oxime of methyl isatin-7-carboxylate. Hydrolysis of (I) with 10% hydrochloric acid gives isatin-7-carboxylic acid and aniline, whilst with 10% sodium hydroxide there are obtained the acid, aniline, and azoxybenzene. H. Burton.

Organic compounds of sulphur. VII. Behaviour of mercaptans towards phenanthraquinone, isatin, and αβ-unsaturated ketones. A. Schönberg and O. Schütz [with G. Arend and J. Peter] (Ber., 1927, 60, [*B*], 2344—2351).—Phenanthraquinone is readily converted by benzyl mercaptan into the *compound* $C_{21}H_{16}O_2S$, which decomposes into its components at about 115°. Since the colour of additive compounds of phenanthraquinone is generally equal to or darker than that of the quinone itself whereas the present compound is less intensely coloured, it is regarded as 10-*keto*-9-*hydroxy*-9-*benzylthiol*-9 : 10-*dihydrophenanthrene* ("*phenanthraquinone benzylsemimercaptol*"); the corresponding *phenyl*, decomp. about 100°, *ethyl*, and n-*butyl* compounds are described. Chrysoquinone yields an analogous *derivative*, $C_{25}H_{18}O_2S$, with benzyl mercaptan, whereas acenaphthaquinone affords the *dibenzylthiol* compound, $\begin{matrix}CO\\C_{10}H_6\end{matrix}>C(S\cdot CH_2Ph)_2$, m. p. 104—105°. Ethyl mercaptan and isatin yield 2-*keto*-3-*hydroxy*-3-*ethylthiolindoline*; the corresponding *benzyl* compound is described. The possibility that the mercaptan is added at the nitrogen atom is excluded by the observation that *N*-acetylisatin gives the *acetyl* derivative of 2-*keto*-3-*hydroxy*-3-*benzylthiol-indoline*. Addition of mercaptans to αβ-unsaturated ketones is realised in the case of 2 : 3-diphenylindone, which gives the corresponding 1 : 1-*diphenylthiol*-, m. p. (indef.) 134—136°, and *dibenzylthiol*-, m. p. 142—143°, derivatives; the latter compound is converted by sulphuric acid in glacial acetic acid into 2 : 3-diphenylindone. H. Wren.

New stereoisomeride (*trans*-) of hexahydrocarbazole. J. Gurney, W. H. Perkin, jun., and S. G. P. Plant (J.C.S., 1927, 2676—2679; cf. A., 1926, 410).—Reduction of tetrahydrocarbazole with tin and hydrochloric acid yields *cis*-hexahydrocarbazole, m. p. 99°, b. p. 280°/769 mm. (*picrate*, m. p. 166°), together with a small quantity (1—2%) of trans-*hexahydrocarbazole*, m. p. 127°, b. p. 286°/769 mm. (*picrate*, m. p. 179°; 9-*acetyl* derivative, m. p. 113°; 9-*benzoyl* derivative, m. p. 133°). The molecule of *trans*-hexahydrocarbazole is under considerable strain, accounting for its formation in small amount. The existence of these stereoisomerides is discussed in relation to the Sachse–Mohr theory of multiplanar rings. M. Clark.

Ammoniated iridodipyridino-salts. M. Delépine (Z. physikal. Chem., 1927, 130, 222—232;

cf. A., 1923, i, 944).—The action of ammonia in the cold on iridium *trans*-dipyridino-tetrachloride, $Ir(C_5H_5N)_2Cl_4$, furnishes the *complexes* $[Ir(C_5H_5N)_2Cl_4][Ir(C_5H_5N)_2(NH_3)_2Cl_2],2H_2O$, red, triclinic, and $[Ir(C_5H_5N)_2Cl_4]_2[Ir(C_5H_5N)_2(NH_3)_3Cl],5H_2O$, which can be separated by levigation, followed by recrystallisation from aqueous solution. Double decomposition of these complexes with pyridine hydrochloride gives rise to the *salts* $Cl[Ir(C_5H_5N)_2(NH_3)_2Cl_2]H_2O$ and $Cl_2[Ir(C_5H_5N)_2(NH_3)_3Cl],4H_2O$. The *iodide, bromide, sulphate*, and *hydrogen sulphate* corresponding with the first of these salts are also described. A carbonate, $CO_3[Ir(C_5H_5N)_2(NH_3)_2(H_2O)Cl],6H_2O$, has also been prepared by the action of silver oxide and carbon dioxide of the air on the monochloride. The *chloride*, $Cl_3[Ir(C_5H_5N)_2(NH_3)_4]$, and a basic salt derived from it are also described.

L. S. THEOBALD.

Synthesis of the "β-acid" (2 : 6-dihydroxyquinoline-4-carboxylic acid) obtained by hydrolysis of crude oryzanin. Y. SAHASHI (Biochem. Z., 1927, **189**, 208—215).—The author's view (A., 1926, 441, 846) that the β-acid of Suzuki, Shimamura, and Odake (A., 1912, ii, 980) obtained by hydrolysis of crude oryzanin is 2 : 6-dihydroxyquinoline-4-carboxylic acid is confirmed by synthesis. Quinic acid is converted by methyl iodide and sodium hydroxide into 2-hydroxy-6-methoxy-1-methylquinoline-4-carboxylic acid (ethyl ester, m. p. 166—167°), identical with the dimethyl derivative of the β-acid obtained by treatment with methyl sulphate. The same compound is also obtained synthetically (starting with a *p*-anisidine, diethylketomalonate condensation) and this compound on demethylation by Zeisel's method gave 2 : 6-hydroxyquinoline-4-carboxylic acid identical with the β-acid.

P. W. CLUTTERBUCK.

Synthesis of 2-carboxymethylquinoline-3-carboxylic acid and of certain of its derivatives. B. BOBRAŃSKI and E. SUCHARDA (Rocz. Chem., 1927, 7, 192—203).—Condensation of *o*-aminobenzaldehyde with ethyl acetonedicarboxylate yields *ethyl 2-carbethoxymethylquinoline-3-carboxylate*, m. p. 62° (*hydrochloride*, m. p. 108°; *nitrate*, m. p. 111°), whence on alkaline hydrolysis is obtained the corresponding acid, which at the ordinary temperature rapidly loses carbon dioxide, yielding 2-methylquinoline-3-carboxylic acid. The *anhydride*, m. p. 255° (decomp.), the *monoamide*, m. p. 218—220° (*acetyl* derivative, m. p. 239°), and the *imide*, m. p. 375°, of 2-carboxymethylquinoline-3-carboxylic acid are prepared, the imide being identical with 1 : 3-dihydroxybenzo-2 : 5-naphthadiazine (Niementowski and Sucharda, A., 1919, i, 354).

R. TRUSZKOWSKI.

Esters of α-phenylcinchoninic acid. S. WEIL and A. JOSKOWICZÓWNA (Rocz. Chem., 1927, 7, 362—368).—The following esters of α-phenylcinchoninic acid have been prepared: p-*chlorophenyl*, m. p. 117—118°, β-*phenylethyl*, m. p. 72°, *pyrocatechyl*, m. p. 178—179°, *guaiacyl*, m. p. 104—105°, *resorcinyl*, m. p. 195—196°, *pyrogallyl*, m. p. 170—171°, *thymyl*, m. p. 110—111°, and the *triphenylcinchoninyl ether* of *quinic anhydride*, m. p. 208°. R. TRUSZKOWSKI.

Manufacture of insoluble azo dyes. I. G. FARBENIND.—See B., 1927, 902.

[Nitro- and amino-acridines.] K. LEHMSTEDT (Ber., 1927, **60**, [*B*], 2413; cf. A., 1927, 575).—A reply to Jensen (A., 1927, 1087). H. WREN.

Isolation of acridine derivatives etc. Preparation of acridine-9-carboxylonitrile. E. WIRTH.—See B., 1927, 925.

Preparation of acridinic [quinoline-2 : 3-dicarboxylic] acid and derivatives. A. KONOPNICKI and E. SUCHARDA (Rocz. Chem., 1927, 7, 183—186).—Acridinic acid is produced in 70% yield by the action of concentrated nitric acid on 2 : 4-dihydroxyacridine. The *anhydride*, m. p. 223°, and *imide*, m. p. 316°, are described. R. TRUSZKOWSKI.

New type of acridone: *para*-acridones. I. TANESCU (Bull. Soc. chim., 1927, [iv], **41**, 1511—1514).—When treated with sulphuric acid in cool benzene solution for 24 hrs. *p*-nitrobenzaldehyde affords mainly *p*-nitrotriphenylmethane, a little 4-nitrotriphenylmethane-2(?)-sulphonic acid, brick-red, m. p. 160°, and traces of a para-*acridone*, $C_{13}H_9ON$, m. p. above 300°. The latter is also obtained by internal condensation from 4-bromo-4′-aminobenzophenone, by heating in presence of copper powder, a little potassium iodide, and amyl alcohol in a sealed tube at 350°. The formation of *m*-nitrotriphenylmethane from *m*-nitrobenzaldehyde in the same way is accompanied by the formation of a little 3-nitrotriphenylmethane-6(?)-sulphonic acid, but no acridone is formed. R. BRIGHTMAN.

Synthesis of the pyridine analogues of quinizarin. S. NIEMENTOWSKI, J. FRÜHLING, and R. JOSZT (Rocz. Chem., 1927, 7, 218—229).—By condensation of quinol dimethyl ether with quinolinic anhydride, 5 : 8-*dihydroxy-α-anthrapyridoquinone* ($+0\cdot5C_6H_6$), m. p. 230°, is produced; with cinchomeronic anhydride the corresponding β-*derivative*, m. p. 209° (*diacetyl* derivative, m. p. 187·5—189·5°; *tetra-acetyl* derivative, m. p. 283°), is obtained.

R. TRUSZKOWSKI.

Manufacture of heterocyclic compounds [naphthaquinolines etc.]. I. G. FARBENIND.—See B., 1927, 903.

α-Amino-*N*-carboxylic anhydrides. V. Side-reactions of the pyridine decomposition. F. WESSELY and M. JOHN (Z. physiol. Chem., 1927, **170**, 38—43; cf. A., 1926, 1235; 1927, 655).—From the ether-soluble portion of the product obtained by heating phenylalanine-*N*-carboxylic anhydride in pyridine there are isolated the two inactive forms of α-(5-benzyl-3-hydantoin)-β-phenylpropionic acid, m. p. 234—235° (corr.) and 170° (sintering 90—100°), respectively. Glycine-*N*-carboxylic anhydride gives in the same way a much smaller quantity of hydantoin-3-acetic acid. The hydantoins are probably the result of addition of the decarboxylated residue, ·NH·CHR·CO·, to the carbimide, CO:N·CHR·CO_2H, formed by isomerisation of the anhydride. No such by-products are obtained when phenylalanine-*N*-carboxylic anhydride is heated with aniline or methyl-

aniline, the evolution of carbon dioxide being quantitatively that required for formation of $\left[CH_2Ph\cdot CH<\begin{matrix}NH\\ CO\end{matrix}\right]_n$. C. HOLLINS.

3 : 5-Hydantoin derivatives as anhydrides of amino-acid diureides. C. GRANACHER and H. LANDOLT (Helv. Chim. Acta, 1927, **10**, 799—815).—The formation of 3 : 5-disubstituted hydantoins, $\overline{CO\cdot CHR'\cdot NH\cdot CO\cdot N}\cdot CHR''\cdot CO_2H$, from dipeptides of the type $CO_2H\cdot CHR'\cdot NH\cdot CO\cdot NH\cdot CHR''\cdot CO_2H$, by elimination of 1 mol. of water proceeds smoothly. Carbamidoglycylglycine ester, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, when heated at 180—190° in a vacuum, affords ammonia and *ethyl hydantoin-3-acetate*, m. p. 120°, which when treated with ammonia gives *carbamidodiacetamide*, $CO(NH\cdot CH_2\cdot CO\cdot NH_2)_2$, m. p. 226—228° (decomp.), also obtainable from ammonia and ethyl carbamidodiacetate. Hydrolysis of the above diacetamide with *N*-hydrochloric acid yields hydantoin-3-acetic acid, m. p. 196—198° (Johnson and Renfrew, A., 1925, i, 583, give m. p. 190—191°), also produced from the above diacetate by treatment with concentrated hydrochloric acid in ether. Hydantoin-3-acetic acid is unaffected by hot hydrochloric acid, but is hydrolysed by *N*-sodium hydroxide to carboxyglycylglycine. *Ethyl 5-benzylidenehydantoin-3-acetate*, m. p. 174° (free *acid*, m. p. 260°), is reduced by sodium amalgam and a trace of acetic acid in aqueous alcohol to *ethyl 5-benzylhydantoin-3-acetate*, m. p. 155° (free *acid*, m. p. 181—183°; *acid amide*, m. p. 216—218°). Similarly, *ethyl 5-*p*-anisylidenehydantoin-3-acetate*, m. p. 182—183° (free *acid*, m. p. 275°), gives *ethyl 5-*p*-methoxybenzylhydantoin-3-acetate*, m. p. 140°. Ethyl α-aminopropionate is converted by carbonyl chloride into *ethyl carbamidodi-α-propionate*, $CO(NH\cdot CHMe\cdot CO_2Et)_2$, m. p. 152°, which when treated with concentrated hydrochloric acid in ether furnishes *α-5-methylhydantoin-3-propionic acid*, m. p. 187—189° after previous sintering. From ethyl carbonyldi-α-amino-γ-methylvalerate (Hugounenq and Morel, A., 1905, i, 178), by distillation at 225—230°/12 mm., there is obtained *ethyl α-5-*iso*butylhydantoin-3-γ-methylvalerate*, whilst treatment with hydrochloric acid in ether yields *α-5-*iso*butylhydantoin-3-γ-methylvaleric acid*, m. p. 148° after sintering at 140°.

H. BURTON.

Action of light on the isomeric modifications of certain polypeptide-hydantoins. D. A. HAHN and J. EVANS (J. Amer. Chem. Soc., 1927, **49**, 2877—2883).—*Methyl 4-benzylidene-3-methylhydantoin-1-acetate* exists in two stereoisomeric forms, m. p. 65·5—66·5° (I) and 98·5—99·5° (II), respectively. When (I) is exposed to daylight or ultra-violet light in presence of a trace of iodine, it is partly converted into (II) and a *polymeride*, m. p. 276—278° (III), whilst some decomposition takes place with formation of benzaldehyde; (II) yields similarly (I) and (III), the change being preceded by an induction period. *4-Benzylidene-3-methylhydantoin-1-acetic acid* also exists in two stereoisomeric forms, m. p. 186·5—187·5° (IV) and 198·5—199·5° (V), respectively. Whilst (IV) does not yield measurable quantities of other products when exposed to light for 5 months, (V) is much more rapidly changed under similar conditions, with production of a small proportion of (IV) and a *polymeride*, m. p. 292—294°, which is also obtained by boiling (II) with hydrochloric acid in glacial acetic acid.

F. G. WILLSON.

Action of tolylhydrazines on dihydroxytartaric acid. F. D. CHATTAWAY and W. G. HUMPHREY (J.C.S., 1927, 2793—2796).—The action of *o*- and *p*-tolylhydrazines on dihydroxytartaric acid, unlike that of other hydrazines (A., 1927, 776), yields pure monohydrazones. When *diketosuccinic acid* o*-tolylhydrazone* (I), m. p. 192° (decomp.), is heated with acetic anhydride, the *anhydride* (II), m. p. 208° (decomp.), is obtained. Crystallisation of (II) from dilute acetic acid regenerates (I), whereas crystallisation from anhydrous alcohol yields the *ethyl hydrogen* ester, m. p. 115°, converted by prolonged boiling with alcohol saturated with hydrogen chloride into the *ethyl* ester (III), m. p. 90°. (III) is alternatively prepared by coupling diazotised *o*-toluidine with the potassium derivative of ethyl oxalacetate. *Diketosuccinic acid* p*-tolylhydrazone* [*anhydride*, m. p. 192° (decomp.); *ethyl hydrogen* ester, m. p. 112°] has m. p. 190° (decomp.). The monohydrazones of dihydroxytartaric acid cannot be converted into pyrazoline derivatives. *Diketosuccinic acid* o*-tolylosazone* (IV), m. p. 170° (decomp.), which cannot be crystallised unchanged, yields, with acetic anhydride, the *anhydride* (V), m. p. 198° (decomp.). Crystallisation of (IV) from acetic acid or acidification of its sodium salt yields *4 : 5-diketo-1-*o*-tolylpyrazoline-3-carboxylic acid 4-*o*-tolylhydrazone* (VI), m. p. 229° (decomp.); (V) is also produced in the former case. The *ethyl* ester of (VI), m. p. 145°, is most easily obtained by boiling (IV) with alcohol containing hydrochloric acid. *Diketosuccinic acid* p*-tolylosazone* [*anhydride*, m. p. 230° (decomp.)] has m. p. 175° (decomp.). *4 : 5-Diketo-1-*p*-tolylpyrazoline-3-carboxylic acid 4-*p*-tolylhydrazone* (*ethyl* ester, m. p. 143°) has m. p. 233° (decomp.).

M. CLARK.

Autocondensation of 1-phenyl-3-methyl-5-pyrazolone. V. IONESCU and V. GEORGESCU (Bull. Soc. chim., 1927, [iv], **41**, 1514—1518).—When heated at 200° for 6 hrs. with alcohol and piperidine, 1-phenyl-3-methyl-5-pyrazolone yields the *bis*-derivative, $\left(\begin{matrix}N{=}CMe\\ NPh\cdot CO\end{matrix}>CH\right)_2 C<\begin{matrix}NPh\cdot N\\ CH_2-CMe\end{matrix}$ (I), m. p. 262°, together with a little of the anhydro-derivative, $\begin{matrix}N{=}CMe\\ NPh\cdot CO\end{matrix}>C{:}C<\begin{matrix}NPh\cdot N\\ CH_2-CMe\end{matrix}$ (II), m. p. 258°, and occasionally, in conditions not yet determined, a little bis-(1-phenyl-3-methyl-5-pyrazolone), m. p. above 300°. When heated at 280° or treated with cold sulphuric acid (I) is converted into (II) and 1-phenyl-3-methyl-5-pyrazolone, a reaction which confirms the above structures (cf. Mohr, A., 1905, i, 676).

R. BRIGHTMAN.

Asymmetric nitrogen atom. LIV. Activation of an asymmetric tertiary base in the form of its salts with optically active acids. E. WEDEKIND and K. A. KLATTE (Ber., 1927, **60**, [*B*], 2325—2334).—The activation of derivatives of tervalent nitrogen includes the problems of the fission of non-

quaternary salts containing an optically active acid, replacement of the active anion by an optically inactive anion, and final removal of the latter with the production of an optically active, asymmetric, tertiary base. The first of these problems has been partly realised in the 4-aminopyrazolone series. Thus the cautious crystallisation of 4-*methylethylamino*-1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*one* d-*camphorsulphonate*, m. p. 142—143°, from ethyl acetate gives a series of fractions which show distinct progressive change in their molecular rotation in aqueous solution, the calculated values for the cation varying from +35·6° to −15·6°. Similar crystallisation of the corresponding d-*bromocamphor*-π-*sulphonate*, m. p. 187—188°, from a mixture of ethyl acetate and acetone gives a most sparingly soluble fraction the cation of which has $[M]_D$ +49°. In one (non-reproducible) instance, a fraction having $[M]_D$ −253° for the cation was produced from the camphorsulphonate; the rotation of this fraction increased to a maximum and then diminished to zero. Salts containing a lævorotatory cation exhibit a gradual change in rotation with time in the sense that the − sign passes to + or to ±, reaching in the first case a maximal value of +17° for the cation, whilst in the second case the observed rotation, +51°, corresponds with that of the camphorsulphonate ion. A case of racemisation of the optically active nitrogenous cation appears to be realised. The rotation of fractions with dextrorotatory cations is independent of the time and unchanged by hydrogen ions or more protracted exposure to relatively high temperature. The apparent stabilisation of the dextrorotatory basic group by the dextrorotatory acidic component is in harmony with the observations of Wedekind and Ney (A., 1912, i, 501), but an explanation of the mutual influence of the groups is rendered difficult by their presence as ions in the solution. Conversion of the head and tail fractions of the *d*-bromocamphor-π-sulphonate into the perchlorate gives a completely inactive *salt*, m. p. 189—191°. 4-Benzylethylamino-1-phenyl-2 : 3-dimethylpyrazol-5-one gives a d-*camphorsulphonate*, m. p. 132—133°, from which a fraction is derived by crystallisation from ethyl acetate having $[M]_D$ +24° for the active cation.

4-*Methylethylamino*-1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*one*, m. p. 92°, is prepared by treating methylaminoantipyrine with ethyl iodide followed by 10% potassium hydroxide. H. WREN.

Glyoxalones and glyoxalidones. II. C. GRANACHER and G. GULBAS (Helv. Chim. Acta, 1927, **10**, 819—826; cf. Granacher and Mahler, A., 1927, 467).—Reduction of 2-phenyl-4-benzylideneglyoxal-5-one with sodium amalgam and acetic acid in presence of alcohol yields 2-*phenyl*-4-*benzylglyoxalid*-5-*one*, m. p. 145—146°, which when treated with hot *N*-hydrochloric acid gives benzaldehyde, phenylalanine, and phenylalanineamide. α-*Benzamidocinnamic acid ethylamide*, m. p. 187°, prepared from ethylamine and the lactimide of benzylidenehippuric acid in alcoholic solution, when heated at 190—200° in a vacuum affords 2-*phenyl*-4-*benzylidene*-1-*ethylglyoxal*-5-*one*, m. p. 110—112°. α-*Benzamidocinnamic acid benzylamide*, m. p. 173—174°, furnishes 2-*phenyl*-1-*benzyl*-4-*benzylideneglyoxal*-5-*one*, m. p. 143—144°. 1 : 2-*Diphenyl*-4-*benzylideneglyoxal*-5-*one* has m. p. 180°. α-*Benzamidocinnamic acid* iso*propylamide*, m. p. 159—160°, when heated in a vacuum does not give the glyoxalone, but yields the lactimide of benzylidenehippuric acid (cf. Granacher and Mahler, *loc. cit.*). α-*Benzamido*-p-*methoxycinnamic acid methylamide*, m. p. 219°, gives 2-p-*methoxyphenyl*-4-*benzylidene*-1-*methylglyoxal*-5-*one*, m. p. 163° (the 1-*ethyl* compound, m. p. 103°, is obtained from the *ethylamide*, m. p. 214°). α-Benzamido-*p*-methoxycinnamanilide has m. p. 254° (Wittenberg, Diss., Basel, 1903, gives m. p. 205°). The lactimide of *p*-anisylidenehippuric acid and ethylenediamine react to form *di*-(α-*benzamido*-p-*methoxycinnamic acid*)-*ethylenediamide*, m. p. 236°, which when heated in a vacuum yields a dark yellow *substance*, m. p. 285—286°, apparently formed by elimination of 1 mol. of water only. H. BURTON.

Sulphonation of glyoxalines. III. G. R. BARNES and F. L. PYMAN (J.C.S., 1927, 2711—2714).—Oxidation of 2-thiolglyoxaline with hydrogen peroxide (Balaban and King, A., 1927, 977) yields *glyoxaline-2-sulphonic acid* (+1H_2O), anhyd. m. p. 303° (corr.) [*barium* salt (+2H_2O)]. This acid differs from the sulphonation product of glyoxaline, which must therefore be glyoxaline-4(5)-sulphonic acid, as previously suggested (J.C.S., 1920, **117**, 1429). Sulphonation of 4(5)-methylglyoxaline yields 4(5)-*methylglyoxaline*-5(4)-*sulphonic acid* (+1H_2O), anhyd. m. p. 278° (corr.) [*sodium* (+3H_2O), *barium* (+3H_2O), and *ammonium* salts], since the product is not identical with 4(5)-methylglyoxaline-2-sulphonic acid (Balaban and King, *loc. cit.*). This acid is readily decomposed by cold bromine water. It fails to react with phosphorus pentachloride at 160°. Like glyoxaline-4(5)-sulphonic acid, it is hydrolysed almost quantitatively when heated for 3 hrs. at 170° with concentrated hydrochloric acid, whereas glyoxaline-2-sulphonic acid shows only a 12% hydrolysis under these conditions. M. CLARK.

Some derivatives of di-(2-pyridyl)amine, and tri-(2-pyridyl)amine. J. P. WIBAUT and G. L. C. LA BASTIDE (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 664—669).—Di-(2-pyridyl)amine (cf. Tschitschibabin, A., 1915, i, 591; Steinhäuser and Diepolder, A., 1916, i, 740) is also obtained by heating 2-chloropyridine with the sodium derivative of 2-aminopyridine at 170—180°. It is nitrated by warm nitric and sulphuric acids to a *dinitrodipyridylamine*, m. p. 195—196°, and is brominated in acetic acid solution, yielding a *dibromodipyridylamine*, m. p. 191° (*dihydrobromide*, m. p. 253—254°). Treatment of several substituted aminopyridines with 2-halogenopyridines under various conditions does not furnish substituted dipyridylamines. 5-*Bromo*-2-*iodopyridine*, m. p. 117°; 2-*bromo*-5-*iodopyridine*, m. p. 122·5°, and 2 : 5-*di-iodopyridine*, m. p. 70·5°, are described. *Tri*-(2-*pyridyl*)*amine*, m. p. 132·5° (*picrate*, m. p. 149°; *mercurichloride*, $C_{15}H_{12}N_4,HCl,HgCl_2$, m. p. 180°), is obtained by heating a mixture of 2-aminopyridine, 2-iodopyridine, mesitylene, potassium hydroxide, potassium, and a trace of copper powder at 150—160°. Tripyridylamine is a feeble base, the order of

basicity for the series, determined by conductivity measurements and p_H values, being tri<mono<di.

H. BURTON.

1 : 5-Naphthyridine and certain of its derivatives. L. KLISIECKI and E. SUCHARDA (Rocz. Chem., 1927, 7, 204—217).—7 : 9 : 10-*Trihydroxybenzo*-1 : 5-*naphthyridine*, m. p. 378° (*acetyl* derivative, m. p. 338°), is prepared by the condensation of aminopicolinic acid with phloroglucinol. Oxidation with fuming nitric acid yields 8-*hydroxy*-1 : 5-*naphthyridine*-6 : 7-*dicarboxylic acid*, decomposing at 170—180° to yield 8-*hydroxynaphthyridine*-7-*carboxylic acid*, which at 340° is converted into 8-*hydroxy*-1 : 5-*naphthyridine*; this sublimes without decomposition at 340° and yields on reduction 1 : 5-*naphthyridine*, m. p. 74°. Dilute nitric acid yields also 6 : 8-*dinitro*-7 : 9 : 10 - *trihydroxybenzo* - 1 : 5 - *naphthyridine*, decomposing explosively at 277°.

R. TRUSZKOWSKI.

Preparation of carbocyanine dyes. F. M. HAMER (J.C.S., 1927, 2796—2804).—The names thiocarbocyanine (cf. Mills, J.C.S., 1922, **121**, 455), oxacarbocyanine, and indocarbocyanine are suggested for the carbocyanine dyes derived from benzthiazole, benzoxazole, and indolenine, respectively. Carbocyanine dyes of every known type are prepared in optimum yield by condensation in boiling pyridine solution of ethyl orthoformate with the appropriate quaternary salt containing a reactive methyl group. The solvent must be dry and four times the calculated quantity of ester is required. No carbocyanine containing two pyridine nuclei has yet been isolated. 2-Methylpyridine ethiodide does not condense with ethyl orthoformate in presence of boiling pyridine. The indocarbocyanines and oxacarbocyanines act, like other cyanine dyes, as photographic sensitisers. The following are described: 2 : 6-*dimethylquinoline alliodide*, m. p. 198—199° (decomp.) [*allobromide*, m. p. 214—215° (decomp.)]; 6 : 6′-*dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine iodide*, m. p. 280—281° (decomp.) [*bromide*, m. p. 281—282° (decomp.)]; 1 : 1′-dimethyl-4 : 4′-carbocyanine iodide, m. p. 290—295° (decomp.); *lepidine alliodide*; 1 : 1′-*diallyl*-4 : 4′-*carbocyanine iodide*, decomp. 150°; 2 : 2′-dimethylthiocarbocyanine iodide, m. p. about 280° (decomp.) (lit. 254°); 1-*methylbenzthiazole allobromide*, m. p. 202° (decomp.); 2 : 2′-*diallylthiocarbocyanine bromide*, m. p. about 260° (decomp.); 2 : 2′ - dimethyloxacarbocyanine iodide, m. p. 275—277° (decomp.) (lit. 259°); 1-*methylbenzoxazole ethiodide*, m. p. 195—197° (decomp.); 2 : 2′-*diethyloxacarbocyanine iodide*, m. p. 277—279° (decomp.); 3 : 3 : 3′ : 3′-*tetramethyl*-1 : 1′-*diethylindocarbocyanine iodide*, pleochroic, m. p. 260—263° (decomp.). Absorption spectra and sensitising action are described.

M. CLARK.

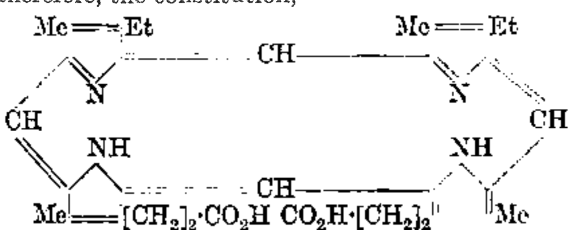
Intramolecular change in 5-amino-1 : 2 : 3-triazoles. O. DIMROTH and W. MICHAELIS (Annalen, 1927, **459**, 39—46).—A reply to Dutt (J.C.S., 1923, **123**, 265) and Carnelley and Dutt (A., 1925, ii, 165). *p*-Nitrophenyl azide condenses with phenylacetonitrile in presence of sodium ethoxide to give 4-*phenyl*-1-p-*nitrophenyl*-5-*amino*-1 : 2 : 3-*triazole* (I), m. p. 182°, which is strongly basic (*hydrochloride*). It was diazotised and coupled with β-naphthol and then gave an *azo*-compound, m. p. 220—225° (decomp.), which must have the formula $NO_2\cdot C_6H_4\cdot N<\begin{matrix}C(NH_2):Ph\\ N{=\!=\!=}N\end{matrix}$. When heated for several min. at 160—170° (I) is converted into the isomeric 5-p-*nitroanilino*-4-*phenyl*-1 : 2 : 3-*triazole* (II), m. p. 164°. Stannous chloride converts (I) into 4-*phenyl*-1-p-*aminophenyl*-5-p-*amino*-1 : 2 : 3-*triazole*, m. p. 166°, and (II) into 5-*amino-anilino*-4-*phenyl*-1 : 2 : 3-*triazole*, m. p. 177° (*hydrochloride*), which by fusion is converted into its isomeride, m. p. 166°. The structure assigned to the amine, m. p. 177°, is confirmed by its ready oxidation with ferric chloride to the *quinoneimine*

These f t are held to disprove the endimino-type of formulæ applied by Carnelley and Dutt (*loc. cit.*) to these compounds.

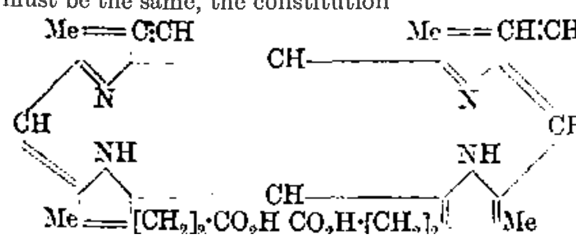
J. W. BAKER.

Syntheses of mesoporphyrin, mesohæmin, and the constitution of hæmin. (Synthesis of porphyrins. XIII.) H. FISCHER and G. STANGLER (Annalen, 1927, **459**, 53—98).—The synthesis of the four possible isomerides of ætioporphyrin has been effected by methods which prove their structure. One isomeride, 1 : 3 : 5 : 7-tetramethyl-2 : 4 : 6 : 8-tetraethylporphin, m. p. 400—405°, has previously been synthesised (Fischer and Klarer, A., 1926, 962). The second, 1 : 4 : 5 : 8 - tetramethyl - 2 : 3 : 6 : 7-tetraethylporphin, identical with *iso*ætioporphyrin (Fischer and Halbig, A., 1926, 963; Fischer, Halbig, and Walach, A., 1927, 469), is synthesised as follows: ethyl propionylacetate is converted into its *iso*-nitroso-derivative which, when reduced with zinc dust in the presence of ethyl acetoacetate, affords *ethyl* 2-*methyl*-4-*ethylpyrrole*-3 : 5-*dicarboxylate*, m. p. 115°. This by hydrolysis of the β-ester group with concentrated sulphuric acid at 40° yields the 3-*carboxylic acid*, m. p. 245°, which, by loss of carbon dioxide, yields *ethyl* 2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, converted by means of hydrogen cyanide and hydrogen chloride into the 3-aldehyde; this is reduced by hydrazine hydrate to hæmopyrrole. The latter reacts with magnesium ethyl bromide and ethyl chloroformate to give *ethyl* 2 : 5-*dimethyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 97°, from which the free *acid*, m. p. 142° (decomp.), is obtained on hydrolysis. Bromination converts the latter into the *hydrobromide*, m. p. 115° (decomp.), of *ethyl* 2-*bromomethyl*-3-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 134°, from which *bis*-(3-*methyl*-4-*ethyl*-5-*carbethoxypyrryl*)*methane* (I), m. p. 148°, is obtained by heating with methyl alcohol. This is hydrolysed to the corresponding *acid*, m. p. 211°, which by aeration in formic acid yields *iso*ætioporphyrin, m. p. 365°. Bromination of (I) yields the *hydrobromide* of *bis*-(2-*bromo*-3-*methyl*-4-*ethyl*-5-*pyrryl*)*methene* (II), m. p. 180° (*picrate*, m. p. 169°), which when heated with bis-(2 : 4-dimethyl-3-ethyl-5-pyrryl)methene and hydrogen bromide in acetic acid at 150° yields the same *iso*ætioporphyrin. The third isomeride, 1 : 3 : 5 : 8-tetramethyl-2 : 4 : 6 : 7-tetraethylporphin, is synthesised as follows: cryptopyrrolealdehyde condenses with hæmopyrrole in warm alcoholic hydrogen chloride to give the *hydrochloride* of (4 : 5-*dimethyl*-3-*ethylpyrryl*)-(2 : 4-*dimethyl*-

3-*ethylpyrrolenyl*)*methene*, m. p. 80° [*picrate*, m. p. 185° (decomp.)], which when heated with bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene and hydrogen bromide in acetic acid at 140°/12—14 atm. yields the *ætioporphyrin*, m. p. 360° (*copper* and *iron* salts; *hexabromo*-compound). The same isomeride is obtained by heating (2-*bromomethyl*-3-*methyl*-4-*ethylpyrryl*)-(2-*bromomethyl*-4-*methyl*-3-*ethylpyrrolenyl*)-*methene hydrobromide* (III), decomp. above 230° (obtained by dibromination of the corresponding methene), and bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene hydrobromide or bis-(2-bromo-4-methyl-3-ethylpyrryl)methene hydrobromide with succinic acid at 190°. The fourth isomeride, 1:4:6:7-tetramethyl-2:3:5:8-tetraethylporphin, m. p. 355° (Fischer, Halbig, and Walach, *loc. cit.*), is similarly obtained from (II) and (2-*bromomethyl*-3-*methyl*-4-*ethylpyrryl*)-(2-*bromomethyl*-3-*methyl*-4-*ethylpyrrolenyl*)-*methene hydrobromide* (IV) (by dibromination of the corresponding methene). When (III) is heated with the hydrobromide of bis-(2-bromo-3-methyl-4-β-carboxyethyl-5-pyrryl)methene (V) and succinic acid at 175—180°, mesoporphyrin, identical in all respects with a pure specimen, is obtained, and has, therefore, the constitution,



When the hydrochloride is heated in acetic acid solution with ferrous acetate, mesohæmin is obtained and therefore the position of the side-chains in hæmin must be the same, the constitution



being assigned to it (cf. Fischer and Lindner, A., 1927, 261). By a similar condensation of (V) with (IV) is obtained *iso*mesoporphyrin, isolated as its *methyl* ester, m. p. 275—279°. Bromination of hæmopyrrole in acetic acid yields the *perbromide* of (2-bromo-4-methyl-3-ethylpyrryl)-(2:3-dimethyl-4-ethylpyrrolenyl)methene, m. p. 141°, from which the free *methene*, m. p. 125°, is obtained by the action of sodium hydroxide on a chloroform solution. The same methene is obtained by bromination, with loss of carbon dioxide, of 2:3-dimethyl-4-ethylpyrrole-5-carboxylic acid. Further bromination affords (2-*bromo*-4-*methyl*-3-*ethylpyrryl*)-(2-*bromomethyl*-3-*methyl*-4-*ethylpyrrolenyl*)*methene hydrobromide*, decomp. 240°. The methene when heated with formic acid gives the ætioporphyrin, m. p. 400°. Bromination of ethyl 2-methyl-4-ethylpyrrole-3:5-dicarboxylate in acetic acid or carbon tetrachloride yields the corresponding -2-*bromomethyl* derivative, m. p. 156°, which, when heated with water, gives formaldehyde and *bis*-(4-*ethyl*-3:5-*dicarbethoxypyrryl*)-2:2′-*methane*, m. p. 130°. By the action of nitrous acid and zinc dust on ethyl propionylacetate is obtained *ethyl* 2:4-*diethylpyrrole*-3:5-*dicarboxylate*, m. p. 97°, from which, by hydrolysis of the β-carbethoxyl group, the corresponding 3-*carboxylic acid*, m. p. 220°, is obtained. This, on dry distillation, yields *ethyl* 2:4-*diethylpyrrole*-5-*carboxylate*, m. p. 49°, which is converted by hydrogen cyanide and hydrogen chloride into the corresponding 3-*aldehyde*, m. p. 84°; this is reduced by hydrazine hydrate, sodium, and alcohol at 160° to 3-methyl-2:4-diethylpyrrole. When a mixture of ethyl 2-methyl-4-ethyl-3-aldehydopyrrole-5-carboxylate, malonic acid, and aniline is heated in alcohol solution, *ethyl* 2-*methyl*-4-*ethyl*-3-β-*carboxyvinylpyrrole*-5-*carboxylate*, m. p. 240°, is obtained, reduced by sodium amalgam and ice water to the corresponding 3-*propionic acid* (3-β-*carboxyethyl* derivative), m. p. 148°. When heated at its m. p. the acrylic acid loses carbon dioxide and yields *ethyl* 3-*vinyl*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 79°, which on catalytic reduction with platinum-black affords *ethyl* 2-*methyl*-3:4-*diethylpyrrole*-5-*carboxylate*, m. p. 75° (also obtained by a Grignard reaction from 2-methyl-3:4-diethylpyrrole). By the action of nitromethane on ethyl 2-methyl-4-ethyl-3-aldehydopyrrole-5-carboxylate with dimethylamine hydrochloride as a condensing agent is obtained 3-*nitrovinyl*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 199° (corr.). Hæmopyrrole condenses with ethyl cyanoformate in the presence of hydrogen chloride to give the *imine hydrochloride*, m. p. 146°, from which *ethyl* 2:3-*dimethyl*-4-*ethylpyrrole*-5-*glyoxylate*, m. p. 83°, is obtained. The free *acid*, m. p. 191° (decomp.), when heated at 190° in a vacuum yields *hæmopyrrolealdehyde*, m. p. 85°; the latter is also obtained by the action of hydrogen cyanide and hydrogen chloride on hæmopyrrole. These products serve as intermediates for the synthesis of coproporphyrins. J. W. Baker.

Condensation of *o*-aminothiophenol with αβ-unsaturated acids. W. H. Mills and J. B. Whitworth (J.C.S., 1927, 2738—2753).—When *o*-aminothiophenol and αβ-unsaturated acids are heated together in an atmosphere of carbon dioxide, β-addition of the thiol group to the ethylenic linking occurs and water is eliminated, giving 4-ketotetrahydro-1:5-heptabenzthiazine derivatives. 4-*Ketotetrahydro*-1:5-*heptabenzthiazine*-2-*acetic acid*, m. p. 235—236° (*ethyl* ester, m. p. 139—140°), obtained from the thiophenol and glutaconic acid, is resolved by brucine and cinchonine into d-4-*ketotetrahydro*-1:5-*heptabenzthiazine*-2-*acetic acid*, m. p. 230°, $[\alpha]_{5790}$ +436·9° in alcohol (l-*brucine* salt, m. p. 164—165°; *ethyl* ester, m. p. 145—146°, $[\alpha]_{5790}^{20}$ +425·5°), and the corresponding l-*acid*, m. p. 229—230°, $[\alpha]_{5780}^{20}$ —435·5° (d-*cinchonine* salt, m. p. 193—195°). Condensation of *o*-aminothiophenol with ethyl α-bromoglutarate yields the isomeric *ethyl* 3-*keto*-2:3-*dihydro*-1:4-*benzthiazine*-2-*propionate*, m. p. 91°. Cinnamic acid and *o*-aminothiophenol react on heating at 160—170° to give 4-*keto*-2-*phenyltetrahydro*-1:5-*heptabenzthiazine*, m. p. 177° (*acetyl* derivative, m. p. 155—156°; *sulph*-

oxide, m. p. 210°; *sulphone*, m. p. 234—235°). Careful heating with small excess of potassium hydroxide solution hydrolyses this benzthiazine to *o-cinnamamidothiophenol*, m. p. 147—148° (*mercurichloride*, m. p. 211—212°), which is reconverted into the benzthiazine on heating at 165—170°. *oo'-Dicinnamamidodiphenyl disulphide*, m. p. 163—164° [*dibromo*-derivative, m. p. 213° (decomp.)], readily formed by oxidation of *o*-cinnamamidothiophenol, is also obtained by reaction of cinnamoyl chloride with *oo'*-diaminodiphenyl disulphide. α-Bromo-β-phenylpropionic acid and ethyl cinnamate each condense with *o*-aminothiophenol, yielding 3-*keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine*, m. p. 159—160°, whilst cinnamoyl chloride and sodium *o*-aminothiophenoxide in absolute alcohol yield 2-styrylbenzthiazole (*picrate*, m. p. 195—196°). This base is also formed when 4-keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine is heated at 240—260° and when cinnamic acid and *o*-aminothiophenol are heated at 210—220°. β-Phenylpropionic acid and *o*-aminothiophenol yield 2-β-*phenylethylbenzthiazole*, m. p. 60—61° (*picrate*, m. p. 132—133°). Crotonic acid reacts with the thiophenol, giving 4-*keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine*, m. p. 205—206° (*acetyl* derivative, m. p. 93°). Acrylic acid and the thiophenol yield 4-ketotetrahydro-1 : 5-heptabenzthiazine, m. p. 215—216° (215—216°), identical with the ε-lactam of *o*-aminophenylthiolpropionic acid, m. p. 87—88° (84°). The hydrochloride, m. p. 173—174° (189°), of this amino-acid is obtained by reduction of *o*-nitrophenylthiolpropionic acid, m. p. 148—149° (145°), which is formed by condensation of acrylic acid and *o*-nitrothiophenol in presence of piperidine. The m. p. given by Mayer and Horst (A., 1923, i, 844) for these compounds are shown in brackets. Maleic, fumaric, and monobromosuccinic acids condense with *o*-aminothiophenol, giving 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic acid*, m. p. 195—196°.

[With G. E. Watts.]—*o*-Aminothioanisole yields with acetic anhydride a *diacetyl* derivative, m. p. 69—70°. Reduction of *ethyl* o-*nitrophenylthiolformate*, a yellow oil decomposing when heated in a vacuum, gives *ethyl*-o-*aminophenylthiolformate* (*hydrochloride*, m. p. 120—122°). This amino-ester, mixed with a little of its hydrochloride and heated at 115°, gives benzthiazolone, which is readily acetylated.

M. Clark.

Quaternary salts in the benzselenazole series. L. M. Clark (J.C.S., 1927, 2805—2809; cf. *ibid.*, 1923, **123**, 2353).—The zinc salt of *o*-aminoselenophenol, which reacts with benzoyl chloride to give phenylbenzselenazole (Bauer, A., 1913, i, 263), reacts similarly with formic acid, giving *benzselenazole* (I), b. p. 154°/45 mm. (*methiodide*, m. p. 188—189°; *methopicrate*, m. p. 173°). The *methiodide*, m. p. 211—212° (decomp.), and *chloroplatinate* of 2-phenylbenzselenazole (II) are described. The methiodides of (I) and (II) react with two equivalents of sodium hydroxide, giving first the carbinol base and afterwards the sodium salt of the ψ-base $COR{\cdot}NMe{\cdot}C_6H_4{\cdot}SeNa$. Oxidation with iodine or potassium ferricyanide then yields *di-o-formylmethylaminodiphenyl diselenide*, m. p. 104°, and *di-o-benzoylmethylaminodiphenyl diselenide* (III), m. p. 170°, respectively. Atmospheric oxidation of the methiodide of (I) in ammoniacal solution gives *di-o-methylaminodiphenyl diselenide*, m. p. 89°, yielding on benzoylation the compound (III). *Di-o-formamidodiphenyl diselenide*, m. p. 174°, obtained as a by-product in the preparation of benzselenazole, is reduced in alcoholic solution by stannous chloride, yielding some benzselenazole by intermediate production of *o*-formamidoselenophenol. When di-*o*-formamidodiphenyl diselenide is heated with phenyl hydrazine, the formyl groups are readily removed with formation of α-formylphenylhydrazine. A satisfactory method for the determination of selenium in organic compounds of this type is described.

M. Clark.

Properties of benzylideneharmine. V. Hasenfratz and R. Sutra (Compt. rend., 1927, **185**, 1048—1050).—Benzylideneharmine reacts with bromine to give two isomeric *hydrobromides*, from which α- and β-*bromobenzylideneharmines*, m. p. 230° and decomp. about 125°, respectively, are obtained. These yield insoluble *chloroplatinates*. A solution of benzylideneharmine in sulphuric acid, when poured into water, gives a precipitate of *benzylideneharmine-N-sulphonic acid*, which forms very unstable salts. The action of methyl iodide on benzylideneharmine, with subsequent hydrolysis, leads to *benzylidenemethylharmine*, m. p. 190° (*hydriodide* and *chloroplatinate* described). Oxidation of benzylideneharmine with chromic acid yields harmic acid, and with nitric acid yields *p*-nitrobenzoic acid.

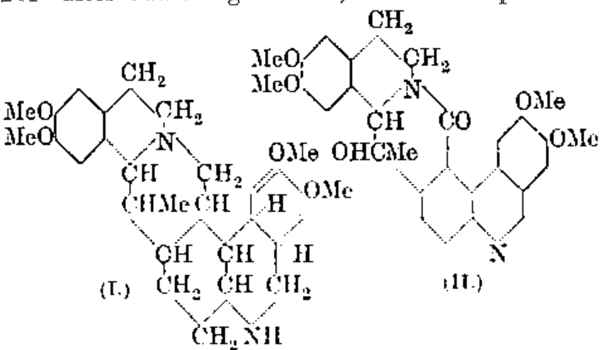
B. W. Anderson.

Determination of ephedrine mixtures by the biuret reaction. C. T. Feng (Chinese J. Physiol., 1927, **1**, 397—406).—The ether-soluble violet pigment obtained by performing the biuret reaction on solutions of ephedrine and ψ-ephedrine has been adapted as the basis of a colorimetric method for the determination of these two substances. The method is extended to the determination of the relative proportions of mixtures of the two alkaloids in solution, since it has been found that together they give less colour than the same amount of either of them when present alone. Examination of the residue left by evaporation of the ethereal solution of the violet pigment leads to the differentiation of ephedrine in solution from ψ-ephedrine; the former leaves a gelatinous residue, the latter rhombic, violet crystals.

E. A. Lunt.

Alkaloids of ipecacuanha. H. Staub (Helv. Chim. Acta, 1927, **10**, 826—837; cf. Spath and Leithe, A., 1927, 471; Brindley and Pyman, *ibid.*, 682).—Emetine hydrobromide, $C_{29}H_{40}O_4N_2,2HBr$ (cf. Carr and Pyman, J.C.S., 1914, **105**, 1591), becomes yellow at 210° and melts to an orange liquid at 248°. Oxidation of emetine with bromine (cf. Carr and Pyman, *loc. cit.*) yields rubremetine bromide, $C_{29}H_{33}O_4N_2Br$ (*methiodide* $+5H_2O$, m. p. 199° after sintering at 174°), which crystallises with 2, 3, or $6H_2O$, according to the solvent used for crystallisation, and is anhydrous from acetone. Careful oxidation of rubremetine bromide with alkaline potassium permanganate yields *dihydroxyrubremetine*, $C_{29}H_{28}O_6N_2$, m. p.

above 305°, a "*substance* D," decomp. 244° after darkening at 220°, and *m*-hemipinimide.



(I.) (II.)

Formula (I) is suggested for emetine and formula (II) for dihydroxyrubremetine. H. BURTON.

Oxyquinine and peroxyquinine. FREREJACQUE (Compt. rend., 1927, **185**, 1052—1055).—In the course of preparation of oxyquinine a *peroxyquinine*, $C_{20}H_{21}N_2O_2{\cdot}O_2,CHCl_3$ (?), m. p. 153°, $[\alpha]_D$ $-60°$, was isolated, having all the properties of a peroxide, but losing them on recrystallisation from acetone. The *N*-oxyquinine prepared by the author differed from Speyer and Becke's product (cf. A., 1922, 674) in having m. p. 188° and $[\alpha]_D$ $-17{\cdot}5°$.

B. W. ANDERSON.

Organic derivatives of silicon. XXXIII. An amorphous variety of octaphenyl*cyclo*silicotetrane. XXXIV. Action of sodium on phenoxydiphenylsilicyl chloride. F. S. KIPPING (J.C.S., 1927, 2719—2728, 2728—2734).—XXXIII. Acetone solutions of the product (*E*) originally obtained, together with the four (*A*, *B*, *C*, *D*) silicohydrocarbons $[SiPh_2]_n$, by heating diphenylsilicon dichloride with sodium (J.C.S., 1921, **119**, 830), continue to deposit crystals of (*B*) during several years. (*E*) is shown to be a mixture of a silicohydrocarbon (E_1) with a considerable proportion of oxygen-containing compounds, arising from impurity in the dichloride (Kipping and Murray, following abstract). (E_1) has the composition $[SiPh_2]_n$, where n ranges from about 7 to 9; it is resinous, melts very indefinitely below 150°, is miscible with acetone, ether, benzene, and chloroform, and behaves like (*B*) towards iodine and nitric acid. When (*B*) is heated for a few secs. above 400°, it melts to a transparent mass, readily soluble in cold acetone; the solution after an interval deposits crystals of (*B*) and the mother-liquors then give with alcohol a flocculent precipitate of an amorphous silicohydrocarbon $[SiPh_2]_n$, closely resembling (E_1). It is concluded that (E_1) is an allotropic form of octaphenyl*cyclo*silicotetrane (*B*), in which the molecules of the (*B*) form have become so entangled by interlocking of the phenyl groups that relatively stable aggregates incapable of forming crystals have been formed. In a single experiment, which could not be repeated, when (*E*) was heated slowly to about 400°, a considerable proportion of (*B*) separated in crystals. When (*E*) is distilled under 5 mm. pressure, a small quantity of oil is obtained. The latter yields triphenylsilicol on oxidation or on treatment with acetone and alkali, hydrogen being evolved in the latter case. This compound is not obtained from unheated (*E*) under similar conditions. The silico-hydrocarbon $[SiPh_2]_n$ is apparently very slowly decomposed at high temperatures, decomposition being accompanied by a transference of phenyl groups from one silicum atom to another, giving triphenylsilicyl $SiPh_3$ or some other compound containing this group.

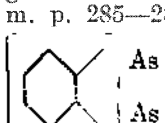
XXXIV. *Phenoxydiphenylsilicyl chloride* (I), b. p. 252—254°/40 mm., and *diphenoxydiphenylsilicane* (II), m. p. 70—71°, are obtained by interaction of phenol and diphenylsilicon dichloride. The compound (I) is immediately soluble in a 5% solution of potassium hydroxide, giving the potassium derivatives of phenol and diphenylsilicanediol. The compound (II) is relatively stable towards 5% sodium hydroxide solution, but is very readily hydrolysed in presence of acetone or alcohol with separation of trianhydrotrisdiphenylsilicanediol. The compound (I) reacts with sodium in hot toluene solution, giving a complex mixture from which octaphenylsilicotetrane, *diphenoxyoctaphenylsilicotetrane* (III), m. p. 215—216°, and diphenoxydiphenylsilicane were extracted by the use of anhydrous solvents. Phenol, diphenylsilicanediol, *hydroxyphenoxyoctaphenylsilicotetrane* (or the corresponding oxide) and *diphenoxytetraphenylsilicoethane* (?) were extracted from the remaining material, using undried solvents. The mechanism of formation of these compounds is discussed. The compound (III) is only very slowly hydrolysed by hydrochloric acid in boiling alcoholic solution, but is completely decomposed by an aqueous solution of piperidine and sodium hydroxide, giving hydrogen and the sodium derivatives of phenol and diphenylsilicanediol. M. CLARK.

Organic derivatives of silicon. XXXV. Preparation of diphenylsilicon dichloride: "Grignard" ether and its action on silicon tetrachloride. F. S. KIPPING and A. G. MURRAY (J.C.S., 1927, 2734—2737).—The impurities (up to 20%) present in diphenylsilicon dichloride prepared by the action of magnesium phenyl bromide on silicon tetrachloride (J.C.S., 1912, **101**, 2113) are ascribed to three possible sources: (1) phenylphenoxysilicon dichloride or diphenylphenoxysilicyl chloride, arising from partial oxidation of the Grignard reagent (A., 1921, i, 140); (2) *diethoxydiphenylsilicane*, b. p. 197—198°/50 mm., 302—304°/767 mm., or ethoxydiphenylsilicyl chloride, formed by reaction of diphenylsilicon dichloride with alcohol present in the "Grignard" ether; (3) ethoxydiphenylsilicyl chloride arising from the interaction product of ether and silicon tetrachloride. Even at the ordinary temperature these substances show slight reaction, probably thus: $SiCl_4+Et_2O \longrightarrow OEt{\cdot}SiCl_3+EtCl$. The b. p. of the ethoxychloride may be expected to approximate still more closely to that of the dichloride than that of diethoxydiphenylsilicane. Separation by distillation would therefore be impossible. An improved method for the preparation of diphenylsilicon dichloride, limiting the operation of these three sources of impurity, is described. The product still contains, however, a small amount of some ethoxy-compound. M. CLARK.

Arseno-organic compounds. E. GRISCHKIEVITCH-TROCHIMOVSKI, L. MATEJAK, and W. ZABŁOCKI (Rocz. Chem., 1927, 7, 230—240).—The following substances were prepared : *Phenyldicyanoarsine*, m. p. 78·5—79·5°, by the action of silver cyanide on phenyldichloroarsine, *α-naphthyldicyanoarsine*, m. p. 159·5—160·5°, *di-α-naphthylcyanoarsine*, m. p. 191·5—192·5°, *methyldicyanoarsine*, m. p. 115·5—116·5°, from cacodyl cyanide and cyanogen bromide, and *phenarsazine cyanide*, m. p. 227—228°. All the above dicyano-derivatives are readily converted by water into the corresponding acids and hydrogen cyanide.
R. TRUSZKOWSKI.

Manufacture of organic compounds of arsenic. R. W. E. STICKINGS, and MAY and BAKER, LTD.—See B., 1927, 925.

Organic compounds of arsenic. III. Tri-o-phenylenediarsine. N. P. MCCLELAND and J. B. WHITWORTH (J.C.S., 1927, 2753—2757).—Diazotised *o*-aminodiphenylarsinic acid couples with phenylarsenious oxide, giving *phenylene*-1 : 2-*diphenylarsinic acid*, unmelted at 310°. Distillation of the product obtained by reduction of this compound with phosphorus trichloride gives *tri*-o-*phenylenediarsine* (regarded as being I), m. p. 295—296° (*mercurichloride*, m. p. 285—286°; *oxide*, unmelted at 360°; *tetrabromide* (II), m. p. 255—256°). The tetrabromide (II) is decomposed when heated under reduced pressure, giving, in addition to bromine and triphenylenediarsine, *o*-dibromobenzene and arsanthrene bromide. Distillation of arsanthrene oxide gives triphenylenediarsine and arsenious oxide. Crystallographic data for the compound (I) are given.
M. CLARK.



(I.)

Azo dyes containing antimony. II. F. DUNNING and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 2869—2877 ; cf. A., 1927, 65).—*p*-Aminophenylstibinic acid is obtained in about 50% yield by diazotising *p*-aminoacetanilide in presence of antimony trioxide and sufficient hydrochloric acid to dissolve the latter, with subsequent decomposition of the resulting precipitated diazonium chloride–antimony trichloride additive product (cf. May, J.C.S., 1912, **101**, 1037) with alkali. Dyes were prepared by coupling diazotised *p*-aminophenylstibinic acid with *dimethylaniline*, brown, *diethylaniline*, purple, *α-naphthol-4-sulphonic acid*, dark red, 2 : 5-*am* -*7-sulphonic acid*, light reddish-brown, 2-*naphthylamine*-3 : 6-*disulphonic acid*, dark brown, 1 : 8-*aminonaphthol*-3 : 6-*disulphonic acid* (*sodium* salt, purple), 2-*naphthol*-3 : 6-*disulphonic acid* (*sodium* salt, orange-brown) and 1 : 8-*dihydroxynaphthalene*-3 : 6-*disulphonic acid* (*sodium* salt, purple). The first two of the above dyes, as well as the six previously prepared (*loc. cit.*), are practically non-toxic to *Trypanosoma equiperdum* in white rats, but the remainder exhibit definite curative properties. Dyeings on wool and cotton with the above products and certain others not isolated indicate that they give fast shades on cotton directly, and that the stibinic acid group is more strongly auxochromic than the sulphonic group. The following additive compounds, obtained by diazotising the appropriate amines in presence of an equivalent of antimony trioxide and excess of hydrochloric acid, were prepared : p-*dimethylaminobenzenediazonium chloride–antimony trichloride*, p-*diethylaminobenzenediazonium chloride–antimony trichloride*, *diphenyl*-4 : 4′-*bisdiazonium chloride–antimony trichloride* (1 : 2), and o-*carbomethoxybenzenediazonium chloride–antimony trichloride*. These were converted, by treatment with aqueous sodium hydroxide at 90°, into the corresponding *stibinic acids*.
F. G. WILLSON.

Mercuration of o-nitrophenol. H. H. HODGSON (J. Amer. Chem. Soc., 1927, 49, 2840—2842).—When heated with mercuric acetate for 4 hrs. at 140—150°, *o*-nitrophenol is converted into 6-*acetoxymercuri*-2-*nitrophenol*, m. p. not below 300°, which, when warmed with iodine in aqueous potassium iodide, affords 6-*iodo*-2-*nitrophenol*, m. p. 110°. The latter yields quantitatively 4 : 6-di-iodo-2-nitrophenol when treated with iodine and mercuric oxide in glacial acetic acid. Treatment of the 3-acetoxymercuri-2-nitrophenol obtained by the method of Raiziss and Proskouriakoff (A., 1922, i, 604) with iodine and potassium iodide as above yields 4-iodo-2-nitrophenol, 4 : 6-di-iodo-2-nitrophenol, and a small proportion of 6-iodo-2-nitrophenol. *Sodium* 6-*hydroxymercuri*-2-*nitrophenoxide*, scarlet, is converted by the appropriate aqueous halogen acids into 6-*fluoro*-, m. p. 187°, 6-*chloro*-, m. p. 185°, and 6-*bromo-mercuri*-2-*nitrophenol*, m. p. 177°. 4-*Fluoro*-, m. p. 195°, 4-*chloro*-, m. p. 205°, and 4-*bromo-mercuri*-2-*nitrophenol*, m. p. 236°, were prepared analogously. 6-*Iodo*-, m. p. 215°, and 4-*iodo-mercuri*-2-*nitrophenol*, m. p. above 300°, were obtained by addition of sulphuric acid to solutions of the appropriate sodium salts in presence of potassium iodide.
F. G. WILLSON.

Reaction of complex chromium salts with magnesium phenyl bromide. F. HEIN and F. PINTUS (Ber., 1927, 60, [*B*], 2388—2390; cf. A., 1927, 549).—In confirmation of previous observations (*loc. cit.*) the compounds $[CrCl_3(EtOH)_3]$, $[CrCl_3[CS(NH_2)_2]_3]$, and $[CrBr_3(C_5H_5N)_3]$, all of which contain the three halogen atoms in direct, non-ionic union with the central atom, react with magnesium phenyl bromide giving compounds regarded as salts of chromium tri-, tetra-, and penta-phenyl hydroxide.
H. WREN.

Side-chain reactions of hæmatin. Conversion of α-hæmatin into hæmatoporphyrin methyl ether, and Morner's method for preparation of hæmatin. O. SCHUMM (Z. physiol. Chem., 1927, **170**, 161—166; cf. Schumm and Mertens, A., 1927, 685).—Priority against Fischer and Lindner (A., 1927, 886) is defended.
C. HOLLINS.

Porphyratin of yeast. IV. Iron porphyratin from oats and yeast. O. SCHUMM [with E. MERTENS] (Z. physiol. Chem., 1927, **170**, 1—5; cf. A., 1926, 1277).—The iron-free porphyratin prepared from flaked oats is identical with hæmatin of animal origin; it shows the same solubilities, the same solution colour and absorption spectra; the hydrochloride, methyl and ethyl esters, and the iron and copper complex compounds all agree in properties with the corresponding hæmatin derivatives. The higher

plants are therefore able to synthesise a hæmatin having all the known properties of blood hæmatin.

C. HOLLINS.

Conversion of hæmatoporphyrin into hæmateric acid, and the "reversible" side-chain reaction of hæmatin. O. SCHUMM [with E. MERTENS] (Z. physiol. Chem., 1927, **170**, 6—12; cf. A., 1927, 685, 886).—The conversion of Nencki's hæmatoporphyrin into hæmateric acid by means of 25% hydrochloric acid (*loc. cit.*) is confirmed and the product completely identified with hæmateric acid from hæmin. The following cycle of reactions is now established: hæmatin (boiled with 1% hydrochloric acid in methyl alcohol) ⟶ tetramethylhæmatohæmatin (removal of iron by hydrazine and acetic acid) ⟶ tetramethylhæmatoporphyrin (boiled with 25% hydrochloric acid) ⟶ hæmateric acid (converted into iron complex salt) ⟶ hæmatin. The cycle of reactions is applicable also to iron porphyratins of vegetable origin, but not to phyllohæmin-β. The second and fourth phases may be omitted, tetramethylhæmatohæmatin being converted directly into hæmatin by 25% hydrochloric acid. Methyl-alcoholic hydrogen bromide or fluoride may be used for the first phase, and 5% potassium hydroxide for hydrolysis in the second phase before removal of iron. For the conversion into hæmateric acid hot glacial acetic acid with 1—10% of sulphuric acid is very suitable. Crude hæmatoporphyrin prepared by Nencki's and Sieber's processes always contains appreciable amounts of hæmateric acid, and should be fractionated with 0·1% hydrochloric acid by Willstätter's method. Hæmatin and other iron porphyratins are converted by ether containing acetic acid into yellow colouring matters, and it is therefore necessary to use carefully purified ether.

C. HOLLINS.

Behaviour of polypeptides and their derivatives towards dilute alkalis and acids. I. E. ABDERHALDEN and H. SICKEL. **II.** E. ABDERHALDEN and H. BROCKMANN. **III. Glycine polypeptides.** E. ABDERHALDEN and S. SUZUKI (Z. physiol. Chem., 1927, **170**, 134—145, 146—157, 158—160).—I. Polypeptides containing a glycine residue are much more readily hydrolysed than others by dilute alkali (*e.g.*, p_H 7·8), the ease of attack becoming greater with increasing p_H and with increasing mol. wt. *l*-Tryptophylglycylglycine is hydrolysed by erepsin at p_H 7·8 as rapidly as by *N*-alkali. Hydrolysis by dilute acids is considerably slower, but here again the presence of a glycyl residue facilitates attack.

II. Chloroacetyl-*dl*-leucine is largely hydrolysed by *N*-alkali at 37°, and the yields in reactions between amino-acids or polypeptides and acid chlorides are appreciably increased by acidifying as soon as the reaction is over. Diglycylglycine is attacked by aqueous ammonia at 37°, and ammations should therefore be performed at lower temperatures. In equal times *N*-alkali liberates more amino-groups from *dl*-α-bromo*iso*hexoyldiglycylglycine than from diglycylglycine. Hydroxides of potassium, sodium, and lithium are equally effective in equivalent concentrations. Water hydrolyses diglycylglycine at 150° in a sealed tube. By the action of *N*-alkali on *l*-leucylglycyl-*d*-alanine either of the terminal groups may be removed; in the case of glycyl-*l*-leucylglycyl-*d*-alanine hydrolysis proceeds from one end only, the products being glycine, *l*-leucine, and glycyl-*d*-alanine.

III. Glycylglycine, diglycylglycine, and triglycylglycine are quantitatively hydrolysed both by *N*- and by 0·5*N*-alkali, more quickly at 37° than at 17°, the rates of hydrolysis increasing with increasing mol. wt. The action of *N*-hydrochloric acid is small.

C. HOLLINS.

Gelatin. IX. Scission of gelatin into constituent proteins. S. B. SCHRYVER and K. V. THIMANN (Biochem. J., 1927, **21**, 1284—1301).—Electrolysis of the hydrochloride of purified gelatin yields a gel with very little nitrogen in the supernatant fluid whilst in the electrolysis of the sodium salt two fractions are obtained, an insoluble fraction (insoluble ana-gelatin) and a soluble fraction (soluble ana-gelatin). The former is soluble in water to the extent of about 15 parts in 100,000 at 15°. The mol. wt. of soluble ana-gelatin is 50,000—60,000. The diamino-nitrogen value of the hydrolysed insoluble fraction is higher than that of the insoluble one. It is not possible to resynthesise a gel by combining the soluble and insoluble ana-gelatins owing to an intramolecular change produced in the process of electrolysis. The irreversible change produced in purified gelatin by heating with water is not accompanied by peptide scission. The name "meta-gelatin" is suggested for the products thus formed. Insoluble gelatin cannot be dispersed in water without undergoing a slight irreversible change and conversion into a soluble form.

S. S. ZILVA.

Gelatin. X. Effect of previous treatment with acid and alkali on the diamino-nitrogen fraction of the hydrolysis products of gelatin. B. THORNLEY (Biochem. J., 1927, **21**, 1302—1304).—The value of this fraction increases with increase of strength of the acid with which the gelatin has been previously treated and decreases again when the acid is stronger than 2·3*N*. With heated gelatin this is not observed. Previous treatment with alkali also increases the diamino-nitrogen fraction. Preparatory treatment with pepsin or trypsin also affects the Hausmann numbers.

S. S. ZILVA.

Combination of proteins with phthalein dyes. L. F. HEWITT (Biochem. J., 1927, **21**, 1305—1313).—Phthalein and fluorescein dyes which change colour on the acid side of the isolectric point of proteins are not discharged or altered as usual on acidification, in the presence of such proteins. This is not due to physical adsorption, but to the chemical combination of the protein with the dye possessing a quinonoid structure and the consequent formation of a coloured oxonium salt. The addition of acid to a mixture of a phthalein or fluorescein dye and a protein solution produces a precipitate at the isoelectric point of the protein which dissolves at about p_H 2·5. The "protein error" of indicators, acid-fast staining of tissue sections, and acid-fast staining of fabrics are discussed.

S. S. ZILVA.

Preparation of an arginine peptide from clupeine. A. KOSSEL and E. STAUDT (Z. physiol.

Chem., 1927, **170**, 91—105).—Prolonged hydrolysis of clupeine with 70% (vol.) sulphuric acid at 37° yields an arginylarginine, readily isolated by means of flavianic acid. The oil has $[\alpha_D]_N$ +29·80° (cf. arginine carbonate, $[\alpha_D]_N$ +40·49°), shows feebly but definitely the Abderhalden picric acid reaction characteristic of diketopiperazines and the biuret reaction, and is hydrolysed quantitatively to arginine by 25% sulphuric acid at 140° in 24 hrs. It thus differs from Fischer's product from arginine methyl ester (Fischer and Suzuki, A., 1906, i, 73; cf. Edlbacher and Bonem, A., 1925, i, 863), which is extremely resistant to hydrolysis, gives no biuret reaction, and a strong picric acid reaction. The action of 70% (vol.) sulphuric acid shows some analogy with the action of trypsin (Kossel and Mathews, A., 1898, i, 612), the protone stage being passed and the products being peptides and free amino-acids. C. HOLLINS.

Elementary organic analysis for carbon and hydrogen without the use of catalysts. I. MAREK (Arh. Hemiju, 1927, **1**, 188—194).—An apparatus for the determination of carbon and hydrogen in organic substances is described, in which combustion takes place in a current of pure oxygen. R. TRUSZKOWSKI.

Determination of sulphur in organic substances. I. MAREK (Arh. Hemiju, 1927, **1**, 194—199).—Sulphur is determined by the combustion of organic substances in a current of moist oxygen and absorption of the acid gases produced in 2% hydrogen peroxide. Sulphuric acid is then determined gravimetrically or volumetrically. R. TRUSZKOWSKI.

Stepanov's method for determining halogens in the benzene nucleus. G. FAVREL and BUCHER (Ann. Chim. anal., 1927, [ii], **9**, 321—324).—A modification of the procedure of Stepanov (A., 1907, ii, 50) for the determination of halogeno-benzene derivatives is described. C. W. GIBBY.

Gas-volumetric determination of SO_2H in organic sulphinic acids. S. KRISHNA and B. DAS (J. Indian Chem. Soc., 1927, **4**, 367—374).—Sulphinic acids react with potassium iodide and iodate as follows, $6R{\cdot}SO_2H+5KI+KIO_3=6R{\cdot}SO_2K+3I_2+3H_2O$. In 19 cases studied there was no elimination of the sulphinic acid grouping, as is the case with sulphonic acids. The details of the method are: to an ice-cold solution of the acid (0·2 g.) in water (40 c.c.) a cold solution of potassium iodide (2 g.) and potassium iodate (0·2 g.) is added gradually. The mixture is warmed to 18—20°, treated with hydrogen peroxide and potassium hydroxide solution, and the evolved oxygen collected and measured. The method gives trustworthy results. H. BURTON.

Analysis of nitrogenous compounds. H. MULLER (Biochem. Z., 1927, **188**, 56—64).—Applications of the author's procedure for the analysis of organic compounds which involves the determination of the nitrogen content and the "oxygen requirement" (A., 1927, 996) to the determination of carbon and hydrogen in nitrogenous substances are described, together with the appropriate procedure for the derivation of empirical molecular formulæ. E. A. LUNT.

Microchemical detection of volatile aldehydes and ketones. C. GRIEBEL and F. WEISS (Mikrochem., 1927, **5**, 146—160).—The paper deals with the identification of aldehydes and ketones such as those present in fruits and essences, by the microchemical examination of derived semicarbazones, *o*-, *m*-, or *p*-nitrophenylhydrazones, or *m*- or *p*-nitrobenzhydrazones. A. R. POWELL.

Hypobromite titration of amino-acid derivatives. C. GRANACHER and G. WOLF (Helv. Chim. Acta, 1927, **10**, 815—819).—When an aqueous solution of about 0·2 g. of (*a*) hydantoin-3-acetic acid, (*b*) α-5-methylhydantoin-3-propionic acid, (*c*) 4-ethoxy-2-methyloxazole, and (*d*) 2-phenyl-4-benzylglyoxalidoneacetic acid is treated with an excess of sodium hypobromite solution at 0° and the number of mols. of reacting hypobromite determined, it is found that in cases (*a*), (*b*), and (*d*) there is an increase in the amount of hypobromite used up to approx. 3 mols. with increase of time of reaction. The value for (*c*) remains steady at about 2 mols. of hypobromite reacted with after 1·75 min. H. BURTON.

Biochemistry.

Limitations of Warburg's theory of the role of iron in respiration. J. W. BUCHANAN (Science, 1927, **66**, 238—239).—Wide divergence between Warburg's theory and the actual facts of respiration is discussed. A. A. ELDRIDGE.

Modification of the Barcroft blood-gas apparatus. L. DRASTICH (Biochem. Z., 1927, **188**, 35—39).—A description of a modified type of Barcroft's blood-gas apparatus for the analysis of 1 c.c. of blood which is so designed that it is also suitable for use as a microrespirometer. E. A. LUNT.

Blood pigment. W. KUSTER and G. F. KOPPENHOFER (Z. physiol. Chem., 1927, **170**, 106—109).—By the alcoholysis of blood pigment at 180° there is obtained, in addition to water-soluble protein degradation products, an insoluble residue containing 4% of iron, in which probably a proline-bearing group of the globin is combined with the iron complex of hæmoglobin. C. HOLLINS.

Tryptoporphyrin. S. FRANKEL and H. PRINZ (Biochem. Z., 1927, **188**, 90—100).—A substance named *tryptoporphyrin* has been prepared by digestion of crystalline oxyhæmoglobin for 3 months with trypsin. It exhibits no absorption bands when examined spectroscopically. The following derivatives have been prepared: the *ethyl* ester and its *hydrochloride*, the *anhydride*, and *hepta-acetyltryptoporphyrin*. The formula $C_{19}H_{14}O_9N_4$ is advanced, but the presence of a small amount of iron in the compound leads to the supposition that there may be two substances present. E. A. LUNT.

Differentiation of the proteins of blood-serum. A. VILA and R. ANCELLE (Compt. rend., 1927, **185**, 1164—1167).—In the separation of proteins, useful control is afforded by determining their sulphur content, which indicates their nature. "Myxoprotein," a complex containing 1·45% of sulphur, was separated by successive flocculations with oxalic acid (thus removing the calcium which stabilises the complex) into serum-albumin (1·84—2·00% S) and serum-globulin (0·90—1·00% S). B. W. ANDERSON.

Antitrypsin of normal serum. L. UTKIN-LJUBOVZOV (Biochem. Z., 1927, **188**, 134—146).—Dog and rabbit sera were heated at 65° for 40 min. in buffered solutions of varying p_H and tested for antitryptic action on tryptic digests of caseinogen. The destruction of antitrypsin on heating at 65° for 40 min. was a maximum at p_H 5·2—4·7 for rabbit serum, 4·5 for dog serum, and 4·4—4·1 for serum-albumin solutions. This destruction optimum lies near the isoelectric point and coagulation optimum for serum-protein but is not displaced by the presence of salts with a bivalent anion, *e.g.*, sodium sulphate. Precipitation of the protein in the serum does not remove its antitryptic properties. E. A. LUNT.

Phosphorus of serum. M. MÂCHEBŒUF (Ann. Inst. Pasteur, 1927, **41**, 1036—1044).—The hypothesis is advanced that a very stable phosphoric ester is present in serum and that some of the phosphoric acid is combined with glyceric acid forming a stable compound fairly resistant to acid hydrolysis. Greenwald's claim to have isolated diphosphoglyceric acid from pig's blood is confirmed. W. ROBSON.

Changes in blood after parenteral administration of foreign proteins. T. ASAKURA (Japan. J. Med. Sci., 1927, **1**, 183—220).—After intraperitoneal administration of sterilised cow's milk or caseinogen solution to rabbits, the following changes in certain blood constituents are observed. There is an increase in the amount of non-protein nitrogen, amino-nitrogen, fibrinogen, sugar, lipase, catalase, and protease, a decrease in serum-protein and antitrypsin. Diastase, complement, and normal hæmolysin remain without definite change. H. D. KAY.

Is kephalin necessary for the activation of prothrombin? C. A. MILLS (Chinese J. Physiol., 1927, **1**, 435—438).—Experimental evidence is cited in agreement with Bordet (Ann. Inst. Pasteur, 1920, **34**, 561) that calcium and kephalin, together with prothrombin, are the necessary precursors to the formation of thrombin. E. A. LUNT.

Origin of indican in fœtal blood. K. SHIBAYAMA (Japanese J. Med. Sci., 1927, **1**, 111—117).—The blood of the fœtus contains more indican than that of the mother. The concentration of indican and of amino-acids in the blood of the fœtus, retroplacental hæmatoma, and cubital vein decreases in the order named, and it would appear that indican is produced in the organism both in intestinal putrefraction and in metabolic processes. *B. coli* appear in the fæces of the newly born 12—24 hrs. after birth.

P. W. CLUTTERBUCK.

Action of low temperatures on the crystalline lens. G. BERGAMI (Atti R. Accad. Lincei, 1927, [vi], 6, 117—121).—At low temperatures, the crystalline lens of the sheep or ox behaves similarly to dialysed blood-serum, undergoing a partial and reversible coagulation and becoming opaque in the central portion. Similar opacity, probably due to dehydration of the lenticular colloids, is produced by hypertonic Ringer's solution, subsequent immersion of the lens in hypotonic Ringer's solution causing the disappearance of the opacity. When acting together, a low temperature and hypertonic Ringer's solution cause opacity, reversible at the ordinary temperature, even in the crystalline lens of the dog, although in this case neither of these agents alone produces the change. T. H. POPE.

Existence of reserve proteins in the mammalian liver. T. CAHN and A. BONOT (Compt. rend., 1927, **185**, 1212—1214).—In guinea-pigs, rabbits, and dogs, the nitrogen content of the proteins in the liver attains, after starvation, a more constant and distinctly higher value than normal, and at the same time the nucleic acid content is raised. These facts prove the presence in the liver of reserve proteins having a different constitution from protoplasmic proteins. B. W. ANDERSON.

Lipoids. P. A. LEVENE and K. LANDSTEINER (J. Biol. Chem., 1927, **75**, 607—612).—The "white matter" of the lipins of horse kidney was separated into pyridine-soluble and pyridine-insoluble fractions. The soluble portion was freed from pyridine, extracted with a mixture of chloroform and methyl alcohol, and the residue purified by dissolution in water and precipitation with Fehling's solution; the resulting substance was free from sulphur and phosphorus. The pyridine-insoluble part, after extraction with chloroform and methyl alcohol, was separated by glacial acetic acid into an insoluble fraction containing 2·55% of sulphur but no phosphorus and a soluble fraction containing 1·89% of phosphorus but no sulphur; the latter substance gave a purple colour with orcinol. C. R. HARINGTON.

Iodine content of thyroid in various animals. T. NOSAKA (Folia endocrinol. japon., 1926, **2**, 878—933).—The iodine content per g. of thyroid is highest in the chicken, but low in the monkey, horse, ox, dog, cat, rabbit, guinea-pig, and snake.

CHEMICAL ABSTRACTS.

Chemistry of the ovary. XIII. Water-soluble extractives of ovarian residue. F. W. HEYL and M. C. HART (J. Biol. Chem., 1927, **75**, 407—415).—Ovarian residue (4·53 kg.) was extracted with ether and then with alcohol; the latter was concentrated, giving a precipitate of *iso*leucine and sodium chloride; the filtrate, on treatment with ether, gave a further precipitate which was extracted with water, as was also the ethereal solution; the combined aqueous extracts contained total creatinine 2·63 g., carbamide 2·99 g., ammonia 1·53 g.; the solution was treated with phosphotungstic acid and the precipitated substances, after recovery from the phosphotungstates, were fractionally precipitated with silver nitrate; there was thus detected adenine, histidine, choline, and δ-aminovaleric acid; from the filtrate from the phosphotungstic acid precipitate there was obtained *d*-lactic acid. The ovarian residue was

further extracted with hot water, and the extract was cleared with tannic acid and precipitated with phosphotungstic acid; the precipitate contained creatinine, guanine, adenine, histidine, arginine, lysine, and carnosine. The filtrate was hydrolysed with sulphuric acid and again treated with phosphotungstic acid; the precipitate contained guanine, adenine, and choline, and the filtrate glycine, alanine, serine, aspartic acid, and proline. C. R. HARINGTON.

Determination of total creatinine in small amounts of tissue. W. C. ROSE, O. M. HELMER, and A. CHANUTIN (J. Biol. Chem., 1927, **75**, 543—548).—The tissue is autoclaved with $2N$-sulphuric acid for 45 min., the solution treated with sodium tungstate, made up to standard volume, and filtered; the creatinine in the filtrate is determined by the method of Folin and Wu (A., 1919, ii, 308); the error of the method is $\pm 4\%$. C. R. HARINGTON.

Use of the starch–iodine end-point in Tunnicliffe's method for the determination of glutathione in tissues. W. A. PERLZWEIG and G. DELRUE (Biochem. J., 1927, **21**, 1416—1418).—The addition of potassium iodide to trichloroacetic acid extracts of tissues permits the employment of the delicate starch–iodine end-point in the titration of glutathione by Tunnicliffe's method (A., 1925, i, 752). S. S. ZILVA.

Activities of a constructed colloidal cell. D. T. MACDOUGAL and V. MORAVEK (Protoplasma, 1927, **2**, 161—188).—Cholesterol–lecithin solutions, together with cholesterol particles with a protective layer of lecithin, have been obtained by using ether as an intermediary, and the mixture has been incorporated in hydratable gels. The properties of such cells in endosmosis, permeability, and p_H are described. CHEMICAL ABSTRACTS.

Cetacea. XXIV. Composition of the urine. T. ICHIMI, S. MORIMURA, Y. MASUMIZU, and T. YAZAWA. **XXV. Oxalic acid content of the urine.** Y. OKAHARA. **XXVI. Relationship between different kinds of whales.** K. HAYASI. **XXVII. Milk of different kinds of whales.** K. TAKEMURA. **XXVIII. Total urinary base.** Y. FURUHASHI. **XXIX. Alkali and alkaline-earth content of different horny tissues. Keratinisation.** H. HAYASHI. **XXX. Function of the liver.** Y. FURUHASHI and T. YAZAWA. **XXXI. Synovial fluid.** K. TAKEMURA. **XXXII. Urinary organic acids.** T. YAZAWA and T. SASAKI **XXXIII. Glycogen content of the liver.** Y. MASUMIZU (Japan. J. Med. Sci., 1927, **1**, 119—124, 125—126, 127—129, 131—134, 135—136, 137—149, 151—152, 153—157, 159—162, 163—164).—XXIV. The total, amino-acid-, and purine-nitrogen, the urea, ammonia, creatine, creatinine, allantoin, uric and hippuric acids, chloride, sulphate, and phosphate contents of the urine of several whales are tabulated, and the composition is shown to be similar to that of a diluted urine of a carnivorous animal.

XXV. The oxalic acid content of three samples of urine varied between 23 and 44 mg./litre.

XXVI. The results obtained by application of the precipitin reaction to the serum of a number of different kinds of whales are tabulated.

XXVII. Milk from three kinds of whales gave the following values: *d*, 1·013—1·041; f. p., −0·751° to 0·789°; solid constituents, 42·28—44·83%; total nitrogen, 1·42—1·887 g.-%; residual nitrogen, 0·152—0·18 g.%; protein (precipitated by tannic acid), 3·73—4·51%; fat, 23·76—37·38%, and sugar, 0·12—0·13%.

XXVIII. The urinary chloride, phosphate, sulphate, and total base for a number of whales are tabulated. The total base is remarkably constant for the different animals.

XXIX. Skin of whales contains much more water than whalebone, the latter being related more closely to horn. The keratin of whale skin has a similar sulphur content to that of land mammals (0·75%), whereas whalebone contains 3·6%. The horn cells of the mucous membranes contain slightly more water and less fat than those of the outer skin, whilst in all tissues protein makes up about the same percentage of the dried material. The fat content of the skin and whalebone is between 3 and 4% and of the mucous membrane of the first stomach, 2%. When the various tissues are compared in the fresh condition, whalebone has the highest ash content, but in the dry state and after removal of fat the latter has the least ash content. The assumption that hardness of horn depends on the deposition of inorganic salts is therefore not valid. In both land and sea animals the formation of hard horn corresponds with the presence of alkaline earths and sulphur-rich keratins. Although there is little difference in the various tissues in total ash content in the dried and fat-free condition, there is considerable difference in respect to the amounts of the constituents of the ash. Whereas in skin the alkalis (especially potassium) predominate, in whalebone the alkaline earths (especially calcium) are present in amounts equal to the alkalis. The alkaline-earth content of whalebone is due to the deposition, in the hardening process, of sparingly soluble calcium compounds of protein containing little water.

XXX. Whale's liver when heated with potassium dihydrogen phosphate gave a protein-free filtrate containing 0·99 g. of soluble nitrogen and 2·3 g. of sugar (after hydrolysis) per 100 g. of liver. A portion of the filtrate was freed from glycogen and then contained 1·3% of sugar. The amount of glycogen therefore by difference corresponds with 1·0% of sugar and a direct determination confirmed this.

XXXI. Synovia contained 0·008—0·013% of sugar, 0·2% of sodium, 0·004% of potassium, 0·06% of calcium, a trace of magnesium, and 0·37% of chlorine. The total nitrogen is 0·27—0·3%, and the residual nitrogen, after precipitation of protein with trichloroacetic acid, 0·089—0·104%. The protein-nitrogen by difference is 0·19%, the percentage of nitrogen in synovial protein being 13%. The weight of protein precipitated by dilute acetic acid corresponds with 1·5—1·7% of the synovial fluid.

XXXII. The total nitrogen and creatinine (in g. per litre) and the organic acids (in c.c. $0 \cdot 1N$-acid per litre) of the urine are tabulated.

XXXIII. The glycogen content of the liver of different whales varied from 3·7% to 0·36%, according as the sampling took place from 6 to 16 hrs. after death. P. W. CLUTTERBUCK.

Cetacea. XXXV. Content of ovarian follicles. K. Hayashi. **XXXVI. Bile.** M. Takata. **XXXVII. Reaction between alcoholic extracts of heart and luetic sera.** M. Matsuura. **XXXVIII. Calcium, magnesium, and phosphorus in various organs [of fin-back whale].** H. Kusakari and H. Tsutsui. **XXXIX. Ambraporphyrin, a red pigment from ambergris.** Y. Okahara (Japan J. Med. Sci., 1927, **1**, 221—234, 235—239, 241—244, 245—246, 247—266). XXXV. Fluid from medium-sized follicles (volume from 0·5 to 1 c.c.) has d^{20} 1·0395—1·0408 and p_H 6·21—6·41. It contains 91·4—92·1% of water and about 6·2% of protein, part of which is precipitated by acetic acid and part is coagulated spontaneously on keeping the original fluid. The latter part is probably not identical with blood-fibrin. The proteins in the fluid may be separated by precipitation with increasing concentrations of sodium sulphate. Of the non-protein nitrogen about two thirds is amino-nitrogen. The fluid contains 0·9% of ether-soluble material and traces of reducing substances. The inorganic constituents have been determined; the sodium content is considerably higher than that of the serum of the same animal (rorqual).

XXXVI. Like that of the majority of mammals, whale (rorqual) bile contains taurocholic and glycocholic acids. The relative quantity of the former to the latter is 6 : 4. Whale bile contains fats, soaps, sterols, and phosphatides in amounts similar to those present in human bile. Since the rorqual has no gall bladder, the secretion of bile into the intestine is probably continuous.

XXXVII. An alcoholic extract of the heart muscle of the rorqual or of *Berardius bairdii*, but not of the sperm whale, contains a substance which is capable of acting as antigen in Meinicke's reaction for diagnosis of syphilis (Münch. med. Woch., 1919, **66**, 932).

XXXVIII. Figures are given for the average total content of calcium, magnesium, and phosphorus per 100 g. of dried pancreas, spleen, liver, kidney, testicles, ovary, brain, and mammary gland.

XXXIX. The red pigment found by Suzuki (A., 1925, i, 1348) in ambergris has been purified and submitted to spectroscopic analysis. Ambraporphyrin in ethereal solution gives an absorption spectrum recalling that of coproporphyrin, although the two substances are not identical. It is, like other porphyrins, unstable, particularly in presence of light. On keeping, even in the dark, before there is any evidence of chemical change in the porphyrin, the four-banded spectrum characteristic of the pure material is changed by the appearance of a new band in the extreme red. H. D. Kay.

p_H of normal saliva. M. Henderson and J. A. P. Millet (J. Biol. Chem., 1927, **75**, 559—566).—The p_H of normal saliva varies regularly during the day, being lowest on awakening, and showing a sharp rise and fall after each meal; the average range of variation is p_H 6·7—7·3. Exertion lowers the p_H of the saliva. C. R. Harington.

Modifications in blood accompanying gastric secretion. III. Carbon dioxide. T. G. Ni and A. C. Liu (Chinese J. Physiol., 1927, **1**, 355—362).—Experiments with fistula, Pavlov-pouch, and Heidenhain-pouch dogs have shown that the prolonged loss of gastric secretion induced by repeated injections of histamine results in an increase in the carbon dioxide content of the arterial blood, the change occurring in the corpuscles as well as in the plasma. The increase in alkali reserve observed after great loss of gastric secretion is not equivalent to the loss of hydrochloric acid involved. E. A. Lunt.

Disgenetic milk. C. Gorini (Compt. rend., 1927, **185**, 970—972).—Milk which has been sterilised at high temperatures and also occasional samples of milk unsterilised and from healthy cows do not function as culture media for certain bacteria, and those introduced therein fail to live. Such "disgenetic" milk is at once made normal in this respect if small amounts of vitamins or other suitable stimulants are added to it. The occurrence of disgenetic milk may explain the discrepancies often encountered in cheese-making etc. B. W. Anderson.

Normal urinary pigment. I. Relationship to diet and metabolism. II. Relationship to basal metabolism. D. L. Drabkin (J. Biol. Chem., 1927, **75**, 443—479, 481—487).—I. Normal urinary pigment was determined colorimetrically by comparison with a standard solution of alizarin mixed with a little aniline-orange. In normal dogs on a basal diet as free as possible from pigment, the average diurnal variation in output of pigment was 4%, and the output was not appreciably affected by addition of pigments such as hæmoglobin and chlorophyll to the diet. The pigment excretion was considerably increased by starvation, by administration of acid, phloridzin, adrenaline, and thyroxine; in the normal animal it was little affected by administration of alkali, whilst it was reduced by thyroidectomy; increased output of pigment was accompanied by diuresis. Except during the period of rapid growth, the output of pigment, in various species, is proportional to the body surface area. In normal human adults, the excretion of pigment is lower in women than in men; it is increased in pregnancy and in exophthalmic goitre, and is normal in diabetes and nephritis except when there is retention of urine. In general, therefore, the urinary pigment appears to be an endogenous product, the output of which is proportional to the endogenous metabolic rate.

II. The above conclusion is supported by investigations of cases of exophthalmic goitre and of fever. C. R. Harington.

Sugar of normal urine. I. Greenwald, J. Gross, and G. McGuire (J. Biol. Chem., 1927, **75**, 491—508).—"Grape nuts," after exhaustive fermentation with yeast, yielded a non-dextrose residue which, however, gave glucosazone; the substance was apparently analogous to the mixture of lævulosan and *iso*saccharosan obtained by heating sucrose (cf. Pictet, A., 1924, i, 1045); ingestion of such substances caused small, but scarcely significant, increases in the urinary sugar; the latter was not increased by administration of dextrose, either alone or in conjunction with a mixed meal; the urinary sugar appears to consist, in part, of non-dextrose

yeast-fermentable substances; it is suggested that it may be of bacterial origin. C. R. HARINGTON.

Rapid determination of sugar in urine. T. J. F. MITSCHKE (Virginia Med. Monthly, 1927, **54**, 251—252).—Benedict's quantitative solution (5 c.c.) is titrated with undiluted urine.
CHEMICAL ABSTRACTS.

Cytolysis in cancer. II. N. WATERMAN and L. DE KROMME (Biochem. Z., 1927, **188**, 65—74).—The lytic factor present in normal serum has been isolated from the organs of the reticulo-endothelial system of the dog, and the variation in its activity with varying p_H has been determined. Its activity is changed by exposure to X-radiation. E. A. LUNT.

Glutathione content of chicken sarcoma. H. YAOI and W. NAKAHARA (Biochem. J., 1927, **21**, 1277—1278).—Polemical. The authors agree with Kennaway and Hieger (A., 1927, 789) that glutathione is present in abundance in malignant tumours. They maintain, however, that this is not true in the case of Rous sarcoma. S. S. ZILVA.

Choline and urea of cerebrospinal fluid in meningocele. H. SIEVERS (Z. Biol., 1927, **86**, 535—541).—The cerebrospinal fluid from a case of myelomeningocele has been examined for choline and for urea. No choline could be detected, although 0·00196% of urea was found. E. A. LUNT.

Storage of cerebrosides in splenomegaly (Gaucher's type). H. LIEB (Z. physiol. Chem., 1927, **170**, 60—67; cf. A., 1925, i, 189).—The identification of kerasin as the cerebroside present in alcoholic extract of spleen from cases of Gaucher's disease is confirmed. No phrenosin (cerebrone) could be detected. Confirmatory experiments of Klercker (Acta Pædiatrica, 1927, **6**, 302—351) are quoted. C. HOLLINS.

Acetone substances in the urine on carbohydrate and fat diets. N. B. DREYER (Proc. Nova Scotian Inst. Sci., 1926—1927, **17**, 26).—On a mixed diet the daily excretion of acetone substances is variable, whilst on carbohydrate diets the amount diminishes until only traces are present. Replacement of the carbohydrate diet by a fat diet results in an increase in excretion of acetone substances which is only tenfold after 24 hrs., the glycogen stores presumably acting as catalyst for the complete oxidation of fatty acids; on the fourth day, however, the increase is several hundredfold. A. WORMALL.

Relative nutritional values of fats. II. J. OZAKI (Biochem. Z., 1927, **189**, 233—241, and Proc. Imp. Acad. Tokyo, 1927, **3**, 439—444).—Further feeding experiments (cf. A., 1926, 1272; B., 1926, 930) on rats with fats containing saturated straight-chain acids show that laurin and myristin have the highest nutritional value. None of the saturated fats has the toxicity of *iso*valerin. The nutritional value of olein, linolein, and linolenin decreases with increasing unsaturation, whilst fats containing $\alpha\beta$-unsaturated fatty acids are of less value than the corresponding saturated fat. In general, fats containing straight-chain acids are better utilised than those having branched-chain acids. The lower aliphatic aldehydes are toxic or of poor, the higher aldehydes (margaric and palmitic) of considerable nutritional value. Methyl and ethyl esters of fatty acids are utilised generally better than, and soaps as well as, the corresponding glycerides. Experiments with fatty acid, fatty acid + glycerol, and glyceride (in corresponding amounts) show that, although little difference is obtained in nutritional value in the case of stearic and palmitic acids, yet there is a considerable increase in value in the order named in the case of myristic and lauric acids. Finally, it is shown that the nutritional values correspond quite clearly with the absorption coefficients of these fats and that the absorption of the fat depends, not only on its m. p., but also much more on its chemical nature.
P. W. CLUTTERBUCK.

Intermediary carbohydrate metabolism. XXII. Formation of lactic acid from malic, fumaric, and maleic acids by the liver. T. IBUKI (Biochem. Z., 1927, **188**, 164—171).—From perfusion experiments on the liver of the normal dog it is concluded that the liver does not convert the sodium salts of malic, fumaric, or maleic acid into lactic acid. E. A. LUNT.

Intermediary carbohydrate metabolism. XXIII. Lactic acid formation by the liver on perfusion with lævulose. Y. HARADA (Biochem. Z., 1927, **188**, 172—177).—Perfusion of the livers of the normal and of the depancreatised dog with solutions containing varying concentrations of either dextrose or lævulose shows that both the normal and the diabetic liver form more lactic acid from lævulose than from dextrose. The increase in lactic acid output on perfusion with lævulose in contrast with dextrose was greater in the diabetic than in the normal liver. E. A. LUNT.

Is there a relation between tonic muscular contraction and lactic acid formation? S. G. ZONDEK and F. MATAKAS (Biochem. Z., 1927, **188**, 40—55).—The increase in lactic acid content and the excitatory effect brought about by immersion of the gastrocnemius of the frog in solutions of potassium salts, quinine, chloroform, ammonium chloride, and acetylcholine have been measured as a function of the time of immersion. Acetylcholine produced no appreciable lactic acid but produced true increased tonus. The other excitants effected increased lactic acid formation, but an irreversible contraction followed by diminution in sensitivity to further stimulation. The time for immersion necessary to produce the maximum excitatory effect does not correspond with that required to produce the maximum amount of lactic acid. It is concluded that lactic acid formation bears no special relation to tonic muscular contraction.
E. A. LUNT.

Ammonia content of blood. IX. Variation of ammonia content with muscular work. J. K. PARNAS, W. MOZOLOWSKI, and W. LEWINSKI (Biochem. Z., 1927, **188**, 15—23).—The ammonia content of blood taken from the cubital vein before and after exercise of the hand and fore-arm has been determined and is shown to increase from 100% to 800%. This variation in the percentage increase is attributed to individual variations in rate of blood-stream and

distribution of capillaries as well as to variation in the duration and the vigour of the exercise. Running results in no increase in ammonia in the blood taken from the arm. E. A. LUNT.

Metabolism of tissues growing *in vitro*. II. Effect of dextrose on ammonia and urea production of kidney tissue. E. WATCHORN and B. E. HOLMES (Biochem. J., 1927, **21**, 1391—1397).—The addition of dextrose to the medium makes no difference to the occurrence of ammonia and urea production by non-growing but surviving embryonic rat-kidney tissue. On the other hand, when this tissue is growing *in vitro* the addition of dextrose inhibits the production of ammonia and urea which would otherwise take place (cf. A., 1927, 479) and frequently actually causes a reduction in the amount of these substances initially present. S. S. ZILVA.

Utilisation of nucleic acids of animal and vegetable origin. T. B. ROBERTSON, C. S. HICKS, and H. R. MARSTON (Austral. J. Exp. Biol., 1927, **4**, 125—150).—The effects of the oral administration of animal and of vegetable nucleic acids to subjects on an otherwise purine-free diet have been compared. The duration of experiment was divided into 4-day periods; during the first 4 days, a purine-free diet was administered to which were added during the second and fourth periods 15 g. daily of animal or of vegetable nucleic acid. The urine was analysed daily, and the daily phosphate content of the fæces was determined. Data are given for four complete experiments in which three different subjects were employed. The average absorption of phosphoric acid from vegetable nucleic acid is 25% in excess of the absorption of phosphoric acid from animal nucleic acid, but the average production of uric acid from vegetable nucleic acid was 100% greater than the production from animal nucleic acid. The loss of renal activity following such a large daily ingestion of nucleic acid rendered the 4-day purine-free period between the administration of the two nucleic acid periods slightly deficient. E. A. LUNT.

Basal metabolism of man on a diet rich in nucleic acid. C. S. HICKS (Austral. J. Exp. Biol., 1927, **4**, 151—154).—The basal metabolism of one subject has been determined over a period of 20 days divided into five 4-day periods, with a diet similar to that described in the preceding abstract. No alteration in basal metabolism was detected.

E. A. LUNT.

Nutritive properties of the Mung bean. V. G. HELLER (J. Biol. Chem., 1927, **75**, 435—442).—Mung beans (grown in Oklahoma) contained protein 23·31%, fat 1·02%, nitrogen-free extract 59·85%, water 9·31%, fibre 3·64%, and ash 2·87%; figures are given for the nitrogen distribution of the protein. Young rats attained maturity on diets in which the whole of the protein was supplied in the form of the beans, although growth was slightly subnormal and reproduction was not satisfactory; the beans contain considerable amounts of vitamin-*A* and -*B*, and their nutritive value is improved by moderate cooking.

C. R. HARINGTON.

Kidney changes in animals with increased blood-pressures while on high-protein diets. F. R. NUZUM (Arch. Int. Med., 1927, **40**, 364—376).—Definite kidney changes were found in animals fed on high-protein diets over a period of 2 years. No similar changes were found in animals kept under similar conditions but fed with lucerne and greens. The urines of the first group of animals were acid, contained albumin and casts, whilst the non-protein-nitrogen and urea-nitrogen contents were increased. Blood-plasma carbon dioxide was decreased and the systolic pressures were increased. The urines from the second group were excessively alkaline, whilst clinical evidences of kidney injury were also evident.

W. ROBSON.

Effect of cystine on the endogenous metabolism of moulting hens. C. W. ACKERSON and M. J. BLISH (Poultry Sci., 1926, **5**, 162—165).—Cystine exerts a protein-sparing effect entirely out of proportion to its nitrogen content.

CHEMICAL ABSTRACTS.

Availability of disulphide acids as supplementing agents in diets deficient in cystine. B. D. WESTERMAN and W. C. ROSE (J. Biol. Chem., 1927, **75**, 533—541).—Neither dithiodiglycollic nor dithiodipropionic acids could replace cystine in the diets of growing rats; the latter of these two acids was entirely without physiological effect, but the former reduced the food consumption of the rats, and, even in presence of cystine, had an inhibitory effect on their growth. C. R. HARINGTON.

Effect of creatine on growth; its distribution in tissues of normal rats. A. CHANUTIN (J. Biol. Chem., 1927, **75**, 549—557).—In normal albino rats the creatine content of the muscles is 0·449%, testes 0·281%, heart 0·174%, brain 0·129%, kidney 0·046%, and liver 0·033%. Addition of creatine to the diet had no effect on growth nor did it cause an increase in the creatine content of any organ except the liver, which is apparently concerned, therefore, in the metabolism of creatine. C. R. HARINGTON.

Zinc and normal nutrition. R. B. HUBBELL and L. B. MENDEL (J. Biol. Chem., 1927, **75**, 567—586).—Figures are given for the content of various food substances in zinc, which metal was present in all cases. Addition of 0·02 mg. of zinc, as sulphate, to a basal diet containing only 0·005 mg. of zinc had a slight stimulating effect on the growth of young mice, which was more evident in females than in males; addition of 0·04 mg. had less favourable results; no significant storage of zinc was observed. It is suggested that the nutritional value of zinc may be due, not to this metal itself, but to its relationship with other metals present in small amounts in the diet. C. R. HARINGTON.

Diurnal variation of gaseous constituents of river waters. II. R. W. BUTCHER, F. T. K. PENTELOW, and J. W. A. WOODLEY (Biochem. J., 1927, **21**, 1423—1435).—The investigation carried out in the spring (cf. A., 1927, 899) has been extended to the summer months. The oxygen curves for May, June, and August are in general similar to those obtained in March and April, although the times of the maximum and minimum values vary to a certain extent. There is a progressive shortening of the period of minimum of oxygen in the curves,

probably due to the variation of the duration of the periods of darkness at the different dates. The time of the increase from the minimum value does not appear to be influenced by the time of sunrise so much as by the meteorological conditions. The current weather conditions have a considerable effect on the times of the maximum and minimum values. The minimum oxygen values in May, June, and August are considerably lower than those of March and April, and it is possible that the larger green plants present during the summer but absent during the spring have caused a decrease in oxygen during the night owing to increased respiration. The outstanding feature in the ammoniacal nitrogen curves was the small differences obtained throughout the 24 hrs. on August 4th—5th. The p_H curves were similar in structure to those of March and April and in general follow the oxygen curves. All the temperature curves show the expected diurnal similarity but over different ranges. A detailed account is given of the vegetation on the rivers Lark and Itchen.

S. S. Zilva.

Effects of polarisation on the steel wire–nitric acid model of nerve activity. G. H. Bishop (J. Gen. Physiol., 1927, **11**, 159—174).—A steel wire rendered passive by immersion in 65% nitric acid has been further investigated, particularly with regard to the effect on it of anodic or cathodic polarisation. As in nerve, the duration of the refractory state is decreased at the anode and increased at the cathode and the duration of activity is increased at the anode and decreased at the cathode. A non-corrosive chrome–nickel steel wire is not rendered active by anodic polarisation in 65% nitric acid, but a type of irritability is observed in 20% nitric acid. Soft iron wire immersed in 65% nitric acid becomes passive only under anodic polarisation and it then exhibits properties resembling those of the passive steel wire.

W. O. Kermack.

Hypoglycæmic action of dihydroxyacetone in man. E. P. Cathcart and J. Markowitz (Biochem. J., 1927, **21**, 1419—1422).—The administration of 50 g. of dihydroxyacetone to a fasting human subject lowers the blood-sugar to about 0·04—0·08% within 40—80 min. S. S. Zilva.

Reaction of the blood-sugar to poisons. F. Bertram (Arch. exp. Path. Pharm., 1927, **126**, 267—283).—Substances influencing the blood-sugar are divided into two classes, namely, those which affect the resting carbohydrate metabolism and those which act only when the latter is abnormal. E. A. Lunt.

Relative toxicity of halogen derivatives of chaulmoogra. B. E. Read (Chinese J. Physiol., 1927, **1**, 345—354).—The saturated dihalogeno-ethyl esters of chaulmoogra have a lethal dose similar to that of the unsaturated ethyl esters. The di-iodo-ester produces albuminuria, but the dibromoethyl ester, in contrast to chaulmoogra esters, does not produce emesis, local irritation, or hypersensitivity and suggests further investigation as a therapeutic in leprosy. These halogen-substituted esters produce a large increase in the urinary neutral sulphur content and no appreciable increase in the urinary ethereal sulphate content. E. A. Lunt.

Effect of therapeutic substances on the p_H of blood. A. Feldt and R. Vara-Lopez (Biochem. Z., 1927, **188**, 112—116).—The modifications of p_H of the blood of syphilitic rabbits on intravenous injection of "salvarsan," "solganol," and "trypaflavine" have been compared with the corresponding effects of similar injections into the normal rabbit. The drugs exert a delayed action on the blood p_H, eventually lowering it in normal animals. The p_H of the blood of syphilitic rabbits is lower than that of the blood of normal animals and is raised by the administration of the above drugs. E. A. Lunt.

Hæmatoporphyrin in urine. F. G. Germuth (Amer. J. Pharm., 1927, **99**, 685—689).—The continued intake of trional leads to a greater amount of hæmatoporphyrin in the urine than the corresponding intake of sulphonal. Salkowski's technique was used for the detection and comparison of the amounts of hæmatoporphyrin present.

E. A. Lunt.

Variations in the ionic equilibrium as factors of pharmacological action. I. Potassium and convulsant drugs. L. Scremin (Atti R. Accad. Lincei, 1927, [vi], **5**, 1011—1016).—Experiments on the effects produced by intravenous injection of pyramidone or codeine hydrochloride into the rabbit show that modification of the equilibrium $Na^+K^+/Ca^{++}Mg^{++}$ by simultaneous injection of potassium chloride results in more pronounced reaction of the cells of the posterior cornu towards the drugs, the specific action of which is to increase the reflex excitability. The cause of this action of potassium ions on the cells of the posterior cornu is not known, but it may be that these ions render the cell walls more permeable and thus facilitate the entry of the drug. T. H. Pope.

Arginase. V. Occurrence of arginase in blood, and the effect of serum on its activity. S. Edlbacher, F. Krause, and K. W. Merz (Z. physiol. Chem., 1927, **170**, 68—78; cf. Edlbacher and Rothler, A., 1925, i, 1505).—Arginase is shown to occur in the erythrocytes of men, oxen, sheep, and pigs. In each case the serum greatly diminishes the activity of the enzyme. The inhibitory effect is largest in alkaline media and reaches a maximum after addition of an optimum (small) amount of serum. The inhibiting agent is not destroyed at 90°, but is completely precipitated by coagulation of the proteins. Arginase is absent from the blood of dogs and rabbits, but serum from these animals contains the inhibiting agent. On the other hand, arginase from the liver of dogs or rabbits is unaffected by serum from dogs, rabbits, oxen, or pigs. It is suggested that the inhibitory effect is due to formation of a system: inhibitor–co-adsorbent–enzyme, the co-adsorbent being absent from dog and rabbit sera.

C. Hollins.

Asymmetric action of phosphatase and the resolution of the *dl*-isomerides of racemic alcohols. C. Neuberg, J. Wagner, and K. P. Jacobsohn (Biochem. Z., 1927, **188**, 227—240).—Vegetable phosphatase hydrolyses the potassium salts of racemic monoborneolorthophosphate into the *dl*-isomerides of borneol with no appreciable decomposition

of either isomeride. The liberation of *l*-borneol occurs in a few hours, the *d*-borneol after several days. By filtration after a few hours' hydrolysis it is possible to effect a partial separation of the optical isomerides.

E. A. Lunt.

Succino-dehydrase. F. G. Fischer (Ber., 1927, **60**, [*B*], 2257—2263; cf. Thunberg, A., 1918, i, 140; ii, 87; 1920, i, 784).—The dehydrase nature of succino-dehydrase is established by the observation that the decolorisation of methylene-blue occurs parallel with the dehydrogenation of succinic acid and leads to the same products as are obtained with oxygen as acceptor. Fumaric acid, amounting to 30% of the succinic acid, and malic acid are obtained by the action of well-washed muscle in the presence of a phosphate buffer on sodium succinate solution containing an equivalent amount of methylene-blue in the absence of oxygen. The products are firmly retained on the tissue by the *leuco*methylene-blue so that their isolation can be effected only by allowing the latter substance to become re-oxidised by exposure to air and repeatedly treating the tissue with boiling water. Dehydrogenation of succinic acid by oxygen affords 25% of fumaric acid and 75% of malic acid. Under the action of fumarase the two acids form an equilibrium mixture. Muscle-tissue in the absence of oxygen converts fumaric acid into *l*-malic acid to the extent of 70% and *l*-malic acid into fumaric acid to 23%. The results obtained are apparently contradictory to those of Bach and Michlin (A., 1927, 591), but their observation that about 300 times as much oxygen is absorbed by muscle as corresponds with the amount of reduced methylene-blue is accounted for by the constant concentration of the solution of the gas throughout the experiment, whereas the concentration of the methylene-blue falls continuously, whilst also *leuco*methylene-blue is deposited on the muscle and diminishes the active surface of the enzyme. Aconitic acid does not appear to be transformed into citric acid in the presence of muscle; the conversion of oleic or elaidic acid into hydroxystearic acid is not observed.

H. Wren.

Biochemical transformation of tyrosine into pyrrole derivatives. A. Angeli (Atti R. Accad. Lincei, 1927, [vi], 6, 87—90).—Consideration of the established facts relating to the pigmentation of pyrrole and its derivatives indicates that aromatic compounds containing in their molecules the grouping (1)·O·C_6H_4·C·C·N(4) should be capable of conversion into melanins. With reference to Bloch and Schaaf's hypothesis that melanins are formed from 3 : 4-dihydroxyphenylalanine by the action of a special enzyme termed "dopa-oxidase" (A., 1926, 87), it is pointed out that 3 : 4-dihydroxyphenylalanine has not yet been found in the animal organism and that extracts of melanotic tumours do not colour tyrosine although they readily blacken pyrrole. It seems probable that, in these cases, the formation of melanin is due to a less complicated oxidation of products diffused throughout the animal organism and containing a ready-formed pyrrole group in their molecules.

T. H. Pope.

Xanthine oxidase. IX. Specificity of the system. II. H. I. Coombs (Biochem. J., 1927, **21**, 1259—1265).—3-Methyl-, 8-methyl-, 9-methyl-, 1 : 3-dimethyl-, and 3 : 8-dimethyl-xanthine, 1-methyl-, 7-methyl-, and 1 : 7-dimethyl-guanine and glyoxaline are not activated by the enzyme; 6 : 8-dihydroxypurine and 2-thioxanthine are activated. These two purines take up one atom of oxygen per molecule in the process of oxidation. The enzyme adsorbs compounds possessing the two-ring purine structure. The introduction of an amino-group strongly favours adsorption and the introduction of methyl groups especially in the glyoxaline ring tends to prevent adsorption.

S. S. Zilva.

Fixation of acetaldehyde. C. Neuberg and M. Kobel (Biochem. Z., 1927, **188**, 211—216).—Data are cited for the use of thiosemicarbazide as a fixing agent for the acetaldehyde produced in the fermentation of dextrose by yeast. The reagent is not toxic and hence does not interfere with the process of fermentation. The separation of the free aldehyde from the carbazone is effected by hydrolysis with phthalic anhydride and subsequent steam distillation, both processes being carried out at low pressure (Biochem. Z., 1902, **35**, 2049). About 9% of the theoretical amount of acetaldehyde can be isolated by this method.

E. A. Lunt.

Fermentation and phosphorylation of sugar anhydrides. A. Gottschalk (Z. physiol. Chem., 1927, **170**, 23—30).—α-Glucosan is readily fermented by top or bottom yeast, the initial velocity being greater than in the case of dextrose; Gelis' negative results (Compt. rend., 1860, **51**, 331) were due to very impure material. In the presence of dipotassium hydrogen phosphate α-glucosan is converted by dried yeast into a hexosephosphate. For both fermentation and phosphorylation the presence of co-zymase is essential. *l*-Glucosan and tetra-α-glucosan are not attacked by fresh yeast or yeast extract, and the former is not converted into a phosphoric ester by the action of dried yeast and phosphate.

C. Hollins.

Existence of cell-free fermentation. A. J. Kluyver and A. P. Struyk (Z. physiol. Chem., 1927, **170**, 110—117).—Contrary to the statement of Kostytschev and his co-workers (A., 1927, 902), fermentation by cell-free preparations does take place. Yeast-juice after passing through a Seitz filter is proved to be free from bacteria but retains its power of fermenting sterilised dextrose solution.

C. Hollins.

Occurrence of calcium citrate crystals in cultures of butyric acid-forming bacteria. Water of crystallisation of calcium citrate. W. H. Peterson, P. W. Wilson, E. McCoy, and E. B. Fred (J. Amer. Chem. Soc., 1927, **49**, 2884—2888).—Crystals of calcium citrate appear in old milk cultures and on potato slants to which calcium carbonate has been added, after fermentation by butyric acid bacteria. Their formation is hastened by changes in hydrogen-ion concentration brought about by the action of the bacteria. Practically all the water of crystallisation of calcium citrate tetrahydrate is lost at 110°, and a dihydrate could not be obtained by heating the tetrahydrate at this temperature (cf. Soldaini and Bertè, A., 1899, ii, 820).

F. G. Willson.

Autolytic power of *B. coli communis*. E. G. Young (Proc. Nova Scotian Inst. Sci., 1926—1927, 17, 79).—Sterile solutions obtained by alternately freezing and thawing emulsions of *B. coli communis* and then filtering through a Berkefeld filter have no action on dextrose in an atmosphere of nitrogen at 37° for several weeks, but effect a very slow hydrolysis of peptone as evinced by an increase in the free amino-nitrogen. A. Wormall.

Toxin and anatoxin of diphtheria. V. Koulikov and P. Smirnov (Ann. Inst. Pasteur, 1927, 41, 1166—1174).—Various amounts of hydrochloric acid have been added to solutions of diphtheria toxin and the mass and relative toxicity of the precipitates so formed have been determined. Maximum toxicity of the precipitate occurs at p_H 4·8, whilst the maximum precipitate is formed at p_H 3·8 to 4·0. The temperature of maximum stability for diphtheria toxin is 20°; precipitation at 37° results in a 66% loss of toxicity and at 0° 75% of toxicity is lost in 3—4 days. The chemical nature of substances neutralising diphtheria toxin and the mechanism of the reaction are discussed. E. A. Lunt.

Metabolism of *B. tetani*. I. H. Sievers and E. Muller (Z. Biol., 1927, 86, 527—534).—Cultures of *B. tetani* were made on a broth–peptone medium at an initial p_H of 7·2. After growth the medium became slightly acid and was found to contain *N*-methylhydantoin, acetic, propionic, and butyric acids, and *r*- and *d*-lactic acids. The origin of each of these products of metabolism is discussed. E. A. Lunt.

Effect of adrenaline on ketosis in phloridzinised and normal rats. A. B. Anderson and M. D. Anderson (Biochem. J., 1927, 21, 1398—1403).—The administration of adrenaline to phloridzinised rats on a protein–fat diet causes a very large temporary increase in the excretion of acetone substances. This is not the case with non-phloridzinised rats on the protein-fat diet or on a standard diet containing carbohydrates. Adrenaline also causes an increase in the ketosis of rats on a fat diet. The addition of sodium hydrogen carbonate to the protein–fat diet does not prevent this effect of adrenaline. It is suggested this effect may be due to a temporary intense stimulus to the oxidation of fat. S. S. Zilva.

The sulphur of insulin. V. du Vigneaud (J. Biol. Chem., 1927, 75, 393—405).—Preparations of insulin, purified by the method of Abel and Geiling (A., 1925, i, 1218) to contain 15—40 units per mg., showed a content of cystine which was roughly proportional to their physiological activity; the figures for cystine were slightly increased after acid hydrolysis of the insulin. The greater part of the sulphur of insulin, but not of its acid hydrolysis products, was eliminated as sulphide on heating with 0·1*N*-sodium carbonate; moreover, the reaction of Sullivan (A., 1926, 1266) for cystine was not given by insulin itself, but was given by the solution of its hydrolytic products; support is therefore given to the view that insulin contains cystine in peptide linking; the sulphur appears to be present as disulphide, which would involve the doubling of the empirical formula for insulin recently proposed by Abel (A., 1927, 701). C. R. Harington.

Ineffectiveness of insulin introduced into the intestine. A. Stasiak (Biochem. Z., 1927, 188, 24—34).—A slight hyperglycæmia follows the direct injection of a solution of insulin into the small intestine of the rabbit. Minced small intestine *in vitro* at 37° destroys the activity of insulin in 3 hrs. E. A. Lunt.

Effect of insulin on fat content of body and organs. S. Omura and K. Nitta (Folia endocrinol. japon., 1927, 2, 103—121).—On injection of insulin into rabbits, the fat in the heart, kidney, and skeletal muscle increases, whilst that in the liver decreases; with mice, or with the use of dextrose and insulin, there is a general increase of fat. Chemical Abstracts.

Intermediary carbohydrate metabolism. XXI. Effect of insulin on dextrose, lactic acid, and phosphoric acid formation by liver tissue. T. Brugsch and H. Horsters (Biochem. Z., 1927, 188, 147—163).—Addition of insulin to suspensions of liver cells from normal, phloridzinised, and depancreatised dogs, rabbits, and guinea-pigs in Ringer's solution with added phosphate results in an average decrease in dextrose content. This decrease is not due to oxidation, production of lactic acid, or the formation of phosphoric esters. E. A. Lunt.

Intermediary carbohydrate metabolism. XXIV. Lack of influence of insulin on the mutarotation of dextrose and lævulose. P. Radt (Biochem. Z., 1927, 188, 178—196).—The effect of insulin on the mutarotation of α- and β-dextrose and of lævulose in aqueous, potassium phosphate, and Ringer solutions has been determined at 18° for 0·1% concentration of insulin and 1% concentration of sugar. No change was observed either in the rate of mutarotation or in the final rotation. E. A. Lunt.

Stereochemical transformation of dextrose by the action of insulin and of muscular tissue. G. Quagliariello and P. De Lucia (Atti R. Accad. Lincei, 1927, [vi], 6, 113—116).—The authors are unable to confirm Lundsgaard and Holbøll's statements that the body-fluids of normal animals contain an unstable form of dextrose ("neoglucose") with a very low rotatory power and that this compound is formed *in vitro* by the simultaneous action of insulin and fresh muscular tissue on dextrose (A., 1926, 1171). T. H. Pope.

Action of insulin on glycolysis and on carbohydrate metabolism of muscle. J. Homma (Japanese J. Med. Sci., 1927, 1, 165—181).—The following phenomena have been investigated in the blood of normal and diabetic dogs and men: (*a*) the difference in sugar content between arterial and venous blood, (*b*) the rate of glycolysis. In the normal dog there is some 10% more sugar in arterial than in venous blood, a difference which is increased during short artificial hyperglycæmia. After pancreatectomy (*a*) practically disappears, whilst (*b*) is much reduced; insulin injected subcutaneously restores (*a*) to its pre-operative value and increases (*b*). Glycolysis of normal blood is not influenced by insulin *in vitro*.

In mild diabetes in man, (*a*) is quite marked, but is scarcely detectable in severe cases; (*b*) is less in severe than in mild diabetes. After insulin injection in severe diabetes, both (*a*) and (*b*) return to the normal. There is no direct relationship between the rate of glycolysis and the presence or absence of lipæmia. H. D. KAY.

Abel's pituitary tartrate. L. HOGBEN (Nature, 1927, **120**, 803—804).—Polemical.
A. A. ELDRIDGE.

Preparation of highly active pancreatic secretin solution. A. B. LUCKHARDT, O. W. BARLOW, and M. WEAVER (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1926, **76**, 182).—The first 100—150 cm. of dogs' intestine, after being washed with tap water, is partly filled with 100—150 c.c. of 0·2—0·4% hydrochloric acid and maintained at the ordinary temperature for 10 min., the extract then being filtered through cotton. CHEMICAL ABSTRACTS.

Mineral nutrition of the living cell and vitamins. Mineral nutrition and natural resistance of vegetable and animals to infectious diseases. M. P. MAZÉ (Ann. Inst. Pasteur, 1927, **41**, 948—981).—A review of the work done in this field by various workers including the author, together with his conclusions. W. ROBSON.

Effects of cod-liver oil on the calcium and phosphorus metabolism of the lactating animal. D. HARVEY (Biochem. J., 1927, **21**, 1268—1276).—The feeding of cod-liver oil to goats improves the balance of calcium by reducing the amount excreted in the fæces (the output of the latter is decreased) and in late lactation increases the percentage and total amounts of calcium in the milk. The fat content of the milk shows no definite change. The effects on phosphorus excretion, on the other hand, are variable. The iodine content of the milk is increased by the administration of either cod-liver oil or potassium iodide. The replacement of cod-liver oil by olive oil plus an equivalent amount of iodine as potassium iodide does not produce the above effects.
S. S. ZILVA.

Influence of fat-soluble vitamins and factors on total and inorganic phosphoric acid in rats' blood. H. VON EULER, T. LOVGREN, and M. RYDBOM (Z. physiol. Chem., 1927, **170**, 79—90).—It is suggested that the antirachitic vitamin is concerned in an enzyme reaction which, with phosphatides and fat-soluble phosphoric acid derivatives as starting material, determines the resorption of phosphates, the formation of bone substance, and the regulation of the equilibrium between calcium and phosphate ions in serum and in cartilage. Rats on a rachitic diet show a phosphate ion content of 8 mg. per 100 c.c. of serum, contrasted with 20 mg. on normal diet. By irradiation of cod-liver oil the activity of the growth-factor is enhanced, but no well-defined alteration of the phosphate content of the blood is produced. Strong overdosage with the antirachitic vitamin produces the same effect on the inorganic phosphate content of the serum as on the growth, *i.e.*, beyond a maximum effect at double the minimum dose, further addition of the vitamin has no marked result. Ox-blood (0·15 mg. per day for young 50 g. rats) is a completely satisfactory antirachitic addendum to the diet. C. HOLLINS.

Antirachitic activation of substances by cathode rays. A. KNUDSON (Science, 1927, **66**, 176—178; cf. Knudson and Coolidge, Proc. Soc. Exp. Biol. Med., 1927, **24**, 363).—Cholesterol acquires antirachitic potency on exposure to cathode rays for 30 sec., and the potency is not destroyed by exposure for 900 sec., but cholesterol purified by way of the dibromide cannot be rendered antirachitic either by cathode rays or by ultra-violet light. Yeast, starch, and cottonseed oil can be activated with cathode rays.
A. A. ELDRIDGE.

Attempted activation of tyrosine by ultra-violet irradiation. S. K. KON and T. MOORE (Biochem. J., 1927, **21**, 1368—1369).—McCollum's diet 3143 containing 0·5% of irradiated tyrosine does not prevent rickets. This is contrary to the statement of Waltner (Magyar Orsovi Arch., 1927, **28**, 19). S. S. ZILVA.

Effects on pigeons of an exclusive diet of rice meal, bran, and polish. R. R. WILLIAMS (Biochem. J., 1927, **21**, 1349—1351).—The above rice mill by-products, although capable of preventing avian polyneuritis when incorporated in a basal diet consisting of polished rice, are distinctly harmful to pigeons when fed as the exclusive diet. This harmful effect varies with different samples. S. S. ZILVA.

Physiological role of vitamin-*B*. V. Relation of inanition to vitamin-*B* deficiency in pigeons. G. F. MARRIAN, L. C. BAKER, J. C. DRUMMOND, and H. WOOLLARD (Biochem. J., 1927, **21**, 1336—1348).—There is a hypertrophy of the adrenal glands in pigeons that are deprived of food, with a proportionate increase of the adrenaline content in most cases whether vitamin-*B* be administered or not. A slight but definite hyperglycæmia is observed in pigeons during most of the course of inanition, and is followed by a hypoglycæmia which is coincident with the premortal fall in body temperature. This variation in the blood-sugar content is independent of the consumption of vitamin-*B*. Nervous symptoms resembling those of avian polyneuritis were observed in a number of starving birds just before death, when the body temperature and blood-sugar were much reduced. The administration of vitamin-*B* or of large volumes of water did not prevent the occurrence of these symptoms. Typical nervous symptoms of beri-beri manifest themselves in about 16 days at a time when the loss of body weight is almost negligible in pigeons forcibly fed on large quantities of a diet deficient in vitamin-*B*. In these birds, although the adrenal glands were hypertrophied, no corresponding increase in their adrenaline content was observed. Vitamin-*B* in this research designates the accessory food factors in yeast. S. S. ZILVA.

Basal metabolism in vitamin-*B* starvation. S. OKADA, E. SAKURAI, T. IBUKI, and H. KABESHIMA (Arch. Int. Med., 1924, **40**, 292—313).—Vitamin-*B* starvation in patients with beri-beri causes aggravation of the symptoms and a decrease in the basal metabolism. Administration of a vitamin-*B* preparation ameliorates the symptoms and increases the

basal metabolic rate. Prolonged vitamin-*B* insufficiency in healthy persons causes typical avitaminosis and decrease in basal metabolic rate. The identification of beri-beri with avitaminosis is discussed.

W. ROBSON.

Influence of the nature of nutritive carbohydrates on the production of acute polyneuritic conditions, recurrent or chronic, obtained in spite of the presence of yeast or yeast extracts. (MME.) L. RANDOIN and R. LECOQ (Compt. rend., 1927, **185**, 1068—1070; cf. A., 1927, 796).—Experiments on three groups of pigeons, fed on balanced artificial diets having the same percentage composition but with different carbohydrates and varying amounts of the two vitamins-*B*, showed that where galactose is the only sugar used, even with large daily doses of brewer's yeast, death occurs in 15—20 days. With other quickly-absorbed sugars, *e.g.*, dextrose, a slight deficiency in these vitamins causes prolonged recurrent polyneuritis followed by death, whilst a deficiency only in the antineuritic vitamin causes chronic polyneuritis. The importance of the nature as well as the amount of essential food constituents is thus shown. B. W. ANDERSON.

The antineuritic vitamin. I. A possible second factor. J. L. ROSEDALE (Biochem. J., 1927, 1266—1267).—Rice polishings were extracted with 1% acetic acid and the extract was precipitated with lead acetate. The fraction from the precipitate cured acute polyneuritis in pigeons; that from the filtrate enabled the birds to maintain growth, health, and natural functions. S. S. ZILVA.

Absorption spectra of oils and oil constituents with special reference to pro-vitamin-*D*. I. M. HEILBRON, E. D. KAMM, and R. A. MORTON (Biochem. J., 1927, **21**, 1279—1283).—By introducing ergosterol into transparent oil showing no selective absorption in the ultra-violet region the three bands at 293·5 μμ, 281·5 μμ, and 270 μμ characteristic of the sterol are obtained. With a 0·2% ergosterol solution the three bands are detected with certainty, whilst with lesser amounts the results are less trustworthy. Utilising this method, a number of oils and oil extracts have been examined for ergosterol and the results are tabulated. Yeast-fat showed the most pronounced absorption of all the oils examined. Groundnut oil varied from sample to sample, no selective absorption being observed in some samples. Where, however, ergosterol bands were plainly present there was also a more or less well-defined band in the neighbourhood of 320 μμ. Sections of skin of 0·1 mm. are not transparent below 297 μμ. S. S. ZILVA.

Induced fluorescence of ergosterol. O. ROSENHEIM (Biochem. J., 1927, **21**, 1335).—Specimens of ergosterol of different origin show a brilliant blue fluorescence when exposed to ultra-violet rays and screened from visible light. Pure cholesterol does not show this phenomenon. There is, however, no connexion between it and the formation of vitamin-*D*, since non-fluorescent ergosterol can be activated. The fluorescence is most probably due to the formation of traces of oxidation products. S. S. ZILVA.

Behaviour of vitamin-*A*. H. STEUDEL (Z. physiol. Chem., 1927, **170**, 13—22).—The growth-factor *A*, as found in brain, is very sensitive to heat except when dissolved with its lipoid complement in fat or other suitable medium. Plant lipins contain little or none of the growth-factor, and the same is true of plant and animal lecithins. A certain relation between growth-factors and sterols is unmistakable. "Promonta," which contains the antirachitic vitamin in considerable amount, rapidly cures experimental keratomalacia without any arrest of growth during treatment. C. HOLLINS.

Absorption of vitamin-*D* from the skin. E. M. HUME, N. S. LUCAS, and H. H. SMITH (Biochem. J., 1927, **21**, 362—367).—Vitamin-*D* in irradiated cholesterol can be absorbed from a small area of undamaged skin to supply the needs of the rat and the rabbit. Rickets was prevented in rabbits fed on a rickets-producing diet and almost normal calcification of the bones was produced, when an area of skin 2·5×3·5 cm. was irradiated for 10 min. three times a week. S. S. ZILVA.

Hydrogenation of "biosterin." Z. NAKAMIYA and K. KAWAKAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 121—142; cf. A., 1925, i, 1365). —On reduction of biosterin by Fokin and Willstatter's method, a solid substance separates, in which nonacosane, batyl alcohol, octadecyl palmitate, and melissyl alcohol have been detected. The greater portion of the product is, however, liquid at the ordinary temperature, and can be separated by distillation into two fractions; it is not possible to ascertain which of these corresponds with vitamin-*A*, as the activity is destroyed by the reduction.

R. CUTHILL.

Indispensable nature of zinc and boron for higher green plants. A. L. SOMMER and C. B. LIPMAN (Plant Physiol., 1926, **1**, 231—249).— Experiments with sunflowers, cotton, barley, buckwheat, castor beans, flax, and mustard grown in culture solutions indicate that for good growth the presence of zinc and boric acid (0·5 in 10^6) is necessary.

CHEMICAL ABSTRACTS.

Effect of temperature on the unequal intake of the ions of salts by plants. A. K. H. PETRIE (Austral. J. Exp. Biol., 1927, **4**, 169—186).—The effect of temperature over the range 4—30° on the absorption by isolated plant-tissue of the ions of single electrolytes has been studied. With rise of temperature the amount of cation absorbed falls and the amount of anion absorbed increases, and these alterations take place proportionally. It is suggested that the absorption of ions by plant cells is a process of base exchange in dissociated colloidal acids or their salts and that a Donnan equilibrium is set up between the colloidal anions of the protoplasm and the external medium. E. A. LUNT.

Hydrogen-ion concentration of plant tissues. III. *Helianthus annuus*. IV. Buffer of sunflower hypocotyl. S. H. MARTIN. **V. *Vicia faba*.** M. W. REA and V. SMALL (Protoplasma, 1927, **1**, 497—521, 522—536; **2**, 45—58). CHEMICAL ABSTRACTS.

Isoelectric point for plant tissue and its importance in absorption and toxicity. W. J. ROBBINS (Univ. Mo. Studies, 1926, **1**, 3—60).

CHEMICAL ABSTRACTS.

Electroendosmosis through wood membranes. A. J. STAMM (Fourth Colloid Symposium Monograph, 1926, 246—257).—A study of Sitka spruce, Alaska cedar, western red cedar, western hemlock, Douglas fir, and yellow poplar woods. The wood/water potential was 0·0136. CHEMICAL ABSTRACTS.

Photocapillary reaction of plant sap. F. HERCIK (Biochem. J., 1927, **21**, 1253—1258; cf. Publ. Fac. Sci. Univ. Masaryk, 1926, No. 74; Biologia Generalis, 1927, **3**, 83; Biol. Listy, 1927, **13**, 108).—The surface tension of the sap of the seedlings of *Sinapis alba* increases on illumination with 1356 lux. When the sap is diluted with distilled water the reverse takes place. In 80% dilution the surface tension at first decreases, then strongly increases and again decreases. In 60% dilution the first increase is smaller and on the contrary the second decrease is more intense. The 20% sap shows practically no increase, the surface tension decreasing in this case almost regularly after illumination. The 10% sap shows a surface tension decrease depicted by a smooth parabolic curve. The changes in the diluted and undiluted sap do not take place in the dark, whilst the surface tension of illuminated saps returns to its initial value in these circumstances. This photocapillary phenomenon is independent of the intensity of the light and can be observed also in the sap of the etiolated seedlings of *Pisum*, *Vicia*, or *Pharbitis*.
S. S. ZILVA.

Alkali tolerance of plants considered as a phenomenon of adaptation. J. F. BREAZEALE (Arizona Agric. Exp. Sta. Tech. Bull., 1926, **11**, 239—256).—The alkali tolerance of plants depends on the amount of alkali required to destroy the enzymes of the roots concerned with growth. Minimal amounts of calcium increase the tolerance of wheat seedlings for sodium chloride and other compounds. Calcium absorbed at one period of growth may effectively "immunise" the plant against alkali at a later period. CHEMICAL ABSTRACTS.

Nitrogen metabolism of the *Coniferæ*. K. MOTHES (Ber. deut. bot. Ges., 1927, **45**, 472—480).—The rate of degradation of protein in leaves of *Vicia faba* and in seeds of *Pinus pinea*, growing in the dark and in the light under various conditions, has been followed. The carbohydrate deficiency induced by darkness results in the decomposition of the protein reserves. It is concluded that the nitrogen metabolism of the *Coniferæ* is analogous to that of the *Gramineæ* and *Leguminosæ*, and that arginine does not take the place of asparagine in the *Coniferæ*. Suzuki's statement that the administration of ammonia as ammonium chloride solution to the pine seedlings results in a great increase in arginine formation could not be confirmed. E. A. LUNT.

Treub's hypothesis. II. L. ROSENTHALER (Biochem. Z., 1927, **190**, 168—180).—No relationship has been found between the amount of illumination and the extent of formation of hydrocyanic acid in cherry-laurel leaves. This does not support the second principle of Treub's hypothesis, which states that hydrocyanic acid is formed from carbohydrates and nitrates, for since the formation of carbohydrate is dependent on the exposure to light, the formation of hydrocyanic acid should be related to the amount of illumination. An increase in hydrocyanic acid content occurs in the young leaves of the cherry-laurel during the development of the leaf buds and this increase is related to protein formation, whilst with *Sambucus nigra*, manuring with amino-acids produces marked increases in the hydrocyanic acid of the stalk and leaves. It is suggested that hydrocyanic acid is formed in plants as a side-reaction of the nitrogen or protein metabolism, when the whole of the simple nitrogenous compounds such as amino-acids cannot be converted into more complex compounds, especially proteins. A. WORMALL.

Speed of autumnal migration of nitrogenous substances from the leaves to the stems of woody plants. R. COMBES and R. ÉCHEVIN (Compt. rend., 1927, **185**, 1060—1062).—There is little or no movement of nitrogenous substances towards the stems and roots of trees until the leaves are definitely turning yellow; during this colour change the process is extremely rapid, 70% of the nitrogen content of the leaves migrating in about 20 days. B. W. ANDERSON.

Isolation and identification of some organic nitrogenous compounds occurring in etiolated maize seedlings. S. L. JODIDI (J. Agric. Res., 1927, **34**, 649—656).—Asparagine has been shown to be present in considerable quantity in maize seedlings germinated and grown in darkness for 5—7 days. Decomposition of the proteins in the seed into amino-acids by the process of germination (A., 1926, 761) appears to be followed by gradual conversion of the latter into asparagine. The occurrence of vernine in the seedlings was also indicated.
C. T. GIMINGHAM.

Comparative plant chemistry. XVIII. *Carex flacca*, Schreb. H. SWIATKOWSKI and J. ZELLNER. **XIX. Chemistry of barks. VI.** J. ZELLNER. **XX. Latex-bearing plants. III.** E. HUPPERT, H. SWIATKOWSKI, and J. ZELLNER (Monatsh., 1927, **48**, 475—478, 479—490, 491—500).—XVIII. The constituents of the fruit of *Carex flacca*, Schreb., have been determined by the usual methods. The air-dried fruit yielded: light petroleum extract 10·28%, ether extract 2·59%, aqueous extract 7·29%, water-soluble ash 3·44%, soluble polysaccharides 1·24%, free acids (as KOH) 1·26%, pentosans 11·19%, methylpentosans 0·36%, starch 23·56%, nitrogen 2·28%, crude proteins 14·25%, total ash 5·37%, and traces of reducing sugars and tannins. The light petroleum extract yielded an oil which is almost completely hydrolysed, the resulting fatty acids, on oxidation by potassium permanganate, yielding a dihydroxystearic acid, m. p. 135°, and a tetrahydroxystearic acid, m. p. 173°; hence the original fatty acids consist mainly of oleic and linoleic acids. The ether extract yielded only a trace of an amorphous substance which gives the cholesterol reaction. The alcohol extract yielded only phlobaphens, tannins, and dextrose or invert-sugar, whilst the aqueous extract contained chlorides, sulphates, nitrates, phosphates, malates, and starch.

XIX. The following barks have been investigated by the usual methods: [with C. L. SCHERZER].—Pur-

ple willow (*Salix purpurea*, L.). The light petroleum extract on hydrolysis yielded 30% of unhydrolysable material which contained a *hydrocarbon*, m. p. 63° (C 84·53; H 14·92%), Hesse's phytosterol, a *substance*, m. p. 240°, and probably ceryl alcohol, whilst the acids separated by hydrolysis consisted of oleic, palmitic, and stearic acids. The alcohol extract (5% of the dried bark) contained phlobaphens, invert-sugar, and a trace of salicin. The aqueous extract (8% of the dried bark) yielded only amorphous products. Robinia (*Robinia pseudacacia*, L.) bark yielded: light petroleum extract 2·95%, ether extract 1·50%, alcohol extract 11·35%, aqueous extract 6·77%, free acids (as KOH) 2·85%, tannins 1·75%, soluble polysaccharides 0·72%, total nitrogen 1·87%, crude protein 11·69%, total ash 7·07%, and traces of reducing sugars. The light petroleum extract on hydrolysis yielded ceryl alcohol, a wax alcohol, m. p. 69—70°, Hesse's phytosterol which was separated into sitosterol (90%) and stigmasterol, and oleic and palmitic acids together with an acid of lower m. p., probably myristic acid. The alcohol extract contained phlobaphens, invert-sugar, and bases of the choline type, whilst the aqueous extract contained a pectin-like carbohydrate, together with phosphates, sulphates, oxalates, and tartrates.

Carob bean tree (*Ceratonia siliqua*, L.). The light petroleum extract on hydrolysis yielded a wax alcohol, m. p. 68—72°, a phytosterol, a *substance*, m. p. 260—262° (*acetyl* derivative, m. p. 164°), and palmitic, stearic, and liquid acids. The alcohol extract contained only phlobaphens, tannins, and invert-sugar.

[With W. ROMANOFSKY.]—Spindle tree (*Euonymus europæa*, L.). The bark was extracted with hot alcohol. The precipitate which separated from the solution on cooling contained dulcitol (1—1·5% of the air-dried bark), which was converted by cinnamoyl chloride and quinoline in chloroform solution into its *hexacinnamate*, m. p. 232—233°, and ceryl alcohol. The alcoholic solution was evaporated to dryness. The light petroleum extract of the residue yielded, after hydrolysis, a *hydrocarbon*, m. p. 63—65°, ceryl alcohol, a phytosterol, and palmitic and stearic acids. The alcohol extract contained invert-sugar, phlobaphens, and a tannin which on fusion with potassium hydroxide yielded an unidentified *substance*, m. p. 195—197°.

[With P. BOMBERG.]—Tree of heaven (*Alianthus glandulosus*, Desf.). The bark yielded: light petroleum extract 4·33%, ether extract 1·41%, alcohol extract 12·18%, total water-soluble matter 34·25%, soluble ash 0·86%, free acids (as KOH) 5·12%, soluble polysaccharides 0·96%, total nitrogen 0·95%, total ash 7·62%. The precipitate which separated from an alcoholic extract of the dried bark consisted essentially of ceryl palmitate and a *hydrocarbon*, m. p. 68°. The light petroleum extract of the alcohol-soluble portion yielded, after hydrolysis, ceryl alcohol (probably contaminated with a lower homologue), and palmitic and stearic acids. The alcohol extract yielded phlobaphens, tannins, invert-sugar, and a bitter principle. The aqueous extract contained polysaccharides and salts of oxalic and inorganic acids.

XX. The whole of the air-dried plant *Euphorbia Cyparissias*, L., with the exception of the root, has been examined, the latex being investigated separately. The air-dried plant yielded: light petroleum extract 5·18%, ether extract 1·49%, alcohol extract 9·12%, aqueous extract 30·64%, soluble ash 6·63%, reducing sugars 2·81%, tannins 3·55%, soluble polysaccharides 3·74%, free acids (as KOH) 1·42%, nitrogen 1·73%, total ash 11·26%. The light petroleum extract, after hydrolysis, yielded ceryl alcohol, amorphous resins, and a substance resembling euphorbone isolated from the latex (below), together with oleic acid and fatty acids of m. p. 67—75°. The ether extract, after hydrolysis, yielded ceryl alcohol, a substance, m. p. 170°, probably stigmasterol, and amorphous products. The alcohol extract yielded phlobaphens, tannins, lævulose, choline, and *euphorbine*, $C_6H_{13}O_2N$, m. p. 240°, which is saturated and has not the reactions of an amino-acid. The aqueous extract contained polysaccharides including pentosans, and salts of tartaric, malic, phosphoric, sulphuric, and traces of hydrochloric acids. The latex (containing 84% of water) from 15 kg. of air-dried plant yielded 60 g. of air-dried substance. The light petroleum extract contained caoutchouc and an alcohol-soluble portion which, after hydrolysis, yielded C-*euphorbone*, $C_{26}H_{16}O$, m. p. 106—107° [*bromine additive* compound, m. p. 155° (decomp.); *acetyl* derivative, m. p. 105°; *benzoyl* derivative, m. p. 117°], which is dextrorotatory, together with amorphous substances and traces of acids. No characteristic products were obtained from the alcoholic and aqueous extracts. The dried latex of *Euphorbia austriaca* kernels was examined. The light petroleum extract yielded caoutchouc and amorphous resins and an alcohol-soluble portion which, after hydrolysis, yielded (after removal of amorphous resins with cold methyl alcohol) A-*euphorbone*. m. p. 88—89° (*acetyl* derivative, m. p. 115—116°). The alcoholic and aqueous extracts yielded only potassium chloride and amorphous substances which could not be characterised. A comparison of the properties of the various euphorbones with those isolated by other workers indicates that *A*-euphorbone is different from *R*-euphorbone.

J. W. BAKER.

Toxic constituent of richweed or white snake-root (*Eupatorium urticæfolium*). J. F. COUCH (J. Agric. Res., 1927, **35**, 547—576).—A disease of cattle and sheep, known as "trembles," is caused by the consumption of the plant *E. urticæfolium*, and milk or milk products from poisoned animals may give rise to "milk sickness" in human beings. A chemical and pharmacological investigation of the plant has led to the isolation of the toxic constituent, *tremetol*, $C_{16}H_{22}O_3$. Tremetol has the properties of an unsaturated alcohol; it is soluble in fats and fat solvents and may be excreted in milk. It gives a characteristic cherry-red colour when a solution in light petroleum is floated on sulphuric acid. The plant also contains a resin acid, which is toxic to rabbits and guinea-pigs but does not cause trembles in sheep; a volatile oil; a crystalline sterol, m. p. 148—149°; inulin; lævulose; an organic base, and a non-toxic glucoside. The tremetol content

rapidly diminishes on drying. Sheep poisoned by the plant or by tremetol develop an acidosis and excrete acetone. C. T. GIMINGHAM.

Variation of the protein content of maize. V. H. B. ARBUCKLE and O. J. THIES, jun. (J. Elisha Mitchell Sci. Soc., 1926, **42**, 113—117; cf. A., 1926, 439).—Immature maize is low in protein. Grains from the middle of the ears are higher in protein than those from the butt or tip. Nitrates slightly increase and phosphates slightly decrease the percentage of protein. CHEMICAL ABSTRACTS.

Methyl alcohol in tobacco smoke. C. NEUBERG and B. OTTENSTEIN (Biochem. Z., 1927, **188**, 217—226).—Data are given for the amount of methyl alcohol in the smoke from various brands of cigars, cigarettes, and pipe tobacco. The greatest amount occurs in cigarette smoke. 90% of the methyl alcohol inhaled dissolves in the saliva, and 20 cigarettes (av. weight 20 g.) yield 42 mg. of methyl alcohol. E. A. LUNT.

Effect of acetate buffer mixtures, acetic acid, and sodium acetate on the protoplasm as influencing the rate of penetration of cresyl-blue into the vacuole of *Nitella*. M. IRWIN (J. Gen. Physiol., 1927, **11**, 111—121; cf. A., 1926, 647; 1927, 72).—The inhibiting effect of sodium acetate–acetic acid buffer mixtures on the rate of penetration of brilliant-cresyl-blue into the vacuole of living *Nitella* is due partly to the specific action of the sodium ion on the protoplasm and partly to the effect of the presence of acetic acid. The rate of penetration of the dye from a borate or phosphate buffer mixture of p_H 7·85 is reduced if the cells have previously been exposed to a solution of acetic acid. This is probably due to the penetration of the undissociated acetic acid into the protoplasm and its subsequent retention and dissociation there. W. O. KERMACK.

Counteraction of inhibiting effects of various substances on *Nitella*. M. IRWIN (J. Gen. Physiol., 1927, **11**, 123—139: see preceding abstract).—The rate of penetration of the dye from a borate buffer mixture at p_H 7·85 is also inhibited by previous exposure to solutions of phosphate buffer mixture, phosphoric acid, hydrochloric acid, sodium chloride, and sodium borate, but this decrease does not occur if the borate mixture contains a sufficient concentration of sodium ions or if a phosphate buffer mixture is substituted for the borate buffer mixture. The inhibiting effect may also sometimes be removed if the dye solution contains certain bivalent cations or if the cells are exposed to such ions. W. O. KERMACK.

Alleged formation of fumaric acid from pyruvic acid by *Rhizopus nigricans*. F. EHRLICH and I. BENDER (Z. physiol. Chem., 1927, **170**, 118—133; cf. Gottschalk, A., 1926, 545).—Careful repetition of Gottschalk's experiments under a variety of conditions shows that *R. nigricans* is unable to grow in a solution of pyruvic acid and mineral salts or to transform pyruvic into fumaric acid. C. HOLLINS.

Production of gluconic acid by *Penicillium luteum-purpurogenum* group I. O. E. MAY, H. T. HERRICK, C. THOM, and M. B. CHURCH (J. Biol. Chem., 1927, **75**, 417—422).—Fungi of the above group grown on media containing 10—30% of commercial dextrose produced, in 14 days, gluconic acid in amounts of 20—60% of the dextrose originally present; *barium gluconate* (+H_2O) has $[\alpha]^{20}$ +9·0°. C. R. HARINGTON.

Nitrogen nutrition of *Penicillium glaucum*. H. COUPIN (Compt. rend., 1927, **185**, 963—965).—In an otherwise suitable medium at 25°, *P. glaucum* assimilated the nitrogen necessary for its growth from proteins, amino-acids, urea, uric acid, and amygdalin, but not from alkaloids, pyrrole, aromatic amines, or cyano-compounds. Among inorganic compounds, ammonium salts and nitrates, but not nitrites, yielded their nitrogen to the fungus. B. W. ANDERSON.

Nutritive value of mushrooms (*Cantharellus cibarius*. J. BARES (Chem. Listy, 1927, **21**, 477—484; cf. A., 1927, 703).—Mushrooms contain 9·58% of dry matter, of which 12·85% is ash and 3·50% is nitrogen, present partly as digestible protein, but to a large extent as chitin. Carbohydrates are present to the extent of 32·7%, chiefly as *d*-mannitol, sorbitol, dextrose, trehalose, cellulose, and pentoses, other carbohydrates also being present. The nutritive value of mushrooms is small. R. TRUSZKOWSKI.

Influence of the soluble silicic acid content of soil on the absorption of phosphoric acid by plants. A NEMEC (Biochem. Z., 1927, **190**, 42—56). —A method is described for the colorimetric determination of silicic acid in aqueous extracts of soil, and the effects of varying the duration of extraction and the amount of water, of drying the soil, and of other factors have been determined. Soil which has been extracted repeatedly with water until the soluble silicic acid is considerably depleted gives, after being air-dried, moistened with water, and kept at the ordinary temperature for 14 days, values for soluble silicic acid which are very near the original value. The water-soluble silicic acid of the soil has a marked influence on the assimilation of phosphoric acid by plants, and with soils poor in silicic acid there is little or no absorption of phosphoric acid. A. WORMALL.

Influence of surface-active substances on wheat grains and spores of *Tilletia tritici*. A. C. WOLF (Biochem. Z., 1927, **188**, 117—133).—The effect of methyl and ethyl alcohols and certain mordants on wheat seeds and the spores of *T. tritici* has been studied. The greatest toxic action with ethyl alcohol was exerted in 40—60% solution; the presence of this surface-active substance increases the toxicity of mercuric chloride. E. A. LUNT.

Rotating dialyser. N. C. WRIGHT and W. RULE (J. Biol. Chem., 1927, **75**, 185—187).—The dialysing membrane is inserted between the mouths of two glass funnels with ground edges and the whole is mounted in an apparatus which can be rotated mechanically. C. R. HARINGTON.

Colorimeter based on the Lovibond colour system and its application to the testing of cod-liver oil and other purposes. O. ROSENHEIM with E. SCHUSTER (Biochem. J., 1927, **21**, 1329—1334).—The standard glasses are arranged in frames containing

ten each of the red, yellow, and blue units, so that they can be rapidly moved horizontally behind a window below the cell which contains the coloured solution to be matched. Details for the colorimetric determination of vitamin-*A* with arsenic chloride or antimony chloride are given. The application of this instrument for other colorimetric work such as the determination of p_H or of cystine is recommended.

S. S. Zilva.

Sucrose and potassium nitrate as plasmolysing agents. W. A. Beck (Protoplasma, 1926, **1**, 15—72).—Measurements of the osmotic value at incipient plasmolysis by sucrose solutions are trustworthy, but those using potassium nitrate are not.

Chemical Abstracts.

Micro-determination of chlorides in biological liquids and organs. E. Tschopp (Mikrochem., 1927, **5**, 161—165).—For liquids, 1 c.c. is treated with 10 c.c. of 0·02*N*-silver nitrate solution, 1 c.c. of 15% trichloroacetic acid solution (to coagulate the protein), and 1 c.c. of nitric acid (*d* 1·4) and the mixture is diluted to 25 c.c. After 30 min. the liquid is filtered through a dry paper and the excess of silver in 20 c.c. of the filtrate is titrated with 0·02*N*-potassium iodide using 1 c.c. of fuming nitric acid and 3 c.c. of starch solution as indicator. For solids, 1 g. is heated with 10 c.c. of the silver nitrate solution, 5 c.c. of nitric acid, and 2 c.c. of "perhydrol" in a micro-Kjeldahl apparatus until dissolution is complete, and, after dilution to 25 c.c., 20 c.c. of the filtrate are titrated as before.

A. R. Powell.

Colorimetric micro-determination of sodium. H. K. Barrenscheen and L. Messiner (Biochem. Z., 1927, **189**, 308—313).—Sodium is precipitated as zinc uranyl sodium acetate (cf. Kolthoff, A., 1927, 436) and determined colorimetrically after conversion into the ferrocyanide. The method is successfully applied to biological material (*e.g.*, serum) by employing the filtrate after treatment with alcoholic zinc acetate to remove protein and phosphate; other cations, *e.g.*, potassium, calcium, magnesium, and ammonium, in their usual concentrations, do not interfere with the determination. The maximal error of determination is + 1·5%.

P. W. Clutterbuck.

Micro-determination of magnesium in biological liquids and organs. E. Tschopp (Helv. Chim. Acta, 1927, **10**, 843—846).—The method depends on the fact that phosphomolybdic acid is readily reduced to molybdenum-blue. After removal of calcium, magnesium is precipitated as magnesium ammonium phosphate. The washed precipitate is dissolved in dilute sulphuric acid and molybdic acid added. Reduction to molybdenum-blue is effected by means of a solution containing "eikonogen," sodium hydrogen sulphite, and sodium sulphite. The resulting colour is compared with that given by a standard solution of phosphoric acid.

J. S. Carter.

Determination of minimal amounts of manganese, copper, and iron in biological investigations. A. Quartaroli (Annali Chim. Appl., 1927, **17**, 361—375).—Copper or manganese in small proportion (as little as 1 : 10,000,000) may be determined by taking advantage of the catalytic action of the metal on hydrogen peroxide. The influence of 1 part of iron in 2000 parts of solution is negligible, and the other elements, occurring in organisms, such as alkali and alkaline-earth metals, are without effect. From 4 to 8 drops of ammonia solution (*d* 0·95) are added to 20 c.c. of the almost neutral liquid, which is kept at 20°, and then about 0·5 g. of powdered glass and 2 c.c. of hydrogen peroxide solution of such concentration that its complete decomposition furnishes about 20 c.c. of oxygen. At intervals of 5 min. from the addition of the peroxide the liquid is shaken vigorously and the volume of the gas evolved read; only when evolution is very slow need these readings be prolonged to 25 or 30 min.

When copper alone is present, 8 drops of the ammonia solution are used. The reaction may be disturbed by the presence of iron, which tends slightly to diminish the action of copper; manganese, which has a slightly lower catalytic effect than copper, and phosphates, especially of magnesium, which may be precipitated on addition of ammonia. With manganese alone, either 4 or 8 drops of the ammonia solution may be used.

This reaction may be employed for the determination of both copper and manganese in presence of only small proportions of iron, and for the determination of iron, manganese, and copper in presence of phosphates, magnesium salts, etc. The procedure is described in each case.

T. H. Pope.

Determination of oxalic acid as urea oxalate in the fluids of the organism. J. Khouri (Bull. Soc. Chim. biol., 1927, 9, 961—969; cf. A., 1923, ii, 795).—A reply to Guillaumin (A., 1927, 475). The method of the author for the determination of oxalic acid is considered to give satisfactory results.

W. O. Kermack.

Determination of free and combined benzoic acid by means of the rocking extraction method. E. M. P. Widmark (Biochem. Z., 1926, **179**, 263—271).—For the determination of free benzoic acid in urine, 40 c.c. of the latter are acidified with 5 c.c. or more of 5*N*-sulphuric acid and rocked in a specially devised glass vessel in contact with 325 c.c. of toluene; the benzoic acid, which passes into the toluene layer, is removed from the latter by 30 c.c. of 0·065*N*-sodium hydroxide in another part of the vessel, which is so constructed that the acid urine and alkali never come into contact with one another. The benzoic acid absorbed by the alkali is determined by titration, suitable allowance being made for the carbon dioxide absorbed from the urine and for the small amount of acid formed from the toluene. The total benzoic acid is determined in a similar manner, the urine (40 c.c.) being first subjected to alkaline hydrolysis (10 c.c. of 6*N*-sodium hydroxide) for 7 hrs. on a boiling water-bath; 10 c.c. of 7*N*-sulphuric acid are then added, and the determination is carried out as before. The method is suitable for determining the daily excretion of benzoic and hippuric acids in small animals such as rats.

J. Pryde.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1928.

General, Physical, and Inorganic Chemistry.

General features of disruptive discharge for obtaining instantaneous spectrograms. H. NAGAOKA, D. NUKIYAMA, and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, 3, 499—502; cf. A., 1927, 1117).—Photographs of the disruptive discharge between metallic electrodes placed in contact show clouds of vapour round the electrodes. The tracks of luminous particles radiate outwards and terminate in dots, the loss in continuity being due to oxidation. Forking is often observed in the tracks, indicating that the particles break up into smaller units. Instantaneous spectrograms show that most lines appear at the first moment as emission, reversal increasing later on, since the vaporisation process is not completed at once. Photographs and spectrograms have been obtained which yield information as to the state of the vapour. Emission depends to some extent on the phase of the electric oscillations; most lines, however, appear at the maximum of the field. Multiple emission of some lines occurs during a half oscillation. R. A. MORTON.

Light excitation [of metallic spectra] by means of the metastable state in atoms of noble gases. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 207—213).—Under certain conditions in a discharge tube, atoms of the rare gases exist in a metastable condition for a relatively long period (10^{-2} sec.). By means of collisions, they can give up energy corresponding with the following voltages: helium 19·72., neon 16·6, argon 11·5. When the discharge tube contains a small proportion of foreign atoms, liberated by heat or electrical sputtering from aluminium, magnesium, zinc, or cadmium, the spectra of these metals are excited by collisions between atoms of metal and metastable rare gas atoms. In the negative glow, neutral atoms are excited, and a considerable number of simple, positively-charged ions of the metallic foreign substance also make their appearance spectroscopically manifest; thus, in addition to arc lines, all the terms of the first spark spectrum are excited provided that they exceed T, where $T-T_0 - E$, T_0^+ being the deepest term of the first spark spectrum of the metal and E the excitation voltage of the rare gas. In the positive glow, more neutral atoms are excited than in the negative glow. In a side tube, branching from near the positive column, it was possible to detect metastable neon atoms (by absorption of the 6402 Å. neon line) at a distance of 2 cm. from the positive light. In this region of the tube, neutral atoms of metal vapour alone undergo excitation. Only such terms in the first spark spectrum as are greater than T' make their appearance, T' being defined by $T'-T_0+T_0^+-E$, T_0 being the fundamental term of the arc spectrum. Excitation therefore seems to be due to collisions, and the emission is much more intense than in experiments using electronic impacts. The interpretation is fully substantiated by the experimental data. R. A. MORTON.

Electrodeless ring discharge in hydrogen. G. HERZBERG (Ann. Physik, 1927, [iv], 84, 553—564).—The discharge produced by placing a bulb containing hydrogen inside a solenoid carrying damped wave-trains of unspecified voltage and frequency has been examined spectroscopically. In the pressure range 0·05—26 mm., three types of bright luminous rings are observed. When the containing bulb is of quartz, a persistent fluorescence is induced in the walls of the bulb by the discharge, which is found to emit, in addition to the hydrogen spectrum, the silicon lines 4131/28 and 3906 Å. R. W. LUNT.

Spectrum of electrodeless ring discharge in hydrogen. G. HERZBERG (Ann. Physik, 1927, [iv], 84, 565—604; cf. preceding abstract).—The spectroscopic data obtained are reviewed at great length. The inner blue ring emits 23 terms of a very pure Balmer series; by reducing the catalytic effect of the walls of the containing vessel the first 18 terms can be obtained without a trace of fine structure. The purity of the Balmer series so obtained has enabled a direct determination to be made of the series limit. The relative intensities of the lines H_α, H_β, H_γ, H_δ, H_ϵ have been found to be 1·00, 0·95, 0·40, 0·14, and 0·15 respectively. R. W. LUNT.

Fine structure of Balmer lines. G. HANSEN (Ann. Physik, 1927, [iv], 84, 688).—Statements criticising Hilger's Lummer–Gehrcke plates appearing in a communication of the author (*ibid.*, 1925, 78, 558) are withdrawn. R. W. LUNT.

Spectrum of carbon arcs in air at high current densities. J. W. RYDE (Proc. Roy. Soc., 1927, A, 117, 164—182).—The degree of excitation provided by carbon arcs cored with metallic salts at high current densities is found to be intermediate between the ordinary arc, in which only the C I line 2478 Å. appears with any intensity, and Merton and Johnson's discharge tubes (cf. A., 1925, ii, 723), in which the two C II doublets at about 3920 and 2837 Å. appear strongly. If the current through such a cored carbon arc is increased, a bright central core develops in the arc stream soon after the limiting current density for ordinary arcs is exceeded. In this core are developed

the spectra of C I, N I, O I, together with the Balmer series and the strongest lines of the red spectrum of argon. Several marked differences in the relative intensities of the C I and N I lines are found compared with those obtained by the discharge tube methods. In addition to the N I line spectrum, the first negative nitrogen bands also appear in the arc stream. Fifty-three new lines have been found, and are attributed to C I, N I, and O I. Five of these complete the N I quadruplet system multiplet $4P-P'$, and two others belong to the $5^1P-P'$ multiplet. Many of the N I and O I lines show considerable broadening and large displacements to the red, amounting in some cases to more than 2 Å. These effects are correlated with the series classifications. The Swan bands are strongly excited close to and inside the positive carbon, but do not appear at all in the arc stream under normal conditions. They show up faintly when a jet of hydrogen is directed on the arc, and very brilliantly when the hydrogen is replaced by coal gas. No lines were observed which could be attributed to helium, even when the arc was run at 250 amp., contrary to the report by Bell and Bassett (Science, 1922, **56**, 512). The seven lines they attributed to helium are really some of the stronger C I, N I, and O I lines, together with the unidentified pair at 4392 and 4385 Å.

L. L. Bircumshaw.

Infra-red radiation of nitrogen. A. H. Poetker (Physical Rev., 1927, [ii], **30**, 812—824).—The first positive group of nitrogen bands has been extended to the region of $1{\cdot}5\,\mu$. The broad radiation maxima corresponding with the 0, +1, and +2 sequences have been analysed into individual bands. The wave-lengths, wave-numbers, and intensities of the principal infra-red lines of the nitrogen spectrum in the ranges 8936·60—7531·06 and 10498·4—8941·7 Å. are tabulated. Birge's assignment of vibration quantum numbers is modified. The oxygen triplet at 9265 Å. has been resolved, the wave-lengths being 9265·67, 9262·61, 9260·31 Å.

A. A. Eldridge.

Density necessary to produce the nebulium spectrum. C. T. Elvey (Nature, 1928, **121**, 12).—It is not known whether a nebular spectrum can be produced when the density of a mixture of oxygen and nitrogen becomes sufficiently low; from astrophysical observations, however, and certain assumptions, it is computed that the mean density at which the nebular spectrum appears is $1{\cdot}8\times10^{17}$ g./c.c.

A. A. Eldridge.

Spectrum of doubly-ionised oxygen (O III). A. Fowler (Proc. Roy. Soc., 1928, **A**, **117**, 317—330).—The spectrum of doubly-ionised oxygen, obtained by using suitably strong discharges in vacuum tubes, has been examined in the region extending from the red to 2228 Å. in the ultra-violet. The lines were distinguished from those of O II by the method of comparing the intensities of the lines under the action of different discharges. More than 300 lines are catalogued, of which about one half have been classified by the author and others. The assigned term values are based on a sequence of three singlet D terms, the deepest term being of the type $^3P_0$. By adopting Bowen's suggestion that the two well-known green lines in the spectra of gaseous nebulæ may represent the irregular combinations $2p^3P_2-2p^1D_2$, $2p^3P_1-2p^1D_2$ of O III (A., 1927, 997), the value 444,661 is obtained for the deepest term $2p^3P_0$. The corresponding ionisation potential of O III is 54·88 volts. The spectrum, as was to be expected, is in general similar to that of N II, and the terms so far determined are in full accordance with Hund's theory. A modified, and more generally applicable, system of notation is suggested.

L. L. Bircumshaw.

Spectrum of fluorine (F I). II. H. Dingle (Proc. Roy. Soc., 1928, **A**, **117**, 407—416; cf. A., 1927, 1).—The previous observations have now been extended farther into the infra-red, and a number of new lines observed. The wave-lengths of 16 lines in the region 7600—8400 Å. have been measured. The additional data have enabled the spectrum to be analysed more thoroughly than was previously possible, and a more complete correlation has been established with the terms to be expected on the Heisenberg–Hund theory. It is shown that de Bruin's scheme (A., 1927, 490) cannot be accepted. The observations of Bowen in the extreme ultra-violet (A., 1927, 285) have led to a slight modification of the analysis previously proposed, the interval 250, proposed by de Bruin for a ^4P term, being adopted as a ^2D interval, and the ^2P term with a separation of 533 being rejected. An ionisation potential of approximately 18·6 volts is indicated. Relative term-values of F I, based on the two metastable states of the core, have been deduced.

L. L. Bircumshaw.

Reversal of neon lines excited at radio-frequency. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1927, **3**, 496—498).—The reversal of neon lines has already been studied for light excited at 50 cycles (A., 1927, 705), and experiments have now been carried out at 10^6 cycles. The length of the luminous column in the capillary tube was capable of ready adjustment, and it was found that the reversal varied in different parts of the tube. In one position the amount of reversal was the same at 50 cycles as at 10^6 cycles, whilst in another position the amount was much smaller at high cycles. The results may depend on the occurrence of metastable neon.

R. A. Morton.

Spectra of phosphorus for different degrees of ionisation. G. Dejardin (Compt. rend., 1927, **185**, 1453—1454).—The variations observed with an electrodeless discharge have enabled the spectra characteristic of different degrees of ionisation of the phosphorus atom to be separated (cf. Millikan and Bowen, A., 1925, ii, 610; Saltmarsh, *ibid.*, 724). The presence of new rays in the ultra-violet region below 2700 Å. is recorded.

J. Grant.

Spark spectra of chlorine. L. Bloch and E. Bloch (Ann. Physique, 1927, [x], **8**, 397—423).—Using an electrodeless discharge tube containing sodium chloride, a large number of chlorine lines have been photographed and classified in accordance with methods already applied to the arc and spark spectra of bromine (A., 1927, 802). The oscillatory discharge allows the lines to be classified as belonging to Cl II and Cl III. Arc lines Cl I corresponding with the spectrum of the neutral atom are observed only very

feebly, if at all, in the condensed discharge. No spark spectra of orders higher than the second (Cl III) are recorded in the photographs. A table is given summarising the present position with regard to the spectrum of chlorine. R. A. MORTON.

Spark spectra of chlorine and of bromine in the Schumann region. G. VAUDET (Compt. rend., 1927, **185**, 1270—1272).—The method of Bloch (A., 1926, 329) has been used to determine the spark spectra of chlorine and of bromine between 2250 and 1300 Å. Lists of rays and their intensities are given, rays common to both elements being due to impurities (cf. Turner, A., 1926, 1071). J. GRANT.

Shifts and reversals in fuse-spectra. A. C. MENZIES (Proc. Roy. Soc., 1927, A, **117**, 88—100).—An account is given of the spectra obtained when wires are suddenly short-circuited so as to carry currents of upwards of 100 amp. The material of the wire is thus vaporised, and the light from the momentary arc is photographed by the spectrograph through the metallic vapour. The method is simple and convenient. For copper, five, possibly six, new terms have been deduced, leading to the allocation of 32 new lines. All those lines which are reversed have final orbits 1^2S_1, $^2D_2$, or $^2D_3$. Lines have a tendency to shift as the current increases, and it is found that the shifted lines having high-level initial terms which are moved to the red come from initial states belonging to (core+s) configurations, whilst those shifted to the violet have initial terms belonging to (core+d) configurations. Measurements made with zinc agreed, on the whole, with those for copper. For iron, the magnitude of the shift depends on the greatness of the term and the electron configuration to which it belongs. Lines the initial terms of which have structure d^6s, s, or d^7, s, will suffer a large shift to the red in the high current arc, and it is predicted that for lines which shift to the violet, the initial terms involved will have structures d^6s, d, and d^7, d.

L. L. BIRCUMSHAW.

Arc spectrum of germanium. C. RICHTER (Naturwiss., 1927, **15**, 266).—The existence of five terms with frequency differences 557·11, 852·81, 5715·33, and 9242·38 is demonstrated.

A. A. ELDRIDGE

Spectra of gallium, germanium, and indium. R. J. LANG (Physical Rev., 1927, [ii], 30, 762—769).—The vacuum-spark spectra of gallium, germanium, and indium were photographed in the ultra-violet. The series spectra of Ga III and Ge IV, already investigated by Carroll, have been re-measured, new lines are included, and term values have been recalculated. The series spectra of Ga II, Ge III, and In II are also tabulated. A. A. ELDRIDGE.

Regularities in the spark spectrum of silver. K. MAJUMDAR (Nature, 1927, 120, 918).—The deepest $^3D_3$ term has a value of about 138,000, corresponding with an ionisation potential of about 17 volts, the consecutive differences being 1577 ($^3D_3-^3D_2$), 2999 ($^3D_2-^3D_1$), and 2306 ($^3D_1-^1D_1$).

The arc spectrum of silver is a purely doublet spectrum. The ionisation potential of Ag^+ is about 22 volts. A. A. ELDRIDGE.

Secondary electron emission from tungsten. H. E. KREFFT (Ann. Physik, 1927, [iv], **84**, 639—673).—The ratio of the number of secondary electrons emitted from a gas-free tungsten surface at temperatures up to 1480° Abs. to the number of incident electrons has been determined as a function of the energy of the incident electrons in the range 0—700 volts. The ratio shows a maximum at 15·3 volts, a minimum at 20 volts, and 18 inflexions in the range above 25 volts. These inflexions agree well with the data for critical excitation potentials for soft X-radiation given by Richardson and Chalkin.

R. W. LUNT.

Spectrum of mercury in the far ultra-violet. G. DEJARDIN (Ann. Physique, 1927, [x], 8, 424—465).—The arc and spark spectra of mercury in the region 2700—1850 Å. have been studied in detail, using as light sources an electrodeless discharge, a condensed spark between copper and mercury electrodes, a three-electrode tube, and an argon-filled quartz mercury-vapour lamp. A large number of new lines are recorded, and these, together with those already known, have been classified into four groups corresponding with different stages of excitation. The first corresponds with the arc spectrum Hg I, and the others, E_1, E_2, E_3, very probably correspond with the spark spectra Hg II, Hg III, and Hg IV. The arc spectrum obtained with the electrodeless discharge is characterised by the development of secondary triplet series and by the appearance of certain combinations forbidden by the selection principle. The variations in wave-length of certain arc lines observed in the condensed discharge are discussed. The electrodeless discharge shows a line at 2269·92±0·05 Å. which may correspond with $1S-2p_1$. The E_1 group of lines supports Carroll's schematic classification (A., 1926, 214), and the 1941·52 Å. line is regarded as the less refrangible component of the first principal doublet of Hg II. The ionisation potential of Hg^+ is 19 volts, in agreement with Carroll's value for the highest spectral term. Earlier work (A., 1924, ii, 709) on the excitation of spark lines by electronic impact is confirmed and extended to the far ultra-violet. The Hg II spectrum can be divided into two sub-groups. R. A. MORTON.

Spectroscopy of the mercury spark produced in a sustained circuit oscillating at high frequency. J. ROSSIGNOL (Compt. rend., 1927, **185**, 1273—1274).—The spectral modifications of the spark produced between an amalgamated copper electrode and a drop of mercury in an oscillating circuit sustained by a three-electrode valve have been studied in relation to variations of the frequency (wave-lengths 2·40—4300 metres). Arc spectra were normally obtained at 3 metres, but at low frequencies (84 metres) first-order spark rays appeared owing to an increase in the self-induction of the circuit. Second-order spark rays appeared at 140 metres, whilst at 200 metres spark rays of Hg^+ (2947·1 and 2916·3 Å.) were obtained. Above this, no further changes were observed. The rays 3914·4, 3027·5, 2534·8, and 2482·1 Å. were produced only at frequencies of about 10^8, and the resonance ray (2536·5 Å.) was always reversed. J. GRANT.

Post-arc conductivity and metastable states in mercury. M. L. Pool (Physical Rev., 1927, [ii], **30**, 848—863).—Post-arc conductivity, ascribed to residual positive ions and electrons, has been observed for 0·1 sec. after a mercury arc has been switched off. The critical restriking potential, previously attributed to the existence of long-lived metastable atoms, is accounted for by the distorted electrical fields which are set up as a result of electron diffusion.

A. A. Eldridge.

Quantum rotation of the mercury atom. R. G. Loyarte (Physikal. Z., 1927, **28**, 904—908).—It has been shown that a number of excitation potentials of mercury can be reproduced by adding 1·4 or multiples thereof to the voltages corresponding with known lines or terms in the arc series (cf. A., 1927, 602). Six excitation potentials discovered by Jarvis (A., 1927, 1119) appear to correspond with 1·4, 2·80, 4·20, and with voltages obtained by subtracting 1·4 or 2·8 from known potentials. It is assumed that the constant difference is to be ascribed to a quantised atomic rotation. By considering 23 lines, extending from the extreme red to the vacuum region, it is shown that all of these can be accounted for by $\Delta\nu$, $2\Delta\nu$, $4\Delta\nu$, and known arc terms to or from which $\Delta\nu$, $2\Delta\nu$, or $3\Delta\nu$ has been added or subtracted. The mean value of $\Delta\nu$, calculated from the spectroscopic data, is 11,316 cm.$^{-1}$, corresponding with 1·390 volts. It would appear that the energy corresponding with an electron jump is in part absorbed in increasing the rotational energy of the atom by one or more quanta, and in part is used up as emission of a light quantum of a certain frequency.

R. A. Morton.

Density of the vapour in the mercury arc and the relative intensities of the radiated spectral lines, with special reference to the forbidden line 2270. B. Venkatesachar (Proc. Roy. Soc., 1927, **A**, **117**, 11—29).—The effect of changing the density of the vapour in a mercury arc (other conditions of excitation being kept unaltered) on the relative and absolute intensities of the radiated lines has been studied within the pressure range 20—0·1 mm. The effect of lowering the vapour density on the series lines (including the intercombination lines) is to increase the absolute intensities of all lines below $m=5$ and to diminish those of all lines above $m=6$. A theory is developed to account for this, based on the assumption that inelastic collisions between excited atoms in lower energy levels and thermally energetic normal atoms form the chief source of the radiators of the higher members. The supply from this source to the radiators of the lower members of a series is regarded as negligible. The forbidden line 2270 behaves like the earlier members of the series lines, and increases in intensity on lowering the density of the vapour, even with current densities of the order of 3 amp. per cm.$^{-2}$ In one set of photometric measurements, the line 4916 showed the greatest intensity change on lowering the vapour density ($I_2/I_1=1{\cdot}40$), followed by the lines 5769 and 5790 ($I_2/I_1=1{\cdot}30$), whilst the smallest increase ($I_2/I_1=1{\cdot}15$) was shown by the lines 5461, 4358, and 4047. These results are consistent with the view that the dimensions of the orbits of the valency electron increase in passing from the state 2^3S_1 to the state 3^1S_0.

Using an arc with a large dead space, it was found that, on raising the pressure by the introduction of air, higher members of series lines were developed. On pumping out the air, higher members beyond $m=11$ disappeared entirely, whilst the forbidden line 2270 and the spark line 2262 became conspicuous. If the density of the vapour is reduced by cooling the arc, many of the spark lines which are excited in the mercury arc are greatly reduced in intensity, whilst others either remain unchanged or gain in intensity. To the second class belong lines the radiators of which are excited atoms in lower energy levels. It is suggested that the lines 2847·8 and 2260·4, which occur in this group, form the first pair of a subordinate series in the spectrum of Hg^+, 1942·5 and 1642·5, according to Carroll, forming the first pair of the principal series.

L. L. Bircumshaw.

Line spectrum of mercury in absorption. Occurrence of the forbidden line 2270 $1^1S_0-1^3P_2$. (Lord) Rayleigh (Proc. Roy. Soc., 1927, **A**, **117**, 294—299; cf. A., 1927, 496, 607).—An arrangement is described by means of which the forbidden mercury line 2270 can be observed as a sharp absorption line in the unexcited vapour. As a source of light, first the continuous hydrogen spectrum was used, then the continuous spectrum accompanying the cadmium spark. It is necessary to employ a high spectroscopic resolving power and the largest possible mass of mercury. The breadth of the line is estimated as roughly 0·08 Å. The breadth of the resonance line 2537 in saturated air at atmospheric pressure is several times as great as that of the forbidden line in pure mercury vapour at atmospheric pressure, and the total radiation absorbed is also several times as great. The forbidden line requires about 10^7 times as much mercury to bring it into evidence as the resonance line. No trace was found of the other forbidden line 2656, and from this it appears that, under equal energy density of incident radiation, a transition from the normal to the 1^3P_0 state has less probability than one to the 1^3P_2 state.

L. L. Bircumshaw.

Fine structure of some mercury lines. W. H. McCurdy (Proc. Nat. Acad. Sci., 1927, **13**, 701—703).—A correction of the fine structure of the lines 3650 and 2967 Å. as given by Nagaoka, Sugiura, and Mishima (A., 1924, ii, 798).

W. E. Downey.

Variation of intensity ratios of optically excited spectrum lines with the intensity of the exciting light. E. A. Baker (Nature, 1927, **120**, 917—918; cf. Wood, A., 1927, 1117).—Experiments on photographic action give results similar to those obtained by Wood for mercury vapour, and place the photographic action among the phenomena of phosphorescence.

A. A. Eldridge.

Strength of anomalous dispersion in the non-luminous vapour of thallium and cadmium. W. Kuhn (Kgl. Danske Videnskab. Selsk. math.-physik. Medd., 1926, **7**, No. 12, 3—87; Chem. Zentr., 1927, i, 2511).—An expression is given for the longitudinal magnetic double refraction for any anomalous Zeeman effect, and data for the anomalous magnetic

rotation-dispersion in non-luminous vapours are recorded as follows: thallium, 3776 Å. ($2p_2-2s$), 0·08; 2768 Å. ($2p_2-3d_2$), 0·20; cadmium, 3261 Å. ($1S_2-2p_2$), $1{\cdot}9\times10^{-3}$; 2288 Å. ($1S-2P$), 1 20. Thallium lines originating from the $2p_1$ state were also observed. Absolute f-values for these and for lines not directly observable were obtained by using the intensity rule for multiplets. A. A. Eldridge.

X-Ray K absorption in elements tungsten (74) to uranium (92), and K screening numbers. J. E. Mack and J. M. Cork (Physical Rev., 1927, [ii], **30**, 741—746).—New values are recorded for the K absorption edges of tungsten, osmium, iridium, platinum, gold, mercury, thallium, lead, bismuth, thorium, and uranium. An attempt to determine Sommerfeld's screening numbers for the K shell has led to the conclusion that Sommerfeld's "relativity correction" does not account for all the curvature of the lines in the Moseley diagram. A. A. Eldridge.

M-Series X-ray absorption spectra of osmium, iridium, and platinum. R. A. Rogers (Physical Rev., 1927, [ii], **30**, 747—754).—The absorption spectra of osmium, iridium, and platinum were investigated from 3·5 to 7 Å., and the following discontinuities (Å.) observed: osmium 6·194 (M_1), 5·975 (M_2), 5·027 (M_3), 4·412 (M_4), 4·037 (M_5); iridium 5·961 (M_1), 5·754 (M_2), 4·851 (M_3), 4·270 (M_4); platinum 5·736 (M_1), 5·541 (M_2), 4·674 (M_3), 3·738 (M_5). Values of $(\nu/R)^{\frac{1}{2}}$ are not in complete agreement with those computed by Bohr and Coster and by Sommerfeld. A. A. Eldridge.

Law of absorption of X-rays by matter. P. Villard (Compt. rend., 1927, **185**, 1415—1419).—Deviations from the law of Bragg and Peirce (A., 1914, ii, 792) have been studied in terms of the variation with λ of the constant C, where $\tau/\rho=C\lambda^3$, the ratio τ/ρ being the partial coefficient of true absorption of X-rays by matter (fluorescence), as distinct from that of simple diffusion. For wave-lengths of the order of 0·1 Å., C passes through a maximum often 40% higher than the constant value it assumes for the longer wave-lengths, and diminishes rapidly for the shorter wave-lengths. The results are explainable by atomic resonance, the exponent 3 in the Bragg and Peirce law being accepted, although the law itself refers only to limiting cases and involves a coefficient which is not constant, but is dependent on resonance phenomena. J. Grant.

Azimuthal distribution of X-rays scattered in an ideal gas. H. Mark and K. Schocken (Naturwiss., 1927, **15**, 139—140; Chem. Zentr., 1927, i, 2391—2392).—Experiments with carbon dioxide and argon show that for constant azimuth the intensities are proportional to the gas pressure. For large angles, the atom factor appears to depress the increase in the total intensity. A. A. Eldridge.

Experimental tests of theories of the absorption of X-rays. F. K. Richtmyer (Physical Rev., 1927, [ii], **30**, 755—761).—Experimental values of $R_L{}^K$, the ratio of the magnitude of the true absorption coefficient on the short wave-length side of, but infinitely near to, the K absorption discontinuity to that on the other side, accord best with Kramers' theory, whereas the absolute magnitude of the absorption discontinuity is given by de Broglie's theory. In the wave-length range $\lambda_K/2<\lambda<\lambda_K$ the absorption coefficients of tin are a linear function of λ^3. A. A. Eldridge.

Absorption of X-rays in various elements. F. K. Richtmyer (Nature, 1927, **120**, 915—916).—The experimental results referred to by Jonsson (A., 1927, 1118) appear to be in conflict with theory. If $\delta_K=E_K/E_{L_1}$, the relative numbers of K- and L-photo-electrons must be independent of the relative numbers of K- and L-electrons in the atom. A. A. Eldridge.

Zeeman effect of the symmetrical top according to wave mechanics. E. U. Condon (Physical Rev., 1927, [ii], **30**, 781—784).—Theoretical. A. A. Eldridge.

Intensities in the Stark effect of helium. II. J. M. Dewey (Physical Rev., 1927, [ii], **30**, 770—780; cf. A., 1927, 180).—The helium atom is regarded as a perturbed hydrogen-like atom, and calculations based on the quantum theory of perturbations are made of the new lines appearing in the Stark effect. The results, although of the correct order of magnitude, deviate considerably from the experimental values. The deviations may be partly due to differences in the number of atoms excited to different states of almost the same energy. A. A. Eldridge.

Application of quantum mechanics to the Stark effect in helium. J. S. Foster (Proc. Roy. Soc., 1927, **A**, **117**, 137—163).—The perturbation theory of quantum mechanics has been applied to the Stark effect in the arc spectra of helium. By means of the theory, the displacements and intensities of the lines emitted by the perturbed system can be calculated without the aid of further information regarding the nature of the inner field, apart from the term values of the unperturbed atom. The first order displacements, calculated for a number of field strengths for Stark components of the eight-line groups $2P-4Q$, $2P-5Q$, $2S-4Q$, $2S-5Q$, and the corresponding orthohelium lines (considered as singlets), are in good agreement with the observations. The ultimate disposition of the components at extremely high fields has been calculated. In very high fields the group patterns for parhelium and orthohelium are nearly identical. The theoretical intensities of the components have been calculated in fields of 10, 40, and 100 kilovolts/cm., and are in agreement with the qualitative observations. In particular, the theory accounts satisfactorily for the observed disappearance of numerous components when the displacement is equal to that of the $2P-nP$ line at zero field. New measurements are recorded of displacements of helium components in fields of 100 and 83 kilovolts/cm., and Lo Surdo photographs of the groups 4922, 4026, and 3965 Å. in high fields are reproduced for the first time. L. L. Bircumshaw.

Thermodynamics, wave-theory, and Compton effect. C. V. Raman (Nature, 1927, **120**, 950—951).—Objections to Compton's explanation of the nature of the Compton effect are summarised, and the author's views, which are being presented and developed elsewhere, are indicated. A. A. Eldridge.

Photo-electric conductivity of sulphur. B. KURRELMEYER (Physical Rev., 1927, [ii], 30, 893—910).—The current produced in sulphur by a given illumination is directly proportional to the applied field from 20 to 15,000 volts/cm. and to the intensity of illumination. No evidence of secondary current was found. On illumination of the crystal, the current reaches its full value rapidly (probably less than 10^{-4} sec.); when the illumination is removed, the current immediately falls almost to zero, a small residual current being due to the motion of positive ions. The initial value, as well as the subsequent shape, of the current–time curve depends on the previous history of the crystal. The curve showing the current per unit of incident energy as a function of the wave-length has a maximum at 470 mμ. The optical absorption curve is unusual, having a point of inflexion near 570 mμ, but asymptotic after 650 mμ. Since substances in which the primary ionisation takes place in the pure crystal material have $n>2$, and the substances having $n>2$ investigated by Gudden and Pohl possessed photoconductivity, the variation of the current in sulphur (where $n_\alpha=1·93$, $n_\beta=2·00$, and $n_\gamma=2·19$ for 768 mμ) with crystal orientation was investigated. The currents in different directions are equal in absolute magnitude, but exhibit a unipolarity along the direction of the acute bisector of the optic axes, with components along other directions. It is suggested that sulphur has a polar axis, if not crystallographically, then at least due to atomic asymmetries. A. A. ELDRIDGE.

Relation between the secondary electron emission from nickel and tungsten and temperature. H. NUKIYAMA and H. HORIKAWA (Tech. Repts. Tohoku Imp. Univ., 1927, 7, 49—56).—The secondary electron emission–temperature curve for nickel has discontinuities in the regions 350—400° and 780—890°. With tungsten, the apparent secondary electron emission remains approximately constant until temperatures at which the primary emission occurs are attained; thereafter it apparently tends to increase with temperature. The temperature relations in this region are, however, somewhat uncertain. The critical potentials of tungsten are 10, 16, 18, 26, 29, 41, 46, and 77·5 volts (cf. Petry, A., 1926, 989). J. S. CARTER.

Chemical action of electrons of moderate velocity on temper films. G. TAMMANN and G. VESZI (Z. anorg. Chem., 1927, 168, 41—45).—The chemical action of electrons having a velocity of 100—150 volts on very thin films of various metallic oxides and halides has been investigated by observation of the colour changes of the film as its thickness alters. The method is much more accurate than that of measuring the change of pressure as gas is evolved; *e.g.*, a change of thickness of 10 μμ, which is easily recognised by the change of colour, corresponds in the case of the reduction of cuprous oxide with an evolution of only 3×10^{-3} mm.^{3} of oxygen per mm.^{2} of surface. The results show that films possessing metallic conductance, *i.e.*, which are transparent to electrons, are unaltered by bombardment with electrons of moderate velocity, whereas those which conduct electrolytically are reduced to metal. H. F. GILLBE.

Diffraction of electrons by a crystal of nickel. C. DAVISSON and L. H. GERMER (Physical Rev., 1927, [ii], 30, 705—740).—A detailed account of the experimental basis of results already published (A., 1927, 492). A. A. ELDRIDGE.

Recoil electrons from aluminium. A. A. BLESS (Physical Rev., 1927, [ii], 30, 871—877).—The values obtained for ν/R (where ν is the frequency of a quantum having the same energy, and R is Rydberg's constant) for electrons ejected from aluminium by the scattering of X-rays of wave-length 0·48 and 0·712 Å., respectively, were 190 and 84·1, in agreement with Compton's, but not Wilson's theory of scattering. A. A. ELDRIDGE.

Excitation of polarised light by electron impact. II. Mercury. H. W. B. SKINNER and E. T. S. APPLEYARD (Proc. Roy. Soc., 1927, A, 117, 224—244; cf. Skinner, A., 1926, 1074).—A continuation of previous work (*loc. cit.*). The percentage polarisations of the individual spectral lines are measured by the methods of photographic photometry, the velocity of the exciting electron stream being varied from 9 to 200 volts. The lines are polarised in various ways; some are polarised positively (*i.e.*, with the electric vector parallel to the electron stream), and some negatively, whilst the lines 4078 and 4108 Å. show no appreciable polarisation. The polarised lines show a characteristic variation of the polarisation with the velocity of the electron stream, the most striking feature being a steep increase in the polarisation with increasing voltage for low velocities, and a subsequent maximum for a velocity corresponding with a few volts above the excitation point. For high velocities there is in most cases a definite reversal of the sign of polarisation. It is shown that the various polarisation effects may be interpreted to give information about the dynamics of the collision process in which an atom is excited by electron impact. L. L. BIRCUMSHAW.

Dark space in high-frequency discharges. S. SMITH (Nature, 1927, 121, 91).

Smallest carriers of electricity in gases. L. B. LOEB (Ann. Physik, 1927, [iv], 84, 689—696).—The criticisms of Schilling (A., 1927, 708) on the author's data for the mobility of ions in air are repudiated at length, and Schilling's experimental values are adversely criticised. R. W. LUNT.

Mobility of ions in gases. M. LAPORTE (Ann. Physique, 1927, [x], 8, 466—554).—In a gas, ions of the same sign exhibit either identical or different mobilities. The alternatives correspond with either a unique constitution for any ion of a given sign, or a series of ions formed from more or less complex aggregates of neutral atoms round the charged centre. Hitherto, no conclusive decision between the two alternatives has been possible. A method analogous in principle to Fizeau's method for determining the velocity of light has been adapted to the problem. The ions are drawn by an electric field across gaps inserted in parallel rotating plates. In all the gases investigated the variations in mobility exceed the experimental error. The apparatus allows the proportions of ions of different mobilities to be deter-

mined, so that distribution curves showing mobility against number of ions can be obtained. In dry air the positive ions show mobilities varying between 0·82 and 2·02, with a maximum at 1·27, whilst the negative ions vary between 1·32 and 3·30, maximum at 2·16 (cm./sec. per volt/cm.). The addition of moisture effects an acceleration of the positive ions and a retardation of the negative ions, the maxima being at 1·47 and 1·79 in air saturated with water vapour. Busse has, however, shown that in perfectly dry air both ions have a mobility of 15 (A., 1926, 1074; 1927, 4). The distribution curves for dry oxygen and nitrogen are the same for the positive ions as for air, but a discrepancy is found for the negative ions, and it is shown that the negative ions in air must be oxygen ions, a result in harmony with the great electronegative affinity of oxygen. The influence of electronic affinity is still more marked with argon, since the distribution curves for negative ions in this gas depend essentially on the degree of purity. Highly purified argon shows a large proportion of very mobile ions which are probably due to free electrons. Indeed, the saturation current in perfectly pure argon can be realised with voltages about 1/50 of those necessary in air. The chemical nature of a gas, and therefore the external electronic configuration of its atoms, is thus of fundamental importance in determining the formation of multimolecular ions.

Many theories postulate an electrostatic polarisation of neutral molecules, by which it would follow that the electrons should exhibit identical behaviour in oxygen, nitrogen, and argon. This consequence is contrary to experience. The work of Busse makes clear the importance of water vapour in the formation of complex ions; the results probably mean that the most active affinity factors are suppressed by complete desiccation. The ions are described as aggregates $M^{+}+nH_2O+pM$, in which n and p are variable and sometimes fairly high numbers.

R. A. Morton.

Absorption of potassium ions in various gases. F. M. Durbin (Physical Rev., 1927, [ii], **30**, 844—847).—The loss by scattering, retardation, or neutralisation suffered by a beam of positive potassium ions, accelerated by 8·5—350 volts, in passing through air, hydrogen, nitrogen, helium, oxygen, or argon has been measured. Curves show the effect of pressure in helium and nitrogen, and the ratio of the mean free path for absorption to its kinetic theory value as a function of the velocity of the ions; oxygen is most, and helium least, effective in weakening the rays.

A. A. Eldridge.

Magneto-chemistry of vanadium. N. Perrakis (J. Phys. Radium, 1927, [vi], 8, 473—480).—An amplification of work previously published (A., 1927, 288, 717, 805).

J. S. Carter.

Relative intensities of positive rays from the isotopes of lithium. J. L. Hundley (Physical Rev., 1927, [ii], **30**, 864—870).—Using Dempster's method of positive-ray analysis, the relative intensities of positive rays from the isotopes of lithium for lithium silicate, lithium aluminate, lithium phosphate and iron oxide, and spodumene were determined for various temperatures. The ratio Li^7/Li^6 decreases with rise of temperature; Li^6 has a greater work function than Li^7.

A. A. Eldridge.

At. wt. and packing effect. S. Meyer (Naturwiss., 1927, 15, 623—625; Chem. Zentr., 1927, ii, 1230—1231).—The atomic nuclei of elements of which the at. wts. are integral multiples of 4 are not necessarily composed of helium nuclei as such. The energy necessary for the disintegration of a helium nucleus must be greater than that available from radium-C' α-particles. Where it has been found possible to liberate protons, these must have been present in the nucleus in an isolated condition, possibly as constituents of "proton shells." The deviations from integers of the at. wts. of the first 24 elements (except aluminium) are positive, and thereafter negative; all elements with negative deviation have odd valency. The at. wts. of the isotopes of elements of even number are nearly always even.

A. A. Eldridge.

Average energy of disintegration of radium-*E*. C. D. Ellis and W. A. Wooster (Proc. Roy Soc., 1927, **A**, **117**, 109—123).—A direct experimental test has been made to decide between the alternative theories as to the mechanism of the β-ray type of disintegration. For the purpose of testing whether, in a β-ray body, every atom gives out the same energy on disintegration, the β-ray emission from radium-E has been analysed by means of a magnetic field and the intensity of the rays of various energies determined by means of an ionisation chamber. A curve is plotted, showing the distribution of energy among the disintegration electrons when they have escaped from the parent atoms, and from this it is deduced that the average energy per disintegration of the emitted particles is 400,000 volts to within 15%. The average energy of disintegration has also been determined by measuring the heating effect of the β-rays, a source of radium-E being enclosed in a calorimeter the walls of which are thick enough completely to absorb the β-radiation. The fact that the value obtained by this method, 350,000±40,000 volts, agrees with that estimated from the distribution curve proves definitely that the disintegration electrons must be emitted from the nucleus with varying energies. If the alternative hypothesis, that the energy of disintegration is a characteristic constant of the atom, were correct, then the heating experiment would have given a value close to 1,000,000 volts, *i.e.*, 2·8 times the actual experimental figure.

L. L. Bircumshaw.

Atomic groupings [of radioelements]. (Mlle.) C. Chamié (Compt. rend., 1927, **185**, 1277—1279).—Atomic groupings of radioelements (A., 1927, 605) have been obtained using a solution of polonium in ammonia, large volumes of water, and cedar-wood oil. The phenomenon is independent of the introduction of silver into mercury activated by polonium, and also of the time of exposure and water-vapour content of the emanation used in the activation of mica. Each group contains on the average 10^6—10^8 atoms of polonium, and the photographs indicate normally a star-shaped structure in which the radial lines correspond with the paths of α-particles.

J. Grant.

Elasticity of the collisions of α-particles with hydrogen nuclei. P. M. S. Blackett and E. P.

HUDSON (Proc. Roy. Soc., 1927, A, **117**, 124—130).—Collisions in which the α-particle and proton approach extremely closely to each other, making forked tracks of narrow angle, are very suitable for accurate study. Two photographs of this type have been measured with considerable accuracy, and it is found that the collisions are elastic within the limits of experimental error. The probable errors of measurement are discussed. L. L. BIRCUMSHAW.

Formation of sulphur trioxide under the action of α-particles. J. E. MAISIN (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, i, 172—177).—The oxidation of sulphur dioxide by oxygen in presence of radon has been followed manometrically. No evidence for the existence of persulphuric anhydride was obtained, sulphur trioxide being apparently the principal reaction product. The ratio of the number of molecules disappearing from the gaseous phase to the number of pairs of ions produced is about 1·5. Assuming the simple reaction $2SO_2+O_2=2SO_3$, this result indicates that each pair of ions produces one molecule of sulphur trioxide. J. S. CARTER.

Powers of retardation of atoms relative to α-particles. S. ROSENBLUM (Compt. rend., 1927, **185**, 1275—1277).—The ratio A_1X_2/A_2X_1 defines the retarding power of an atom relative to α-particles, where A and X refer to the superficial densities and the atomic weights, respectively, of two elements producing the same loss of relative velocity. Gold is taken as the standard of comparison, and X may be substituted by the constant K of the author's equation (A., 1927, 1120). It is then shown for a number of elements that the expression $N/(N+4)^{\frac{1}{2}}$ measures the retarding power of an element in terms of its atomic number (N). The electronic absorption of energy decreases when N increases, and the α-particles liberate most energy when in collision with loosely-held electrons. J. GRANT.

γ-Ray emission and the law of radioactive transformation. J. C. JACOBSEN (Nature, 1927, **120**, 874—876).—In the author's method of determining the period of transformation of radium-C' (A., 1924, ii, 142), the number of α-particles was found to decrease approximately exponentially with increasing distance from the source, whereas Barton's curve (A., 1927, 86), obtained with a differently constructed apparatus, rose from zero to a maximum position, and then fell. The origin of the disagreement is discussed, and Barton's curve is considered to be free from error. Such a curve is obtained when the γ- and α-transformations are assumed to take place according to an exponential law, the constants λ_γ and λ_α being suitably adjusted. These constants appear to be of the same order of magnitude; if they are considered to be equal, and the velocity of the recoil atoms is taken as 2×10^5 cm. per sec., λ_γ is 10^5 sec.$^{-1}$, the recoil due to the emission of the γ-rays being disregarded. A. A. ELDRIDGE.

Measurement of penetrating radiation. K. BÜTTNER (Naturwiss., 1927, **15**, 158—160; Chem. Zentr., 1927, i, 2391).—Absorption measurements were made under various conditions. A. A. ELDRIDGE.

Pleochroic haloes and the age of the earth. F. LOTZE.—See this vol., 150.

Limits of the periodic system. A. VON ANTROPOFF (Z. Elektrochem., 1927, **33**, 475—476; cf. Meyer, A., 1927, 710).—Polemical.

Limits of the periodic system. E. MEYER (Z. Elektrochem., 1927, **33**, 476; cf. preceding abstract).—A reply to Antropoff. H. J. T. ELLINGHAM.

Quantum theory of molecules. M. BORN and R. OPPENHEIMER (Ann. Physik, 1927, [iv], **84**, 457—484).—Mathematical. R. W. LUNT.

Diameters of atoms and ions. A. FERRARI (Nuovo Cim., 1927, **4**, 39—47; Chem. Zentr., 1927, i, 2626).—Using Goldschmidt's values of atomic radii, the "absolute densities" of certain ions have been calculated. In particular sub-groups of the periodic classification, the values generally increase with increasing at. wt., and are greater for the right than for the left sub-groups. Magnesium belongs in this respect to the right sub-group. Fluorine and oxygen have higher densities than have the homologues immediately following. Increasing the charge of positive ions greatly increases the density. A. A. ELDRIDGE.

Effective cross-section of gas molecules in chemical kinetics. G. KORNFELD (Z. physikal. Chem., 1927, **131**, 97—104).—It has been shown by Nordheim (A., 1926, 654) that in the transfer of energy by collisions between atoms and molecules there must be an effective cross-section for these which is appreciably greater than that determined from elastic collision. This variable effective cross-section must be important in certain groups of chemical reactions where it is not a question of double decomposition between molecules, but of energy transfer from one to another. This is the case, for instance, in sensitised reactions in which the energy necessary for the reaction, which is greater than the available thermal energy, is supplied by foreign molecules. Even in purely thermal reactions, the variable effective cross-section may be all-important, *e.g.*, in unimolecular reactions, or, in fact, whenever the continuance of the reaction is dependent on the supply or removal of energy by collision. Finally, catalytic reactions which depend on the action of a trace of foreign substance may be included. In the case of the catalytic influence of a trace of water vapour on the combination of chlorine and hydrogen, the lower limiting value of the effective radius of the water molecule has been calculated from the available data to be at least thirty times that calculated from the kinetic theory of gases. M. S. BURR.

Structure of the Swan bands. J. D. SHEA (Physical Rev., 1927, [ii], **30**, 825—843).—Theoretical. A detailed quantum analysis is based on published data. The moment of inertia of the Swan band carrier for infinitely small vibration is $15{\cdot}84\times10^{-40}$ g. cm.^{2} for the initial state in the emission process, and $17{\cdot}03\times10^{-40}$ g. cm.^{2} for the final state. Johnson's suggestion that the Swan bands may be due to acetylene is criticised, and a compound C—C or, if possible, C^-—C^- is suggested as carrier. A. A. ELDRIDGE.

Ultra-violet band system of carbon monosulphide and its relation to those of carbon monoxide (the "4th positive" bands) and silicon monoxide. W. JEVONS (Proc. Roy. Soc., 1928, A, **117**, 351—375; cf. Martin, *ibid.*, 1913, **89**, 127).—A quantum analysis has been made of the band-heads in the system discovered by Martin (*loc. cit.*) in the region 2837—2436 Å. in the tube discharge through carbon disulphide vapour and in the carbon arc fed with sulphur. An examination of Martin's spectrograms leads to a Deslandres scheme for the band-heads and to the assignment of the vibrational quantum numbers n', n''. The bands are probably of the simplest type, with single R, Q, and P branches. From a study of the variation of the interval between the two heads of each double-headed band with n' and n'', the two heads are ascribed to the R and Q branches, respectively, the less refrangible Q head being the less intense. The bands of the progression $n'-1$ are abnormal, their R heads being less intense than their Q heads, and the separations of the two heads of each band being abnormally large. Moreover, the distance of the $n'=1$ vibrational level in the initial state from the $n'=0$ level is abnormally large compared with that indicated by the spacing of the other n' levels. Similar anomalies have been found by Birge (cf. A., 1927, 184) for the final state of the CO Ångstrom system, which is also the initial state of the CO 4th positive system. Several points of similarity between the latter and the CS system are discussed. It is shown that the ultra-violet systems of SiO and CS both resemble the 4th positive system of CO, in that (*a*) the bands of all three systems show degradation to the red, and (*b*) the ratio of the system-origin to the resonance line of the comparable atom is approximately the same for each system. The three systems are therefore ascribed to the electronic transition $1^1P \rightarrow 1^1S$, where 1^1S is the normal state and 1^1P the second excited state of the molecule. There is an even closer resemblance between the CO and SiO systems than between the CO and CS systems as regards (*a*) the ratio of system-origin to comparable atomic line, (*b*) the proportional increase of vibrational frequency, and (*c*) the intensity distribution and proportional decrease of moment of inertia in the transition $1^1P \rightarrow 1^1S$. L. L. BIRCUMSHAW.

Radiation from explosions of carbon monoxide and oxygen to which hydrogen has been added. W. E. GARNER and F. ROFFEY (Nature, 1928, **121**, 56—57).—The radiation from an explosion of an equimolecular mixture of carbon monoxide and oxygen falls sharply when 0·07% of hydrogen is present, and continues to fall slowly when the percentage of hydrogen is gradually increased to 2%. The effect is not due to absorption in front of the explosion wave, and is probably not due to the absorption by water vapour formed in the wave-front. A. A. ELDRIDGE.

Shape of the carbon dioxide molecule. K. L. WOLF (Z. physikal. Chem., 1927, **131**, 90—96).—Theoretical. The shape of the carbon dioxide molecule is discussed on the basis of the existing data for molecular heat, infra-red absorption, and dielectric constant, the last being determined experimentally or deduced from dispersion data. The evidence is in favour of a molecule in which the atoms are arranged symmetrically in a straight line (cf. Eucken, A., 1926, 882; Barker, A., 1922, ii, 805). M. S. BURR.

Electronic states and band spectrum structure in diatomic molecules. VI. Theory of intensity relations for case *b* doublet states. Interpretation of CH bands, 3900, 4300 Å. R. S. MULLIKEN (Physical Rev., 1927, [ii], **30**, 785—811; cf. A., 1927, 607, 916).—Theoretical intensity equations are obtained for all possible branches in transitions between doublet electronic states falling under Hund's case *b*, and a revised notation is proposed. The energy differences between F_1 and F_2 terms (s parallel or antiparallel to j_k) are considered qualitatively for a series of cases between *a* and *b*, for normal and inverted doublets. The structure and intensity relations of the CH band at 4300 Å. agree with the theoretical for a case *b* $^2D \rightarrow {}^2P$ transition; for the 3900 Å. band, agreement with theory is equally good for a case *b* $^2S \rightarrow {}^2P$ transition. Initial term values for both bands are given. It is considered likely that the ^2P, ^2D, and ^2S levels of CH are derived respectively from the three lowest states, ^2P, ^1D, and ^1S of carbon. A. A. ELDRIDGE.

Continuous absorption of light in potassium vapour. R. W. DITCHBURN (Proc. Roy. Soc., 1928, A, **117**, 486—508).—A spectrophotometric method is described for measuring relative absorption coefficients of a vapour for different wave-lengths without keeping the vapour pressure absolutely constant. Results are given for potassium over the range 4000—2200 Å. and under widely different experimental conditions. The total experimental error is nearly all photographic and is about 2—3%. The main features of the results are explicable on the view that the measured absorption is the sum of that due to the potassium molecule and that due to the atom. The changes in the experimental curves caused by changes of the vapour pressure of potassium, the pressure of the filling gas, and the temperature are indicated, and the results are discussed in connexion with the theory of atomic and molecular absorption. An attempt has been made to separate the atomic and molecular absorptions on the assumption that the molecular absorption is directly proportional to the molecular concentration and the atomic absorption to the atomic concentration, but it is found that in general these assumptions are not justified, and a satisfactory quantitative separation is not possible. The fact that the amount of atomic absorption appears to be much less than that expected may possibly be due to the partial or total re-emission of the absorbed radiation. An experiment in which continuous absorption produces line fluorescence is described, and is explained by assuming that the molecule is ionised into one neutral atom, one ionised atom, and one electron. The heat of dissociation of the potassium molecule is derived from the absorption curves and used to calculate the degree of association in potassium vapour under different conditions of temperature and vapour pressure. L. L. BIRCUMSHAW.

Relative intensity of the principal doublet (*H*, *K*) and of the diffuse doublet (*X*) in the

spectrum of the calcium chromosphere. C. DAVIDSON (Month. Not. Roy. Astr. Soc., 1927, **88**, 30—33).—A series of photographs with varying exposures of the chromospheric spectrum in the neighbourhood of these lines has been obtained by focussing an image of the sun tangential to the slit of the spectrograph. After correcting for the superimposed continuous spectrum from Planck's formula, for $T=5000°$, it was found that the intensity of the line, 8542 Å., of the diffuse doublet is somewhat greater than that of K_1 at a level between 1000 and 2000 kilometres above the photosphere. At heights above 4000 kilometres, X rapidly ceased to be recorded. The results, although incomplete, are therefore in agreement with Milne's prediction, derived from a consideration of the mechanics of the ionised calcium atom, that the infra-red lines (X) should be more intense than H, K at low levels, whilst at high levels they should be fainter. G. A. ELLIOTT.

Spectrophotometric observations on the growth of oxide films on iron, nickel, and copper. F. H. CONSTABLE (Proc. Roy. Soc., 1928, **A**, **117**, 376—387; cf. A., 1927, 930).—The growth of oxide films has been studied on thin films of iron, nickel, and copper supported on china clay rods and on massive rods of these metals, comparative spectrophotometric observations being made of the character of the reflected light at frequent intervals during the oxidation. The colour sequence shown during the oxidation of the reduced metals brightens considerably during activation, owing to the increase in the reflecting power of the metallic films. Experiments on the oxidation of a copper rod composed of surfaces of burnished, sand-papered, and electrolytically deposited metal showed that the composite nature of the reflected light was practically independent of the irregular nature of the surface, only its intensity being altered. The brightness of the colour sequences varied in the same way as the brightness of the metal surface on which they were formed. The colour sequence on copper shows the red colours much more strongly than the blue, due partly to the strong reflexion of red light by metallic copper. On nickel no reds are observed, their place being taken by brown, and the blue colours are strongly accentuated. This effect is ascribed to the strong specific absorption of nickelous oxide. The colours on iron are normal, but after the first blue the sequence is distorted by the strong specific absorption of the oxide film, the dispersion of the oxide, and the tendency of the oxide to form a detached coating over the surface. The thicknesses of homogeneous films of a given colour have been calculated from the experimental data, using Kundt's values for the refractive indices and Cauchy's formula. The tables are used, with observations of the rate of formation of the colours, to show that from 300° to 500° the velocity of oxidation decreases in the order copper, iron, nickel.

L. L. BIRCUMSHAW.

Displacement of absorption bands of organic dyes, dissolved in different alcohols with constant and varying concentrations of dye. L. HIRSCHLER (Biochem. Z., 1927, **190**, 411—423).—Very few dyes were found which, when dissolved in a homologous series of alcohols, did not show displacement of the absorption bands in passing up the series, the shift being in most cases towards the red. With most dyes showing this displacement, there occurs, with change of medium, an asymmetric change of the width of the bands. The far greater displacement of the bands obtained by varying the concentration of the dye is explained as an asymmetric change in the width of the bands.

P. W. CLUTTERBUCK.

Spectrum of CaSrS-samarium mixed phosphors. M. TRAVNIČEK (Ann. Physik, 1927, [iv], **84**, 823—839).—The phosphorescent system $[Ca_mSr_n]S–Sm+LiF$ has been investigated. The calcium phosphor shows a sharp red emission line at 6058·6 Å., whilst the strontium phosphor has a corresponding line at 6036·8. Using this emission as a criterion, it is found that the transition through mixtures of calcium and strontium is perfectly continuous, as is to be expected if the phosphorescence centre is a definite compound. Each component of the phosphor exercises some effect on the emission. In exactly the same way, the X-ray investigation shows the lattice constant to vary continuously. The crystalline nature of the sulphide diluent is of great importance in determining emission from the phosphor, since lattice constant and frequency vary in the same sense.

Freshly-prepared mixed phosphors are unstable, showing ageing phenomena. Striking differences are recorded between fresh and one-year-old magnesium sulphate–, barium sulphate–, and magnesium oxide–samarium phosphors both in respect of wave-length and intensity of the emission bands. The interpretation of the results is discussed.

R. A. MORTON.

Dielectric constants of four electrolytes as given by the Carman electrometer method. C. C. SCHMIDT (Physical Rev., 1927, [ii], **30**, 925—930).—Curves showing the relation between the dielectric constant and concentration of aqueous solutions of sodium chloride (up to $0·018N$) and potassium chloride (up to $0·01N$) exhibit a minimum, and corresponding curves for barium chloride (up to $0·024N$) and copper sulphate (up to $0·028N$) exhibit two minima. In all cases the dielectric constant reaches a value greater than that of water (cf. Walden, Ulich, and Werner, A., 1925, ii, 512, 773).

A. A. ELDRIDGE.

Arrangement of the electrometer method for measuring the dielectric constants of electrolytes. A. P. CARMAN and C. C. SCHMIDT (Physical Rev., 1927, [ii], **30**, 922—924).—An adaptation of Carman's method (A., 1924, ii, 809) is described.

A. A. ELDRIDGE.

Dielectric constants of aqueous solutions of electrolytes. H. ZAHN (Physikal. Z., 1927, **28**, 916—918).—Polemical. The investigations of Hellman and Zahn (A., 1926, 778; 1927, 7) are not consistent with results obtained by Pechhold (A., 1927, 919) and show much better agreement with the work of Skancke and Schreiner (A., 1927, 932). Pechhold found that the curves showing dielectric constant plotted against temperature all exhibited a minimum. It is claimed that only a few electrolytes really show

this minimum and that Pechhold's results are vitiated by the employment of too low a frequency. Fürth contests the criticism in a discussion.

R. A. MORTON.

Dielectric constants of ammonia, phosphine, and arsine. H. E. WATSON (Proc. Roy. Soc., 1927, **A**, **117**, 43—62).—A detailed description is given of the apparatus and method used for obtaining absolute values of dielectric constants. All possible sources of constant error were explored. Determinations were made at high frequency, the change in capacity with pressure of a condenser containing gas being compensated by a variable condenser in series so as to keep the frequency of the system constant. An exact setting was obtained by the method of beats with a second oscillating system. Measurements of the dielectric constants of ammonia, phosphine, and arsine were made at approximately $-47°$, 16°, and 100°, and at three frequencies, and the variation of dielectric constant with pressure was also examined. The following mean values of $(\varepsilon-1)\times10^5$ at 1 atm. and at $-47°$, 16°, and 100°, respectively, were obtained: ammonia, 1099, 659, 406; phosphine, 337·3, 238·1, 168·7; arsine, 251·0, 191·6, 146. From these, the value of BN in Debye's equation, $\varepsilon-1=N(A+B/T)$ was calculated, and finally μ, the electric moment. The absolute values found for ammonia are considerably higher than those obtained by Jona (A., 1919, ii, 130), but the value calculated for μ is approximately the same in each case. Ammonia and phosphine conform approximately with Debye's formula, whilst for arsine the value of B is substantially zero, so that this gas is similar to the permanent gases so far as its dielectric constant is concerned. μ is much smaller for phosphine than for ammonia and smallest for arsine.

L. L. BIRCUMSHAW.

Molecular volumes of liquids at their b. p. A. E. ARBUSOV (Z. physikal. Chem., 1927, **131**, 49—60).—An apparatus for the determination of the density of a liquid at its b. p. is described. Using the most recent at. wt. data, the molecular volumes of the following liquids at the b. p. have been determined: methyl, ethyl, propyl, *iso*propyl, and *iso*butyl alcohols, *iso*butyl iodide, chloroform, and benzene. The results are in good agreement with the best data of earlier investigators; they make it possible also to explain some of the errors in the older determinations.

M. S. BURR.

Atomic volume relations in certain isomorphous series. A. F. HALLIMOND (Min. Mag., 1927, **21**, 277—284).—The molecular volumes of several series of salts of potassium, rubidium, and cæsium are tabulated, and it is shown that the ratio of the differences (Cs—K)/(Rb—K) is a constant. Also for the chlorides, bromides, and iodides of the alkalis and the alkaline earths the ratio of the differences in molecular volumes (I—Cl)/(Br—Cl) is a constant. From these data are calculated the atomic volumes of the metals and the volumes of the acid radicals, showing that the volume of any one metal varies in its different salts. The general conclusions reached are (1) that in any two isomorphous salt-series formed from the same eutropic elements the volume of an element in one series bears to its volume in the other series a ratio which is the same for all members of the group, and (2) that the eutropic replacement of one element by another of different volume does not alter the volume of the rest of the molecule.

L. J. SPENCER.

Specific volumes of low-melting picrates. P. WALDEN, H. ULICH, and E. J. BIRR (Z. physikal. Chem., 1927, **130**, 495—515).—The appropriate technique for the determination of the true specific volume of low-melting solids at temperatures below 220° is described with the preparation and purification of the following ammonium picrates: ethyl-, propyl-, *n*-butyl-, *iso*butyl-, *n*-amyl-, *iso*amyl-, *n*-heptyl-, dimethyl-, methylethyl-, diethyl-, dipropyl-, di*iso*amyl-, triethyl-, tripropyl-, tri*iso*propyl-, dimethyldipropyl-, triethylpropyl-, diethyldipropyl-, methyltripropyl-, ethyltripropyl-, tetrapropyl-, and tetra*iso*amyl-. It is shown that for these substances the true specific volume, φ, is more accurately represented by the expression $\varphi_\theta=\varphi_0(1+\alpha\theta)$, where θ is the temperature, than by Mendeleev's formula. It is also shown that for the picrates of primary, secondary, and tertiary amines the molecular volume at 150°, V, is related to the number of carbon atoms in the ammonium group, N, by $V=157+18{\cdot}8N$; for quaternary ammonium bases the equation $V=152+18{\cdot}4N$ applies.

R. W. LUNT.

Volumes and the homologue characteristic. I. and II. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 6—9, 73—76; Chem. Zentr., 1927, i, 2791—2792).—I. The homologue characteristic R applicable to a particular aliphatic series applies also to series with a benzene, naphthalene, or anthracene ring. Each increase of two hydrogen atoms depresses the value of R by 10 units; each ring depresses it by 30 units. The formula $R-3M/d_4^0-16n=73+10C-5H-30A$ (where C, H, and A, respectively, are the numbers of carbon atoms, hydrogen atoms, and rings) is given.

II. Phenylethyl-, but not *s*-trimethylphenyl-, 1-methyl-4-*iso*propylphenyl-, *p*-tolyl-, *p*-xylyl-, or *p*-*iso*propylphenyl-acetylene or phenylallylene, is a normal homologue of phenylacetylene. Penta- and hexa-alkylbenzenes are dicyclic.

A. A. ELDRIDGE.

Change in the refractive index of air when an electric glow discharge is passing through it. J. B. SETH (Nature, 1927, **120**, 880).—The change, which is local, and maximal at a pressure of 25 mm., was studied by observing the shift in the interference fringes obtained by Jamin's plates.

A. A. ELDRIDGE.

Periodic anomalies in the properties of long-chain compounds. W. B. LEE (Trans. Faraday Soc., 1927, **23**, 630—640).—From an examination of the available data relating to molecular rotatory power, static friction, density, heat of crystallisation, packing density of unimolecular films, viscosity, toxicity, esterification constants of acids, double refraction, X-ray spacings, b. p., capillary activity, dielectric constant, and many other properties, it is found that a well-defined irregularity is evident in certain series of long-chain compounds on the addition of the fifteenth carbon atom to the chain, although a departure from the normal behaviour may begin at the

fourteenth. Similar, but less pronounced, irregularities may also be frequently observed at the fifth and tenth carbon atoms. This applies to certain optically active carbinols, as well as to normal fatty acids and their salts. To account for these anomalous properties in homologous series, it is suggested that the carbon atoms are disposed in space in the form of a spiral or helix, in such a way as to cause a periodicity in those properties of the molecule which ultimately depend on residual affinity. This conception, therefore, requires that polarity should influence molecular rotatory power, a view which is supported by the experiments of Rule and Smith (A., 1925, ii, 1120). The model suggested does not agree with that deduced from X-ray analysis, which applies, however, only to the solid state. It is possible that, in solution or in the molten state, rotation of the carbon atoms and their linkings may take place to produce the open-pentagonal type of structure required. On this hypothesis the increments in molecular volume for each CH_2 group added to the chain should become non-alternating with respect to odd and even members of a series above the m. p. A certain amount of evidence confirms this conclusion. M. S. BURR.

Rectilinear diameter of ethylene. E. MATHIAS, C. A. CROMMELIN, and H. G. WATTS (Compt. rend., 1927, **185**, 1240—1242).—The deviations of ethylene from the law of rectilinear diameter are of the order of about 1% and are of the same nature as observed for argon and carbon dioxide, *i.e.*, the diameter is slightly concave for temperatures near the critical point and slightly convex for lower temperatures. The angular coefficient of the diameter is -0.00061277, and the critical coefficient 3·524. J. GRANT.

Experimental test of Maxwell's distribution law. J. A. ELDRIDGE (Physical Rev., 1927, [ii], **30**, 931—935).—Measurements of the velocity distribution of molecules in cadmium vapour give results which agree, within the experimental error, with Maxwell's law. A. A. ELDRIDGE.

Rotating-crystal X-ray photographs. G. GREENWOOD (Min. Mag., 1927, **21**, 258—271).—An outline is given of the rotating-crystal X-ray method, and it is shown how the constants of the crystal are related to the distances between the "layer-lines" and the spaces between the spots. The method is applied to the examination of the tetragonal crystals of tetramethylammonium iodide and tetraethylammonium iodide. The former has the cell dimensions $a=8.05$, $c=5.75$ Å., containing two molecules of NMe_4I, and the space-group probably V_d^3 (not holohedral as given by Vegard in 1917). The latter is scalenohedral V^5 with $a=12.29$, $c=6.82$ Å., containing four molecules of NEt_4I. L. J. SPENCER.

Difficulties in the quantitative determination of the scattering power of atoms for incident X-rays. J. M. BIJVOET (Chem. Weekblad, 1927, **24**, 574—579).—A discussion of the relative advantages of the single-crystal and crystal-powder methods of measuring scattering power. S. I. LEVY.

Grating spectrograph for X-rays of long wave-length. J. THIBAUD (J. Phys. Radium, 1927, [vi], **8**, 447—450).—A vacuum spectrograph involving a diffraction grating with tangential incidence and suitable for the spectroscopic examination of X-rays of long wave-length is described. The theory of such an instrument has already been given (A., 1927, 286). Data previously recorded (*ibid.*, 803) are discussed in greater detail. J. S. CARTER.

Radiograph of a crystal having the face-centred cubic lattice. M. MAJIMA and S. TOGINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 75—78).—Laue photographs with X-rays incident at various angles on an aluminium crystal are reproduced. The orientation of the axis of any crystal having a face-centred cubic lattice can then be determined by a comparison of its radiograph with these photographs. A more accurate result is obtained, however, if various crystal faces are identified in the radiograph under examination by means of the standard photograph, and the orientation of the axis is determined from these by calculation. R. CUTHILL.

Relation of the surface of crystals to their mass and volume. C. HRYNAKOVSKI (Arb. Komm. Math. Naturwiss. Posen, 1925, *A*, **2**, 1—27; Chem. Zentr., 1927, i, 2626—2627).—The relative rapidity of growth of single planes in an individual crystal is a function of its mass, although this rule is valid only for a particular stage of growth. The quotient of the actual and hypothetical (spherical) surfaces is constant for each crystal; the value falls (1·593—1·229) with increasing symmetry in the triclinic, monoclinic, and regular systems. In twinning and overgrowth higher values are obtained. The quotient of the actual surface and mass or volume becomes disproportionately smaller with increase in the latter. A. A. ELDRIDGE.

Crystal lattice of lithium nitride, Li_3N. R. BRILL (Z. Krist., 1927, **65**, 94—99; Chem. Zentr., 1927, i, 2629—2630).—There are four molecules in the elementary cell; the space-group appears to be T^4, that of ammonia, so that the two molecules are analogous. A. A. ELDRIDGE.

X-Ray study of magnesium oxychloride cement. T. MAEDA.—See B., 1928, 54.

Alkylamine alums, and other substitutions in ammonium aluminium sulphate. K. SPANGENBERG (Fortschr. Min. Kryst. Pet., 1927, **11**, 344—347; Chem. Zentr., 1927, i, 2630).—A discussion of the lattice structure of the alums and their derivatives. A. A. ELDRIDGE.

Analysis of mixed crystals and alloys. A. ERDAL (Z. Krist., 1927, **65**, 69—82; Chem. Zentr., 1927, i, 2707).—In the system potassium bromide–ammonium bromide true mixed crystals of the sodium chloride type are formed when 0—40% of ammonium bromide is present. Vegard's additivity rule is valid. Ammonium bromide has a 6.87×10^{-8} cm. In the system copper–silver true mixed crystals are formed only when the components are nearly pure. A. A. ELDRIDGE.

X-Ray examination of iron nonacarbonyl, $Fe_2(CO)_9$. R. BRILL (Z. Krist., 1927, **65**, 85—93; Chem. Zentr., 1927, i, 2629).—The crystals are hexagonal, a 11·08, b 6·45, c 15·8 Å., with four molecules in the elementary cell. A. A. ELDRIDGE.

Crystal structures of two intermetallic compounds [of copper with magnesium and with aluminium]. J. B. Friauf (J. Amer. Chem. Soc., 1927, **49**, 3107—3114).—The structures of the compounds Cu_2Mg and $CuAl_2$ were calculated from Laue, rotation, and powder photographs. The former compound has a unit cube of edge 6·99 Å. containing 8 molecules. The structure is derived from the space-group O_h^7 (Wyckoff's notation), the atoms having the same arrangement as the metal atoms in spinel (Bragg, Phil. Mag., 1915, [vi], **30**, 305). The unit cell of $CuAl_2$ is tetragonal, with a=6·04 Å. and c=4·86 Å., and contains 4 molecules (cf. Jette, Phragmen, and Westgren, B., 1924, 299). The atomic arrangement may be derived from the D_{4h}^{18} and other space-groups. S. K. Tweedy.

Crystallography of double nitrates of neodymium and praseodymium. R. B. Ellestad and F. A. Gray (Z. Krist., 1927, **65**, 140—141; Chem. Zentr., 1927, i, 2797).—The double nitrates, $2R(NO_3)_3,3M(NO_3)_2,24H_2O$, scalenohedral trigonal, hygroscopic, have the following values of c/a: neodymium-zinc 1·569, -nickel 1·579, -magnesium 1·576, -manganese 1·580, -cobalt 1·584; praseodymium-zinc 1·584, -nickel 1·576, -cobalt 1·567, -manganese 1·565, -magnesium 1·562. Etch-figures on the (111) faces form equilateral triangles. A. A. Eldridge.

***X*-Ray and electrical investigation of the system palladium-hydrogen.** J. O. Linde and G. Borelius (Ann. Physik, 1927, [iv], **84**, 747—774).—The lattice constant of pure palladium is given by $a=3\cdot888+4\cdot6\times10^{-5}(t-20)$ Å. Using a modified Debye method, the lattice constants of palladium in an atmosphere of hydrogen have been determined at 100°, 150°, and 200° over the pressure range 0·1—4 atm. The results are consistent with two phases: (i) hydrogen dissolved in palladium, lattice constant 3·888—3·92 Å., concentration of hydrogen below c=0·5H/Pd; (ii) palladium hydride Pd_2H, lattice constant 3·978. Two forms of palladium hydride Pd_2H probably exist. Under certain conditions, a third phase appears which is a continuation of the first phase, *i.e.*, it is a hydrogen solution with the concentration greater than c= 0·5H/Pd.

When palladium is made the cathode in the electrolysis of, *e.g.*, sulphuric acid, the amount of hydrogen absorbed will vary with current density, time, and temperature. A number of palladium samples so treated have been studied by the Seeman–Bohlin method. As the hydrogen content increases, the system shows two phases at first, followed by a phase exhibiting a lattice constant of 4·034, which rises to 4·07 Å. with supersaturation. The relation between lattice constant and hydrogen concentration is approximately linear. The resistance of the palladium-hydrogen system increases regularly up to a concentration c=0·75H/Pd, and then decreases, the fall being very marked from c=0·85 onwards; whence it is concluded that the compound PdH has a relatively small resistance. From the pressure-concentration diagram it is concluded that the system is best envisaged as a metallic mixed-crystal system with the components Pd and PdH. R. A. Morton.

Notation of mercurammonium salts. M. François (Ann. Chim., 1927, [x], **8**, 341—362).—The theories of Rammelsberg (A., 1889, 347) and of Pesci (A., 1890, 1211; 1891, 268) concerning the structures of complex mercurammonium salts are criticised mainly in view of the author's work (A., 1899, ii, 657; 1900, ii, 208; 1906, i, 484). If in a system composed of one to four ammonium groups two hydrogen atoms are replaced by a mercury atom, it is possible to formulate all complex salts containing one to eight atoms of mercury, the majority of which are known. The additive compounds of mercuric halides and ammonia should be formulated as for other metallic salts, and not as dimercurammonium ammonium iodides; thus the instability of the compound obtained by passing ammonia over red mercuric iodide points to the formula $HgI_2,2NH_3$ and not $Hg_2NI,3NH_4I$ (Pesci, *loc. cit.*). H. Burton.

Lattice constant of thallous iodide. T. Barth (Z. physikal. Chem., 1927, **131**, 105—106; cf. A., 1926, 896).—By comparison with sodium chloride, the lattice constant of thallous iodide has been corrected to 4·198±0·002 Å. If the value of the exponent n (*loc. cit.*) be taken as 8, the corrected values for mixed crystals of thallous bromide and iodide are in agreement with the lattice theory of Grimm and Herzfeld (Z. Physik, 1923, **16**, 79). M. S. Burr.

Crystal structure of linneite, polydymite, and sychnodymite. G. Menzer (Fortschr. Min. Kryst. Pet., 1927, **11**, 315—316; Chem. Zentr., 1927, i, 2639).—Linneite is face-centred cubic, with edge of unit cube, containing 8 molecules of Co_3S_4, 9·398± 0·007 Å., space-group probably O_h^7. Polydymite, $(Ni,Fe,Co)_4S_5$, has a 9·405±0·007 Å., and sychnodymite, $(Co,Cu,Ni)_4S_5$, has a 9·434±0·007 Å. Polydymite and sychnodymite are not considered to be essentially distinct from linneite. A. A. Eldridge.

Crystal structure of berzelianite. W. Hartwig (Fortschr. Min. Kryst. Pet., 1927, **11**, 307—308; Chem. Zentr., 1927, i, 2639).—Berzelianite, Cu_2Se, is face-centred cubic, the structure being probably that of fluorite with the atom positions: Se (0, 0, 0), Cu ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$)($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$); edge of unit cube containing 4 molecules, 5·731+0·008 Å. Natural berzelianite contains small quantities of silver and sulphur. A. A. Eldridge.

Crystal structure of the chondrodite series. W. H. Taylor and J. West (Proc. Roy. Soc., 1928, **A**, **117**, 517—532).—A qualitative *X*-ray examination by the rotating-crystal method and by the ionisation spectrometer has been made of crystals of chondrodite, humite, and clinohumite. The chondrodite group is of interest since it supplies a good example of morphotropy, the c/a or c/b ratio changing in a simple, progressive manner with additions of the molecule Mg_2SiO_4 (olivine) on passing through the series, whilst the a/b ratio remains unchanged. Furthermore, all three crystals are based on the hexagonal form of the two possible close-packed arrangements of oxygen atoms, and the Mg_2SiO_4 portion of the crystals is found to possess the olivine structure. The dimensions of the unit cells, includ-

ing that of olivine, are as follows (the crystallographic b axis is taken as the a axis and *vice versa*, and c' denotes the thickness of the unit cell perpendicular to the c face): chondrodite (2 molecules in the unit cell, space-group probably C_{2h}^{5}, possibly C_{2h}^{4}), a—4·733, b=10·27, c=7·87, c'=5×1·488 Å., α=109° 2′; humite (4 molecules in the unit cell, space-group V_{h}^{16}), a=4·738, b=10·23, c=20·86, c'=14×1·490 Å.; clinohumite (2 molecules in the unit cell, space-group probably C_{2h}^{5}, possibly C_{2h}), a—4·745, b=10·27, c=13·68, c'=9×1·492 Å., α=100° 50′; olivine (4 molecules in the unit cell, space-group V_{h}^{16}), a—4·755, b=10·21, c=5·98, c'=4×1·495 Å. From an examination of the X-ray rotation photographs, it appears that the crystals of the chondrodite series consist of alternate layers, parallel to the c face, of $Mg(OH)_2$ and Mg_2SiO_4, based on an arrangement of oxygen atoms and OH-groups in hexagonal close packing. The oxygen atoms appear to determine the dimensional relations of the unit cell, whilst the magnesium and silicon atoms control the pattern and thus the cell symmetry. The $Mg(OH)_2$ layer has the same thickness in each crystal, but that of the olivine layer (measured perpendicular to the c face) has the ratio of 2 : 3 : 4 in chondrodite, humite, and clinohumite, respectively. The layers of olivine structure in humite, unlike those in chondrodite and clinohumite, are bisected by reflexion planes parallel to the c face. This causes alternate layers of $Mg(OH)_2$ in humite to be mirror images of each other, and explains the orthorhombic symmetry of the crystal.

L. L. Bircumshaw.

Crystallography of sucrose. G. Vavrinecz (Z. Krist., 1927, **64**, 543; Chem. Zentr., 1927, i, 2406).—New determinations give the ratios $a : b : c$—1·2518 : 1 : 0·89458; β=102° 55·24′.

A. A. Eldridge.

Crystal form of carbamide nitrate. A. Hestermann (Z. Biol., 1927, **86**, 561—568).—Crystallographic data are cited from which it is concluded that carbamide belongs to the monoclinic system.

E. A. Lunt.

Crystallography of some simple benzene derivatives. W. A. Caspari (Phil. Mag., 1927, [vii], **4**, 1276—1285).—The lattice dimensions of crystals of the phenylenediamines and aminophenols are recorded. R. Cuthill.

New kinds of mixed crystals. VI. D. Balarev [with R. Kaischev and G. Kratschev] (Z. anorg. Chem., 1927, **168**, 154—162; cf. this vol., 7).—When barium sulphate is precipitated in presence of increasing amounts of alkali metal chlorides or potassium nitrate, the amount of alkali salt included in the precipitate first increases to a maximum, at which the crystalline form of the precipitate changes, then falls again, these results being in agreement with Grimm's observations on the inclusion of potassium permanganate (A., 1924, ii, 828). On the author's theory, the maximum corresponds with the point at which the foreign salt adsorbed on the exterior of the sulphate crystals commences to influence their porosity. In support of this view, it is further found that the amount of foreign salt in the crystals is, in general, the greater the more water they contain. These facts also lend confirmation to the theory that the occlusion by barium sulphate of various salts of a different crystalline form is a purely mechanical effect, depending on the existence of an internal surface within the sulphate crystals. As a cause of this porosity of the sulphate particles, the existence of two different forms of the salt suggested itself, the transition from one to the other in the solid state increasing the fineness of capillaries already present, and also producing new ones; this was found to be so by experiment. By precipitating barium chloride with sulphuric acid at the b. p. in a solution acidified slightly with hydrochloric acid, or in the cold, a form of barium sulphate is produced having a solubility at 18—20° of 2·3 mg./litre of water, which agrees with the accepted value obtained by the conductivity method. From a solution very strongly acidified with hydrochloric acid, however, a form with a solubility of 3·3 mg. at 18—20° separates, this being in aqueous solution at the ordinary temperature metastable in respect of the other variety, and passing into it either spontaneously or on addition of nuclei or barium chloride solution to its saturated solution. R. Cuthill.

Free energies of solid compounds deduced from their crystal structure: with special reference to calcite and aragonite. J. L. Buchan (Trans. Faraday Soc., 1927, **23**, 672—676).—By considering the simplest lattice, determined from X-ray measurements, from which the crystal can be built up, regarding the ions as point charges, and calculating the work required to bring up each ion from an infinite distance to its place in the lattice, the value for the free energy of formation of calcite from Ca^{++} and CO_3^{--} ions is found to be −4060 g.-cal/mol. at 18°, and for aragonite −3680 g.-cal./mol. Hence, at 18°, aragonite is unstable with regard to calcite, and the free energy of transition from aragonite to calcite is −380 g.-cal./mol. (cf. this vol., 133). The value for the free energy of formation of calcite from the elements calcium, carbon, and oxygen has also been calculated and compared with that deduced from thermochemical data. In the same way the free energies of aragonite, ferrous and manganous carbonates, sodium nitrate, ammonium iodide, and sodium chloride have been calculated, and the results tabulated. M. S. Burr.

Evaporation and dissolution phenomena of zinc. G. Aminoff (Z. Krist., 1927, **65**, 23—27; Chem. Zentr., 1927, i, 2707).—Only facets corresponding with the lattice planes (0001), (10$\bar{1}$1), (11$\bar{2}$0), and (10$\bar{1}$0) give goniometer reflexions. The rate of dissolution in sulphuric acid is lowest in the direction of the c-axis. A. A. Eldridge.

Magnetic properties of single crystals of nickel. W. Sucksmith, H. H. Potter, and L. Broadway (Proc. Roy. Soc., 1928, **A**, **117**, 471—485).—The crystals were prepared from Mond pellets by slow cooling from the molten liquid contained in a long cylindrical alundum crucible, and the specimens were subsequently ground by hand on a fine oil-stone. Measurements were made of the component of magnetisation parallel to the applied field (I_P) and perpendicular to the field (I_N) in the principal

crystal planes, and of the variations of these two vectors on rotating the field in the plane of the disc. The ballistic method employed by Honda and Kaya was used for the measurement of I_P, whilst I_N was determined by Weiss' torsion method. It is shown that the existence of directional properties in the crystal invalidates the use of the torsion method for the measurement of I_P. The magnetisation coincides with the field when the latter is applied along the symmetry axes, the direction of easiest magnetisation being along the trigonal axis. The results are compared with the data for iron obtained by previous investigators. L. L. BIRCUMSHAW.

Magnetic properties of single crystals of nickel. S. KAYA and Y. MASIYAMA (Nature, 1927, **120**, 951—952).—A record of experiments performed with crystals ($7\times2\cdot3$ cm.) of nickel grown by slowly lowering out of an electric furnace a crucible of the molten metal. A. A. ELDRIDGE.

The metallic state. W. HUME-ROTHERY (Phil. Mag., 1927, [vii], 4, 1017—1045).—The various theories of the metallic state are discussed critically with special reference to properties other than those of electrical or thermal nature. Only the electron lattice theory of Lindemann (A., 1915, ii, 47) gives a rational picture of the way in which the crystal lattices of metals are built up, and the same theory is in general agreement with the compressibility data and tensile properties. This theory is the only one giving an explanation of the plasticity of metals, which is regarded as due to the relatively great difference in size of the positive ions and negative electrons from which the lattice is built up. Owing to the precessional motion of the elliptical electronic orbits, the zones of repulsion round the metallic ions will vary periodically, and a motion of this type is thought to be the cause of supraconductivity in some metals at the temperatures of liquid helium. This conception is in agreement with the fact that supraconductivity is shown by some metals and not by others. Relations between the inter-atomic distances in metals and salts are pointed out.

W. HUME-ROTHERY.

Cohesion: a general survey. C. H. DESCH (Trans. Faraday Soc., 1927, **24**, 53—64).—A general review of phenomena in connexion with cohesion, summarised under the following headings: (1) relations between tenacities of substances measured by different kinds of tests, (2) elastic limit, (3) failure by fatigue, (4) hardening effect produced by the cold working of metals, (5) dependence of the manner of deformation on the rate of application of stress and the time for which it is applied, (6) nature of the crystal boundaries in metals, and the intercrystalline cement theory, (7) nature of crystal surfaces, (8) adhesion of solders or other materials, thin films of which can unite solid masses, also the adhesion of electrodeposited material, (9) diffusion in solids, (10) nature of cohesion and the application of the equation of van der Waals. W. HUME-ROTHERY.

Properties of non-metallic elements in relation to their cohesive forces. A. M. TAYLOR (Trans. Faraday Soc., 1927, 24, 157—159).—In non-metals the linkings are homopolar and the cohesive force in the solid is due to electrical doublets arising from the deformation of the electronic shells. In polar salts the linkings are heteropolar and the cohesive force is due to the ionic charges plus the above electrical doublets. The doublets are produced under the influence of an electric field of intensity E by deformation of the electronic shells, and their moments may be written $p-\alpha E$, where the constant α may be found by measurement of the atomic refractivity, or from the correction of the Rydberg number in the formulæ for the series spectra. The attractive force between two doublets falls off as the inverse fourth power of the distance, which results in a greater value for the compressibility k than when the inverse square law alone is concerned. Hence, in salts, an increase in α leads to an increase in k, and this is confirmed experimentally for potassium chloride, bromide, and iodide. In non-metals, both α and k are high, and the force F between two doublets may be written $F=cp^2/r^4-\beta/r^n$, which on differentiating and eliminating β from the equilibrium condition ($F=0$, $r=r_0$) leads to $F^1=-cp^2(4-n)/r^5$, the corresponding expression for polar compounds being $F^1=-(er)^2(2-n)/r^5$. The quantity F^1 varies rapidly with r, and more rapidly in non-metals than in polar compounds, indicating that the restoring force on a displaced particle is more anharmonic in the non-metals. In agreement with this, the thermal expansion of non-metals is higher than that of salts. When high values of k are found in non-metallic elements or in polar compounds, it is probable that the units possess considerable electrical moment.

W. HUME-ROTHERY.

Relation of fatigue to cohesion in metals. H. J. GOUGH (Trans. Faraday Soc., 1927, **24**, 137—148).—A summary of recent work carried out at the National Physical Laboratory on cyclical stress relations, the nature of deformation by plastic strain slip, the hardening produced by slip, and the manner of the initiation and propagation of fatigue cracks. R. W. LUNT.

Relation of hysteresis to cohesion and fatigue in metals. B. P. HAIGH (Trans. Faraday Soc., 1927, 24, 125—137).—Experiments are described in which metallic rods have been subjected to approximately sine-wave form tensile stresses of frequency 2000 cycles per sec. Annealed ductile metals are characterised by three well-defined sections of the hysteresis–time curve: a brief evolution of heat during not more than $2\cdot5\times10^5$ cycles, during which period the hysteresis falls to a low but slowly rising value which constitutes the second stage; in the third stage the hysteresis rapidly increases followed by fracture. Curves typical of a number of metals are discussed. R. W. LUNT.

Plasticity problems in metals. G. SACHS (Trans. Faraday Soc., 1927, **24**, 84—92).—Mathematical analyses of a number of characteristic types of distortion in metals produced by shear are reviewed and discussed with particular reference to cases of industrial importance. R. W. LUNT.

Relation between cohesion and tensile and dielectric strength. A. F. JOFFÉ (Trans. Faraday Soc., 1927, **24**, 65—72).—Experiments are described

in which, by avoiding surface cracks, the tensile strength of rock salt is 160 kg./mm.; the value deduced from Born's theory is 200 kg./mm. The discrepancy between the observed values of the dielectric strength of glass, mica, rosin, picein, oil, and benzene and those predicted by theory (approx. 10^8 volts/cm.) has been shown to be non-existent by investigating the dielectric strength of thin sheets of these substances. The accepted values refer to sheets of greater thickness than 5 μ; these low values are attributed to the heat dissipated in the dielectric in an intense field by existing ions and by new ions formed by collision in the relatively long path between the electrodes, since it is known that the dielectric strength diminishes rapidly as the temperature rises. R. W. LUNT.

Mechanical and electrical cohesion and molecular forces. A. JOFFÉ (Physikal. Z., 1927, **28**, 911—916).—Born's electrical theory of the solid state appears to break down in respect of cohesion since rock salt comes apart under a tension of 0·4 kg./mm.^{2}, whereas according to the theory 200 kg./mm.^{2} should be required. If a crystal of rock salt is suspended in hot water and its resistance to tension then determined, it is found that the moist crystal can withstand up to 30—160 kg./mm.^{2} without breaking. It is argued that inequalities in the crystal surface tend to disappear as the layers of salt are dissolved and that the high resistance of the perfect crystal is in accordance with theory. Similarly, a globule of salt was subjected to cooling in liquid air and then plunged into hot water or molten lead. The crystal withstood in this way pressures of 25 and 70 kg./mm.^{2} without disintegration.

The resistance of crystals to electrical forces shows that whilst 10×10^7 volts/cm. represents the theoretical voltage, actually only 3×10^5 volts are required for disruption of rock salt. The discrepancy is general and the following factors may operate in causing it: (1) the higher the temperature the greater the tendency to disruption under lower voltages, and as heat may be developed by the current, this factor will tend to lower the disrupting voltage; (ii) excitation of ions by collisions with the ions first formed; (iii) local concentration of the electrical field; (iv) widening of the breach by mechanical effects following the original effect. It is shown that very thin films of dielectrics will actually withstand voltages not much less than those predicted by the electrical theory. R. A. MORTON.

Incidence of chemical attraction on cohesion. T. W. RICHARDS (Trans. Faraday Soc., 1927, **24**, 111—120).—Following an historical review it is suggested that mechanical equilibrium in atomic contacts is determined by an expression of the following form: $p+\Pi_0(v_0/v)^m=\Pi_P(v_0/v)^n+$ where p is the external pressure, Π_0 the sum of all intrinsic compression effects, Π_P the intrinsic distending pressure, $P_e-T\alpha/\beta$ the thermodynamic thermal pressure, where α and β are the coefficients of expansion and compression respectively, v is the volume, and v_0 the volume at some standard state at which Π_0 is defined. It follows that $\beta-1/\Pi_0(n-m)$. In the case of a binary compound the following expression is advanced for $\beta:x/(n-m).[x/\Pi_1+(x-1)/\Pi_2]$, where x is the fraction of each atom subjected to a cohesive pressure Π_1, and $1-x$ the fraction subjected to intense chemical pressure Π_2. This analysis indicates the existence of internal pressures in non-volatile solids of the order of the tensile strength of glass; such values are consistent with the heats of formation and of evaporation of such substances. R. W. LUNT.

Interweaving of crystal gratings. G. VON HEVESY and G. RIENACKER (Ann. Physik, 1927, [iv], **84**, 674—688).—The diffusion of silver iodide into cuprous iodide, and *vice versa*, has been investigated at 480°; the process is found to be reversible, the cuprous iodide being uniformly distributed throughout the entire mass after a period of 12 hrs. The velocity of diffusion has been determined from measurements of the conductivity of the diffusing layers. If a layer of cuprous iodide be placed in contact with a layer containing an equivalent amount of silver sulphide, then after 4 days the iodide layer contains 7·8 mol.-% of cuprous iodide and 92·2 mol.-% of silver iodide; the sulphide layer contains 8·2 mol.-% of silver sulphide and 91·8 mol.-% of cuprous sulphide. Approximately the same composition of iodide and sulphide layers is observed if a layer of silver iodide is allowed to diffuse into a layer containing an equivalent amount of cuprous sulphide. These results show that the process is reversible and that a true equilibrium is reached, the crystal grating becoming interwoven. R. W. LUNT.

Radiate crystallisation. B. POPOV (Fortschr. Min. Kryst. Pet., 1927, **11**, 320—321; Chem. Zentr., 1927, i, 2627).—The phenomenon was investigated with malonamide and resorcinol. A. A. ELDRIDGE.

Temperature factors of X-ray reflexion for sodium and chlorine in the rock-salt crystal. I. WALLER and R. W. JAMES (Proc. Roy. Soc., 1927, **A**, **117**, 214—223).—Theoretical. If F_1 and F_2 are the average atomic scattering factors, at a given angle, for chlorine and sodium, respectively, at 0° Abs., then the amplitude factor at a temperature T, for spectra where the waves scattered by the chlorine and sodium atoms are in phase, will be $F_1e^{-M_1}+F_2e^{-M_2}$, and for spectra where they are out of phase, $F_1e^{-M_1}-F_2e^{-M_2}$, M_1 and M_2 being functions of T. It is shown that if allowance is made for the different values of M for the two atoms, Waller's theoretical formula for the temperature coefficient (A., 1927, 816) agrees with experiment in the case of rock salt from 86° to 500° Abs. L. L. BIRCUMSHAW.

Focal structure of smectic substances. R. GIBRAT (Compt. rend., 1927, **185**, 1491—1492).—Assuming that the forces acting on each element of homogeneous matter of a smectic body are constant in magnitude and direction, and may be represented by a single resultant, the positions of such resultants are given by an ellipse and a hyperbola placed focally to one another. This structure is often seen in practice, *e.g.*, when an isotropic liquid is cooled. J. GRANT.

Salts with low m. p. II, III, and IV. Electrical conductivity, viscosity, and molecular

state of fused picrates. P. WALDEN, H. ULICH, and E. J. BIRR (Z. physikal. Chem., 1927, **131**, 1—48; cf. this vol., 107).—An apparatus is described for the measurement of the electrolytic conductivity of small quantities of fused salts. Measurements of the conductivity of twenty-two alkylammonium picrates, at temperatures between 40° and 220° at intervals of 10°, have been made. At the higher temperatures, the dependence of equivalent conductivity on temperature may be indicated by the formula $\lambda=A(t-\theta)^2$, where A and θ are characteristic constants. With increase in the number of $:CH_2$ groups, but the same degree of substitution, the equivalent conductivity decreases, but the value also depends on the character of the molecule, *e.g.*, *n*-butyl- or *n*-amyl-ammonium picrate has a higher conductivity than the corresponding *iso*-compound. The degree of substitution has also a marked influence. For the same mol. wt., the conductivities of the salts of the primary, secondary, tertiary, and quaternary amines are approximately in the ratio of 1 : 2 : 1·7 : 7. The temperature coefficient of conductivity is $2/(t-\theta)$ or $2\sqrt{A}/\theta$. Thus, at equally reduced temperatures $t-\theta$, all the salts have the same temperature coefficient. The results bear out the observations of Kohlrausch on solutions, and of Biltz on conductors of all kinds (A., 1924, ii, 515), that the conductivity temperature coefficient in all conductors is greater the smaller the conductivity. For the primary and quaternary amines, θ is approximately constant, the mean values being 76·7 and 41·7, respectively. The viscosities of the same picrates have been determined by Poiseuille's method in an apparatus which is described. The fluidity $\varphi=1/\eta$ may be represented with considerable accuracy by the formula $\varphi=a(t-\delta)^2$, where α and δ are characteristic constants. The mean values for δ in the primary and quaternary groups are 83·7 and 49, respectively, only a little higher than the corresponding values for θ in the conductivity formula. The values of α, however, are very much larger than the values of A for the same salts. With increasing mol. wt., and the same degree of substitution, the viscosity first diminishes and then increases. For the same mol. wt., when the number of $:CH_2$ groups is between 7 and 10, the viscosities of the normal primary, secondary, tertiary, and quaternary amines are approximately in the ratio of 4 : 1·6 : 1·2 : 1. The salts with the greatest fluidity have the smallest temperature coefficient. The molecular state of the fused substituted ammonium picrates is discussed. By comparison of the conductivity data for the fused salts with those for infinitely dilute solutions, it is concluded that the picrates of the quaternary bases are practically completely dissociated, whilst those of the secondary are 50% and of the tertiary and primary 20% dissociated. The effect of increasing size of cation is similar to that in infinitely dilute solution, and may be explained by decreasing mobility of the ion with increasing size, without at the same time any appreciable change in degree of ionisation. In accordance with Bjerrum's conception, a non-ionised molecule is regarded as a pair of ions which, through marked reciprocal deformation, have acquired properties very different from those of the free or associated ions. M. S. BURR.

Theory of electric and magnetic birefringence in liquids. C. V. RAMAN and K. S. KRISHNAN (Proc. Roy. Soc., 1927, **A**, **117**, 1—11).—It has been shown that the Langevin–Born theory of electrical birefringence fails to give the magnitude of the Kerr constant in liquids correctly in terms of the constants of the molecule as determined in the gaseous condition (A., 1927, 397), and a modification of the theory is suggested. According to Langevin and Born, whilst the individual molecule is anisotropic, the polarisable matter present round it is so distributed that the local polarisation field acting on the molecule is independent of its orientation in the field. This assumption cannot be correct in a dense fluid, and it is now suggested that the orientation of the molecule determines the distribution of matter around it, and therefore also the local polarisation field acting on it. When the Langevin–Born theory is modified so as to take into account this "anisotropic" polarisation field, the resulting expression is in better accordance with facts than the original expression. In general, the influence of the anisotropy of the polarisation field is to diminish the magnitude of the Kerr effect to be expected. This is explained as being due to the fact that the longer geometrical dimension of a molecule tends to be also the direction of maximum electrical and optical susceptibility. The distribution of the molecules in a dense fluid therefore tends to be such that their mutual influence is equivalent to an apparent diminution in the anisotropy of the molecules.

L. L. BIRCUMSHAW.

Dispersion of metals in solid salts under the action of an electric current. T. PECZALSKI (Compt. rend., 1927, **185**, 1588—1591).—An iron tube filled with a salt (potassium, barium, or strontium chloride) and containing a copper rod placed axially, was heated to a temperature below the m. p. of the salt, and the iron and copper portions were then connected to a source of current. Above 300° the conductivity increased rapidly after 1 hr. when the copper was made positive, and copper was detectable in the salt. When the copper was negative the increase was slower and iron was detectable in the salt. The use of aluminium and alumina in place of the copper and the salt, respectively, gave negative results except for an increase in conductivity in the former case when the iron was positive. The results are explainable by emission of ions of the metal, whilst there is also evidence of electrolysis of the salt vapours, with the formation of unstable compounds between the metal and the cations and subsequent deposition of the former in the salt.

J. GRANT.

Inductive power in the gaseous state. CORDONNIER and GUINCHANT (Compt. rend., 1927, **185**, 1448—1450).—Measurements for 33 gases of inductive power, K, relative to air, have shown that for mixtures with air or carbon dioxide the dielectric excess, $K-1$, is a linear function of the partial pressure of one of the constituents and that the relation is subject to the same degree of accuracy as Dalton's law. The ratio L/R (L the Lorenz constant, R the molecular refractivity) is an index of chemical constitution. For normal substances it is 1, whilst the substitution

of hydrogen by a methyl group increases R by 4·6, although the increase is much greater if the molecule contains an electronegative group. If $L>R$, the value of L is usually greater for the gaseous than for the liquid state at the same temperature. For pairs of isomerides the compound containing an enolic or a replaceable hydrogen atom has the highest inductive power. J. GRANT.

Effect of X-rays on the crystallisation of antimony. M. CAMPA (Nuovo Cim., 1927, **4**, 28—31; Chem. Zentr., 1927, i, 2630—2631).—Antimony subjected during solidification to moderately hard X-rays has a Hall coefficient 15% smaller than the normal. A. A. ELDRIDGE.

Magnetic analysis. O. VON AUWERS (Physikal. Z., 1927, **28**, 871—882).—A summary of published work in which the advantages of magnetic analysis are stressed. The theoretical basis is discussed together with the relationship between magnetic and mechanical properties. Various types of practical application are instanced. R. A. MORTON.

Thermo-electric effect in single-crystal bismuth. R. W. BOYDSTON (Physical Rev., 1927, [ii], **30**, 911—921).—The thermal $E.M.F.$ against constantan of single-crystal bismuth was determined for various orientations, and the thermo-electric power and Peltier heat were computed. The Peltier heat and difference in Thomson coefficients for Bi$\perp$ against Bi$\|$ were also computed. Polycrystalline bismuth and zinc give results in accord with Linder's formula. A. A. ELDRIDGE.

Permeability of iron at high frequencies. C. GUTTON and (MLLE.) J. MIHUL (Compt. rend., 1927, **185**, 1197—1198; cf. A., 1927, 614).—The mean magnetic permeabilities for a constant frequency of soft iron and piano wires are constant for small field strengths (up to about 1 gauss) and then increase with the field strength. J. GRANT.

Toluoylenol. S. RÖSCH (Fortschr. Min. Kryst. Pet., 1927, **11**, 327—328; Chem. Zentr., 1927, i, 2641).—Enolic toluoylbenzoylmethane, $C_6H_4Me\cdot C(OH):CHBz$ or $C_6H_4Me\cdot CO\cdot CH:CPh\cdot OH$ forms rhombic tablets, $a:b:c=3\cdot092:1:1\cdot166$. The refraction increases from the red to the violet: α 1·635—1·690, β 1·644—1·805, γ 1·932—2·359. The double refraction is very great: $\beta-\alpha$ 0·009—0·015, $\gamma-\alpha$ 0·297—0·669, $\gamma-\beta$ 0·288—0·554. A. A. ELDRIDGE.

Temperature measurements and catalytic wall effects in the glow discharge. R. SEELIGER and H. STRAEHLER (Physikal. Z., 1927, **28**, 894—904).—The temperatures within a discharge tube have been measured by means of inserted thermo-elements and by a manometric device based on the sagging of a thin sheet of mica under pressure. Using pure neon and pure hydrogen, curves have been obtained showing the temperature developed at points from 0 to 15 mm. from the axis of the discharge tube with discharges running under known currents and with defined gas pressures. When the thermo-element was protected from actual contact with the discharge by means of a glass sheath, the results were fundamentally divergent from those obtained with a bare thermo-element. Provided, however, that the outside of the glass sheath was covered with a thin film of metal it was found that the results with the bare thermo-element could be reproduced. Experiments with gases containing traces of impurities showed that the temperatures developed in the discharge tube were consistently higher for the bare thermo-element than for the sheathed element. Pure gases showed little sign of this discrepancy. It is concluded that the results are not due to experimental error, but to a real difference in temperature brought about by the catalysing action of the metallic surface. R. A. MORTON.

Critical temperatures of boron trichloride and silicon tetrachloride. T. W. PARKER and P. L. ROBINSON (J.C.S., 1927, 2977—2981).—The critical temperatures of these substances, purified by vacuum fractionation, were determined by means of an improved form of apparatus. The temperature recorded at the appearance of the meniscus in the cloud during the change from vapour to liquid was taken as the critical temperature. The mean values are 178·8±0·2° for boron trichloride and 233·6±0·2° for silicon tetrachloride. Slightly lower values were, however, obtained by maintaining the substance near the critical temperature for some time, or after heating it at a higher temperature. G. A. ELLIOTT.

Thermal conductivities of certain liquids. G. W. C. KAYE and W. F. HIGGINS (Proc. Roy. Soc., 1928, **A**, **117**, 459—470).—The thermal conductivities of a number of common liquids have been determined by a plate method, over a range of temperatures up to 200° (where feasible). The apparatus consisted of two aluminium blocks, the upper "hot block" containing an electric heating coil and the lower "cold block" being provided with radiating fins. The test liquid was contained in a small trough running round the upper end of the cold block, and formed a layer, about 20 cm.^{2} in area and up to 0·5 mm. thick, between the two blocks. An aluminium guard plate containing a subsidiary heating coil was mounted above the hot block and separated from it by a thin film of air, and by adjusting the current through the subsidiary coil it was arranged that the energy supplied to the main heating coil should be almost all transmitted downwards through the test liquid. Corrections were applied for lateral heat loss from the hot block, heat transferred through the liquid in the trough, and heat lost by evaporation from the liquid in the trough. The following results were obtained for the conductivity at 20° and the temperature coefficient α in the expression $K_t=K_0(1+\alpha t)$, respectively: water, 0·0014, +0·001; glycerol, 0·00068, +0·0005; castor oil, 0·00043, −0·0005; aniline, 0·00041, 0·0000; olive oil, 0·00040, −0·0003; cylinder oil, 0·00036, 0·0004; transformer oil, 0·00032, −0·0006; "B.P." paraffin, 0 00030, −0·0001; paraffin oil, 0·00029, −0·0005. L. L. BIRCUMSHAW.

M. p. of the substituted amides of dibasic acids. C. R. BARNICOAT (J.C.S., 1927, 2926—2929).—The dibasic acids and their amides, anilides, o- and p-toluidides, and p-bromoanilides, up to the

C_{13}-member, have been prepared and their m. p. determined. The successive members of each of these series show alternation in m. p. For the free dibasic acids this alternation is considerably greater than for the corresponding monobasic acids, but it diminishes with increasing mol. wt. With the anilides the alternation appears to exhibit an unusual arrangement in groups of four members, whilst for the toluidides and *p*-bromoanilides it is less marked and more regular. An explanation of these variations on the theory of alternating polarities is put forward. The following new compounds are described: *Dicarboxylamides* of n-*nonane*, m. p. 173°, and n-*decane*, m. p. 189°; *dicarboxyanilides* of n-*nonane*, m. p. 156°, n-*decane*, m. p. 191°, and n-*undecane*, m. p. 158°; o-*toluidides* of *glutaric*, m. p. 222°, *adipic*, m. p. 222°, *pimelic*, m. p. 174°, *suberic*, m. p. 185°, *azelaic*, m. p. 171°, and *sebacic*, m. p. 179°, acids; *dicarboxy*-o-*toluidides* of n-*nonane*, m. p. 164°, n-*decane*, m. p. 164°, and n-*undecane*, m. p. 142°; p-*toluidides* of *glutaric*, m. p. 218°, *adipic*, m. p. 241°, *pimelic*, m. p. 206°, *azelaic*, m. p. 198°, and *sebacic*, 201°, acids; p-*bromoanilides* of *succinic*, m. p. 284°, *glutaric*, m. p. 256°, *adipic*, m. p. 268°, *pimelic*, m. p. 240°, *suberic*, m. p. 248°, *azelaic*, m. p. 225°, and *sebacic*, m. p. 225°, acids; *dicarboxy*-p-*bromoanilides* of n-*nonane*, m. p. 215°, n-*decane*, m. p. 213°, and n-*undecane*, m. p. 202°.

G. A. ELLIOTT.

Glass. I. Transition between the glassy and liquid states in the case of some simple organic compounds. G. S. PARKS and H. M. HUFFMAN (J. Physical Chem., 1927, **31**, 1842—1855).—The specific heats of *n*-propyl alcohol and propylene glycol in the liquid and in the supercooled states have been determined by the method previously described (A., 1925, ii, 491). There is a sharp change in specific heat during the transition between the glassy and the liquid states. The specific heat–temperature curves are similar in form to those of ethyl alcohol (*loc. cit.*) and of glycerol (Gibson and Giauque, A., 1923, ii, 124), the sharp rise in specific heat occurring at higher temperatures as the number of hydroxyl groups in the molecule increases. The specific heat and thermal conductivity in the glassy state are the same as in the crystalline condition, but are different from the values observed for the liquid state. A temperature range, 17° for *n*-propyl alcohol, 30° for propylene glycol, and 40° for glycerol, marks the transition between the glassy and liquid states.

L. S. THEOBALD.

Density of molten magnesium. K. ARNDT and G. PLOETZ (Z. physikal. Chem., 1927, **130**, 184—186). —The density of magnesium, determined by a sinker method in an atmosphere of hydrogen, is found to range from 1·58 to 1·51 over the temperature interval 666—720°. The work of Edwards and Taylor (B., 1923, 608) is in good agreement, and the final values given are 1·601, 1·536, and 1·470 at 650°, 700°, and 750° respectively.

L. S. THEOBALD.

Physical properties of some derivatives of *cyclo*hexane. N. N. NAGORNOV and L. A. ROTINJANC (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 162—173; cf. A., 1925, ii, 646).—Results are given of measurements of the vapour pressures at different temperatures, the critical temperatures, the m. p., and the specific volumes from the b. p. to the m. p. for methyl*cyclo*hexane, chloro*cyclo*hexane, and *cyclo*hexanol. For *cyclo*hexane, t_c 281·0°, the vapour pressure is given by $\log P=7{\cdot}01516-1306{\cdot}4/(235{\cdot}24+t)$; $dP/dt=22{\cdot}89$ mm. at the b. p. For methyl*cyclo*hexane, b. p. 100·8°, t_c 301·5°, the specific volume is given by $1{\cdot}27143/(1-0{\cdot}001084t-0{\cdot}000000126t^2-0{\cdot}0000000033t^3)$ and the vapour pressure by $\log P=6{\cdot}50393-1089{\cdot}9/(200{\cdot}0+t)$; $dP/dt-21{\cdot}1$ mm. at the b. p. For chloro*cyclo*hexane, b. p. 142·9°, m. p. −43·9°, t_c 314—325°, the specific volume is expressed by $0{\cdot}98228/(1-0{\cdot}0009564t+0{\cdot}0000001758t^2-0{\cdot}00000000303t^3)$; $\log P=7{\cdot}15895-1619{\cdot}5/(235{\cdot}6+t)$ and $dP/dt-19{\cdot}9$ mm. at the b. p. For *cyclo*hexanol, b. p. 160·6°, t_c 377°, the specific volume is $1{\cdot}05929/\{1-0{\cdot}0007856(t-25)-0{\cdot}000001472(t-25)^2\}$; $\log P=6{\cdot}80369-1199{\cdot}1/(145{\cdot}0+t)$, $dP/dt=22{\cdot}5$ mm. at the b. p. Except for *cyclo*hexanol, which is associated, the values of the ratio between the temperature Abs. and volume is almost constant for these compounds.

Albertosi's formula, $d^{5/3}=A-BT$ (A., 1916, ii, 214), may be converted into the form $V=V_{T=0}/(1-CT^{3/5})$, where V and $V_{T=0}$ are the specific volumes at $T°$ Abs. and 0° respectively, and C is a constant, equal to A/B. In this form, the expression differs from Mendeleev's law for the expansion of liquids principally in the exponent in the denominator. When this law is applied over a wide temperature range at low temperatures, deviations are observed, the magnitudes of these increasing as the temperature is lowered. For liquids obeying Cailletet and Mathias' law of the linear dependency on the temperature of one half of the sum of the densities of liquid and vapour, at temperatures corresponding with low vapour pressures the vapour pressure may be neglected, as it falls within the limits of accuracy of ordinary measurements of liquid density. In such case the law of expansion becomes $d-a-bt$ or $V=V_0/(1-kt)$, which is Mendeleev's law. As the vapour pressures of most organic compounds for pressures up to 100 mm. vary around 0·0004, this law should hold under these conditions, and this is actually confirmed by the data for methyl*cyclo*hexane. If it is assumed that the coefficient k of Mendeleev's formula depends on the temperature and this dependency is expressed by $k=a+bt+ct^2$, the formula becomes $V=V_0/(1+at+bt^2+ct^3)$, which agrees very accurately with the experimental data for any temperature interval nearly to the b. p.

T. H. POPE.

Relation of vapour pressure to particle size. S. L. BIGELOW and H. M. TRIMBLE (J. Physical Chem., 1927, **31**, 1798—1816).—Thomson's equation connecting vapour pressure with particle size is critically examined and is considered to have a very restricted range. Microscopical examination of sulphur droplets shows that whenever clear zones appear, as in Ostwald's experiment, the central, growing particle is always crystalline. No measurable distillation occurs when all droplets are kept in the liquid state, at a constant temperature, which is contrary to the requirements of Thomson's equation. Other liquids which wet glass show no distillation at a constant temperature, and it is concluded that such

liquids form droplets in equilibrium with a continuous film of the liquid itself on the wetted solid. With mercury, however, large globules were found to increase in size at the expense of the smaller drops, but this distillation ceased at the end of a few days before the complete disappearance of the latter. With iodine, naphthalene, and camphor, such growth could not be detected at a constant temperature, but it could be always observed when slight temperature differences were not eliminated. Distillation between a large and small meniscus in the case of benzene, toluene, ether, or water is too slow to permit the determination of the equilibrium position of the meniscus. The utility of Thomson's equation is questioned. L. S. THEOBALD.

Equation of state for easily liquefied hydrocarbons. II. Weight of a litre of *n*-butane. M. BECKERS (Bull. Soc. chim. Belg., 1927, **36**, 559—590).—A repetition of van Bogaert's determination of the weight of a litre of *n*-butane (A., 1927, 719) at 0° and under 710 mm. pressure has given the value 2·5192 g. R. CUTHILL.

Change of compressibility with pressure. L. H. ADAMS (J. Washington Acad. Sci., 1927, **17**, 529—533).—The compressibilities, β, of a number of elements and minerals have been determined directly or, when possible, from the change in length produced by pressure, P, the latter method being the more sensitive. When β is plotted against $d\beta/dP$ a curve is obtained from which the order of magnitude of the pressure coefficient of compressibility may be determined if the mean compressibility over a given pressure range is known. Tellurium and the alkali halides do not fall on the curve. J. GRANT.

Effect of temperature on the viscosity of air. R. S. EDWARDS (Proc. Roy. Soc., 1927, **A**, **117**, 245—257; cf. Williams, A., 1926, 234; Rankine, *ibid.*, 671).—The measurements were made in order to test Williams' conclusions (*loc. cit.*) respecting the validity of Sutherland's law of the variation of viscosity with temperature. A constant-volume method was used, the bulb containing the air and the capillary tube being surrounded by a vapour jacket to obtain definite temperatures. The following mean values were obtained for $\eta_\theta \times 10^4$ (c.g.s.u.): 1·7846 at 15°, 2·181 at 100°, 2·529 at 184·4°, 2·954 at 302·0°, 3·425 at 444·5°. The ratios of the viscosities, η_θ/η_{15}, show good agreement with the results of previous investigators with the exception of Williams. Sutherland's formula is strictly obeyed over the range considered, and no evidence is found of the breakdown discovered by Williams in the neighbourhood of 300°. The value of 118 is found for Sutherland's constant. L. L. BIRCUMSHAW.

Internal friction in solids. A. L. KIMBALL and D. E. LOVELL (Physical Rev., 1927, [ii], **30**, 948—959).—The internal friction constant has been determined for the following materials: rubber, celluloid, tin, maple wood, zinc, glass, aluminium, brass, copper, tungsten, iron, steel, phosphor-bronze, molybdenum, nickel, nickel-steel, and monel metal. Constants for some of these materials and bronze are also calculated from the results of other investigators. A. A. ELDRIDGE.

Method for comparing the times of mixing of two transparent liquids in different proportions, and some experimental results, particularly with gasoline and carbon disulphide. L. E. DODD (J. Physical Chem., 1927, **31**, 1761—1789).—A method of measuring the time of mixing of two or more transparent liquids, in which use is made of the optical effects produced by striæ on a beam of transmitted light, is described. The abrupt disappearance of the striæ makes possible the determination of this time with an accuracy of 3%. The data obtained with gasoline and carbon disulphide are reported and discussed, and results with water and a salt solution indicate the possibility of a wider application of the method. L. S. THEOBALD.

Refractometry of binary liquid systems. I. and II. V. J. ANOSOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 379—404, 455—457; cf. A., 1926, 234).—I. Three types of refractive-index curves are distinguished: (1) for ideal mixtures—a straight line or a curve closely approximating thereto; (2) for systems in which dissociation of the component occurs—a curve convex to the axis of concentration, and (3) for systems with reciprocal chemical action—a curve concave to the concentration axis.

Results are given for six binary liquid systems. For ethyl acetate–stannic chloride and piperidine–allylthiocarbimide in which the components react strongly, chemical combination is characterised by change in direction and by a maximum divergence from additivity. The piperidine–allylthiocarbimide curve exhibits a singular point.

II. The refractive index of mixtures of acetone and chloroform at 13° gives a curve slightly concave to the axis of composition (cf. Zawidzki, A., 1901, ii, 6). The values for the system acetic anhydride–water show a minimum for the composition $C_2H_4O_2$ and a maximum between 60 and 70 mols.-% H_2O, possibly indicating the formation of the compound orthoacetic acid, $CMe(OH)_3$. For benzene–glyceryl trinitrate, the refractive index isotherm at 12·5° exhibits concavity towards the axis of composition, the glyceryl nitrate probably undergoing association. T. H. POPE.

Magnetic susceptibility of binary liquid systems. N. A. TRIFONOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 434—435; cf. A., 1926, 234).—The magnetic susceptibility for the system allylthiocarbimide–dimethylaniline is related linearly to the molecular composition. Acetone–carbon disulphide gives a curve convex to the axis of abscissæ, whilst for acetone–chloroform the curve is concave and exhibits a maximum. For strengths of magnetic field 14—17 kilogauss and for temperatures 10—30°, the magnetic susceptibility is independent of both field strength and temperature. T. H. POPE.

Magnetic rotation of the plane of polarisation by binary liquid mixtures. N. A. TRIFONOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 436—440).—For the mixtures allylthiocarbimide–dimethylaniline, acetone–carbon disulphide, acetone–chloroform, allylthiocarbimide–piperidine, and acetic anhydride–water, the magnetic rotation curves are

symbatic to the viscosity curves. With systems in which the components react with one another, there is considerable deviation of the isotherms from rectilinearity. T. H. POPE.

Certain physical properties of mixtures of solutions of hydrochloric acid with sodium and potassium hydroxides. N. A. TRIFONOV, K. I. SAMARINA, V. J. ANOSOV, and S. I. TSCHERBOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 441—442).—The values of the specific gravity, coefficient of viscosity, magnetic rotation, refractive index, and electrical conductivity are given for an approximately $5N$-hydrochloric acid solution to which gradually increasing amounts of potassium (or sodium) hydroxide solution of similar concentration were added. The curve expressing each property in relation to the composition of the mixed solution consists of two branches meeting at an angle at the point corresponding with neutrality, the deviation from additivity being greatest at this point. T. H. POPE.

Eutectic f.-p. depression in binary mixtures. III. E. KORDES (Z. anorg. Chem., 1927, **168**, 177—188; cf. A., 1927, 1132).—The rule that the relative eutectic depressions of the f. p. of the components of a binary mixture are in the inverse ratio of the concentrations of the components in the eutectic mixture is applicable to many binary mixtures in which compound formation occurs. Divergencies arise, however, if either of the eutectic constituents decomposes on fusion; nevertheless, in such cases, the rule is generally valid if it is assumed that dissociation occurs completely. The hypothesis of partial dissociation will, however, explain the facts equally well in most instances. In a few cases where the eutectic temperature does not obey the rule even if decomposition is assumed to take place, it seems probable that solvate formation occurs. The rule is also applicable to binary systems which in the sense of the phase rule consist of more than two components. R. CUTHILL.

Binary azeotropic mixtures of ethyl alcohol with petroleum hydrocarbons. Y. TANAKA and T. KUWATA (J. Fac. Eng. Tokyo, 1927, **17**, 117—126).—A study of the azeotropic mixtures formed by ethyl alcohol and hydrocarbons shows that a simple relation exists between the b. p. of hydrocarbons or the mean b. p. of their mixtures, and the compositions and the mean b. p. of the azeotropic mixtures formed by the hydrocarbons or their mixtures and ethyl alcohol. The relation between the b. p. of hydrocarbons and the weight percentage of ethyl alcohol in azeotropic mixtures can be represented by a straight line corresponding with $W_H=(160-T_H)/1{\cdot}15$ for paraffin and naphthene hydrocarbons and with $W_H=(140-T_H)/0{\cdot}89$ for aromatic hydrocarbons, where W_H is the weight percentage of hydrocarbon in the azeotropic mixture and T_H the b. p. of the hydrocarbon. These results were arrived at from distillation experiments with azeotropic mixtures of ethyl alcohol with the following purified hydrocarbons: *n*-hexane, *cyclo*hexane, *cyclo*hexene, *n*-heptane, methyl*cyclo*hexane, benzene, toluene, and purified commercial gasoline samples of b. p. 117—119°, 129—131°, and 146—150°, respectively. The observed values of the weight percentage of hydrocarbons contained in azeotropic mixtures agree with the calculated values to within $\pm 3\%$. Hydrocarbons or their mixtures with b. p. below 45° or above 160° cannot form azeotropic mixtures under atmospheric pressure.

The relations between the b. p. of hydrocarbons and azeotropic mixtures are represented by a hyperbolic curve of formula $(T_H-T_{AZ})(81-T_{AZ})=K$, where T_{AZ} is the b. p. of azeotropic mixture and K is a constant equal to about 236 for paraffin and naphthene hydrocarbons, and about 150 for aromatic hydrocarbons. The b. p. of azeotropic mixtures can thus be calculated from the b. p. of the hydrocarbon contained in the azeotropic mixtures to within $\pm 1\%$.

For commercial gasoline having a wide range of b. p., good agreement is shown between the observed and the calculated values of T_{AZ}. The formulæ given above are equally applicable to hydrocarbon mixtures having a wide range of b. p. provided T_H and T_{AZ} are taken as mean the b. p. of the hydrocarbon mixture and of the azeotropic mixture, respectively. R. A. PRATT.

Azeotropism in binary systems containing an amide. M. LECAT (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, ii, 87—97).—The azeotropic data for binary systems containing acetamide or propionamide are collected and discussed. Empirical formulæ are given for the azeotropic lowering in systems containing hydrocarbons, esters, halogen compounds or ethers, and acetamide. J. S. CARTER.

New binary azeotropes. IX. M. LECAT (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, i, 149—158).—A further list of binary azeotropic mixtures and non-azeotropic systems is given. J. S. CARTER.

Partial vapour pressures of benzene–toluene and benzene–ethylbenzene mixtures. T. BELL and R. WRIGHT (J. Physical Chem., 1927, **31**, 1884—1886).—The partial pressures of the above mixtures have been determined at 20° using the air-current method and analysing the condensed liquid by means of the effect on the f.-p. depression of an added quantity of benzene. Complex formation, if any, occurs only to a slight extent. L. S. THEOBALD.

Viscosity of fused metals and alloys. I. L. LOSANA (Notiz. Chim.-Ind., 1927, 2, 1—4; Chem. Zentr., 1927, i, 2706).—A description of methods. A. A. ELDRIDGE.

Copper–silicon alloys of high copper content. W. GEISS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1927, **168**, 31—32).—The electrical resistance R, the temperature coefficient α of the resistance, and the tensile strength of copper–silicon alloys containing up to 6% Si have been measured between 20° and 100°. $R\alpha$ is approximately constant up to 5% Si; above this limit R increases very rapidly, but the change in α is very small. The rate of corrosion of the alloys in air decreases with increase of silicon content. H. F. GILLBE.

Rate of evaporation of small spheres as a method of determining diffusion coefficients. Diffusion coefficient of iodine. B. TOPLEY and R. WHYTLAW-GRAY (Phil. Mag., 1927, [vii], **4**, 873—

888).—An experimental arrangement is described for measuring the rate of evaporation of freely-suspended spheres of volatile material. It is shown that the diffusion coefficient of the vapour, D, is given by the equation $-dS/dt=8\pi MDp/\rho Rt$, where S is the surface area of the sphere at a time t, M the mol. wt., p the saturation pressure of the vapour, and ρ the density of the sphere. The correction applied for the self-cooling of the sphere is given by $T_2-T_1-pD\lambda/RT'_2k$, where k is the specific conductivity of the gas through which diffusion takes place and λ the specific heat of the material. The values of D for iodine measured at 4 temperatures showed good agreement with direct measurements in straight tubes, the mean values being 0·0851, 0·0814, 0·0808, and 0·0767 at 30·05°, 25·05°, 20·00°, and 14·00° respectively. C. J. SMITHELLS.

Reciprocal action between dissolved gases and solvent on the basis of the dependence of gas solubility on temperature. G. TAMMANN (Z. Elektrochem., 1927, **33**, 425—428).—Theoretical. The solubility of gases in water is closely related to the presence of the polymerised molecules, $(H_2O)_6$, and the form of the temperature–solubility curves for the commoner gases, as well as the formation of crystalline hydrates, are discussed in reference to this view. L. S. THEOBALD.

Traube's rule in connexion with hydrotropy. [Influence of salts of alkylbenzenesulphonic acids on the solubility of benzoic and phthalic acids.] H. FREUNDLICH and G. V. SLOTTMAN (Biochem. Z., 1927, **188**, 101—111).—Measurements have been made at 20° of the solubility of benzoic and phthalic acids in water in the presence of varying concentrations of sodium benzenesulphonate, *p*-toluenesulphonate, and *p*-ethylbenzenesulphonate. The ratio of the increase of solubility ΔL to the solubility L_c is a function of the concentration C of the added salt of the form $\lambda_c=\lambda_0c^n$, where $\lambda_c=\Delta L/L_c$ and λ_0 and n are constants specific to the system concerned. The ratio of the concentration of sodium benzenesulphonate to that of sodium *p*-toluenesulphonate, and of sodium *p*-toluenesulphonate to that of sodium *p*-ethylbenzenesulphonate which produce the same increase in solubility of benzoic acid has a mean value of 1·54 throughout the range examined. In the case of phthalic acid this ratio has a mean value of 1·61. These results therefore provide a further illustration of Traube's rule for an homologous series. E. A. LUNT.

Ionic distribution coefficients. E. LARSSON (Svensk Kem. Tidskr., 1927, **39**, 122—130; Chem. Zentr., 1927, ii, 1231—1232).—The solubility of silver acetate, propionate, benzoate, phenylacetate, hydrocinnamate, phenoxyacetate, benzilate, α-naphthoate, and triphenylpropionate in water and alcohol at 25° was determined by titration with thiocyanate; values of $P(A)$ in the equation $P(\mathrm{Ag})+P(A)=2\log l_1/l_2-0\cdot4l_1^{1/3}+4l_2^{1/3}$, where and l_2 are the solubilities and $P(\mathrm{Ag})=2\cdot1$, are tabulated. The greater the number of benzene rings in the anion, the smaller (in general) is the distribution coefficient; anions containing hydroxyl or carboxyl groups yield larger values. For a monobasic tartaric ion the value 3·8 is computed; for succinic acid 3·0, and for propionic acid 1·6. A. A. ELDRIDGE.

Adsorption. IV. Adsorption by coconut charcoal from binary mixtures of saturated vapours. The systems methyl alcohol–benzene, ethyl alcohol–benzene, *n*-propyl alcohol–benzene, and *n*-butyl alcohol–benzene. F. G. TRYHORN and W. F. WYATT (Trans. Faraday Soc., 1928, **24**, 36—47).—The experimental method was the same as that used for ethyl alcohol–benzene mixtures (A., 1926, 788). A review of the results for the four systems confirms the theory of three-stage adsorption already put forward (*loc. cit.*). The sharpness and extent of the second stage vary greatly from system to system. For the methyl and ethyl alcohol mixtures this stage is usually well defined, but is indistinguishable in the propyl alcohol mixtures. In the butyl alcohol mixtures it becomes more prominent and extensive as the concentration of alcohol in the liquid increases. This tendency towards second-stage masking also occurs in the methyl and ethyl alcohol mixtures, when the initial liquid mixtures are near to those of the minimum b. p., and an explanation is offered which suggests that the replacement of alcohol by benzene molecules (or *vice versa*) in the adsorbate is synchronous with a steady increase in the number of molecules adsorbed. The cause of the replacement is to be found in the tendency of the liquid adsorbate to come into equilibrium with the remaining liquid mixture. As equality of composition is never reached, it is inferred that the selective properties of a charcoal modify the vapour pressures of adsorbed substances in different degrees (cf. Baker, J.C.S., 1927, 949). A quantum mechanism based on energy transfer in the infra-red region is suggested for this effect. L. F. GILBERT.

Selective adsorption [of electrolytes during precipitation]. M. GELOSO and (MLLE.) L. S. LÉVY (Compt. rend., 1928, **186**, 35—37).—The distribution of electrolytes between the solid and liquid phases produced by the precipitation of manganese dioxide from an acid solution containing ferric and cupric sulphates has been studied. The distribution of each electrolyte between the solid and liquid phases does not appear to be modified by the presence of the other electrolyte. J. GRANT.

Adsorption by metallic hydroxides. V. Comparative study of the adsorptive power of iron, aluminium, and chromium hydroxides for acids and alkali. K. C. SEN (J. Physical Chem., 1927, **31**, 1840—1841).—The adsorption of citric, racemic, oxalic, malic, succinic, hippuric, benzoic, and sulphuric acids and of arsenious oxide by chromium hydroxide is much greater than by ferric and aluminium hydroxides. Except for sulphuric acid, ferric hydroxide shows a greater adsorptive power than aluminium hydroxide. L. S. THEOBALD.

Adsorption of acids by filter-paper. II. S. G. MOKRUSCHIN and E. J. KRYLOV (Kolloid-Z., 1927, **43**, 387—389).—On the basis of the theory of electrical adsorption (Mokruschin and Essin, A., 1926, 573) an explanation is given of the fact that for small amounts of adsorption the maximal adsorption is reached at

low concentrations. Curves are given for the adsorption of citric, formic, phosphoric, arsenic, acetic, monochloroacetic, and trichloroacetic acids by filter paper. The experimental results are in complete agreement with the formula previously derived (*loc. cit.*). E. S. HEDGES.

Adsorption on dissolved molecules. II. M. S. MARINESCO (J. Chim. phys., 1927, **24**, 593—620; cf. A., 1927, 1135).—The viscosities and diffusion coefficients of solutions of certain fluorescein derivatives etc. in water and in various alcohols have been measured. To obtain the diffusion coefficients a microcolorimeter of special design was used. The results are interpreted in terms of Einstein's theory (Z. Elektrochem., 1908, **14**, 235—239), and indicate the formation of an adsorbed layer of the solvent on the surface of the large solute molecules. This layer is approximately unimolecular for all the solvents considered, although the degree of adsorption depends to some extent on the electrical properties of the solvent and of the solute. In alkaline solutions of fluorescein a layer of hydroxyl ions may be adsorbed and adsorption of the solvent is then prevented. G. A. ELLIOTT.

Absorption of water by gelatin. D. J. LLOYD and W. B. PLEASS (Biochem. J., 1927, **21**, 1352—1367).—Sodium chloride in the presence of hydrochloric acid and up to a concentration of 0·01M suppresses the swelling of gelatin due to acid; at greater concentrations it causes a coagulation of the acid gelatin. The maximum of acid swelling is at p_H 2·6. In the presence of sodium hydroxide the salt also suppresses the swelling due to the alkali. The salt has no further action even at high concentrations (2M). The maximum alkaline swelling is at p_H 9·8. The swelling of gelatin due to acid or alkali increases as an exponential function of the temperature. The point of minimum swelling of ash-free gelatin (isoelectric point) is at p_H 5·0. At this point sodium chloride promotes water absorption, swelling being proportional to the logarithm of the concentration of the salt. At p_H 5 in the absence of salts swelling increases slowly with rising temperature up to 15° or 18°, after which with further rise there is a decrease of swelling at the same p_H. Sodium chloride increases swelling slowly with temperature up to about 18°, after which there is very rapid increase ending at about 20° in complete dissolution of the gelatin. The greater the concentration of sodium chloride present the lower the temperature at which dissolution occurs. At p_H 7 in the absence of salts gelatin shows some swelling due to the alkali present. The addition of sodium chloride up to 0·01M causes a suppression of swelling; at greater concentrations the salt, as at p_H 5·0, induces a swelling which is in logarithmic ratio to its concentration. At p_H 7 in salt solutions stronger than 0·01M the effect of temperature on swelling resembles that at p_H 5. When the concentration of sodium chloride is less than 0·01M, or in the absence of salts, the effect of temperature on swelling at p_H 7 is intermediate between its effects in the alkaline and in the isoelectric zones. When gelatin is in solution as electrically-charged particles the effect of adding sodium chloride is mainly electrostatic, but when present in electrically neutral forms the salt acts by adsorption and hydration. The theoretical aspects of swelling are discussed. S. S. ZILVA.

Heat of adsorption of oxygen on charcoal. A. F. H. WARD and E. K. RIDEAL (J.C.S., 1927, 3117—3128).—An apparatus for the determination of the heat of adsorption and the amount of adsorption of oxygen by charcoal is described, and values have been obtained for four different charcoals. The rates of autoxidation have been measured at 40° by the method of Rideal and Wright (A., 1925, ii, 806). The area of methylene-blue adsorption, the ash content, and the true and apparent bulk densities have also been determined. High initial heats of adsorption were observed, due to the existence of patches of more active charcoal surface. The extent of these was measured by the amount of oxygen adsorbed, and was found to be proportional to the rate of autoxidation of the charcoal. From data previously obtained (*loc. cit.*), it is possible to calculate the amount of amyl alcohol necessary to poison the autoxidation of the charcoals considered. This bears a constant ratio to the amount of oxygen adsorbed with the initial high heat of adsorption. The behaviour of one charcoal of high ash content was exceptional and seems to indicate an instability of the carbon surface. M. S. BURR.

Determination of the value of adsorbents. W. BACHMANN and L. MAIER (Z. anorg. Chem., 1927, **168**, 61—72).—Determination of the adsorption maximum of an adsorbent does not give complete information as to its value, especially for industrial purposes. Complete sorption and desorption curves are necessary. Such curves may be obtained for silicic acid gels by Gustaver's method with considerable accuracy, and in 1/20th—1/30th of the time usually required. The characteristic hysteresis curves are obtained. H. F. GILLBE.

Absorption of butyric acid on water surfaces. C. R. BURY (Phil. Mag., 1927, [vii], **4**, 980—984).—Calculations of the amount of butyric acid absorbed on water surfaces, from measurements of surface tension, have assumed that the activity of the acid is proportional to its concentration. This assumption is unjustified and new calculations using Jones and Bury's values for activity (this vol., 128) are given. Butyric acid forms saturated surface layers at the water-air surface, in which the area occupied by a molecule of acid is independent of concentration over a wide range, but increases slightly with temperature. The area occupied by a molecule at the water–hexane interface is smaller than at the water–air surface, but larger than that occupied by the higher fatty acids and alcohols. There is no evidence of the formation of a saturated surface layer at the water–benzene interface. C. J. SMITHELLS.

Adsorption. XXI. Influence of similarly charged ions on the coagulation of sols of Congo-red, benzopurpurin, and cerium hydroxide. S. GHOSH and N. R. DHAR (Kolloid-Z., 1927, **43**, 389—395).—In their behaviour towards coagulation, sols may be divided into two groups, which the authors term "anomalous" and "normal." The anomalous

sols require more of a univalent positive ion for coagulation in dilute than in concentrated solution, and the coagulating power of a mixture of electrolytes with ions of different valencies is not additive towards such a sol. Congo-red is an anomalous sol, and cerium hydroxide behaves as a normal sol. Benzopurpurin occupies an intermediate position, since it behaves normally towards mixtures of electrolytes, but gives an anomalous dilution effect.
E. S. HEDGES.

Sorption. M. TARLE (Bull. Chem. Soc. Japan, 1927, 2, 304).—A reply to Sameshima (A., 1927, 1135).
R. CUTHILL.

Hydrolytic adsorption and equilibrium displacement. D. TALMUD (Kolloid-Z., 1927, 43, 386—387).—When a solution of aluminium sulphate is agitated with activated charcoal, adsorption of sulphuric acid occurs and the excess of aluminium hydroxide remains in colloidal solution. The amount of sulphuric acid adsorbed can be determined by washing out the charcoal with an emulsion of light petroleum in water and then titrating with sodium carbonate. Using a mixed solution containing 0·66% of aluminium sulphate and 4·01% of potassium sulphate, the amount of sulphuric acid adsorbed by charcoal is greater than the sum of the amounts adsorbed from the two solutions separately.
E. S. HEDGES.

Adsorption anomalies. WO. OSTWALD (Kolloid-Z., 1927, 43, 268—276).—From a consideration of published data it is shown that adsorption anomalies occur both for very small and very large amounts of the adsorbent. The relative adsorption decreases for small amounts of the adsorbent and has a maximum value for a critical amount of solid phase. When a large excess of the adsorbent is used, the relative adsorption again falls, but later passes through a minimum and begins to rise again. The behaviour is explained as being due to the dispersion of some of the adsorbent, so increasing the surface; with very small amounts of adsorbent, the adsorption causes the coagulation of this dispersed material, corresponding with the fall in the relative adsorption. The anomaly in the region of large amounts of adsorbent is explained as a normal function of the curve connecting x/m with m, where x is the amount of adsorbed material and m the amount of adsorbent.
E. S. HEDGES.

Derivation of an adsorption equation from Langmuir's theory of residual valencies. M. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1927, 43, 377—386).—The following adsorption equation is derived: $a/A=(\alpha\mu/K)^{1/n}/[1+(\alpha\mu/K)^{1/n}]$, where α is the adsorption coefficient, μ the number of molecules striking against the surface, a the adsorbed amount, A the maximal adsorption, and n the valency of the adsorbed ions. It follows from the equation that for strong adsorption the degree of adsorption will increase with the valency of the ion, but for slight adsorption the multivalent ions will be adsorbed least. For small concentrations of the adsorbed substance the equation approximates to the ordinary logarithmic equation. The equation shows that the diminution of adsorption by the presence of a foreign substance is the greater the less the substance is adsorbed. This has been established experimentally. The theory is in good agreement with experiments on the adsorption of various electrolytes by manganese dioxide and by the hydroxides of iron, aluminium, and chromium.
E. S. HEDGES.

Cohesion in surface films. N. K. ADAM (Trans. Faraday Soc., 1927, 24, 149—154).—The nature of the cohesive forces in surface films of long-chain substances on water, aqueous solutions, and hydrochloric acid is discussed. These films are of three types, the condensed type with close-packed, nearly vertically oriented molecules, the gaseous type, in which the molecules are flat in the surface and move independently, and the expanded type, intermediate in area and properties between the first two. The author's previous suggestion (A., 1926, 1002), that, in the expanded type, the molecules have their chains coiled in helices with vertical axis, is rejected because liquid-expanded films have now been found with areas different from the 48 Å.^{2}, which was previously considered to be a constant for this type of film, this supposed constancy being the foundation for the helical theory. These films probably contain tilted molecules, but the peculiar properties of each head determine primarily the spacing of the heads, and secondly the tilting of the chains. In the condensed films the rigidity increases with the length of the chain, the temperature of expansion at which the condensed film breaks down being raised about 10° near 0°, and 7° near 60° for each additional carbon atom. The lateral adhesion also depends on the heads and end groups. The attraction of the end group for water is one of the chief factors in determining the stability of a film, the following being a rough classification; (*a*) very weak attraction, no film formed: hydrocarbon, $\cdot CH_2I$, $\cdot CH_2Br$, $\cdot CH_2Cl$; (*b*) weak attraction, films unstable (groups in increasing order of attraction for water): $\cdot CH_2{\cdot}OMe$, $\cdot C_6H_4{\cdot}OMe$, $\cdot OAc$; (*c*) strong attraction: $\cdot CH_2{\cdot}OH$, $\cdot CO_2H$, $\cdot CN$, $\cdot CO{\cdot}NH_2$, $\cdot CH{:}N{\cdot}OH$, $\cdot C_6H_4{\cdot}OH$, $\cdot CH_2Ac$. It is probable that the intermolecular forces in these films are of the same nature as those in the crystals of the substances concerned, and relations between the m. p. are traced in this way.
W. HUME-ROTHERY.

Effect of the acidity of the support on the structure of unimolecular films. H. EGNER and G. HAGG (Phil. Mag., 1927, [vii], 4, 667—670).—The dissociation constants of the fatty acids are all in the region of 10^{-5}, and it has been shown by Adam (A., 1921, ii, 488) that a palmitic acid film on water exhibits a maximum spreading tendency when the p_H of the water is less than 5·5. It is suggested therefore that for films of fatty acid on water the hydrogen-ion concentration at which the spreading is most rapid is numerically equal to the negative logarithm of acid dissociation constants of the fatty acid. The possible application of the principle to the determination of the dissociation constants of sparingly soluble substances is indicated.
A. E. MITCHELL.

Electrostatically charged limiting surfaces. R. AUERBACH (Kolloid-Z., 1927, 43, 114—131).—The diminution in surface tension of liquids bearing simple electrostatic and double-layer charges has been

studied theoretically, and investigated experimentally for water, mercury, acetone, and *iso*butyl alcohol. Under certain definite conditions reproducible negative values for the surface tension were obtained.

The energetics of electrical dispersion are discussed. By means of electrical charges, liquids may be dispersed in air or insulating liquids, resulting, in the latter case, in emulsions of the water-in-oil type, in which the disperse phase carries free charges. It is possible to recover these charges so that the system may be regarded as an "accumulator" for free electrical energy. The evidence for this view is that an electroscope may be discharged or a Geissler tube made to glow from the emulsion. R. A. MORTON.

Surface tension of protein solutions. III. J. H. ST JOHNSTON (Biochem. J., 1927, **21**, 1314—1328).—As in the case of gelatin (cf. A., 1925, ii, 659; 1926, 1092) the surface tension of caseinogen and egg-albumin solutions varies with the p_H. There is a maximum at the isoelectric point and secondary maximum at a lower ; the minimum corresponds with the maxima of other properties. Neutral salts in low concentration lower the surface tension of the above proteins in acid solution but raise it in a greater concentration. Denaturation of egg-albumin lowers its surface tension. There is a rapid fall at first in the surface tension of freshly made up acid or alkaline solutions of caseinogen, the equilibrium not being reached until nearly 24 hours. The bearing of these results on the Donnan equilibrium is discussed.

S. S. ZILVA.

Permeability of membranes. IV. Variations of transfer numbers with the dried collodion membrane produced by the electric current. L. MICHAELIS and A. A. WEECH (J. Gen. Physiol., 1927, **11**, 147—158; cf. A., 1927, 727).—When an electric current is passed through a collodion membrane separating a solution of potassium chloride on the cathode side from a solution of potassium nitrate on the anode side the transfer number for chlorine ions depends on the concentration of potassium chloride, also on the strength of the current and on the previous treatment of the membrane.

W. O. KERMACK.

Permeability of gelatin membranes. R. COLLANDER (Protoplasma, 1927, **3**, 213—222).—Although the living protoplasm is much more readily permeable to surface-active, and incidentally lipoid-soluble, substances than to inactive substances, such differences are not observed with membranes of copper ferrocyanide or collodion (A., 1925, ii, 201; 1926, 791). The behaviour of these two classes of substances towards a gelatin membrane has therefore been investigated to ascertain whether a membrane composed of protein substance resembles the living protoplasm in its selective permeability. Such investigations have been carried out by Traube and co-workers (cf. A., 1925, i, 735), but it is claimed that their results are inconclusive since the molecular dimensions of the substances investigated are small compared with the pore dimensions of the gelatin gel. No such criticism can be levelled against the present data, which have reference to thick membranes and to organic substances of high mol. wt. A surface-active and -inactive substance were allowed to diffuse simultaneously through the same membrane, measurements being made with aqueous and methyl-alcoholic solutions. The measurements show that molecular size (as measured by molecular refraction) is the main factor governing the rate of diffusion, the capillary-active or -inactive nature of the substance being relatively unimportant. The differences between the present results and those obtained with the living protoplasm are briefly discussed, and the present data interpreted as supporting the lipoid theory.

J. S. CARTER.

Dialysis. I. Law of decrease in dialysis. II. Course and rate of dialysis as a function of the "specific surface." H. BRINTZINGER (Z. anorg. Chem., 1927, **168**, 145—149, 150—153).—I. It is found that if c_0 is the concentration of a diffusible ion or molecule at the commencement of a dialysis, the concentration c_t after a time t is given by the expression $c_t = c_0 e^{-\lambda t}$. Here λ is a constant if the liquid being dialysed is kept well mixed, the specific surface is not too small, the concentration difference of the diffusible ion on the two sides of the membrane is maintained maximal, and considerable temperature variations do not occur. From the above equation, the rate of dialysis at time t may be shown to be given by the relation $d(c_0 - c_t)/dt = \lambda c_t$.

II. For a particular dialysis, λ is directly proportional to the specific surface, from which it may be deduced that the times required to reach a given concentration are inversely proportional to the specific surface, and also to λ. R. CUTHILL.

Filtration phenomena. A. SIMON and W. NETH (Z. anorg. Chem., 1927, **168**, 221—254).—Experiments have been made on the rate of filtration of water and aqueous solutions of electrolytes, chiefly acids and bases, through various types of crucible with porous bottom, including Schott crucibles with sintered glass bottoms, Berlin crucibles with porous porcelain plates, Haldenwanger porous porcelain crucibles, and a Neubauer platinum crucible. In filtering with the aid of suction, it is found that as the amount of liquid which has passed through the crucible increases, the rate of filtration, even of pure water, diminishes, gradually at first, then more and more rapidly, until the crucible becomes practically stopped up. The rate at which stoppage is approached is different for different liquids, and in some instances a particular liquid may temporarily promote the subsequent filtration of a different liquid. Hydroxide solutions appear to be particularly effective in blocking up the filter, yet the phenomenon is not entirely ionic, since it is observed with non-electrolytes, such as acetone. With all the liquids examined, it is found that a second filtration following soon after the first occurs at a steady rate, without the crucible becoming choked. If, however, the first filtrate is kept for 20—30 hrs. in a closed vessel, or boiled, on being filtered again it behaves as if it were a fresh unfiltered liquid, so that it cannot be suspended matter in the solutions which retards filtration. Under comparable conditions, the rate of filtration of a freshly-filtered liquid is greater than that of the

same liquid unfiltered. When unfiltered water is filtered under hydrostatic pressure without suction, the rate of filtration first rises, then passes through a maximum, and ultimately falls below the initial rate. Using water which has previously been filtered, however, the rate of filtration remains steady at the maximum value, indicating that the fall observed with unfiltered water must be due to the same causes as the phenomenon manifested in filtration by suction, rather than to the separation of air in the pores of the filter, as Zakarias has suggested (A., 1925, ii, 862). The initial rise must be due to the wetting of the capillaries and removal of air, since it is absent when boiled-out water is filtered in a vacuum with a crucible the pores of which have previously been filled with water. In order to arrive at an explanation of the various phenomena observed, attempts were first made to detect electrification of the sintered mass. After water had been filtered through it, it was found to hold a positively-charged silver iodide hydrosol, but to allow a similar sol with a negative charge to pass. Application of a *P.D.* across the mass showed little more than an ordinary electro-osmosis effect. Attempts to detect static charges were also fruitless. No evidence could be obtained of any swelling of the filtering material. It appeared probable that stoppage of the crucible might be brought about by the larger species of water molecules, since the refractive index of water was slightly increased by filtration, but this effect was subsequently found to be due to the removal of dissolved gases. No satisfactory explanation of the above phenomena has therefore been obtained. R. CUTHILL.

Relationship between the viscosity of water and the pressure and that of solutions and the concentration. G. TAMMANN and H. RABE (Z. anorg. Chem., 1927, **168**, 73—85).—The viscosities of solutions of potassium chloride, bromide, and iodide and of ammonium chloride and nitrate have been determined by the Ostwald viscosimeter at 0°, 10°, 30°, and 75° at concentrations of 1—5*M*. The change of the relative viscosity of the solutions, referred to water as unity at each temperature, has been calculated as a function of the difference ΔK between the internal pressure of the solution and of the solvent; ΔK is interpolated from coincident pressure values of the isobars of water under a pressure ΔK and those of the solutions. The differences between the curves showing the relationship between viscosity η and external pressure yield linear curves for all the potassium salts investigated. The relationship between the viscosity of water at 0° and the pressure p is given with considerable accuracy for the pressure range 0—2000 atm. by the equation $\eta=1-0{\cdot}1349\times10^{-3}p+0{\cdot}5778\times10^{-7}p^2$. For the potassium halide and nitrate solutions the equation $\eta=1-0{\cdot}1349\times10^{-3}\Delta K+0{\cdot}5778\times10^{-7}\Delta K^2+\sigma_\eta\,.\,\Delta K$ is valid, η being the viscosity of the solution and σ_η a constant characteristic of the salt. Similar equations hold at higher temperatures.

The variation with pressure of the interionic friction in a solution is similar to, but not identical with, that of the viscosity, the constant σ_η being different. Further, the influence of temperature on the viscosity is greater than that on the interionic friction. H. F. GILLBE.

Preparation of colloidal sulphur by means of hydrazine. WO. OSTWALD and I. EGGER (Kolloid-Z., 1927, **43**, 353—355).—Stable sols of sulphur can be prepared by the action of hydrazine hydrate on sulphur and then dispersing in hot water, or by pouring the sulphur–hydrazine solution into water and then dialysing. E. S. HEDGES.

Kinetic studies on the formation of starch paste. I. Formation of starch paste in the cold. WO. OSTWALD and G. FRENKEL (Kolloid-Z., 1927, **43**, 296—312).—A study has been made of the formation of paste from starch suspensions under the influence of various added substances, and of the effect of varying the concentration, temperature, moisture, and previous treatment. The substances which facilitate the change are sodium, potassium, and ammonium thiocyanates, sodium and potassium hydroxides, hydrochloric acid, sodium salicylate, and carbamide. The viscosity curve of the process is S-shaped, like that of the setting of plaster of Paris. The experimental curves can be divided into three groups, according to the portion of the S-shaped curve which can be realised. The addition agent becomes effective at a certain critical concentration and has a large " concentration coefficient." The concentration of the starch suspension and the temperature are also of great influence on the velocity of formation of paste. Different velocities were found for different kinds of starch, and thus this effect can serve as a means for the characterisation of starch.
E. S. HEDGES.

Aqueous extracts of seeds as agents in the preparation of silver sols. E. V. MILLER and R. P. HIBBARD (Plant Physiol., 1926, **1**, 409—413).—Stable, negatively-charged silver sols are obtained by adding 2 drops of 0·1*N*-silver nitrate solution to the filtered aqueous extracts of various seeds. The reduction, which is probably due to proteins, with sugar as stabiliser, is accelerated by exposure to sunlight, although over-exposure precipitates the silver.
CHEMICAL ABSTRACTS.

Colours of colloidal silver, especially on flocculation. E. WIEGEL (Koll.-Chem. Beih., 1927, **25**, 176—230).—The colour of colloidal solutions is discussed with particular reference to the many colours which are characteristic of silver sols. Using *p*-hydroxyphenylglycine as a reducing agent, silver sols having a variety of colours can be produced. Comparison of the colour of such unprotected sols with that of sols prepared in presence of gelatin shows that the colour is in no way due to the relations between the gelatin and silver in the colloidal particle. The particles are anisotropic, giving rise to a stream-double refraction. Unpurified silver sols prepared by Carey Lea's method using dextrin undergo a colour change on keeping for some months, the colour in transmitted light changing from yellow to orange, purplish-red, violet, and then blue. It is shown that this change is due to a slow coagulation of the colloidal silver, and the velocity of the change depends on the electrolyte content of the sol. With progressive coagulation there occurs a displacement

of the absorption maximum in the region of greater wave-lengths and a broadening of the absorption band. When the coagulated silver is dried, a product is formed the colour of which is complementary to the colour of the sol in transmitted light. The stream-dichroism observed in the silver sols on slow coagulation shows that the particles are anisotropic, and comparison of the experimentally obtained extinction curve with theoretical curves leads to the conclusion that the particles are leaf-like. The anisotropy becomes stronger with increasing age of the sol. Experiments were also carried out on Carey Lea's silver sols prepared by the citrate method. It was observed that the flocculating power of bivalent cations is about 100 times that of univalent cations. In sols prepared both by the dextrin method and also by the citrate method, flocculation by bivalent cations is accompanied by the normal colour sequence: yellow, red, violet, blue; but with univalent cations an anomalous colour sequence is observed: yellow, yellowish-green, dark green, blue. These anomalous colours appear to be mixed and are probably due to partial flocculation. Addition of a small amount of silver nitrate to an old, reddish-violet, slightly alkaline silver sol produces a colour change to green. This is due to the adsorption of silver oxide by the silver particles, because the same effect can be produced by direct addition of a silver oxide sol, and also the reddish-violet colour returns after addition of ammonia or sodium thiosulphate. The particles of the green sols are negatively charged. The light absorption of the two components of the particles is not additive. The dextrin silver sols, especially those having an orange colour, are sensitive to light. The most effective rays are the blue and violet, flocculation taking place in a few seconds. E. S. HEDGES.

[Refractive] indices of colloidal solutions. A. BOUTARIC and [MLLE.] G. PERREAU (Rev. gen. Colloïd., 1927, **5**, 658—662).—An illustration of the applicability of an interferential refractometer to the study of colloidal solutions. The difference between the refractive index of a sol and that of the intermicellar liquid obtained by dialysis increases linearly with the concentration of the sol. In presence of electrolytes the refractive index of a sol remains constant until actual precipitation commences. Adsorption during sedimentation may be followed refractometrically.

J. S. CARTER.

Emulsions with refraction colours. I. D. BHALLA, S. S. BHATNAGAR, and N. A. YAJNIK (Kolloid-Z., 1927, **43**, 366—377).—The authors describe experiments on the formation of emulsions with refraction colours in which the influence of the volume of both phases, the nature and concentration of the emulsifier, and the temperature has been studied. Stable gels of a gelatin solution in glycerol were prepared, showing refraction colours. Two types of coloured emulsions can be distinguished: (*a*) those which on rise of temperature undergo a colour change from blue, through green, to yellow, (*b*) those which undergo the reverse colour change. The view put forward by Holmes and Cameron (A., 1922, ii, 269) that such a coloured emulsion requires equality of refractive indices of the two phases but a difference in optical dispersion, has been established experimentally. E. S. HEDGES.

Viscosimetry of colloidal systems. WO. OSTWALD (Kolloid-Z., 1927, **43**, 190—209).—Consideration of data published elsewhere shows that similar results are obtained for the structure viscosity effect when different forms of apparatus are used. The agreement between the results obtained with the Couette apparatus and the capillary viscosimeter is at variance with accepted views. The author attempts an explanation. E. S. HEDGES.

Viscosity anomalies of sols in the Couette apparatus. WO. OSTWALD (Kolloid-Z., 1927, **43**, 210—214).—Anomalies are shown by the sols of gelatin and starch in the Couette apparatus, which are not met with when the capillary viscosimeter is used. It is claimed that the non-reproducibility of the anomalies in the capillary viscosimeter is not at variance with the author's experiments, which indeed show that the observed results are due to the special construction of the Couette apparatus. In the case of the gelatin sol the effect is due to the adsorption of the colloid on the inner cylinder, so increasing the roughness of the wall. In the case of the starch sol the anomaly is explained by the destruction of the structure of the sol in carrying out the measurement by the Couette method. E. S. HEDGES.

Structure and formation of colloidal particles. H. FREUNDLICH (Trans. Faraday Soc., 1927, **23**, 614—623).—The application of *X*-ray measurements to the determination of the state of aggregation and the crystalline form of colloidal particles, and the various optical methods for determining their shape, with special reference to the use of the azimuth diaphragm, are discussed. An account of the different possible structures of colloidal particles, the factors influencing their formation, and the changes which they undergo after formation, is also given.

M. S. BURR.

Sols with structure-viscosity. I. Viscosimetry of ammonium oleate sols. II. Structure-turbulence of sols of cotton-yellow and mercury sulphosalicylate. WO. OSTWALD, R. AUERBACH, and J. FELDMANN (Kolloid-Z., 1927, **43**, 155—181, 181—187).—I. An account is given of very extensive measurements of the viscosity of ammonium oleate sols, using many different forms of apparatus. The reproducibility of the results compares favourably with that obtained with other sols, *e.g.*, gelatin. The viscosity curves obtained for ammonium oleate sols are compared with those for gelatin sols; on the whole, there is no essential dissimilarity. The behaviour of sols of ammonium oleate as regards turbulence and structure viscosity depends on the concentration of the sol, structure-viscosity becoming more prominent in the more concentrated sols. Mechanical treatment reduces the viscosity for high and medium velocities. Heating at 65° destroys completely the usual viscosity relations of ammonium oleate sols. These results are discussed from a theoretical point of view. The measurements carried out by means of the capillary viscosimeter confirm those obtained by Hatschek and Jane (A., 1926, 240), using the Couette apparatus.

II. The structure-turbulence anomaly shown by the viscosity of ammonium oleate sols (preceding abstract) is found also in sols of cotton-yellow (whether purified or containing salts) and in gels of mercury sulphosalicylate. The effects are obtained using either the Couette apparatus or capillary viscosimeters of various types. Cotton-yellow sols containing sodium sulphate at various concentrations develop structure-turbulence, which disappears again at higher concentrations. There is a maximum viscosity at about 1·3%. Sols showing well-defined structure-turbulence also show marked shear-elasticity. E. S. HEDGES.

Jelly formation of ceric hydroxide hydrosol. W. BILTZ (Z. anorg. Chem., 1927, **168**, 96).—A claim for priority over Chakravarti, Ghosh, and Dhar (A., 1927, 934). H. F. GILLBE.

Relation between viscosity and electrolytic dissociation of colloidal solutions. I. Behaviour of gelatin hydrosols before and after treatment with proteolytic substances. S. VISCO (Arch. sci. biol., 1926, **8**, 471—479; Chem. Zentr., 1927, i, 2402).—From p_H 4·6, the viscosity of gelatin solutions increases with addition of hydrochloric acid to a maximum value at p_H 2·8 and thereafter diminishes. After treatment with trypsin, the gelatin solutions did not exhibit this maximum. The changes in viscosity are hence ascribed to changes, possibly the presence of sub-microscopic particles, in the protein solution, and not to ionisation variations. A. A. ELDRIDGE.

Viscosity factor in emulsification. R. C. SMITH (Phil. Mag., 1927, [vii], **4**, 820—826).—It is pointed out that it is not the viscosity of the dispersion medium but rather the viscosity of the interfacial film between the suspensoid and the dispersion fluid which is the limiting factor in emulsification. An examination of a large number of suspensions of solids in liquids has shown that solids which are readily emulsifiable exhibit as a rule high interfacial tensions with the dispersion medium. A. E. MITCHELL.

Solubility of cellulose esters. I. II. Solubility of cellulose acetate in acetone. I. SAKURADA and T. NAKASHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 153—164, 165—171).—I. Di- and tri-esters of cellulose with palmitic, stearic, and lauric acids, which are partly soluble in organic liquids, have been prepared by the action of the acid chloride on cotton cellulose in a mixture of pyridine and benzene. By heating the insoluble portions of the stearic esters in naphthalene at 200°, or with stearic acid or benzenesulphonic acid, they are rendered more or less completely soluble. Since this process is in no case accompanied by hydrolysis, and since the cellulose regenerated from the esters corresponds in properties with Hess' cellulose-*A*, it is concluded that the change in solubility is associated with physical changes, probably in molecular arrangement. Determinations of the mol. wt. in camphor by the cryoscopic method indicate that the soluble esters are associated.

II. By acetylation of secondary cellulose acetate which is soluble in acetone, it becomes partly insoluble. From a comparison between the solubilities of the cellulose acetates and the cellulose esters of the fatty acids, and the methods by which the solubility may be increased, it appears probable that in both sets of compounds the changes in solubility must be due to the same causes. By means of this hypothesis, some explanation of the "ripening" of primary cellulose acetate can be derived (cf. Ost, B., 1919, 355). R. CUTHILL.

Application of the Aitken effect to the study of aerosols. H. L. GREEN (Phil. Mag., 1927, [vii], **4**, 1046—1069).—A continuous-action Wilson cloud apparatus has been devised in which the counting of the particles is effected by a photographic method. The apparatus has been used for the study of ammonium chloride and cadmium oxide clouds. In the case of ammonium chloride the rate of coagulation of the cloud could be expressed by the equation $1/n=1/n_0+Kt$, where n is the number of particles per c.c. at time t, n_0 is the initial number of particles, and K the coagulation constant. K decreases as the initial concentration increases and it is suggested that the degree of dispersion of a cloud depends both on the degree of supersaturation of the vapour and the number and size of the nuclei present in the air. Similar results were obtained with cadmium oxide clouds. The results have been verified with a visual ultramicroscope. A. E. MITCHELL.

Structural-chemical contributions to colloid-chemical problems. M. BERGMANN (Gerber, 1926, **52**, 195—196; Chem. Zentr., 1927, i, 2520).—Simple molecules can assume the properties of proteins. Alanylserine anhydride, by loss of a molecule of of water, yields three methylenedioxymethylpiperazines, having mol. wt. 140, of which two are very sparingly soluble in water. From the *iso*-form a substance is obtained with formaldehyde which yields colloidal solutions in water, gelatinises, and precipitates tannin. The postulate of very large "principal valency molecules" is unnecessary in protein chemistry. A. A. ELDRIDGE.

Change in viscosity and electrical conductivity of sols on ageing, and formation of gels of inorganic substances. N. R. DHAR and D. N. CHAKRAVARTI (Z. anorg. Chem., 1927, **168**, 209—217).—With increasing age, sols of thorium hydroxide (prepared either in the hot or in the cold), ceric hydroxide (prepared in the hot), ferric hydroxide (prepared in the cold), and benzopurpurin manifest increasing conductivity and decreasing viscosity, thus behaving like the other hydrophobic colloids previously examined (A., 1927, 629). Gelatin sols, however, first become more viscous, and do not change in conductivity. With silicic acid sols prepared either in the hot or in the cold, both viscosity and conductivity increase, this phenomenon being attributed to the aggregation of particles of molecular dispersity on the one hand, and to the release of adsorbed electrolytes on the other. A ceric hydroxide sol prepared in the cold, and kept until it has stiffened to a gel (*ibid.*, 934), ultimately becomes mobile again, the conductivity increasing at the same time; silicic acid sols behave similarly. If to a dilute solution of ferric or chromic chloride or aluminium nitrate are

added sodium acetate, and then, after the mixture has been partly neutralised with ammonia, a little ammonium sulphate, a stiff gel of the corresponding hydroxide ultimately results. It is considered that the particles in gels such as these, which are formed by the slow coagulation of sols through the whole of their mass, are not arranged in a network. The arsenate gels, however, obtained by adding dipotassium hydrogen arsenate to manganous or zinc sulphate have probably a honeycomb structure, and are more stable. Von Weimarn's gels represent the third and least stable group. R. CUTHILL.

Effect of the degradation products of gelatin on its separation by sulphosalicylic acid, and a technical method for testing gelatin. WO. OSTWALD and R. KOHLER (Kolloid-Z., 1927, **43**, 345—348).—The volume of liquid separating out from a gelatin sol on addition of sulphosalicylic acid is less after the gelatin sol has been heated. The volume of separated liquid falls linearly with the amount of degradation products contained in the gelatin. The effect can be used as a method of characterising different grades of gelatin. E. S. HEDGES.

Separation of gelatin sols into two liquid layers by sulphosalicylic acid in relation to the phase rule. WO. OSTWALD and R. KOHLER (Kolloid-Z., 1927, **43**, 131-150).—For a given concentration of gelatin, separation occurs between two limiting concentrations of the sulphosalicylic acid, these limits becoming narrower for higher concentrations of gelatin. The effect is not observed in gelatin sols more concentrated than 14%. The two liquid layers do not have a constant composition, but the variation is least for a given concentration of gelatin when the concentration of sulphosalicylic acid is near one or other of the limiting values. Greater differences in composition of the layers are noticed at low concentrations of gelatin than in concentrated solutions. Rise of temperature diminishes the difference between the layers, ultimately leading to the formation of a single liquid phase. Although at first sight the behaviour of the system appears to be similar to that of a ternary molecularly dispersed system, comparison of the equilibrium diagram of the system gelatin–sulphosalicylic acid–water with that of the system potassium carbonate–alcohol–water reveals important differences. The two-phase system gelatin–sulphosalicylic acid–water has at least one degree of freedom more than is to be expected from the point of view of the phase rule. E. S. HEDGES.

Effect of neutral salts on the formation of two liquid layers from the system gelatin–sulphosalicylic acid–water. WO. OSTWALD and R. KOHLER (Kolloid-Z., 1927, **43**, 151—155).—The separation of gelatin–sulphosalicylic acid mixtures into two liquid phases on the addition of potassium nitrate, chloride, bromide, and thiocyanate, and ammonium sulphate at a concentration of 4 g.-mol. per litre has been examined at 25°. Small quantities of the neutral salts are favourable to the separation, larger amounts exert a preventive influence, whilst still larger quantities again assist the separation. The relative effects of the different salts are in accordance with their position in the Hofmeister series. Gelatin solutions separate into two layers, not only on addition of sulphosalicylic acid, but also by addition of any acid the anion of which falls near the thiocyanate end of the Hofmeister series. E. S. HEDGES.

Gelation of silicic acid. Formation of gas bubbles and drops in silicic acid during gelation. H. A. FELLS and J. B. FIRTH (Trans. Faraday Soc., 1927, **23**, 623—630).—The form taken by bubbles, or by drops of liquid such as chloroform or mercury, passing through a silicic acid sol during the process of gelation has been studied, and the pressure required to blow the bubbles at various stages has been measured. The spherical shape assumed by the bubble or drop before gelation gradually flattens to a thin film in succeeding bubbles as gelation proceeds. Once a bubble or drop is formed in the gel the shape is permanent, and the air or liquid can be withdrawn or replaced at will. Any subsequent development of the bubble or drop appears as a growth on the original. After gelation, up to the condition for the formation of the extremely thin, film-like bubble which causes a permanent fracture in the gel, the only apparent change in the latter is that of continued increase of rigidity. After this stage there is external syneresis. The pressure required to blow a bubble increases as the gel ages, and once a bubble passes through the semi-rigid gel, subsequent bubbles follow the same path and pass with reduced resistance because the gel is fractured. Syneresis takes place along the path, due to the pressure caused by the first bubble. From the form of the bubbles or drops produced in different portions of the same sol, it is evident that gelation does not take place uniformly, but round a series of gelation centres. The water present in the gel is of two types, "fixed" and "free" (cf. A., 1927, 935). With the passage of time fixed water changes to free and is lost by evaporation, when the gel shrinks and ultimately forms anhydrous crystalline silica or quartz (Zsigmondy, A., 1911, ii, 880). Silicic acid gel has been found naturally, side by side with quartz, in the Simplon Tunnel (Z. Krist., 1901, **34**, 289). M. S. BURR.

Influence of salts on the optical rotation of gelatin. I. D. C. CARPENTER (J. Physical Chem., 1927, **31**, 1873—1879).—The specific rotations of 0·7% solutions of potassium gelatinate (calfskin) containing potassium chloride, bromide, or iodide have been measured at p_H 6·0 and at 0·5° after 1, 2, and 7 days, and also at 40°. Each salt produces a characteristic lowering of the optical activity, the effect being in the descending order, iodide, bromide, and chloride. The change is attributed to the equilibrium between the gel and sol forms of gelatin, together with the changes in the equilibrium of water produced by the added halide. L. S. THEOBALD.

Solvation of the disperse phase in jellies. H. GAUNT and F. L. USHER (Trans. Faraday Soc., 1928, **24**, 32—36).—The degree of hydration of the disperse phase in silicic acid jellies has been derived from the changes in the concentration of indifferent solutes (sulphuric and nitric acids, chloride and oxalate ions) which occur on gelatinisation (cf. McBain and

Jenkins, J.C.S., 1922, **121**, 2336). The necessary data were obtained from a comparison of the original liquid and the intermicellary liquid which exudes from the jellies by syneresis. The degree of hydration of "precipitated" silicic acid, ferric hydroxide, and aluminium hydroxide was also determined, the broken materials being allowed to remain in contact with the reference liquids for several days. Attempts to prepare jellies of stannic, cupric, mercuric, and arsenic sulphides were unsuccessful.

L. F. GILBERT.

Method for determining the tensile strength of gelatin jellies. A. ROSINGER and J. J. VETTER (J. Amer. Chem. Soc., 1927, **49**, 2994—3003).—The tensile strength of gelatin jellies is determined by measuring the dimensions of the spherical segment which is produced when a circular membrane of the jelly, supported rigidly at its circumference, is subjected on one side to air pressure. A suitable apparatus is described, which can also be used to study the time of relaxation of stretched membranes.

S. K. TWEEDY.

Influence of hydrolysed gelatin on the precipitation of silver chromate. T. R. BOLAM and B. N. DESAI (Trans. Faraday Soc., 1928, **24**, 50—52; cf. A., 1926, 1005).—The influence of hydrolysed and unhydrolysed gelatin on the separation of silver chromate from aqueous solutions of silver nitrate and potassium chromate has been studied. The time for the appearance of a precipitate is decreased by hydrolysis. Evidence is adduced that this is not due to the slight change in acidity which occurs (cf. Ganguly, A., 1927, 19). With hydrolysed gelatin the precipitate appears uniformly at all parts, whereas with the unhydrolysed substance the precipitate is formed locally at certain points and settles comparatively rapidly. It is obvious that protection and inhibition are not closely associated.

L. F. GILBERT.

Influence of alkalis on the coagulation of silica and clay suspensions by alkali chlorides. H. B. OAKLEY (J.C.S., 1927, 3054—3065; cf. this vol., 16).—The addition of alkalis decreases the turbidity of a clay suspension as measured in a Klett nephelometer. The effect increases in the order: barium, calcium, ammonium, potassium, sodium, and lithium. The effect of mixtures of hydroxides with the corresponding chlorides on the coagulation of clay suspensions has been investigated. Below a certain alkalinity, increasing concentration of the mixtures results first in flocculation, then failure to flocculate, and finally flocculation again. The phenomenon is also shown by kaolin, and by silica coagulated by a small quantity of alumina, but not by pure silica, the flocculating powers of the chlorides considered increasing in the order: lithium, sodium, potassium, and calcium, calcium being about ten times as powerful as sodium. Between p_H 9 and 10 there is a pronounced maximum in the concentration of sodium chloride required to flocculate clay, kaolin, or aluminated silica. The behaviour observed is probably the outcome of two opposing factors in the stability of clay. The formation of a sodium compound tends to stabilise the suspension, the effect reaching a maximum at p_H 9—10 (*loc. cit.*). The presence of the electrolyte, on the other hand, tends to flocculate it. Calcium chloride behaves similarly to sodium chloride in the coagulation of clay, but the maximum is at p_H 7. Clay is more readily flocculated by calcium hydroxide than by calcium chloride at equivalent concentrations, provided these exceed $0{\cdot}003N$. At lower concentrations the opposite is the case. A suspension of silica is coagulated by calcium or sodium chloride in an alkaline medium only, and the minimum concentration required for flocculation rises rapidly as alkalinity diminishes. Silica is flocculated by $0{\cdot}0001M$-aluminium chloride. Greater concentrations give a stable electropositive suspension, whilst subsequent addition of increasing quantities of sodium hydroxide at first flocculates the suspension, and then gives a stable electronegative suspension. The flocculating powers of sodium hydroxide, carbonate, and hydrogen carbonate have been compared, and decrease in the order given.

M. S. BURR.

Kinetic investigation of the peptisation of aluminium hydroxide. WO. OSTWALD and H. SCHMIDT (Kolloid-Z., 1927, **43**, 276—295).—The course of the peptisation of aluminium hydroxide gel prepared from ammonium alum was followed by gravimetric and potentiometric methods. The general character of the peptisation–time curves resembles that of a coagulation–time curve, being autocatalytic, or S-shaped. No relation could be found between peptisation and hydrogen-ion concentration, the effect depending rather on the anion of an acid. Buffer solutions of the same hydrogen-ion concentration but containing different amounts of neutral salt behave quite differently. Many strong acids, such as sulphuric acid and phosphoric acid, do not peptise aluminium hydroxide.

E. S. HEDGES.

Thixotropy of concentrated ferric oxide sols. H. FREUNDLICH and W. RAWITZER (Koll.-Chem. Beih., 1927, **53**, 231—278).—A study has been made of the thixotropy of ferric oxide sols, especially with regard to the limiting concentrations of ferric oxide and sodium chloride. Below a certain concentration of sodium chloride no change in the viscosity of the system occurs, and above a critical ratio of sodium chloride to ferric oxide thixotropy is replaced by irreversible syneresis. The inhibitive action of amino-acids is not shared by other organic compounds. This effect is reversible and can be removed by dialysing away the amino-acid; it is due to an adsorption of the amino-acid. The inhibitive action of the amino-acid increases with the number of CH_2 groups contained therein. The amino-acids have no effect, however, on the velocity of cataphoresis. The curve connecting the velocity of gelation of ferric oxide sols with the concentration of sodium chloride reaches a maximum, which is independent of the concentration of the ferric oxide. A study was also made of some physical properties of ferric oxide sols. Using an apparatus similar to that of Couette, the tensile strength was found to increase during gelation to a constant end-point. The final value is different from that obtained when the transformation merely appears to have come to an end. The modulus of elasticity increases with the load

but the extension is still quite reversible. During the measurement of viscosity in the Couette apparatus, the degree of liquidity of the sol depends on the shear gradient, and an end-point is reached by the stirring which is not the same as that produced by shaking the sol. E. S. Hedges.

Influence of serum on the diffusion of acid dyes in gelatin gel. H. Bennhold (Kolloid-Z., 1927, **43**, 328—335).—Serum has the power of radically changing the diffusion of acid dyes, in the sense that highly-dispersed substances diffuse slowly in its presence. Naphthol-yellow-*S* is almost completely dissociated in solution, whilst brilliant-Congo-*R* is at the other extreme, since it exists as a coarse dispersion. The two dyes exhibit widely different rates of diffusion in the presence of gelatin gel, but if serum is used in certain defined proportions the rates of diffusion become almost identical. Sera from different animals all possess this property, so that the phenomenon may possess biological significance.
R. A. Morton.

Influence of acids on the water-binding capacity of serum. A. Adler (Kolloid-A., 1927, **43**, 313—328).—The integral water-binding capacity (sol-swelling+sol osmosis) of sheep-blood serum in the presence of 19 different acids has been investigated. When the acids are placed in the order of their optimal swelling effects on the serum, the series is approximately the same as for the swelling of gelatin. The dissociation constant or the hydrogen-ion concentration of an acid does not determine the water-binding power of the serum. Weak organic acids may show larger effects than strong mineral acids. The biologically important acids, phosphoric, lactic, β-hydroxybutyric, and glycollic acids, exhibit the phenomenon more strongly than the other acids investigated. R. A. Morton.

Proteins and acids. F. Modern (Anal. Asoc. Quím. Argentina, 1927, **15**, 160—186).—Previous work on the effect of the addition of small amounts of acids to proteins stable in the isoelectric zone (cf. Modern and Pauli, A., 1925, ii, 518; Pauli, A., 1927, 19) has been supplemented by some observations of the displacement of the isoelectric point (determined by minimum viscosity) reached by addition of acids, towards a lower C_H with lower concentrations of proteins, and of the "fixation" of acid added to pure proteins.

These results are discussed in the light of Michaelis' theory and an adaptation of Bjerrum's theory (A., 1923, i, 444). The latter affords an explanation on the assumption that the protein solution contains

$NH_3 \cdot R \cdot CO_2H$ (A^+), $NH_3OH \cdot R \cdot COO$ (A^-), $NH_3 \cdot R \cdot COO$ ($^+A^-$), and neutral molecules (A). The reaction $A^- + HCl \longrightarrow {}^+A^- + Cl^- + H_2O$ then accounts for the disappearance of the hydrogen ion of added acid and the necessity of adding 150 times the calculated quantity of acid to bring the solution to the isoelectric point, whilst the accompanying increase of conductivity is due to chlorine ions, and the migration of the protein to the cathode (Pauli and Samec, Biochem. Z., 1914, **62**, 247) is due to residual A^+ ions. The formation of neutral particles as acid is added explains the displacement of the point of minimum viscosity.

When more acid is added to solutions of ovalbumin, the p_H of which is less than that of the isoelectric point, the "fixation" of hydrochloric acid by the protein increases with addition of acid up to $0{\cdot}025N$, and then remains constant. The activity of the chlorine ion of the protein salt also increases to a maximum at a concentration of $0{\cdot}01N$ of added acid and then falls slowly. R. K. Callow.

Viscosity and hydration. III. Kinetics of syneresis. S. Liepatov (Kolloid-Z., 1927, **43**, 396—400).—The velocity of syneresis of geranin gel was followed by measuring the volume of liquid phase produced after various time intervals. The velocity increases with rise of temperature and with the concentration of the gel. With more concentrated gels, syneresis starts earlier and the total amount of liquid phase produced is less. Syneresis is not observed in gels more concentrated than 3%. Addition of alcohol accelerates the process of syneresis, the degree of acceleration increasing with the amount of alcohol. The results agree with the view that the particles are hydrated and tend to grow together. The degree of hydration calculated from the syneresis agrees with that calculated from the viscosity by means of Hatschek's equation. E. S. Hedges.

Theory of electrolytic dissociation. W. Nernst (Z. Elektrochem., 1927, **33**, 428—431).—Recent measurements (Nernst and Orthmann, A., 1926, 579; 1927, 733) of heats of dilution, Q, of dilute salt solutions show that the data for lithium chloride solutions can be represented approximately by the relation $Q=320\sqrt{c}$ for concentrations up to $c=0{\cdot}1N$, a relation of the form to be expected from Debye's theory of strong electrolytes. But with potassium nitrate solutions, Q is positive only in very dilute solutions and becomes increasingly negative with increasing concentration. This behaviour is ascribed to incomplete electrolytic dissociation and the relation $Q=320\sqrt{c}-Q_0(1-\alpha)$ may therefore be expected to hold, where α is the true degree of dissociation and Q_0 the heat of dissociation. From the temperature coefficient of the heat of dilution, Q_0 for potassium nitrate is estimated to be 4000 g.-cal. and $1-\alpha=0{\cdot}05$ when $c=0{\cdot}1$. Values of Q calculated from these figures agree approximately with the observed values. Values of $1-\alpha$ are also obtained for $0{\cdot}1N$-solutions of sodium nitrate, sodium chloride, and potassium chloride. The apparent degree of association $(1-\alpha')$ from f.-p. data being 0·13 for $0{\cdot}1N$-lithium chloride, the addition of 0·13 to the true degrees of association of other salts gives values which are compared with the corresponding data for $1-\alpha'$, and an approximate agreement is obtained. Hückel's development of the Debye theory is criticised. H. J. T. Ellingham.

Theory of concentrated solutions. IV. Rosanov's method for the study of the composition of the vapour phase in equilibrium with a binary mixture of volatile liquids. E. Pahlavouni (Bull. Soc. chim. Belg., 1927, **36**, 533—547).
Rosanov's method has been modified to give accurate results when only about one quarter of the usual quantity of liquid is employed. The new method has been tested and results are given for mixtures of carbon disulphide and carbon tetrachloride, dichloro-

ethane and benzene, *cyclo*hexane, and acetone, and butyl alcohol and benzene. H. F. GILLBE.

Change of the mass action law for strong electrolytes. P. GROSS (Oesterr. Chem. Ztg., 1927, **30**, 207—210).—A survey of modern views on strong electrolytes. H. F. GILLBE.

"Ebullioscopic paradox." A. MAZZUCCHELLI (Gazzetta, 1927, **57**, 856—858).—The ebullioscopic paradox (cf. Berthoud, Briner, and Schidlof, A., 1927, 1029) is explained in the author's text-book ("Elementi di chimica fisica," Turin, 1923).

E. W. WIGNALL.

Dilution law for strong electrolytes. R. T. LATTEY (Phil. Mag., 1927, [vii], **4**, 831—836).—The formula $\lambda_0-\lambda=A/(\beta+V^{\frac{1}{2}})$, where A and B are constants peculiar to the solution in question, has been shown to be applicable, over a wide range, to the conductivity of strong electrolytes. According to Debye and Hückel A should be expressible in the form K where and K_2 are factors depending only on the solvent and l_1 and l_2 are the mobilities of the ions of the salt. According to Onsager (A., 1927, 1031) the mobility term above should be replaceable by another term b independent of the salt. A should therefore be either a linear function of $\lambda_0 b$ or of It is shown, however, that A is additive only and can be expressed as the sum of terms which are characteristic of the anion and cation, respectively. From the approximately linear relationship between λ_0 and A for potassium chloride, sodium chloride, and sodium fluoride a linear relationship between a and l for the ions K^+, Na^+, Cl^-, and F^- has been assumed and values of A have been calculated for all the salts examined and found to be in fair agreement with actual determinations. B can still be regarded only as a correction term.

A. E. MITCHELL.

[Electrolytic] dissociation of α-keto-acids. R. BARRE and A. CORNILLOT (Ann. Chim., 1927, [x], **8**, 329—339).—The electrolytic conductivities of phenylglyoxylic and phthalonic acids and of their sodium salts in aqueous solutions have been measured at various dilutions. The conductivity–dilution curve from v=40—1000 for the former acid differs from those obtained by Bader (A., 1891, 257) and by Böeseken and Felix (A., 1921, i, 844) and approaches asymptotically the value Λ_∞ —352, which is in good agreement with the value (353) calculated from the curve for the sodium salt, which approaches the value =83. Hence the anion has a mobility of only 41, the value obtained by the application of Ostwald's law being 64. With the above value of Λ_∞ for the acid, the dissociation constant has a value 10×10^{-2}, phenylglyoxylic acid being a strong acid, and in agreement with this a sharp neutralisation point is obtained by electrometric titration of the acid with sodium hydroxide solution. Similar results are obtained in the case of phthalonic acid (v=12·9—648), the curve approaching the value Λ_∞=352, the acid ionising in accordance with the scheme

$$C_6H_4(CO_2H)\cdot CO\cdot CO_2H \longrightarrow H+C_6H_4\left\langle\begin{matrix} C(OH)\cdot CO_2' \\ >O \\ CO \end{matrix}\right.$$

whence k=3·2×10⁻², and the mobility of the anion is 39, in disagreement with the value 64 calculated on the basis of Ostwald's law. For the neutral sodium salt the value Λ_∞=217 is found experimentally, in moderate agreement with the value 242 calculated on the assumption that the bivalent ion has twice the mobility of the univalent ion. Electrometric titration shows a well-defined minimum corresponding with the monosodium salt, no subsequent minimum being obtained on further addition of sodium hydroxide. The supposed anomalies in the dissociation of α-ketonic acids are due to the erroneous values which have been assumed for the ionic mobilities and have no real existence. J. W. BAKER.

Dissociation constants of cystine, cysteine, thioglycollic acid, and α-thiolactic acid. R. K. CANNAN and B. C. J. G. KNIGHT (Biochem. J., 1927, **21**, 1384—1390).—The apparent constants at 30° at different stages of dissociation have been determined for the above compounds, the methylene-blue–methylene-white electrode being used in the case of cystine and the hydrogen electrode for the other compounds. S. S. ZILVA.

Pseudo-electrolytes. Condition of ammonia in aqueous solution. E. BAARS (Samm. chem. u. Chem.-tech. Vortrage, 1927, **29**, 53 pp.; Chem. Zentr., 1927, i, 2792—2793).—The equilibrium between ammonia and water in an indifferent medium (nitrobenzene) was investigated the solubility of ammonia in dry and aqueous nitrobenzene and of water in benzene was determined. Values of $K=[NH_4OH]/[NH_3][H_2O]$ increase with the ammonia concentration. Values of K' for the reaction $2NH_3+H_2O=2NH_3,H_2O$ change to a similar extent, but in the opposite sense. Hence both hydrates are considered to be present. The partial pressures of water and ammonia over solutions of ammonia, and the contraction on admixture of ammonia and water vapour at the ordinary temperature were also investigated.

A. A. ELDRIDGE.

F. p. of concentrated solutions. II. Solutions of formic, acetic, propionic, and butyric acids. III. Solutions of phenol. E. R. JONES and C. R. BURY (Phil. Mag., 1927, [vii], **4**, 841—848, 1125—1127; cf. A., 1927, 619).—The activities of formic, acetic, propionic, and butyric acids have been determined by the f.-p. method over a wide range of concentration. In general the results are in agreement with those of other observers. The rapid change of the activity of butyric acid with the concentration is attributed to the close proximity of the f.-p. curve to the critical solution point, which lies in the metastable region within a degree of and below the curve.

III. Previous work has been extended to the determination of the activity of phenol by the f.-p. method. From the results the free energy of formation of phenol hydrate, $2PhOH,H_2O$, from ice and solid phenol at about −1° is −306 g.-cal. per g.

A. E. MITCHELL.

Hydrolysis of solutions of sodium palmitate as measured by extraction with *p*-xylene. J. W. MCBAIN and R. BUCKINGHAM (J.C.S., 1927, 2679—2689).—The hydrolysis of soap solutions has been investigated by studying the distribution of palmitic acid between water and *p*-xylene. Two

kinds of experiments are described, viz., those in which soap solutions are extracted with the non-aqueous solvent and therefore changed in composition, and those in which the right amount of fatty acid is previously added to the non-aqueous layer, so that the final equilibrium is determined without appreciable alteration of the aqueous solution. The results show that true equilibrium is attained, and that a soap solution, even when it is appreciably hydrolysed, contains only the merest trace of uncombined fatty acid, which is completely dissolved and not in the emulsified or free condition. Practically all the fatty acid corresponding with the hydrolysis alkalinity is in combination as insoluble acid soap. Soap solutions are excellent buffers, as their hydrolysis alkalinity is less dependent on extraneous additions than is usually the case with standard buffers. The effect of electrolytes is to diminish the extractability, and probably the hydrolysis, of dissolved soap. O. J. WALKER.

Superacid solutions. I. Use of chloranil electrode in glacial acetic acid and strength of certain weak bases. N. F. HALL and J. B. CONANT (J. Amer. Chem. Soc., 1927, **49**, 3047—3061).—Superacid solutions (*i.e.*, solutions of substances, like salts of amides, in which salt formation is exceptionally complete) are investigated with the aid of cells of the type Pt|tetrachlorobenzoquinone (satd.), tetrachloroquinol (satd.), HX (*c*) in acetic acid|LiCl in acetic acid|aqueous calomel electrode. Such cells have large *E.M.F.*, which are uniformly reduced on addition of basic substances, thus permitting the titration of the various acids with bases. Titration curves for sulphuric acid with many bases (pyridine, carbamide, acetanilide, etc.) are recorded; they resemble the curves obtained in water systems, and the bases studied are arranged in order of increasing strength and characterised by constants allied to the hydrolysis constants of their salts in water solution. The dissociation constants at 25° of *p*-toluidine and triethylamine are $1{\cdot}29\times10^{-9}$ and $5{\cdot}62\times10^{-4}$, respectively. The activity coefficients of molar solutions in acetic acid of trichloroacetic, sulphuric, and perchloric acids are 6·7, 700, and 25,000. The cause of superacidity in a solution is attributed to abnormally high hydrogen-ion activity. The *E.M.F.* of the above cells are depressed on addition of alcohol and especially of water to the acetic acid solution.

S. K. TWEEDY.

Superacid solutions. II. Chemical investigation of the hydrogen-ion activity of acetic acid solutions. J. B. CONANT and N. F. HALL (J. Amer. Chem. Soc., 1927, **49**, 3062—3070).—Data are recorded for five arylcarbinols and five unsaturated ketones with the aid of acetic acid buffer solutions containing sulphuric acid and very weak bases. The results, which are consistent with those obtained by the methods of the preceding abstract, show that the substances used constitute a graded series of indicators suitable for use in superacid solutions. Addition of alcohol seems to produce an alcoholysis of the carbinol salt besides diminishing the acidity of the solution. The rate of sucrose inversion in 98% acetic acid ion activity as measured either by the chloranil electrode or by means of indicators. The chemical behaviour of acids and bases in different solvents is discussed. S. K. TWEEDY.

Oxidation-reduction. XI. Potentiometric and spectrophotometric studies of Bindschedler's-green and toluylene-blue. M. PHILLIPS, W. M. CLARK, and B. COHEN (U.S. Public Health Service, Suppl. 61).—The equilibrium potentials of mixtures of Bindschedler's-green and its leuco-compound and of toluylene-blue and its leuco-compound in buffered solutions have been determined. Electrode equations have been derived relating the potentials to the hydrogen-ion concentration and the dissociation constants of the reactants. These constants have been evaluated from the electrode data and checked by hydrogen electrode titration curves of the leuco-compounds or by spectrophotometric observations. Bindschedler's-green is subject to spontaneous decomposition the rate of which is a function of the hydroxyl-ion concentration and leads to serious drifts of potential beyond about p_H 9·5. The behaviour of the indamines is compared with that of the thiazines. The basic indamines form useful alternative indicators to the acidic indophenols for the determination of oxidation-reduction intensity in biological systems. R. K. CANNAN.

Oxidation-reduction. XII. Schardinger reaction. W. M. CLARK, B. COHEN, and M. X. SULLIVAN (U.S. Public Health Rep., Suppl. 66, 1927). —The observations of Clark, Cohen, and Gibbs (A., 1925, ii, 1164) on the changes in electrode potential which occur on the addition of aldehyde to fresh milk have been confirmed. Various possible causes of failure in the experiments of Kodama (A., 1926, 1175) are discussed and illustrated experimentally. Kodama's observation that the addition of hypoxanthine to xanthine oxidase does not lead to the development of increased negative potentials is confirmed. R. K. CANNAN.

Dissociation of some organic and inorganic substances at high temperatures. G. M. WOOD and T. C. POULTER (Proc. Iowa Acad. Sci., 1926, **33**, 172—173).—Vapours were passed through a tube (at 500°) provided with wire electrodes to which a *P.D.* of 1—15 volts was applied, and the current was measured. The following showed a significant conductivity: glacial acetic acid, ethyl acetoacetate, hydrogen chloride, "AmOH," iodine, and nitrobenzene. Conductivity could be detected with 75% acetic acid, amylene, carbon tetrachloride, chlorobenzene, formic acid, bromine, bromobenzene, and methyl acetate. Conductivity was not observed with benzene, methyl alcohol, ammonia, toluene, chloroform, water, ethyl alcohol, benzaldehyde, or ethyl bromide. CHEMICAL ABSTRACTS.

Equilibrium diagram of the system thallium-phosphorus. Q. A. MANSURI (J.C.S., 1927, 2993—2995).—Molten thallium alloys with phosphorus, especially above 400°. When more than 2·5% of phosphorus is added, two layers are formed. The upper layer is a dark, brittle, homogeneous solid X, melting at 420° and dissolving excess of phosphorus

to form solid solutions which freeze at temperatures above 420° and over a temperature range. The excess phosphorus may be present as the yellow variety, since the alloys inflame when rubbed on emery paper. The lower layer is a solution of a small quantity of X in thallium, but on cooling it gradually loses phosphorus and freezes at the m. p. of thallium. The substance X tends to dissociate into its constituents at all temperatures. A high pressure is, therefore, necessary for its formation.

M. S. Burr.

Vapour pressures of potassium amalgams. R. W. Millar (J. Amer. Chem. Soc., 1927, 49, 3003—3010).—The mercury vapour pressures of amalgams containing a mol. fraction N_2 of potassium are given by $\log p(\text{mm.})=a-b/T$. Corresponding values of N_2, a, and b are 0·0492, 7·799, 3125; 0·0552, 7·779, 3125; 0·0877, 7·717, 3125; 0·180, 7·569, 3212; 0·321, 7·968, 3950. The activities of the mercury, a_1, are calculated for each amalgam at 200°, 250°, 310°, and 390° and van Laar's relation between a_1/N_1 and N_1/N_2 is shown to hold at each temperature (cf. Hildebrand, "Solubility," p. 45). The deviations from Raoult's law are among the greatest yet observed and decrease with rising temperature. The heat of vaporisation of mercury from amalgams containing up to 8 mols. % of potassium is equal to that of pure mercury; possibly a mercuride is formed which behaves as a perfect solute with respect to pure mercury as solvent. At concentrations above 8 mols. % the partial molal heat content of the mercury is negative.

S. K. Tweedy.

Vapour pressure of sodium and cæsium amalgams. H. E. Bent and J. H. Hildebrand (J. Amer. Chem. Soc., 1927, 49, 3011—3027; cf. preceding abstract).—The vapour pressures were measured between 554° and 651° Abs., the mol fraction of mercury, N_1, varying between 1 and 0·5. The correction of experimental errors is discussed. If $\log a_1/N_1=0{\cdot}5\beta N_2^2$, then β (a function of T) expresses the deviation of both solvent and solute from Raoult's law (cf. Hildebrand, A., 1927, 936) and its values are compared for sodium, potassium, cæsium, and barium. From the connexion between β and T the relations $\log a_1/N_1=-(1965/T+3{\cdot}42)N_2^2$, $=-5815N_2^2/T$, $=-7810N_2^2/T$ are derived for the first three amalgams. The activities of the alkali metals are determined by integration of the Duhem equation and the *E.M.F.* of cells in which alkali metal is transferred to amalgam are calculated. On the assumption that each molecular species obeys Raoult's law and that dissociation occurs in accordance with the mass action law, the formation of the compounds $NaHg_2$, $NaHg_4$, and $NaHg_6$ will explain the vapour pressures of amalgams from $a_1=0{\cdot}1$ to 0·9, whilst in very dilute amalgams the compound $NaHg_{16}$ will account for both the vapour pressure and the *E.M.F.* data (cf. Poindexter, A., 1926, 897). The apparent molal volume of mercury in cæsium is negative when the mercury concentration is less than 30 mols.-%.

S. K. Tweedy.

Volatile hydrides. Formation of a compound HCl,HBr, and the binary system hydrogen chloride–nitrous oxide. A. Klemenc and O. Kohl (Z. anorg. Chem., 1927, 168, 163—176).—Pressure measurements have shown that at −85° to −75° hydrogen chloride and hydrogen bromide give a solid *compound*, HCl,HBr, which in the vapour state or in solution in either of its components is practically completely dissociated. Down to −120°, its vapour pressure, P, is connected with the temperature (Abs.), T, by the relation $\log P=-811/T+6{\cdot}818$. Attempts to detect the formation of a compound between hydrogen chloride and nitrous oxide in the liquid state in the same way have been unsuccessful.

R. Cuthill.

Equilibrium of the system potassium oxalate–water. N. K. Voskresenski (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 458; cf. A., 1926, 898).—The eutectic point of this solution, −6·3°, corresponds with a solution containing 25·19 g. of the salt per 100 g. of water. At ordinary atmospheric temperature the saturated salt solution boils at 107°.

T. H. Pope.

Equilibria in certain binary systems of 2 : 4 : 6-trinitromethylnitroaniline (tetryl). N. N. Efremov and A. M. Tichomirov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 269—301).—Binary systems of tetryl with the following compounds have been subjected to thermal analysis. (1) *o*-Nitrophenol (m. p. 44·9°); eutectic point, 40·2°, corresponds with 87·8 mols. % of nitrophenol; the mixtures are stable, and solid solutions, containing up to about 5·5% of tetryl, are formed. (2) *p*-Nitrophenol (m. p. 113·8°); mixtures are viscous and prone to supercooling; eutectic point, 80·6°, corresponds with 50·6 mols. % of nitrophenol; mixtures are not very stable, and solid solutions containing up to 8·5 mols. % of *p*-nitrophenol and up to 10·5 mols. % of tetryl are formed. (3) *p*-Nitrotoluene (m. p. 52·4°); mixtures are stable and colourless; eutectic point, 46·6°, corresponds with 84·7 mols. % of *p*-nitrotoluene (cf. Giua, A., 1915, i, 950); no solid solutions are formed. (4) *o*-Nitroaniline (m. p. 69·4°); mixtures are yellowish-red and, after crystallisation, violet; they show only slight stability; eutectic point, 49·7°, corresponds with 73·2 mols. % of *o*-nitroaniline. (5) *m*-Nitroaniline (m. p. 114·0°); mixtures are unstable and are yellow when fused and grey when crystallised; eutectic point, 78·3°, corresponds with 55·3 mols. % of *m*-nitroaniline; no solid solutions are formed. (6) *p*-Nitroaniline (m. p. 147·3°); mixtures, yellow when fused and brown when crystallised, are unstable, and the eutectic point, 87·2°, corresponds with 40·6 mols. % of *p*-nitroaniline. (7) *m*-Dinitrobenzene (m. p. 89·5°); mixtures are colourless and no solid solutions are formed; eutectic point, 65·5°, corresponds with 66·5 mols. % of *m*-dinitrobenzene. (8) 2 : 4-Dinitrotoluene (m. p. 68·0°); mixtures are stable and pale yellow, and no solid solutions are formed; eutectic point, 59·1°, corresponds with 79·5 mols. % of the dinitrotoluene. (9) 2 : 4-Dinitrophenol (m. p. 111·4°); solid solutions containing 0—16% of tetryl and 0—18·5% of dinitrophenol are formed; eutectic point, 83·1°, corresponds with 57·7 mols. % of dinitrophenol. (10) Picric acid; mixtures are stable, and the eutectic point, 75—77°, corresponds with about 43 mols. % of picric acid. (11) Styphnic

acid (m. p. 175·5°); mixtures with 73—90% of the acid are unstable, and solid solutions are probably formed; eutectic point, about 83°, corresponds with about 25·5 mols. % of the acid. (12) 2 : 4 : 6-Trinitrotoluene; eutectic point, 58·8°, corresponds with 63·4 mols. % of trinitrotoluene, and there is no reason to assume the existence of a molecular compound of the two components; this result differs from that obtained by Giua (A., 1915, i, 950). (13) 2 : 4 : 6-Trinitrocresol (m. p. 101·2°); eutectic point is about 78° and corresponds with 63—64 mols. % of trinitrocresol. T. H. Pope.

Gas–solid equilibria. I. Pressure–temperature equilibria between benzene and (*a*) ferric oxide gel, (*b*) silica gel in sealed systems of known and unalterable total composition. B. Lambert and A. M. Clark (Proc. Roy. Soc., 1927, A, **117**, 183—201).—The equilibria between benzene and ferric oxide gel and silica gel, respectively, have been investigated by a method involving (1) the introduction into an all-glass apparatus, part of which consists of an evacuated mercury manometer, of an accurately known weight of the "activated" gel; (2) evacuation of the system, followed by the distillation into the apparatus of a known weight of benzene; (3) heating the sealed system in a vapour-bath to definite temperatures (30—130°), the equilibrium pressure for each temperature being read on the manometer. A series of such closed systems was investigated, containing gradually increasing weights of benzene per g. of gel used. Details are given for the weighing of portions of gel in a vacuum, the construction of evacuated mercury manometers, and the introduction of accurately known weights of benzene into the system. The pressure–concentration relationships derived from the pressure–temperature curves are described. L. L. Bircumshaw.

Thermal decomposition of ferrous sulphate. E. Greulich (Z. anorg. Chem., 1927, **168**, 197—202.)—The dissociation pressure of anhydrous ferrous sulphate between 235° and 698° has been determined, the pressure reaching 1 atm. at 680°. Using available data for the relation between the constant of the equilibrium $2SO_3 \rightleftharpoons 2SO_2 + O_2$ and the temperature, T, to calculate the partial pressure, p, of sulphur trioxide in the gaseous phase resulting from the dissociation, the results agree with the equation $\log p = -2691{\cdot}8/T + 5{\cdot}1526$. From this equation, the heat of dissociation between 316° and 554° is calculated to be 12·3 kg.-cal., giving 189·5 kg.-cal. for the heat of formation of ferrous sulphate. R. Cuthill.

Reactions in the solid state at high temperatures. III. Heterogeneous equilibria in systems in which gas is evolved. W. Jander (Z. anorg. Chem., 1927, **168**, 113—124; cf. A., 1927, 1037).—The gas pressures corresponding with the equilibrium $BaCO_3 + SiO_2 \rightleftharpoons BaSiO_3 + CO_2$ have been determined at various temperatures, and found to obey the Nernst approximation formula satisfactorily if the heat of reaction from left to right is taken as −34 kg.-cal. at 0° Abs. R. Cuthill.

System lime–alumina–silica. E. Janecke (Z. Elektrochem., 1927, **33**, 477; cf. Hansen, Dyckerhoff, Ashton, and Bogüe, A., 1927, 519).—Evidence for the existence of the compound $8CaO,Al_2O_3,2SiO_2$ is discussed and the conclusions of Hansen and collaborators are disputed. H. J. T. Ellingham.

Crumbling of fused masses in the system calcium oxide–alumina–silica. T. Suzuki and K. Kasai (Sci. Papers. Inst. Phys. Chem. Res. Tokyo, 1927, 7, 173—188).—The crumbling after solidification of molten mixtures of calcium oxide, alumina, and silica has been examined, the extent to which the phenomenon occurs being measured by the relative amount of the mass which is converted into powder. By measurements of refractive indices, it is found that the powder resulting from masses containing little alumina consists mainly of Rankin and Wright's γ-$2CaO,SiO_2$ (A., 1915, ii, 50), whereas in mixtures rich in alumina the compound $3CaO,Al_2O_3,SiO_2$ preponderates. Of the mixtures examined, that containing 32 mols. % of silica and no alumina crumbled most readily. R. Cuthill.

Ternary systems copper acetate–acetic acid–water and lead acetate–acetic acid–water at 25°. K. Sandved (J.C.S., 1927, 2967—2974).—Investigation of the system copper acetate–acetic acid–water at 25° indicates that the following three compounds are capable of existence: (1) $Cu(OAc)_2,H_2O$; (2) $Cu(OAc)_2,AcOH,H_2O$; (3) $Cu(OAc)_2,AcOH$. The ternary invariant point between (1) and (2) lies at 0·79% of copper acetate and 74·06% of acetic acid, and that between (2) and (3) at 0·17% and 95·40%, respectively. The solubility of copper acetate in water at 25° is 6·79% and it is depressed by the addition of acetic acid. The system belongs to the same type as the alkali acetate–acetic acid–water systems examined by other investigators. When lead acetate is substituted for copper acetate, totally different behaviour is observed. The solubility of lead acetate trihydrate increases on addition of acid, the latter reaching a maximum at 28·99%, when the concentration of the anhydrous salt is 52·1%. At 67·90% of salt and 22·01% of acid there appears to be a ternary point between the trihydrate and the anhydrous salt. No acid salt has been identified. The results are discussed with reference to other data on the solubility of lead salts and also on the conductivity of electrolytes in acetic acid. The solutions of lead acetate in concentrated acetic acid probably contain very soluble complex salts of the type xAcOH,yPb(OAc)$_2$, dissociated to a small extent only into complex ions. M. S. Burr.

Systems uranyl nitrate, alkali nitrate, water, at 25°. A. Colani (Compt. rend., 1927, **185**, 1475—1476).—The double nitrates of uranyl and sodium or potassium do not crystallise from aqueous solutions in the cold. The ammonium double salt $UO_2(NH_4)_2(NO_3)_4,2H_2O$ separates, in slowly deliquescing crystals which are decomposed by water. The anhydrous double salt $UO_2NH_4(NO_3)_3$ probably results from the crystallisation of an equimolecular mixture of the above nitrates from cold nitric acid (d 1·33), but is readily decomposed by cold water. J. Grant.

Empirical formula expressing mutual solubility of two salts with a common ion. T. S.

WHEELER (J.S.C.I., 1927, **46**, 420—423T).—The expression $s_0-s=kx^m$, where s_0 is the solubility of the saturating salt in a unit volume of its own aqueous solution at temperature t, s is the quantity of the saturating salt dissolved in a unit volume of solution at temperature t in presence of a quantity x of added salt (s_0, x, and s are in the same units), and m and k are empirical constants, expresses within the limits of experimental error the mutual solubility in water of salts with a common ion, provided that the salts separate from the aqueous solution in crystals containing no water of crystallisation, and that there is no formation of mixed crystals or double salts. The constant m depends only on the saturating salt.

Calcium cyanamide. II. Equilibrium of the reaction $CaC_2+N_2 \rightleftharpoons CaCN_2+C$. H. FRANCK and H. HEIMANN (Z. Elektrochem., 1927, **33**, 469—475).—The system has been investigated by measurements of the pressure of nitrogen developed at 940—1300°, calcium cyanamide of 99·6% purity being obtained by the reaction between calcium oxide and hydrogen cyanide. The curves obtained by plotting the pressure of nitrogen against temperature show two branches, the lower, corresponding with a solid solution of cyanamide and carbide, being exponential, and the upper, corresponding with the molten system, being linear. The lowest value of the "break" occurs at 1146°, and is assumed to indicate the m. p. of the eutectic, cyanamide–carbide. The break also corresponds with an arrest in the cooling curve. The addition of calcium fluoride depresses this break and also the pressure of nitrogen. The value of the heat of the reaction obtained from the curves is 68,400 g.-cal. between 1080° and 1130°, in good agreement with that obtained directly by Franck and Hockwald (B., 1926, 88). L. S. THEOBALD.

Liquid immiscibility in the system $FeO-Fe_2O_3-Al_2O_3-SiO_2$. J. W. GREIG (Amer. J. Sci., 1927, [v], **14**, 473—484).—The occurrence of two liquid phases in the system $FeO-Fe_2O_3-SiO_2$ has been studied; fusion of iron oxide with silica results in general in the formation of two liquid layers, of which the more siliceous layer is the less fluid. Over a small temperature interval in the neighbourhood of 1660° cristobalite is in equilibrium with the two liquids. Mixtures having a ferrous : ferric ratio of about 1 : 1 are the least miscible. The quantity of aluminium oxide necessary for the production of a homogeneous liquid varies with the ferrous : ferric ratio and with the silica content, a maximum of about 6·5% being required for a 1 : 1 ratio. It is shown that the hypothesis of siliceous magmas separating into two liquid layers is incorrect. The bearing of the results on the problems of furnace linings is discussed. Addition of iron oxide to a mixture of silica and alumina may in certain cases raise the fusion temperature of the whole. H. F. GILLBE.

Determination of the composition of the solid phase in equilibrated systems. V. P. SCHISCHOKIN (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 421–425).—The graphic method devised by Schreinemakers (A., 1893, ii, 260) for determining the composition of a solid phase in equilibrium with a liquid phase does not give exact results for small angles between the two straight lines, representing respectively the composition of the liquid phase and of the residual mixture of solid and liquid phases. This defect may be remedied by expressing the composition in terms of a fixed weight of the solvent. This modified procedure is applied to the systems guanidine nitrate–silver nitrate–water, and ammonium chloride–cupric chloride–water (cf. Rivett and Clendinnen, J.C.S., 1923, **123**, 1634). T. H. POPE.

Analytical and graphical methods of investigating complex equilibrium systems. V. P. SCHISCHOKIN (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 333—369).—Algebraic and geometric methods are considered. It is shown that various physical properties, and the relation between the concentrations of the components of systems which are formed by the mixing of m components may be expressed as linear non-homogeneous functions with m variables. On removal of n complexes from a system with m components, the relation between the concentrations of the components is, in the general case, determined by a linear non-homogeneous function with $(m+n)$ variables.

For determining the connexion between the concentrations of the components of complex systems, use may be made of the graphical methods of ordinary descriptive geometry and those of Fedorov's new graphical geometry (parallel vectors). In operations involving four or more variables Bieberbach's method is simpler than Federov's inclined vector method. The group to which a system belongs may be determined by D'Ocagne's and Masso's nomographic methods.

From the character of the relations between the concentrations of the components of a complex system, it is possible to judge, both qualitatively and quantitatively, of the physico-chemical processes which have taken place in the system prior to the establishment of the existing equilibrium.

These analytic and graphic methods are applied to the solution of several hydrological and chemico-mineralogical questions. Various mineral springs are shown to be formed by the mixing of two different waters, one more saline that the other and both resulting from metamorphosis of the water of the Black Sea. The formula attributed to tourmaline by Penfield and by Foote is readily verifiable by means of the characteristic equation for the mineral.
T. H. POPE.

Concept of substance and the phase rule. R. WEGSCHEIDER (Z. anorg. Chem., 1927, **168**, 33—40).—A substance, in the sense of the phase rule, is defined as including all homogeneous bodies the properties of which, after subjection to variations, become the same when they are subjected to identical external conditions; the changes produced when the bodies are subjected to changes of external conditions, at least within certain limits, are not concerned with changes of composition. H. F. GILLBE.

Theory of static and dynamic displacement. II. D. REICHINSTEIN (Z. Elektrochem., 1927, **33**, 455—469; cf. A., 1926, 130).—Theoretical. The author's displacement theory is further extended and set out as a unified system. The theory not

only applies to the statics and dynamics of adsorption processes, but also serves to characterise solutions and solid solutions. The philosophical significance of the theory is discussed and its applications to adsorption, solubility, passivation of metals, and decrease in velocity of oxidation with increasing concentration of oxidising agent are demonstrated.

H. J. T. ELLINGHAM.

Equations of state of adsorbed phases. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1927, **2**, 299—303; cf. A., 1927, 199).—On the assumption that the equation of state for an adsorbed substance involves the potential energy due to intermolecular forces as well as the thermal energy of the adsorbed molecules, and applying the theory of dipoles, the term kE in Cofman's equation (A., 1926, 674) is converted into the form iRT. Applying Volmer's surface correction (A., 1925, ii, 539), the value of i for the adsorption of various organic substances at liquid–gas and liquid–liquid interfaces is found not to exceed 1, indicating that the adsorbed molecules attract each other. In the adsorption of acetic acid at a water–carbon interface, on the other hand, the acid molecules apparently repel each other, the value of i being greater than 1.

R. CUTHILL.

Reaction regions. XVII. Reaction regions in which a dichromate is the substance supplying oxygen. W. P. JORISSEN and G. M. A. KAYSER (Rec. trav. chim., 1927, **46**, 885—890; cf. this vol., 21).—Reaction regions in the systems potassium dichromate–sulphur–iron and potassium dichromate–sulphur–aluminium have been investigated and are represented diagrammatically. In presence of silica, the narrow neck in the reaction region of the system ammonium dichromate–sulphur–iron becomes a gap and the reaction space becomes divided into two regions.

J. S. CARTER.

Free energy of transition in the system calcite–aragonite. J. L. BUCHAN (Trans. Faraday Soc., 1927, **23**, 668—671).—The *E.M.F.* at 25° of a cell consisting of two hydrogen electrodes dipping into saturated solutions of calcite and aragonite, respectively, in *N*-potassium chloride solution containing 25% of alcohol, and connected by the same potassium chloride solution, is 0·009 $\pm$0·0002 volt, the electrode in the calcite solution being positive. The value of the free energy of transition of aragonite to calcite, calculated from this, is -414 cal./g.-mol., which is in approximate agreement with that determined from Kohlrausch's solubility data (A., 1903, **ii**, 528).

M. S. BURR.

Methods of determining the heat equivalent of calorimetric bombs. W. SWIENTOSLAWSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 563—565).—The merits of a universal relative determination of heats of combustion using benzoic acid as a standard are discussed and compared with methods used for determining absolute values.

A. RATCLIFFE.

Methods of determining the heat equivalent of calorimetric bombs. A. SCHUKAREV (J. Russ. Phys. Chem. Soc., 1927, **59**, 567—572).—Disadvantages of relative determinations of heats of combustion are discussed (cf. preceding abstract).

A. RATCLIFFE.

Calorimetric researches. XIV. Heats of combustion of successive members of homologous series: the normal primary aliphatic alcohols. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1927, **46**, 903—917; cf. A., 1926, 686, 1210).—In order to substantiate the suggestion that alternation is confined to the crystalline state, the heats of combustion of seven normal aliphatic alcohols have been determined. All the heats of combustion relate to isothermal reactions at 19·5°. The values thus obtained for the molecular heats of combustion (kg.-cal. 15°) at constant pressure, Qp, are: butyl, 639·5; amyl, 795·6; hexyl, 951·9; heptyl, 1108·4; octyl, 1265·0; nonyl, 1420·9; decyl, 1576·9. Combining these results with those of Richards and Davis (A., 1920, ii, 589) for the lower alcohols it is found that there is no indication of any alternation, the increment due to each increase of CH_2 being 156·3 kg.-cal. Contrary to previous experience, it is found that initial terms with abnormally high energy contents are missing.

In order to investigate the variation in molecular volume with mol. wt. the densities of nine normal alcohols were determined. The values of $d_4^{19\cdot5}$ thus obtained are: butyl, 0·7986; amyl, 0·8041; hexyl, 0·8082; heptyl, 0·8116; octyl, 0·8146; nonyl, 0·8174; decyl, 0·8198; undecyl, 0·8217; dodecyl, 0·8234. The derived molecular volumes show a constant increment of the order 16·59—16·80 c.c. Neither the b. p. nor the molecular refractivities (existing data) show any indication of alternation.

Approximate values for the degrees of association of the normal aliphatic alcohols have been calculated by standard methods. Whilst such values are admittedly approximate they nevertheless show that the degree of association decreases as the series is ascended. Possibilities whereby variation in degree of association may be reconciled with constant increment in physical constants are discussed.

J. S. CARTER.

Thermochemistry of organic compounds. E. BERNER (Arch. Math. Naturvidenskab., 1926, **39**, 6; reprint).—The heats of combustion of a series of stereoisomeric racemic and *meso*-compounds of the types represented by racemic acid and mesotartaric acid have been determined in a specially designed bomb calorimeter. Temperatures were measured by a platinum resistance thermometer and the substances were carefully purified by alternate crystallisation and distillation in a vacuum. In all cases, it was found that the *meso*-isomerides have the greater heats of combustion when corrections are applied for the difference in the lattice energy of the solids; these corrections were derived from measurements of the heats of dissolution of the isomerides. Calculations from existing data indicate that the energy of the atomic linkings in paraffins, at any rate in those containing less than ten carbon atoms in the molecule, is constant. The energy of the unsaturated linkings in unsaturated aliphatic compounds is nearly constant, and the energy in these linkings is in agreement with the ease with which they are attacked chemically. Alicyclic hydrocarbons containing five or more carbon atoms in the molecule have normal linking energies; the configuration of the rings is therefore

multiplanar, and it is suggested that isomeric forms of these compounds may be detectable at low temperatures. G. A. ELLIOTT.

Fictitious heat of dissolution of thallous sulphate. F. ISHIKAWA (Bull. Chem. Soc. Japan, 1927, 2, 294—299).—If the *E.M.F.* of the cell 50% thallium amalgam|saturated solution of thallous sulphate in equilibrium with the solid, mercurous sulphate|mercury and the similar cell with an unsaturated solution of thallous sulphate are E_A and E_B, respectively, application of the Gibbs–Helmholtz equation shows that the differential heat of dissolution, Q, of thallous sulphate is given by the expression $Q=nF[(E_B-E_A)-T\{(dE/dT)_B-(dE/dT)_A\}]$, where n, F, and T have their usual significance. By extrapolation to the saturation concentration of the values of Q obtained from *E.M.F.* measurements with the above cells, values of the fictitious heat of dissolution are obtained which approximate closely to those derived previously by another method (A., 1923, ii, 537). R. CUTHILL.

Heats of dilution of strong electrolytes in the limiting region of the Debye–Hückel theory. W. LANGE and G. MESSNER (Z. Elektrochem., 1927, 33, 431—440).—By means of an adiabatic differential calorimeter reading to about a millionth of a degree, measurements have been made at 25° of the heats of dilution, Q, of dilute solutions of the following salts: (1) potassium chloride, sodium chloride, lithium chloride, lithium bromide; (2) calcium nitrate, sodium sulphate; (3) magnesium sulphate, calcium sulphate; (4) potassium nitrate, cæsium chloride. Concentrations, c, as low as 0·001 g.-mol./litre were used in some cases. Salts of group (1) all gave practically identical values of Q at $c=0{\cdot}01$, but these values are definitely lower than the calculated value. Since the latter involves the temperature coefficient of the dielectric constant of water, however, it may be somewhat inaccurate. For salts of group (2), values of Q agree with each other, but are also less than the calculated value, whereas values obtained for group (3) are considerably higher than the theoretical and these salts are definitely anomalous. In all cases, Q is positive at sufficiently low concentrations as required by the theory, and for lithium bromide Q is practically proportional to $\sqrt{c}$ up to $c=0{\cdot}1$. With salts of group (4) the Q–$\sqrt{c}$ graphs are definitely curved and exhibit a maximum, Q eventually becoming negative with increasing concentration, for potassium nitrate at any rate. For potassium chloride and lithium bromide measurements of Q were also made at lower temperatures and for each salt the ratio of the values of Q at two different temperatures agreed closely with the theoretical value. From the data for lithium bromide it is shown that the partial molal heat capacity of water, c_{p_1}, in solutions of this salt is given by $c_{p_1}=17{\cdot}98-0{\cdot}098c^{1{\cdot}5}$, a relation of the same form as that obtained empirically by Randall and Ramage (A., 1927, 208), the value of the constant (0·098) being of the same order as that found by these authors for sodium chloride solutions. H. J. T. ELLINGHAM.

Free energy and heat of dilution of concentrated solutions. R. FRICKE and L. HAVESTADT (Z. Elektrochem., 1927, 33, 441—455).—Vapour pressures of aqueous solutions of various substances, including electrolytes and non-electrolytes, at various concentrations have been measured by a differential method at 0° and at either 10° or 15°. For each solute at each temperature values of vapour pressure, p, are plotted against the dilution, φ, of the solution (g.-mol. of water/g.-mol. of solute) or against the mol. fraction of the water. For solutions of carbamide and silver nitrate, values of p are higher in concentrated solutions than those corresponding with the mixture law, $p=p_0\varphi/(\varphi+1)$, where p_0 is the vapour pressure of water, but in more dilute solutions values for carbamide approach the theoretical values closely. For most of the other substances examined the vapour pressures were notably lower than the theoretical, especially in the more concentrated solutions of substances having a high positive heat of dilution. From the data obtained, the free energy of dilution, A, and the heat of dilution, U, were calculated for each solution, values of U being obtained by means of Kirchhoff's equation. For each solute values of A and U were plotted against φ. For silver nitrate and the salt $2KI,HgI_2$, U is negative and the A and U curves diverge with increasing concentration. Most of the other substances examined have a high positive value of U, and in these cases the A and U curves intersect, A being $>U$ in more dilute solutions but $<U$ in more concentrated solutions. In no case do the A and U curves run parallel over a considerable range of concentration so that the "theory of the ideal concentrated solution" (Nernst) cannot be applied without further considerations to concentrated solutions with a high positive heat of dilution. H. J. T. ELLINGHAM.

Diffusion coefficients and ionic mobilities. E. N. GAPON (Z. anorg. Chem., 1927, 168, 125—128).—Examination of some of the existing data for the diffusion coefficients, D, of organic substances in water shows that if n is the number of atoms in the molecule the relation $D\sqrt{n}$=constant is approximately true, the value of the constant being rather greater for associated substances than for non-associated substances. A similar empirical formula, $u\sqrt{n}$= constant, connects n with the ionic mobility, u, in the case of numerous electrolytes. This latter expression may be used to calculate ionic hydrations, the results being in general in agreement with those obtained by the usual methods. R. CUTHILL.

Transport numbers of hydrochloric and picric acids. T. ERDEY-GRUZ (Z. physikal. Chem., 1927, 131, 81—89).—The transport numbers of picric and hydrochloric acids at 25° in water, ethyl alcohol, acetone, and glycerol, and in aqueous solutions of the last three as well as of mannitol, chloral hydrate, dextrose, and sucrose, have been determined by an electrometric method. The transport number of the hydrogen ion in alcohol and glycerol solutions at first increases with the concentration of the solutions, and then decreases. In the acetone solutions there is a continual decrease. Similar variations are observed in the other solutions. The results are explained on the assumption that the picrate ion is non-hydrated and non-solvated, and that, in the

hydrochloric acid solutions, the hydration or solvation has relatively less influence on the chlorine ion than on the hydrogen ion. The changes must therefore be due principally to a diminution in hydration of the hydrogen ion with increasing concentration of the non-electrolyte, followed by increase in solvation. The large value of the transport number in pure water, compared with the low value in pure acetone, glycerol, or alcohol, is explained by supposing that transport in aqueous solution is mainly of the Grotthus type, whilst this plays only a small part, or none at all, in transport in other solvents. M. S. BURR.

Electrolytic transport of water in solutions of hydrochloric and hydrobromic acids. A. WAGNER (Chem. Listv, 1927, **21**, 543—548).—By means of transport experiments with Baborovsky's apparatus the following values have been obtained for the transport number of the cation, and the transport of water, respectively: *N*-hydrochloric acid, 0·874, 0·43; 0·1*N*-hydrochloric acid, 0·873, 0·64; *N*-hydrobromic acid, 0·878, 0·50. The transport numbers are probably somewhat too high, owing to electro-osmosis at the membranes. Assuming, however, that this effect is negligible in *N*-solutions, and that in such solutions the chloride ion fixes 4 molecules of water, the hydrogen ion is calculated to fix 1 molecule, and the bromide ion 3 molecules. R. CUTHILL.

Electrical conductivity of binary liquid systems. S. I. TSCHERBOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 459—460).—The electrical conductivities of the system aniline–acetic acid at 21° are in agreement with those given by Konovalov (A., 1893, 356). The curve expressing the conductivity of the system acetic anhydride–water at 17° consists of two branches intersecting at an obtuse but distinct angle at a point corresponding with 50 mols. % of water. The conductivity isotherm recalls the viscosity isotherm for this system (cf. Kurnakov, J. Russ. Phys. Chem. Soc., 1918, **50**, 157), except that the conductivity exhibits a pronounced maximum for 96 (not 75) mols. % of water.
T. H. POPE.

Electrochemistry of non-aqueous solutions. VIII. Conductivity of dilute organic solutions of silver nitrate, silver thiocyanate, and lithium bromide. R. MULLER, V. RASCHKA, and M. WITTMANN (Monatsh., 1927, **48**, 659—672).—The work of Muller, Griengl, and Mollang (A., 1926, 1212) is extended, and the results are again in agreement with the Debye–Hückel theory. The following figures give respectively the dielectric capacity of solvents, from recorded data, followed by (each at 25°) the solubility of silver nitrate in the solvent (in g. per litre), the range of v in conductivity measurements, the lowest value of v at which the square root law is valid, and the value of Λ_∞: *o*-toluidine, 6·3, 0·128, 1327—170,000, 15,000, 11; piperidine, 5·8, 40·07, 10—20,000, 320, 0·24; acetonitrile, 35·8, 875·7, 10—80,000, 78, 270; methyl ethyl ketone, 17·8, 1·72, 100—100,000, 12,000, 140; acetophenone, 18 or 15·6, 0·0755, 2250—144,000, 6,000, 36. Since phenylthiocarbimide is attacked explosively by silver nitrate, silver thiocyanate is used as solute; the respective figures are: 11, 0·926, 1·724—220,000, 13,000, 21·5; the results are uncertain, especially when v exceeds 100,000. For lithium bromide in benzaldehyde solution, the figures are: 18·0, 136·28, 0·637—1632, 10, 6·3. E. W. WIGNALL.

Specific adsorption volume and the electromotively effective space. D. REICHINSTEIN (Z. anorg. Chem., 1927, **168**, 189—196).—Theoretical. The conception of electromotively effective space previously developed in connexion with the determination of the rate of reactions occurring at electrodes during the passage of a current (A., 1923, ii, 468) has been applied to the elaboration of a theory of galvanic polarisation. It is found that it is really an adsorption problem which is involved, and the electromotively effective space is, in fact, equal to the adsorption space on the electrode. An equation for the polarisation *E.M.F.* is derived, which accounts for Le Blanc's point of inflexion on the voltage curve.
R. CUTHILL.

Decomposition potentials of the fused halides of the alkali and alkaline-earth metals. II. L. CAMBI and G. DEVOTO (Gazzetta, 1927, **57**, 836—855).—Further experiments have been made by the method described (cf. Giorn. Chim. Ind. Appl., 1926, **8**, 303). In addition to further observations on the chlorides, results are given for lithium, sodium, potassium, and barium bromides and iodides, calcium and strontium bromides, and magnesium iodide between 600° and 1000° with graphite anodes and nickel cathodes. Further measurements are also recorded for calcium, strontium, and barium chlorides with nickel and iron cathodes. The decomposition potentials at 800° are: (chlorides) potassium 3·37, lithium 3·30, sodium 3·20; (bromides) potassium 2·98, lithium 2·95, sodium 2·83; (iodides) potassium 2·53, lithium 2·48, sodium 2·30. The decomposition potentials of the fluorides of lithium, potassium, and calcium are much lower than those of the corresponding chlorides or bromides. The results indicate the occurrence of depolarisation phenomena. Neumann's method (cf. A., 1925, ii, 797), which gives markedly lower values of the decomposition potential, is criticised. Two thermodynamic methods of calculating the decomposition potential are given and the results, as exemplified in the case of sodium chloride, are in good agreement with the experimental figures. O. J. WALKER.

Current density–potential curves and time phenomena in the passivation of various metals. W. J. MÜLLER (Z. Elektrochem., 1927, **33**, 401—406).—The influence of the method of experiment on the form of current density–potential curves for anodes exhibiting active and passive states is discussed. The importance of the time factor is emphasised and a method of drawing the curves to show time effects is indicated. Curves for chromium are similar in form to those for iron and nickel, but at given current density passivity sets in after a very much shorter active period. True passivity, as shown by these metals, is regarded as due to a change in the atoms of the metal itself. The formation of a non-conducting film of salt, basic salt, or hydroxide causes high current densities at points which are not covered by the film, and passivity is brought about by the high

current density. Metals which do not exhibit true passivity may show "mechanical passivity," but in such cases the high anode potential is due merely to the ohmic resistance of a film, the metal being really still active. H. J. T. ELLINGHAM.

New method of measuring overvoltage. L. J. P. BYRNE (Trans. Faraday Soc., 1927, 23, 661—667).—A new method for measuring overvoltage while the current is flowing is described. The *P.D.* E between the electrodes, the current I flowing through the cell, and the ohmic resistance R of the cell are all determined simultaneously. The overvoltage is $E-IR$. The method gives the true overvoltage existing during electrolysis without introducing extraneous factors, and is applicable over a wide range of current densities. Curves are given showing the relation between current density and overvoltage at copper electrodes in neutral and acid copper sulphate solutions of various concentrations, and at platinised platinum electrodes in sulphuric acid solution. A method is suggested by which oxygen and hydrogen might be obtained by using alternating current. M. S. BURR.

Electrolytic reduction potentials of organic compounds. I. Polarographic method. II. *iso*Valeraldehyde. III. Pyridine. IV. Nicotinic acid. M. SHIKATA (Mem. Coll. Agric. Kyoto, 1927, 4, 1—8, 9—18, 19—33, 35—48).—I. A description is given of the use of polarograms, produced by the automatic registration of current-voltage curves on a rotating drum, for the determination of the reduction potentials of organic compounds at the dropping mercury cathode.

II. [With I. TACHI.]—Polarographic measurement of the reduction potential - of *iso*valeraldehyde shows the equation $\pi=-(RT/2F)\log[k'/\{[H^{\cdot}]^2\times C_{R\cdot CHO}\}]$ to be valid; thus the reduction is reversible, in both acid and alkaline solution. For a 0·1868*M*-solution in 0·1*N*-hydrogen chloride, $\log k'=34{\cdot}672$. Corrected for adsorption the equation becomes $\pi=-(RT/2F)\log[k'/\{[H^{\cdot}]^2\times C_{R^{m}\cdot HO}\}]$ in which for a strongly acid solution m is 1·380, for neutral solution 0·287, for alkaline solution 1·33, and for a solution in ammonium chloride 0·272. The results suggest negative adsorption of *iso*valeraldehyde at a mercury cathode in neutral solution. Schiff's reaction for the detection of aldehydes is only one twentieth as sensitive as the polarographic method. The influence of *iso*amyl alcohol on the reduction potential suggests that this substance is the product of the reaction.

III. [With I. TACHI.]—The two waves in the current–voltage curves obtained in the reduction of pyridine are due to reduction of the pyridine ion and molecule respectively. In acid solution moderate agreement exists between the theoretical and observed values of the reduction potential, although greater deviations occur than when the reduction is reversible. In neutral and alkaline solutions the agreement is less satisfactory. For moderate pyridine concentrations the adsorption coefficient m of the pyridine ion is 0·219 in acid solution and 0·089 in neutral solution. For the molecule in alkaline solution m is 0·223.

IV. [With I. TACHI.]—The reduction of nicotinic acid at the dropping mercury cathode takes place in two stages, of which the first is the reduction to aldehyde of the carboxyl group and the second the reduction of the pyridine ring. Reduction does not occur in presence of an excess of alkali, owing probably to desorption of the negatively-charged nicotinic acid ion at the cathode. A study of the reduction potential of benzoic acid indicates that the pyridine ring facilitates the reduction of the carboxyl group to a greater degree than does the benzene ring. H. F. GILLBE.

Applications of the polarographic method. I. Analysis of abnormal mineral constituents. II. Copper complex salts. III. Microanalysis of reducible substances in fermentation products. M. SHIKATA (Mem. Coll. Agric. Kyoto, 1927, 4, 49—57, 59—74, 75—90).—I. [With I. TACHI and N. HOZAKI.] The polarographic method is applicable to the micro-detection of lead and copper.

II. The deposition potentials of copper complexes have been determined. On the assumption of the formation of lithium trichlorocuprate in solutions of cupric and lithium chlorides, the equilibrium constant $K=[Cu^{\cdot\cdot}][Cl']^3[CuCl_3']$ is $3{\cdot}98\times10^{-9}$ for lithium chloride concentrations from 0·05*N* to *N*. The equilibrium constants of sulphate complexes are in general greater than those of chloride complexes. The existence of current maxima and minima in the current–voltage curves is ascribed to varying adsorption of the copper complexes.

III. [With K. SHOJI.]—Reducing substances such as cinnamaldehyde, furfuraldehyde, and acetaldehyde in various fermented liquids may be detected by the polarographic method. H. F. GILLBE.

Behaviour of nickel anodes. F. FOERSTER and F. KRUGER (Z. Elektrochem., 1927, 33, 406—425).—Solutions of nickel sulphate containing varying amounts of nickel chloride and 2% of boric acid were electrolysed at 20° between nickel electrodes at fixed current densities, the electrolyte being well stirred. The bath voltage, anode potential, anodic and cathodic current efficiencies, and the p_H value of the electrolyte were measured during each electrolysis. When the current density is low or the chloride concentration high, the anode is continuously active and dissolves with high current efficiency at potentials (ε_h) between $+0{\cdot}40$ and $+0{\cdot}58$ volt, the p_H value of the electrolyte increasing gradually during the process. With high current density or low chloride concentration, the anode is in a permanently passive condition, for although it still dissolves with a current efficiency of 15—35%, its potential lies between $+1{\cdot}69$ and $+1{\cdot}75$ volt: the p_H value of the electrolyte falls rapidly at first but eventually approaches a constant low value. Under intermediate conditions, the p_H value decreases at first to a minimum and then rises again, whilst the anode exhibits temporary passivity. At first the anode potential varies periodically between a value which corresponds with activity and one somewhat less than that which is characteristic of permanent passivity, these higher values being more persistent; but as electrolysis proceeds the frequency of the pulsations decreases and the active phases become more persistent until permanent activity is eventually established. The

maximum current density at which the anode remains continuously active increases rapidly with the chloride concentration, but decreases somewhat with increase in the sulphate concentration; it was also found to be higher with technical anodes than with specially prepared electrolytic anodes. High anode potentials are attributed to the partial covering of the anode surface by the observed peroxide film, but true passivity is regarded as due to a change in the electronic structure of the nickel atoms, a change which is produced by local high current densities, but which can persist in the presence of oxygen even if the current density falls owing to dissolution of part of the film. In "temporary passivity" the film forms but redissolves by interaction with chloride ions before true passivity is established. The current density–potential relations for a nickel anode in a nickel chloride solution and in a solution containing chloride and sulphate were also investigated.

As long as the p_H value of the electrolyte is below 5·5 good cathodic deposits of nickel are obtained. Flaking and cracking, which occur at high p_H values, are ascribed to strains due to inclusion of nickel hydroxide in the deposit. Presence of the hydroxide also enables hydrogen bubbles to adhere to the cathode and hence leads to pitting. The cathodic current efficiency runs parallel with the anodic efficiency, but is somewhat greater than the latter unless the anode is permanently active. The best conditions for electrodeposition of nickel in practice are discussed. The chloride concentration must be sufficient to avoid temporary passivity; the p_H value must be kept down, a condition favoured by low current concentration, and the iron content of the solution kept as low as possible, since iron in the deposit leads to flaking, and deposition of ferric hydroxide to pitting. H. J. T. Ellingham.

Electroendosmosis of aqueous solutions through glass diaphragms. H. C. Hepburn (J.C.S., 1927, 3163—3164).—The measurements by Fairbrother and Varley (A., 1927, 826) of the electro-endosmosis of dilute hydrochloric acid through a diaphragm of sintered Jena glass powder are criticised and their apparently inconsistent results corrected for the lowering of the electrokinetic potential produced by given concentrations of hydrochloric acid. Consecutive series of measurements then show good agreement, and, contrary to the view of Fairbrother and Varley, do not indicate any change in the effective size of the diaphragm pores corresponding with a progressive swelling process at the glass surface. Errors are introduced by failure to remove the last traces of adsorbed electrolyte remaining from the strong acid used in cleaning the diaphragm between the series of observations. The use of an entirely fresh diaphragm for each series of measurements is recommended. R. A. Pratt.

Flame and combustion. A. Egerton (Nature, 1928, **121**, 10).—A general view of gaseous combustion is presented. Reaction will commence when a sufficiently energetic molecule of fuel combines momentarily with an energetic oxygen molecule, forming a peroxide in a high energy state. Resulting breakdown may involve the formation of an aldehyde and water; these molecules would possess not only the initial energy of activation but also the reaction energy, and on their next encounter with other fuel (or oxygen) molecules would communicate sufficient energy to enable combination to occur, and so start a reaction chain. This view is discussed. A. A. Eldridge.

Ionisation and chemical change during slow combustion. J. A. J. Bennett and E. W. J. Mardles (J.C.S., 1927, 3155—3161).—The temperatures of spontaneous ignition in a heated tube of vapour or spray of *m*-xylene, *n*-butyl alcohol, undecane, benzyl alcohol, amyl ether, and cymene are recorded, and it is concluded that a system containing liquid droplets is more ionised and more sensitive to ignition than the corresponding vapour mixture. Similarly, chemical changes occurring below the ignition temperature were usually more marked and occurred at lower temperatures with the liquid drops present than with the vapours alone. Slight ionisation was shown at higher temperatures with some gaseous mixtures. It is concluded that a thermionic emission occurs at the commencement of combustion, followed during combustion by the formation of centres of chemical change from ions as soon as they are liberated. The formation of peroxides from hydrocarbons is indicated. The action of iron carbonyl, lead tetraethyl, and other "anti-knocks" inhibits peroxide formation during the period of slow combustion. Experiments with hydrogen, and with hydrogen–air, hexane–air, coal gas–air, and acetylene–air mixtures, with and without puffs of "anti-knocks," were made at temperatures up to 600°, when no appreciable increase in ionisation was found. R. A. Pratt.

Decomposition of diacetone alcohol in alkali hydroxide solutions. G. Åkerlöf (J. Amer. Chem. Soc., 1927, 49, 2955—2981).—The velocity of the above decomposition was measured by a physical method which gave reasonably accurate results with reaction velocities having half-periods up to 35 sec. The velocity/alkali concentration ratio as a function of increasing concentration (0·1—2·2N) shows an almost continual decrease for lithium hydroxide, but for solutions of the other two hydroxides used it passes through a minimum between 0·6N and 1N, afterwards increasing, rapidly for potassium hydroxide but comparatively slowly for sodium hydroxide solutions. The corresponding activity coefficient–concentration curves for the pure hydroxides behave similarly, indicating that the above decomposition velocity is proportional to the hydroxide activity.

The experiments were repeated after addition of the corresponding chlorides, the total salt concentration being kept constant (up to 6N); log (velocity constant/alkali concentration) was a linear function of the hydroxide concentration, as in the case of the pure hydroxides, the lines being parallel for each alkali metal. Extrapolation of these lines to zero salt concentration gave values for the velocity of decomposition of diacetone alcohol in very concentrated alkali solution which agreed with those calculated from activity coefficients. An expression is deduced for the reaction velocity in solutions of high electrolyte concentration which agrees with Hückel's simplified general equation for the activity

coefficient of a strong electrolyte (A., 1925, ii, 513) and holds also for the conversion of acetylchloroaminobenzene into *p*-chloroacetanilide in acid solution (Harned and Seltz, A., 1922, ii, 631). The decomposition velocity of diacetone alcohol seems to be a function of the activity of the electrolytes present at all concentrations. A review of relevant results is given. S. K. TWEEDY.

Velocity measurements on the opening of the lactone ring in derivatives of phthalide. A. TASMAN (Rec. trav. chim., 1927, 46, 922—924).—Errors in the calculation of the velocity coefficients previously published (A., 1927, 1186) are corrected. The conclusions remain valid and some of the "exceptions" now accord better with the general scheme. J. S. CARTER.

Inactivation of the surface of metals by diffusion. III. Diffusion of tungsten into iron and the resistance limits of iron-tungsten alloys. G. GRUBE and K. SCHNEIDER (Z. anorg. Chem., 1927, **168**, 17—30).—The extent of the diffusion of tungsten into iron when a bar of the latter is heated in contact with finely-divided tungsten for 15—72 hrs. at 1280°, 1330°, and 1400° has been determined by analysis of successive layers, each of thickness 0·05 mm., ground from the surface of the bar. The curves showing the relationship between the distance below the surface and the percentage of tungsten present exhibit a well-defined break at a point corresponding with a depth which increases with the time and temperature of heating. The mean diffusion coefficients for a short period of heating at the three temperatures given are 3·2, 21, and 26×10^{-5} cm.^{2}/day respectively, but the coefficient increases very greatly with increased time of heating, *i.e.*, with increase of the depth of penetration of the tungsten. It is suggested that the thin film of foreign matter deposited on the crystals of iron greatly influences the diffusion velocity.

Corrosion measurements have been made on iron-tungsten alloys containing 0—75% of tungsten, prepared by fusing a compressed mixture of the finely-divided metals, tempering the alloy at 1350° for 72 hrs., and cooling fairly slowly. Immersion of the alloys in *N*-hydrochloric acid for 24 hrs. and measurement of the weight of metal dissolved show that as the tungsten content increases up to 6% the amount of corrosion decreases to a value of about 0·33 of that of pure iron, and thereafter remains practically constant until 68·7% of tungsten, corresponding with Fe_3W_2, is approached, when the corrosion rises to a maximum and finally diminishes. Similar results are given by sulphuric acid. In 0·1*N*-nitric acid the amount of corrosion diminishes continuously as the tungsten content increases up to about 40%, and thereafter rises to a maximum.

Alloys containing up to 8% of tungsten consist of homogeneous mixed crystals; from 8% to 33% the structure exhibits large mixed crystals interspersed with small crystals of Fe_3W_2. The diminished susceptibility of the alloys to corrosion is ascribed to the formation of a protective film of tungstic oxide. H. F. GILLBE.

Corrosive effect of nitric, hydrochloric, and sulphuric acids on pure lead and lead containing small amounts of copper and antimony. J. C. OLSEN, M. H. QUELL, and W. G. HOLLEY (Trans. Amer. Inst. Chem. Eng., 1926, **18**, 19—36).—Corrosion in sulphuric acid increases with the temperature (20—100°) and concentration, and is minimal when the lead contains 0·1% of copper. With hydrochloric acid, corrosion is least with pure lead and greatest with lead containing antimony. Pure lead is least attacked by nitric acid, and least by concentrated acid. CHEMICAL ABSTRACTS.

Paradox of corrosion and protective film [on iron] theory. T. FUJIHARA.—See B., 1927, 967.

Theory of intermediate reaction ions. I. H. VON EULER and A. OLANDER (Z. physikal. Chem., 1927, **131**, 107—126).—The reactivity of a substance is greatly increased by its ionisation. Hence the reaction is catalysed by a compound which, by salt-formation with the reacting substance, causes the increased formation of suitable ions of the latter. This does not exclude the possibility that the neutral substance may be reactive, or that it can form compounds with other substances, *e.g.*, neutral salts, which possess a higher specific reactivity than the free molecule. Substances catalysed by either acids or bases may function as amphoteric electrolytes and possess an isoelectric point. The acid amides are typical examples of this group. The basic dissociation constant of acetamide has been determined electrometrically. If no correction is made for the change in activity of the hydrogen ion in presence of the undissociated acetamide, the basic dissociation constant is $2\cdot5\times10^{-15}$ at 20° and $2\cdot0\times10^{-14}$ at 50°. If correction is made on the assumption that the acetamide has the same effect on the hydrogen-ion activity as an equal percentage of sucrose, the values are $3\cdot8\times10^{-15}$ and $3\cdot1\times10^{-14}$, respectively. The rate of hydrolysis of acetamide at 50° has been determined, under conditions of approximately constant p_H, in presence of different concentrations of hydrochloric acid between 0·1*N* and 3·12*N*. The ratio of the velocity coefficient to the amount of ionised acetamide, calculated from the corrected dissociation constant, is practically constant up to a concentration of acid of 2·0*N*, above which it falls rapidly. If calculated, however, from the uncorrected value, although approximately constant it shows a gradual small decrease with increase of hydrochloric acid. The ratio of the velocity coefficient to the hydrogen-ion concentration shows that the former increases more slowly than the latter. The mechanism of the reaction is discussed. It probably depends on the reaction with water of the intermediate ion $CH_3\cdot CONH_3^+$, or an isomeride of this ion, the velocity of hydrolysis being proportional to the concentration of the acetamide ion, and not to that of the hydrogen ion. The system ethyl ether–hydrochloric acid–water has been studied electrometrically, and it is concluded that the basic dissociation constant of ethyl ether is less than 3×10^{-16}. This is much smaller than the value suggested by Skrabal (A., 1927, 943). M. S. BURR.

Organic catalysts with hydrogen-ion optimum. G. LJUNGGREN (XII Int. Cong. Physiol., 1926, 97—98; Chem. Zentr., 1927, i, 2505).—Amino-compounds

exert a catalytic effect on the decomposition of acetoacetic acid; the optimal p_{H}, which is near the neutral point, varies for different amines. The reaction is unimolecular. The effect is due chiefly to the primary amino-group; the total concentration of the solution is of importance. A. A. ELDRIDGE.

Catalytic action of aluminium chloride. H. J. PRINS (Chem. Weekblad, 1927, **24**, 615—619).—A theoretical discussion of the causes of the activity of aluminium chloride as a catalyst. S. I. LEVY.

Nickel as catalyst in thermal decomposition of methane. B. YAMAGUTI (Bull. Chem. Soc. Japan, 1927, **2**, 289—294).—Metallic nickel prepared by precipitating nickel sulphate solution with sodium carbonate and heating the precipitate in a current of hydrogen is most effective in catalysing the thermal decomposition of methane if the reduction temperature is about 600°, and if about 20% of oxide is left unreduced. The carbon produced by the decomposition of the methane does not appear to affect the activity of the catalyst. R. CUTHILL.

Auto-poisoning phenomenon shown by catalytically active copper at moderate temperatures. F. H. CONSTABLE (J.C.S., 1927, 2995—3000; cf. A., 1926, 250; 1927, 839).—When a copper catalyst is used to dehydrogenate alcoholic substances above 280° the activity decays with time. The dehydrogenation of ethyl alcohol was studied over ranges of temperature 270—350° and 375—400° and the corresponding decay curves were plotted, but no simple law of decay could be deduced. The initial rate of decay fell rapidly as poisoning of the catalyst proceeded. The results indicated the possibility of this being a particular case of the selective poisoning of a distribution of centres of activity. R. A. PRATT.

Catalysts and their effects on the oxidation of mineral oils. G. W. CUPIT.—See B., 1927, 960.

Hydrogen activated by the electrical discharge. A. DE HEMPTINNE (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, i, 143—149).—In a continuation of previous work on the reduction of metallic oxides by hydrogen in presence of an electrical discharge (A., 1923, ii, 121) it is shown that lead dioxide and mercuric oxide, but not copper oxide or lead monoxide, are reduced when not directly exposed to the electronic or ionic bombardment. The values of N/N' are, however, smaller. These observations are interpreted as indicative of the existence of non-ionised, active hydrogen, monatomic, triatomic, or excited, in the tube. Reduction at the cathode is effected by means of positive ions and at the anode by the intervention of negative ions or by non-ionised active hydrogen. Actual bombardment favours the reduction. J. S. CARTER.

Salt of bivalent silver. G. A. BARBIERI (Ber., 1927, **60**, [*B*], 2424—2427).—Electrolysis in a divided cell in which the anolyte is an 8—10% solution of silver nitrate containing 40% of pyridine and the catholyte 10—15% sulphuric acid, the anode and cathode being respectively a platinum capsule and a thick platinum wire, gives small yields of the unstable, orange-red, crystalline *compound*, $Ag(NO_3)_2,4C_5H_5N$, which liberates iodine from potassium iodide and oxidises chromium and manganous salts to chromic and permanganic acids. H. WREN.

Comparison of certain methods for determining the ultra-violet intensity of a light source. A. E. GILLAM and R. A. MORTON (J.S.C.I., 1927, **46**, 417—420T).—Various chemical methods for the determination of ultra-violet intensity have been described and the influence of screens of window-glass and vitaglass in retarding the reactions has been investigated. Webster, Hill, and Eidinow's acetone-methylene blue gauge is sensitive chiefly to rays between 200 and 280 $\mu\mu$, as only some 12% of the chemical change can be ascribed to rays transmitted by vitaglass. The effective rays in the photolysis of potassium nitrate are also very largely absorbed by vitaglass.

The photolysis of oxalic acid sensitised by uranyl salts is much more sensitive to wave-lengths in the near and middle ultra-violet. Mackenzie and King have suggested that the photochemical decomposition of pure carbon tetrachloride can serve as a useful actinometric reaction, but it is found that rays of wave-length longer than 265 $\mu\mu$ do not bring about decomposition. With shorter radiations the method works well. The possibility of using the decomposition of hydrogen peroxide is discussed and certain difficulties are indicated. Experiments on the deterioration of mercury-vapour lamps show that the output of ultra-violet radiation may fall to 60% or even 40% after 150 hrs. (See this vol., 140.)

Self-integrating chemical actinometry for ultra-violet dosage or other specific purposes. M. J. DORCAS and G. S. FORBES (J. Amer. Chem. Soc., 1927, **49**, 3081—3086).—Reddish-purple Corex glass, backed with a 1 cm. layer of 0·00025*M*-picric acid solution, transmits, at each frequency, a light-wattage proportional to the efficiency in producing erythema (sunburn) in human skin. A 50% solution of benzoquinone in alcohol was photolysed behind this filter, which was compensated, at each wave-length, for the photochemical efficiency of this photolysis. By this means changes in total intensity and in spectral energy distribution are integrated. If y is the iodine value of the benzoquinone photolysed per hr., and x is the reciprocal of the times in which the same sources, without filters, produce a standard erythema, then $y=ax$ approximately, or, for the more efficient light sources, $y=ax+b$, where a and b are constants, b being very small. Thus, the reciprocity law does not appear to hold exactly for the erythema reaction (cf. Hausser and Vahle, Strahlentherapie, 1923, **13**). S. K. TWEEDY.

Interaction of chlorine and sulphur monochloride. Preparation of sulphur dichloride. Use of antimony pentachloride as catalyst. R. P. BOTHAMLEY (Trans. Faraday Soc., 1928, **24**, 47—50).—The period of induction during the reaction between sulphur monochloride and chlorine (cf. A., 1906, ii, 157) is reduced by substituting sunlight for diffused daylight, and the reaction proceeds more rapidly thereafter than under the latter conditions. The reaction is catalysed by antimony pentachloride (cf. A., 1905, ii, 22). In experiments carried out at the ordinary temperature, absorption of chlorine

ceased when the liquid contained about 70% of chlorine (SCl_2=68·9% Cl). At 0°, however, absorption proceeded beyond this point. L. F. GILBERT.

Formation of nitrite from nitrate as a measure of ultra-violet intensity. A. E. GILLAM and R. A. MORTON (J.S.C.I., 1927, **46**, 415—417T).—The photolysis of potassium nitrate buffered at p_H 9·4 may be used as an actinometer for measuring the ultra-violet output of mercury-vapour lamps. The Griess–Ilosvay colorimetric method of determining nitrite concentration has been adapted for the purpose. The photolysis is primarily sensitive to wave-lengths in the far ultra-violet, so that it is suitable for detecting the first stages in the ageing of the lamps. It is also suitable for controlling the bactericidal action and other reactions occurring in the same spectral region. The use of a screen of vitaglass enables the test to be used as a theoretically sound method for controlling the output of a light source in respect of the stimulative rays. The reaction is, however, too slow for general use as an easy routine test for dosage in actinotherapy. (See this vol., 139.)

Photochemical studies. VI. Photochemical reaction between oxygen and mercury vapour at relatively low pressures. W. A. NOYES, jun. (J. Amer. Chem. Soc., 1927, **49**, 3100—3106).—The above reaction occurs largely between ozone and mercury vapour. The former, it is shown, cannot be produced by both sensitised and unsensitised reactions (cf. Dickinson and Sherrill, A., 1926, 485), and it is suggested that a relatively unstable complex of excited mercury and oxygen is formed which yields ozone through collision with activated or unactivated oxygen molecules or with ozone molecules. S. K. TWEEDY.

Influence of radiation on thermal unimolecular reactions. J. E. MAYER (J. Amer. Chem. Soc., 1927, **49**, 3033—3046).—A detailed account of previously published results (Lewis and Mayer, A., 1927, 948). The absorption coefficients of nitrogen pentoxide at low pressures for black-body radiation (cf. Daniels, A., 1926, 108) are the same whether the black body is at 100° or 200° and are of the same order of magnitude as the coefficients for wave-lengths less than 7 μ. The velocity coefficient of thermal decomposition is calculated to be 1×10^{10} sec.$^{-1}$, which is $2{\cdot}5\times10^{-6}$ times the experimental value (cf. Lewis and Smith, A., 1925, ii, 799). Pinene at low concentrations is not racemised at 830—1053° Abs. by a molecular stream of radiation. The concentration of the latter over the greater part of the frequency range exceeds that in a hohlraum at a temperature high enough to produce racemisation within the time of exposure used. Thus for both reactions the rate of activation by radiation alone is of insufficient rapidity to account for the observed decomposition rate, although a theory necessitating both radiation and collision is not incompatible with the experimental results. Recalculation of Kroger's results (A., 1926, 41) shows that the rate of dissociation of iodine by radiation is lower than the rate of reaction normally found in thermal reactions of the same activation energy. S. K. TWEEDY.

Supposed photoactivity of irradiated substances. O. BECK (Monatsschr. Kinderheilk., 1926, **33**, 320—329; Chem. Zentr., 1927, i, 2396).—The observed darkening of the photographic plate is due to ultra-violet rays of relatively long wave-lengths. Irradiation of cod-liver oil and milk produces an extension of the absorption spectrum towards the ultra-violet, and that of paraffin oil a contraction. The iodine value of cod-liver oil, but not of paraffin, suffers a temporary reduction. A. A. ELDRIDGE.

Light effect in the system caoutchouc–sulphur. H. POHLE (Naturwiss., 1927, **15**, 162—163; Chem. Zentr., 1927, i, 2396).—Exposure to light of caoutchouc–sulphur mixtures results in a separation of the sulphur; the effect, which is due to the violet and blue rays, can be followed ultramicroscopically, and the beginning of vulcanisation can be observed. Except in the presence of substances which absorb the blue and violet rays, the effect is observed so far below the surface as the light penetrates.
A. A. ELDRIDGE.

Activation of hydrogen by electric discharge. G. GLOCKLER (Nature, 1927, **121**, 93).—Elliott's observations (A., 1927, 187) may be due to the hydrogen leaving the discharge tube carrying ions (H_2^+, H^+, or both) and electrons, the latter then combining with the sulphur atoms, and hydrogen sulphide being produced by simple ionic combination.
A. A. ELDRIDGE.

Reduction of alkali carbonates by carbon, and action of alkali metals on carbon. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1927, **168**, 218—220).—Heating curves of mixtures of sugar charcoal or graphite with sodium carbonate or potassium carbonate have points of inflexion, indicating that the carbonate has commenced to "wet" the carbon, at 1040—1085°. Gas-carbon rods exposed to the vapour of sodium or potassium above about 500° begin to crumble, probably owing to the formation of solid solutions of the alkali metals in the carbon. Sodium vapour begins to act on porcelain at 570°, and at a particular temperature acts more rapidly than potassium, and less rapidly than lithium.
R. CUTHILL.

Oxidation of sodium amalgam by means of oxygen. A. FELDMANN.—See B., 1928, 12.

Formation and constitution [and anti-tubercular action] of sodium aurosulphite. B. ODDO and Q. MINGOIA (Gazzetta, 1927, **57**, 820—826; cf. Rosenheim, Hertzmann, and Pritze, A., 1908, ii, 860).—*Sodium aurosulphite*, $Na_5Au(SO_3)_4(+5H_2O)$, is obtained by neutralising an aqueous auric chloride solution with sodium hydroxide and adding a solution of sodium sulphite; on adding alcohol to the filtered liquid, a yellow compound with a reddish-green fluorescence is obtained. Determinations of mol. wt. cryoscopically in water give a value $\frac{1}{8}$ to $\frac{1}{10}$ of the theoretical; μ_∞=720. It is therefore concluded that the substance dissociates thus: $3SO_3^{--}+AuSO_3^{+}+5Na^{+}$, the ion $AuSO_3^{+}$ having the structure $O{:}S{<}_{O}{>}Au^{+}$ and the conductivity 88·5 (cf. Mollgaard, "Chemotherapy of Tuberculosis," Copenhagen, 1924).

The substance is completely absorbed from hypodermic or intramuscular injection; whilst there is a

definite bactericidal action on Koch's bacillus, the anti-tubercular action is not great. In man the optimum tolerated dose is 0·1—0·2 g.

E. W. WIGNALL.

Magnesium peroxide. H. KREPELKA and J. CERVINKA (Časopisu ceskosloven. lek., **6**, No. 11—12, 14 pp.; Chem. Zentr., 1927, i, 2404).—Treatment of ethereal (concentrated) hydrogen peroxide with magnesium hydroxide yields a hygroscopic substance of composition between MgO_2,H_2O and $MgO_2,2H_2O$, passing into the dihydrate and then into the compound MgO_2,MgO,H_2O, and in one case into $4(MgO_2,2H_2O),MgO$, but in absence of water into indefinite compounds with evolution of oxygen.

A. A. ELDRIDGE.

Colour changes of double iodides when rubbed. G. TAMMANN and G. VESZI (Z. anorg. Chem., 1927, **168**, 46—48).—The transient red colour produced when an emulsion of silver mercuric iodide, $2AgI,HgI_2$, in gelatin, deposited on a glass plate, is rubbed is due to local rise of temperature to above 50°, the transition temperature of the double salt. The same is true of the change from red to violet of cuprous mercuric iodide, $2CuI,HgI_2$, which takes place at 65°.

H. F. GILLBE.

Chemical effects of high-frequency sound waves. I. Preliminary survey. W. T. RICHARDS and A. L. LOOMIS (J. Amer. Chem. Soc., 1927, **49**, 3086—3100; cf. Phil. Mag., 1927, [vii], **4**, 417; A., 1927, 849, 1008).—The chemical effects of high-frequency (289,000 $sec.^{-1}$) compression waves are considered. Many sensitive metastable systems are discharged; *e.g.*, nitrogen trichloride is exploded and yellow mercuric iodide becomes red below 120°. Superheated liquids evaporate with explosive violence and substances at a liquid or gas interface are readily dispersed; *e.g.*, fairly stable emulsions of mercury in water may be prepared. Mercurial thermometers and thermocouples give readings elevated by several degrees, and air-free liquids boil below their normal b. p. Dissolved gases are expelled from solution to the pressure lowering in the tensional region of the waves. Some chemical reactions are accelerated, *e.g.*, the hydrolysis of methyl sulphate and the iodine "induction period" reaction. Tentative explanations of the above phenomena are offered.

S. K. TWEEDY.

Action of sodium amalgam on carbon disulphide. B. FETKENHEUER [with H. FETKENHEUER and H. LEOUS] (Ber., 1927, **60**, [*B*], 2528—2537).—Carbon disulphide when shaken with 0·8% mercury amalgam forms a complex mixture of compounds which cannot readily be separated into its methylated derivatives after treatment of the product with methyl sulphate. The crude material is therefore treated with 90% alcohol, which leaves undissolved a product (not yet completely investigated) containing almost all the mercury. The solution is treated with methyl chloride, thus leading to the isolation of the following substances: methyl sulphide; *methyl tetrathio-oxalate*, $(CS\cdot SMe)_2$, m. p. 100·9°, b. p. 210°/0·1 mm. (decomp.), d_4^{20} 1·619, hydrolysed to oxalic acid [Sakurada's observation that ethyl tetrathio-oxalate is formed by the action of hydrogen chloride and cyanogen followed by hydrogen sulphide on an ethereal solution of ethyl mercaptan could not be confirmed (cf. A., 1926, 950)]; *methyl methylxanthate*, $C_3H_5OS_2$, b. p. 168°/765 mm., converted by alcoholic ammonia into ammonium thiocyanate; methyl trithiocarbonate, b. p. 224°/760 mm.; an isomeric *methyl tetrathio-oxalate*, m. p. 71·6°, d_4^{20} 1·658, apparently stereoisomeric with that described above; *tetramethylthiolethylene*, $(SMe)_2C:C(SMe)_2$, m. p. 61·5°, d_4^{18} 1·397 (corresponding *bromo*-derivative, $C_6H_{12}Br_4S_4$). The production of methyl methylxanthate is due to a subsidiary reaction, since the compound is not produced when the crude product of the reaction is treated directly with methyl sulphate. The production of sodium sulphide is not accompanied by the separation of carbon and the mechanism cannot at present be explained. Carbon disulphide appears able to add sodium, giving the compounds $\cdot CS\cdot SNa$ and $:C(SNa)_2$. Sodium in the absence of mercury does not react with carbon disulphide in a sealed tube at 150°, the slight brown layers formed being due to unavoidable production of layers of oxide or hydroxide on the surface of the metal. Sodium–potassium alloy forms yellowish-brown, exceedingly explosive crusts. When carbon disulphide is added to a solution of sodium in liquid ammonia, a vigorous action results in the production of a brown mass which, with methyl sulphate, affords the two forms of methyl tetrathio-oxalate, methyl trithiocarbonate, tetramethylthiolethylene, and methyl sulphide.

H. WREN.

Frosting of glass by mixtures containing hydrofluoric acid and alkali fluorides. C. D. SPENCER and L. OTT.—See B., 1928, 52.

Behaviour of thorium oxide in tungsten filaments. W. GEISS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1927, **168**, 107—112).—Thorium oxide in tungsten filaments is reduced at temperatures above 2700° Abs. to metallic thorium, which does not form mixed crystals with tungsten. Diffusion of thorium oxide to the outer portions of the filament takes place through the interstices between the tungsten particles, and not through the crystal lattice.

H. F. GILLBE.

Preparation of $Th(OH)_4$ from the solution of a salt as function of the hydrogen-ion concentration. J. A. ATANASIU (Ber., 1927, **60**, [*B*], 2507—2509).—Thorium hydroxide is quantitatively formed when pyridine is added to the solution of a thorium salt at about its neutral point (p_H 7); the solution may be very feebly acid or alkaline. The quantity of pyridine has no marked effect on the precipitate. The metals of the cerium group and the ordinary heavy metals are not precipitated under these conditions.

H. WREN.

Appearance of visible impurities in chemical preparations with lapse of time. G. KASSNER (Festschr. A. Tschirch, 1926, 80—84; Chem. Zentr., 1927, i, 2523).—The cause of a white preparation of bismuth nitrate becoming grey after 1 year proved to be the separation of tellurium effected by decomposition products of the cellulose of the filter paper employed.

A. A. ELDRIDGE.

Reaction between potassium carbonate and sulphur in alcoholic solution. T. L. DAVIS and

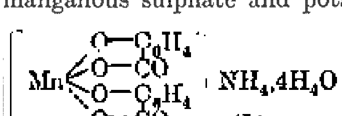
J. W. Hill (J. Amer. Chem. Soc., 1927, **49**, 3114—3116).—The reaction is essentially the same as in aqueous solution; it is of much greater rapidity, however, since alcohol dissolves an appreciable amount of both substances, whereas water dissolves only a minute quantity of sulphur. 100 C.c. of ethyl alcohol solution contain, at 25°, 0·1114 g. of anhydrous potassium carbonate, 0·0088 g. of anhydrous sodium carbonate, and 0·03926 g. of sulphur.

S. K. Tweedy.

Seleno-compounds of tungsten. V. Lenher and A. G. Fruehan (J. Amer. Chem. Soc., 1927, **49**, 3076—3080).—The saturation of cold, concentrated ammonium tungstate solution with hydrogen selenide yields green orthorhombic crystals of *ammonium selenotungstate*, $(NH_4)_2WSe_4$; incomplete saturation yields red, triclinic crystals of *ammonium diselenotungstate*, $(NH_4)_2WSe_2O_2$. Both salts are readily soluble in water (the solutions decomposing slowly in air), somewhat soluble in alcohol, and insoluble in ether, benzene, and carbon disulphide. Crystallographic properties are recorded. S. K. Tweedy.

Oxidation of iodic acid by compounds of bivalent silver. G. A. Barbieri (Ber., 1927, **60**, [*B*], 2427—2428).—Oxidation of a boiling solution of iodic acid by potassium persulphate in the presence of silver nitrate affords silver periodate. When a dilute solution of silver nitrate is treated with sodium carbonate and potassium persulphate at 70—80°, silver peroxide is precipitated; in the presence of an iodate, almost homogeneous silver periodate, Ag_3IO_5, is nearly quantitatively precipitated in place of the oxide. H. Wren.

New compounds of tervalent manganese. G. A. Barbieri (Ber., 1927, **60**, [*B*], 2421—2424).—When an ammoniacal solution of ammonium salicylate is treated successively with aqueous solutions of manganous sulphate and potassium persulphate the *compound* (I) is precipitated as a grey mass. It liberates iodine from potassium iodide; its brown solutions in dilute sulphuric acid are decolorised by hydrogen peroxide, sulphurous acid, hydrazine, and other reducing agents; it is converted by potassium cyanide into potassium manganicyanide. The presence of a relatively stable complex containing tervalent manganese is established by the formation of *precipitates* after addition of solutions of silver, thallium, and *luteo*-cobalt salts. Ammonium manganisalicylate is transformed by warm pyridine into the green *compound*, $Mn[CO_2H{\cdot}C_6H_4{\cdot}O]_2NH_4,3C_5H_5N,5H_2O$, which loses part of its pyridine when treated with chloroform and is converted by addition of glacial acetic acid to its saturated alcoholic solution into the *substance* $Mn[CO_2H{\cdot}C_6H_4{\cdot}O]_2H,2C_5H_5N,2H_2O$.



(I.)

H. Wren.

Oxides of iron, especially ferrous oxide. H. Groebler and P. Oberhoffer.—See B., 1928, 12.

Reduction of metallic oxides by hydrogen. III. Nickel oxide. IV. Cobalt oxide. G. Gallo.—See B., 1928, 56.

Black nickel oxide. M. Le Blanc and H. Sachse (Z. anorg. Chem., 1927, **168**, 15—16; cf. Lunde, A., 1927, 815).—Polemical. H. F. Gillbe.

Bivalent ruthenium. H. Gall and G. Lehmann (Ber., 1927, **60**, [*B*], 2491—2497; cf. A., 1927, 123).—Repetition of the experiments of Remy (A., 1921, ii, 209) and Remy and Wagner (A., 1927, 328) on the reduction of ruthenium trichloride by sodium amalgam shows that the consumption of hydrogen never exceeds one equivalent proportion and that under these conditions only bivalent and metallic ruthenium are produced, whereas univalent ruthenium is incapable of existence. The green colour regarded by Remy as indicative of a definite valency stage is only a mixed colour produced whenever the blue solution of ruthenium dichloride is mixed with ruthenium trichloride. It invariably appears when reduction is effected slowly and its apparent dependence on the acidity of the solution is attributed to the variation caused thereby in the ratio of molecular to atomic hydrogen evolved by the amalgam. The behaviour of ruthenium dichloride when heated in a current of carbon dioxide at 200° excludes the possibility that it can have the composition $HRuCl_2$. Oxidation of the blue solutions of ruthenium dichloride by alkaline permanganate (cf. Ruff and Vidic, A., 1925, ii, 480) shows a consumption of four equivalents of oxygen indicating the transition from the bivalent to the sexavalent state, but the results are not very accurate, since the permanganate is partly transformed into manganate with liberation of gaseous oxygen. The use of manganate, however, yields exact and confirmatory results. H. Wren.

Platinum metals. VII. Reduction of ruthenium trichloride by sodium amalgam and by alcohol. H. Remy and T. Wagner (Z. anorg. Chem., 1927, **168**, 1—14).—Water-soluble ruthenium trichloride may be converted into potassium pentachlororuthenate without loss of chlorine by evaporation of a solution of the trichloride with the theoretical quantity of potassium chloride. Titrations of sodium amalgam with solutions of the ruthenate yield the same results as when ruthenium trichloride is employed, the successive changes of valency being clearly indicated. Assuming a valency of three for ruthenium in the trichloride and in the pentachlororuthenate, the first stage in the titration corresponds with a change to the bivalent, and the second stage to the univalent state. The deep blue solution formed when insoluble ruthenium trichloride is treated with aqueous alcohol contains ruthenium in the same valency state as the blue solution obtained by reduction with sodium amalgam; a complex acid H_2RuCl_3 is probably present. Pure anhydrous ruthenium trichloride may be prepared from the dark brown solution formed when ruthenium tetroxide is treated with hydrogen chloride by evaporation to constant weight at about 150—160° in a current of dry hydrogen chloride. The product, which contains free hydrogen chloride and water, is heated at 400° in a high vacuum in presence of soda-lime for 2—2·5 hrs.

H. F. Gillbe.

Platinum compounds of hydrazine and carbylamines. L. A. Tschugaev, M. S. Skanavi-

GRIGOREVA, and A. POSNJAK (Ann. Inst. Platine, 1926, No. 4, 299—305).—Compounds of the type

$$\left[(CH_3\cdot NC)_4,Pt{<}{\genfrac{}{}{0pt}{}{NH\cdot NH_2}{NH\cdot NH}}{>}Pt,(CH_3\cdot NC)_4\right]X_2,nH_2O$$

are described: *chloride* ($8H_2O$), red, emerald-green when heated; *iodide* ($4H_2O$), emerald-green; *perchlorate* ($2H_2O$), strawberry-red; *azide*, dark blue. With ethylcarbylamine: *nitrate* ($2H_2O$), red; *perchlorate*, red; *iodide*, yellow; *chloroplatinate*, red; *chloride*, orange-yellow. Treatment of the chlorides with concentrated hydrochloric acid yields the *compounds* $4CH_3\cdot NC,Pt_2,2N_2H_3,2HCl,Cl_2$ and $4C_2H_5\cdot NC,Pt_2,2N_2H_3,Cl_2,2HCl$, respectively.

CHEMICAL ABSTRACTS.

New series of acido-amido-tetrammine derivatives of quadrivalent platinum. L. A. TSCHUGAEV (Ann. Inst. Platine, 1926, No. 4, 37—43).—Chloropentammineplatinic chloride and alkali yield *chloroamidotetrammineplatinic chloride*, $[Pt,4NH_3,NH_2,Cl]Cl_2$; the corresponding (chloro-) *bromide* and *nitrate* and *bromoamidotetrammineplatinic bromide* were prepared. CHEMICAL ABSTRACTS.

Use of the quinhydrone electrode in electrometric acid titration. A. KLIT (Z. physikal. Chem., 1927, **131**, 61—80).—The following acids have been titrated, using the quinhydrone electrode: hydrochloric, oxalic, acetic, malonic, and citraconic acids, and potassium dihydrogen phosphate. As comparison electrode a quinhydrone electrode in $0\cdot01N$-$HCl+0\cdot09N$-KCl was used (cf. Veibel, J.C.S., 1923, **123**, 2203). A weak acid, of initial concentration $0\cdot1N$, may be titrated by this method with $0\cdot1N$-base, provided its dissociation constant is not less than 10^{-7}. If the initial concentration is $0\cdot005N$ the dissociation constant must not be less than 10^{-6}. To avoid any error due to carbonic acid, a stream of nitrogen must be passed through the solution during titration. The dissociation constants (in the case of the polybasic acids the second dissociation constants) calculated on the basis of the p_H value when half-neutralised, and taking into account the ionic strengths concerned, are in good agreement with existing data.

M. S. BURR.

Apparatus for potentiometric titrations. J. F. SPENCER (J.S.C.I., 1927, **46**, 423—424T).—An apparatus for carrying out titrations in highly coloured solutions, and suitable for use in general volumetric work, is described. A rheostat is used as a potentiometer, its ends being connected through a switch to an accumulator, and a sliding contact enables any fraction of the potential drop across the potentiometer to be opposed to the *E.M.F.* between the electrodes in the titration cell. When these are equal (no deflexion on the galvanometer) the *E.M.F.* is read on a voltmeter, and readings are made after each addition of standard solution until the end-point is passed, the end-point being found from the curve in which the *E.M.F.* is plotted against the volume of solution added. W. J. POWELL.

Permanently saturated electrode for p_H determination. SWYNGEDAUW (Compt. rend. Soc. Biol., 1927, **96**, 693—695; Chem. Zentr., 1927, i, 2756).—An arrangement is suggested whereby permanent hydrogen saturation is possible, and the p_H determination carried out in the original vessel.

A. A. ELDRIDGE.

[Platinum electrodes.] S. POPOFF and A. H. KUNZ (Proc. Iowa Acad. Sci., 1926, **33**, 169).—The optimal conditions for plating platinum-black deposits are described. "Poisoned" hydrogen electrodes are restored by treatment with concentrated nitric acid.

CHEMICAL ABSTRACTS.

Electroanalysis. H. PAWECK and R. WEINER (Z. anal. Chem., 1927, **72**, 225—248).—The novel feature of the method described is the use of electrodes of fusible alloy—Wood's or Lipowitz' metal. Electrolysis is carried out at a temperature at which the cathode is fluid, and when deposition is completed cold water is added to the electrolyte to cause the cathode to solidify. The deposited metal alloys with the fusible alloy and the button of solidified metal is washed quickly with water, alcohol, and ether in succession, dried at 50° in a vacuum desiccator, and weighed. The procedure recommended for the determination of copper, zinc, cadmium, mercury, bismuth, and lead is described in detail, and except for lead and cadmium does not vary appreciably from that previously described when using a mercury cathode (A., 1924, ii, 562). The deposition in most cases is effected more smoothly owing to the overvoltage of hydrogen on Wood's metal being higher than on mercury. Cadmium is deposited from a sulphate solution containing 10 g. of ammonium oxalate with a current of 2—3 amp. at 4·5—6 volts. For the deposition of lead the acetate solution is treated with 10—15 g. of ammonium oxalate, 10—15 c.c. of hydrochloric acid, and 0·5 g. of hydroxylamine hydrochloride and electrolysed for 2 hrs. with 3—4 amp. A. R. POWELL.

Stirrer for rapid electro-analysis. H. ROM (Chem.-Ztg., 1927, **51**, 985).—The stirrer consists of a rod covered with vulcanite and provided with means for attaching any type of electrode at its lower end and with three driving pulleys of different diameters at its upper end, the whole being mounted on a suitable support. A number of stirrers connected together with a common driving belt may be operated by one motor. A. R. POWELL.

"Greasy" burettes. W. LOWSON (Nature, 1928, **121**, 14).—Inaccuracy due to "greasiness" is avoided by the addition of a trace of saponin to standard acid. A. A. ELDRIDGE.

Mercury method of calibrating microburettes. E. SCHILOV (Z. anal. Chem., 1927, **72**, 261—263; cf. A., 1927, 221).—In the method previously described the limiting diameter of the burette is 3 mm.; this may be increased to 4·2 mm. by supporting the mercury on a column of air above the lower column of water. A. R. POWELL.

Determination of p_H of fluids containing carbon dioxide at different partial pressures. A. BECK (Biochem. Z., 1927, **190**, 75—83).—A full description of the apparatus and method is given.

A. WORMALL.

Use of sodium borate instead of sodium hydroxide in the titration of weak bases. H.

BAGGESGAARD-RASMUSSEN and C. E. CHRISTENSEN (Festschr. A. Tschirch, 1926, 263—282; Chem. Zentr., 1927, i, 2756).—Sodium borate is substituted for sodium hydroxide in the titration of excess of acid in the determination of alkaloids or ammonia.

A. A. ELDRIDGE.

Determination of hydrogen in fire-damp. HEYER.—See B., 1928, 42.

Reaction between iodic and hydriodic acids in very dilute solution and the titration of the liberated iodine with thiosulphate. P. PUTZEYS (Ann. Soc. Sci. Bruxelles, 1927, 47, *B*, i, 159—172; cf. Vosburgh, A., 1922, ii, 863; Rice, Kilpatrick, and Lemkin, A., 1923, ii, 574; Bray and Miller, A., 1924, ii, 870; Popoff and Whitman, A., 1925, ii, 1093).—An investigation of reactions involved in iodometry, primarily concerned with their application to micro-analysis. The reaction occurring in solutions about $0{\cdot}001N$ with respect to iodate and containing excess of iodide and acid has been investigated, special attention being devoted to the elimination of the oxygen error, and it is shown that the theoretical quantity of iodine is liberated and a satisfactory end-point obtained on subsequent titration only when the product of the concentrations of iodide and acid lies between certain limits. In the present instance these limits are 0·01 and 0·075 and apply to measurements made in artificial light. The limits are narrower for daylight. As the concentration of iodate is increased the quantity of iodine determined by titration becomes more independent of these factors. Reacting mixtures should be kept for 5 min. before titration. Although reaction between sodium thiosulphate and iodine is practically instantaneous, it is, nevertheless, advisable to add the thiosulphate rather slowly towards the end of the titration, especially when extremely dilute solutions are involved. Owing to the relative slowness of the reaction, titration with very dilute solutions of arsenite should be avoided. Alkaline absorption of iodine commences at p_H 6. Dilute solutions of thiosulphate should be prepared by dilution of $0{\cdot}1N$-solution with water approximating to conductivity water, and although when protected against acid vapours such solutions are not markedly unstable, they should be standardised immediately prior to use by means of a solution of potassium iodate of corresponding concentration, the quantities of potassium iodide and acid added to this latter being in accordance with the conditions stipulated above. $0{\cdot}1N$-Solutions of thiosulphate should be standardised by the dichromate-iodide method (Vosburgh; Bray and Miller, *loc. cit.*). J. S. CARTER.

Determination of the constituents of a gaseous mixture containing hydrogen sulphide, carbon dioxide, hydrogen arsenide and phosphide, and acetylene. M. WILMET.—See B., 1928, 13.

Determination of selenium by rapid electro-analysis. A. JILEK and J. LUKAS (Chem. Listy, 1927, 21, 576—583).—The nitric acid solution containing not more than 50 mg. of selenium as selenious acid is treated with a solution of copper or bismuth nitrate containing at least as much copper or three times as much bismuth as there is selenium present; 3 c.c. of nitric acid and 3·5—5·5 g. of tartaric acid, dissolved in water and neutralised with sodium hydroxide, are added, followed by water to give a volume of 120—150 c.c., and the solution is electrolysed at 18° with a current of a few centiamperes at 2·0—2·2 volts in a Classen crucible using a rotating platinum spiral as anode. The deposited copper or bismuth contains all the selenium and adheres well to the cathode; it is washed with a stream of cold water without breaking the current, then with alcohol, dried at 100°, and weighed. The weight of selenium is obtained by subtracting from this weight the weight of the copper or bismuth added.

A. R. POWELL.

Qualitative precipitation of phosphoric acid with lead salts. G. G. KANDILAROV (Z. anal. Chem., 1927, 72, 263—264).—After removal of the hydrogen sulphide from the solution obtained by digesting the ammonia and ammonium sulphide precipitate with dilute hydrochloric acid, the liquid is diluted to 150—200 c.c. and treated drop by drop with a dilute solution of lead acetate until no further precipitate forms. All the phosphoric acid is thus removed as lead phosphate. The filtrate is treated with ammonium sulphide and the precipitate digested with dilute sulphuric acid to remove the lead from the zinc, iron, and manganese. Chromium is mainly precipitated with the lead phosphate and should therefore be tested for in a separate portion of the original solution (cf. Balarev, A., 1922, ii, 525; 1924, ii, 700).

A. R. POWELL.

Electrometric titrations: chloramine-*T* as a titrating agent. A. MCMILLAN and W. EASTON (J.S.C.I., 1927, 46, 472T).—" Chloramine-*T* " may be used for analytical work (Noll, A., 1925, ii, 66) in the oxidising operations involving the use of iodine to replace the latter if a few drops of potassium iodide containing a little starch are added to serve as indicator. The same substance may be used as titrating reagent in conjunction with the electrometric apparatus for the determination of arsenic, antimony, tin, and iron, no indicator being required in this case.

Volumetric determination of arsenic acid. K. PEDERSEN-BJERGAARD (Dansk Tidsskr. Farm., 1928, 2, 1—7).—A discussion of the reaction $H_3AsO_4+3I'+2H^{\cdot} \rightleftharpoons H_3AsO_3+I_3'+H_2O$ involved in the volumetric determination of arsenic with respect to the mass-action equation $K=([H_3AsO_4][H^{\cdot}][I'])/([H_3AsO_3][I_3'])$, the results of previous workers being briefly cited. In the direct determination of arsenic acid by reduction with hydriodic acid and subsequent titration of the liberated iodine, the reaction is affected adversely by dilution, which leads to low results. The solution should contain $4N$-hydrochloric acid and 1% of potassium iodide, and should be kept at the ordinary temperature for 15 min., when the liberated iodine is titrated with thiosulphate solution, using starch as indicator. If a mixture of arsenious and arsenic acids be present, the former is first determined in a portion of the solution by titration with iodine in presence of sodium hydrogen carbonate. Another portion is acidified strongly with hydrochloric acid, some ferrous sulphate and potassium bromide are added, and the whole of

the arsenic is distilled off as chloride. The arsenious acid in the distillate is determined as above, and the arsenic acid found by difference. H. F. HARWOOD.

Determination of the purity of elementary boron. J. W. ANDREWS.—See B., 1928, 51.

Determination of carbon monoxide by means of mercuric oxide. P. N. GRIGORJEV (Z. anal. Chem., 1927, 72, 263—266).—The determination of carbon monoxide by oxidation with yellow mercuric oxide at 100° (cf. Moser and Schmid, A., 1914, ii. 384) yields high results if the gas mixture contains aldehydes or hydrocarbon vapours. These may be removed by passing the gas successively through concentrated sulphuric acid and liquid paraffin cooled below 0°. A. R. POWELL.

Determination of carbon monoxide with iodine pentoxide. J. TAUSZ and K. JUNGMANN.—See B., 1928, 13.

Solubility of magnesium oxalate, and its importance for separation of calcium and magnesium. M. BOBTELSKY and (FRAU) MALKOWA-JANOWSKI (Z. angew. Chem., 1927, 40, 1434—1436).—The solubilities of magnesium oxalate in solutions of ammonium oxalate, oxalic acid, and ammonium chloride at 15° and 100° are recorded; from the data, a table of corrections for the determination of magnesium by precipitation as oxalate is given. Determination of the calcium becomes inaccurate if the amount present is too low, but may be carried out accurately if the proportion is increased by addition of a known quantity of a calcium chloride solution. S. I. LEVY.

Precipitation of magnesium ions by tropæolin-*OO* and the use of this reaction for its colorimetric determination. J. ZAHRADNICEK (Biochem. Z., 1927, 191, 61—73).—Tropæolin-*OO* precipitates magnesium ions from solution, the maximum precipitation being obtained in 30 min. The best reaction is obtained with 2 c.c. of 0·1% tropæolin with 1 mg. of magnesium at a reaction p_H 6·8—7·0. In the absence of other electrolytes, 0·001 mg. of magnesium may be detected, but in their presence the reaction is interfered with, potassium sulphate inhibiting least and sodium phosphate most. Most other salts and salts of the alkaline earths react with the dye only in very concentrated solution and the precipitate dissolves on dilution. Organic solvents inhibit the reaction. The use of the dye is adapted to the determination of magnesium in small amounts of serum, plasma, blood, and tissues. P. W. CLUTTERBUCK.

Potentiometric determination of silver, copper, and gold. E. ZINTL, G. REINACKER, and F. SCHLOFFER (Z. anorg. Chem., 1927, 168, 97—106).—In absence of other metals, silver may be determined in a sulphate solution by potentiometric titration with chromous sulphate solution. Silver and copper, when both present, may be determined by the same method after addition of ammonium chloride, sodium acetate, and acetic acid; two breaks in the potential curve are obtained, corresponding with the successive reduction of the silver and copper salts. Mixtures of silver with lead, quadrivalent tin, or tervalent gold or arsenic may be determined in the same manner.

The velocity of reduction of auric chloride being less than that of the catalytic decomposition of the chromous salt by the finely-divided metallic gold, accurate results cannot be obtained by direct titration. The presence of a cupric salt in the solution renders the titration quantitative; lead, cadmium, bismuth, mercury, and silver do not interfere. Gold and copper may be determined simultaneously in presence of lead, cadmium, or bismuth. Consecutive determination of gold, copper, and mercury in a solution containing 2—5% of hydrochloric acid may be effected by titration with chromous sulphate first of the gold, and then, after addition of bismuth and ammonium chlorides, of the copper and mercury. Copper and gold may be titrated directly in presence of silver and 2—5% of hydrochloric acid; the silver may then be determined by rendering the solution alkaline with ammonia, adding sodium acetate and ammonium chloride, and, after keeping the solution for several hours, continuing the titration with chromous chloride. H. F. GILLBE.

Detection and determination of metals by means of 8-hydroxyquinoline ("oxine"). I. M. KOLTHOFF (Chem. Weekblad, 1927, 24, 606—610).—The isoelectric point of the pure compound is at p_H 7·2, and the solubility at this point at 18° has the minimum value of about $3 \cdot 6 \times 10^{-3}$ g.-mol. per litre; solubilities have been determined for the p_H range 6·0—8·4. The sensitiveness of the reagent under various conditions towards metals is tabulated. In alkaline solution (with sodium potassium tartrate to hold the metal oxide in solution if necessary) copper, cadmium, zinc, and magnesium are completely precipitated, cobalt and nickel nearly so; zinc and magnesium may be completely separated by precipitating the former first in acetic acid solution, the latter afterwards in ammoniacal solution.

Various gravimetric determinations are described, in which the metal compound of 8-hydroxyquinoline is precipitated under suitable conditions, dried, and weighed as such; aluminium is readily determined in presence of calcium and magnesium. The volumetric method with bromine is best carried out by adding excess and titrating back; the determination of zinc, magnesium, calcium, and aluminium in this way is described. S. I. LEVY.

Applications of the polarographic method. M. SHIKATA.—See this vol., 136.

Determination of rare metals and separation from other metals. X. Three new gravimetric determinations of beryllium, and separations depending thereon. L. MOSER and J. SINGER (Monatsh., 1927, 48, 673—687).—A method for preparing pure beryllium sulphate, depending on the use of tannic acid (cf. A., 1927, 846), is described.

Beryllium may be determined gravimetrically as oxide in three ways. The first, precipitation by ammonia (cf. Bleyer and Boshart, A., 1912, ii, 1211), gives low values, since the solubility of beryllium hydroxide is 2·0 mg. of oxide per litre, rising to 4·5 mg. in presence of 1% of ammonia, even when 1% of ammonium chloride is also present; it is unsatisfactory owing to the ease with which impurities are adsorbed on the hydroxide (which is furthermore

very difficult to filter), and is abandoned. A second method is adapted from that used by Schirm (A., 1909, ii, 834) for the determination of aluminium, and consists in the precipitation of the hydroxide from neutral solution by an ammonium nitrite solution; when this is used for beryllium, the hydroxide forms a compact precipitate, easily filtered, but low values are obtained, owing to the formation of nitric acid by decomposition of the nitrous acid liberated. This is avoided by adding methyl alcohol, and thus eliminating nitrous acid in the form of its very volatile methyl ester. The beryllium hydroxide is washed with hot water, ignited to the oxide, and weighed; accurate results are obtained.

Thirdly, tannic acid may be used. Whereas aluminium is precipitated (and separated from beryllium; cf. A., 1927, 846) by tannic acid in weakly acid solutions, beryllim is purecipitated from a solution by adding ammonium nitrate and then tannic acid, followed by ammonia solution. The precipitate is washed and ignited; accurate values are obtained, provided that the solution contains no other metal (except the alkali metals) and no acetate. The method is applicable to the smallest quantities of beryllium.

A satisfactory method of determining beryllium as pyrophosphate is now described (cf. Travers and Perron, A., 1924, ii, 677). By analogy with magnesium, which forms a crystalline ammonium phosphate only in neutral or weakly acid solutions (Schmitz, A., 1925, ii, 67), beryllium ammonium phosphate can be prepared crystalline if an acetate is present. The beryllium solution is treated with a solution of diammonium hydrogen phosphate, ammonium nitrate, and ammonium acetate. After heating, enough nitric acid is added to dissolve the precipitate; dilute ammonia solution is then added very slowly while cloudiness develops, and then rapidly. The crystalline beryllium ammonium phosphate is washed with ammonium nitrate solution and is ignited. Precipitation can also be obtained in presence of sulphosalicylic acid, but not of tartaric acid.

Beryllium is separated from ferric iron and from chromium, thorium, and tungsten by precipitating these as tannic acid complexes in acid solution (cf. A., 1927, 846), and similarly from titanium and vanadium, which form tannic acid complexes insoluble in concentrated acetic acid, and from zirconium, which forms a complex insoluble in concentrated acetic acid or even dilute hydrochloric acid. Beryllium cannot be separated from molybdenum by the tannic acid method, and is accordingly precipitated by ammonium nitrite, a little ammonia solution being added to dissolve any adsorbed molybdenum compound.

E. W. Wignall.

Potentiometric determination of cerium. K. Someya (Z. anorg. Chem., 1927, **168**, 56—60).—Cerous sulphate solution, containing free sulphuric acid, is boiled with sodium bismuthate, and the resulting solution, after cooling and diluting, is titrated with ferrous sulphate solution.

H. F. Gillbe.

Separation and determination of tin in the analysis of stannates by their decomposition in a current of hydrogen chloride. G. Jander and F. Busch (Ber., 1927, **60**, [*B*], 2594—2597).—Determination of sodium and barium in their respective stannates is accurately effected by gently heating the salts in a current of hydrogen chloride and weighing the residual chloride. The volatilised tin tetrachloride is absorbed in two tubes containing water and dilute ammonia, respectively; the tin is determined as stannic oxide after precipitation with ammonia and ammonium nitrate. Attempts to determine tin volumetrically by a reductive process gave low results since volatile tin compounds were carried away by the gases evolved during the process.

H. Wren.

Germanium. XXV. Arc spectrographic detection and determination of germanium. Occurrence of germanium in certain tin minerals. Enargite as a possible source of germanium. J. Papish, F. M. Brewer, and D. A. Holt (J. Amer. Chem. Soc., 1927, **49**, 3028—3033).—The arc spectrum lines of germanium are tabulated for germanium solutions of different concentrations. Except when the germanium is present in very low concentrations the presence of tin has no influence. Certain tin minerals are found to contain small quantities of germanium (0·005, 0·001%). Some specimens of enargite contain 0·1% of the metal, and a method of extraction from this mineral is described.

S. K. Tweedy.

Electrolytic separation of bismuth at low potential. J. Lukas and A. Jilek (Chem. Listy, 1927, **21**, 541—543).—To 3 c.c. of concentrated nitric acid, containing not more than 0·3 g. of bismuth, is added a solution of 6 g. of tartaric acid neutralised with 20% sodium hydroxide, and the mixture is electrolysed at 70° in a Classen capsule with a rotating gauze anode with a current of 0·1 amp. and a *P.D.* of 2 volts. When the current has fallen to a few hundredths of an ampere, indicating the completion of the separation, the deposit is washed with water without stopping the current, then with alcohol, and dried at 100°.

R. Cuthill.

Red-sensitive photo-electric cells. C. C. Paterson (Nature, 1928, **121**, 58).—Photo-electric cells of the Elster–Geitel type sensitive to the extreme red.

A. A. Eldridge.

Application of interference refractometer to the measurement of the concentration of dilute solutions. R. Macy (J. Amer. Chem. Soc., 1927, **49**, 3070—3076).—The necessary precautions attending the use of the Zeiss interference refractometer for determining the concentrations of dilute solutions are described and discussed (cf. Barth, A., 1926, 779). The instrument is more sensitive to aromatic than to aliphatic compounds.

S. K. Tweedy.

Method for the determination of specific heats and heat tone from temperature-time curves. W. M. Cohn (Z. angew. Chem., 1927, **40**, 1557—1559).—The substance under examination is placed in a small crucible containing also a thermo element within an electric furnace. The method is intended principally for silicates and ceramic masses for which variations in the thermal conductivity may be neglected. Then the rate of transmission of heat to

the substance $dQ/dt - f(t,G)$, where t is the temperature of furnace and G the temperature difference between the furnace walls and the crucible. This function is a constant for a given furnace. A substance is chosen the specific heat of which has been ascertained. For the same substance the temperature–time curve is measured and thus dQ/dt is obtained. A series of curves is produced for varying values of G, and the temperature–time relations for various substances are transformed into temperature–heat quantity relations. Specific heats are determined by tangents and the thermal effect of any chemical reactions which occur can be measured. C. IRWIN.

Mercury oscillating pump. J. T. DONNELLY, C. H. FOOTT, H. NIELSEN, and J. REILLY (J.S.C.I., 1927, **46**, 437—438T).—A column of mercury in a U-tube is kept in oscillation by a water suction pump. The suction applied to one leg of the U-tube draws the mercury upwards. When the mercury reaches a certain height a float opens a valve to the atmosphere which breaks the partial vacuum. The mercury then drops to its original position, closes the valve, and restarts the cycle.

Micro-method for the determination of surface-tension and density. V. R. DAMERELL (J. Amer. Chem. Soc., 1927, **49**, 2988—2991).—The technique of the micro-determination of density and surface-tension with simple apparatus is described. About 0·1 c.c. of liquid is required; the accuracy is of the order of 1%. S. K. TWEEDY.

Distillation cooler. W. SCHULEMANN (Chem.-Ztg., 1927, **51**, 985).—The apparatus, which is for use in vacuum distillations, consists of a round-bottom flask the neck of which is narrowed and constricted at the upper end and turned downwards into a bulb-shaped tube; this is provided with outlets at its upper end for the insertion of a thermometer and for conducting the vapours to the condenser, and at its lower end to return condensed liquid and spray into the lower part of the round flask away from the stream of vapour which is admitted through a small tube on the opposite side of the neck of the flask. A. R. POWELL.

Apparatus. H. J. FUCHS (Biochem. Z., 1927, **190**, 241—246).—An apparatus for preparation of pure, sterile distilled water, an improved stalagmometer, and an apparatus for bubbling the same quantity of gas through several liquids in the same time, are described. P. W. CLUTTERBUCK.

Apparatus for removal of dissolved gases from water. J. R. LORAH, K. T. WILLIAMS, and T. G. THOMPSON (J. Amer. Chem. Soc., 1927, **49**, 2991—2994).—An apparatus is described in which the advantages of the Van Slyke apparatus (A., 1917, ii, 422) are combined with those of Treadwell's. S. K. TWEEDY.

Platinum electrode for laboratory and demonstration use. S. WIECHOWSKI (Chem.-Ztg., 1927, **51**, 984—985).—The electrode comprises a rectangular platinum sheet, 25×12 mm., to which is welded a piece of stout platinum wire 3·5 cm. long which is sealed into a small glass test-tube. The end of the wire in the tube is flattened and turned up to form a small hook into which a similar hook of brass or copper wire is fixed and the joint hammered flat. The brass wire is held in position by a plug of cement in the mouth of the tube and is provided with a brass contact and screw for making connexion with the source of current. A. R. POWELL.

Change of state on heating of silver mirrors deposited on glass. I. SAWAI and O. MORISAWA (Z. anorg. Chem., 1927, **168**, 49—55).—The distance between the particles forming a silver mirror on glass is on heating altered to an extent which varies with the temperature of heating, the thickness of the mirror, and the nature of the atmosphere in which the heating is conducted. H. F. GILLBE.

Cover-glass for conducting microchemical reactions in the Zeiss quartz cell. J. JOCHIMS (Z. wiss. Mikroskop., 1927, **44**, 214—216; Chem. Zentr., 1927, ii, 1285).

Illinium. W. A. NOYES (Z. anorg. Chem., 1927, **168**, 264).—Polemical against Rolla and Fernandes (A., 1927, 501). R. CUTHILL.

Geochemistry.

Theory of the upper atmosphere and meteors. (EARL OF) BERKELEY (Nature, 1927, **120**, 954).

Composition of the air in the streets of Paris. D. FLORENTIN (Compt. rend., 1927, **185**, 1538—1541).—The air of the streets in the centre of Paris contains about 0·5 litre/m.^{3} of carbon dioxide and small quantities of carbon monoxide. The actual amounts depend on the atmospheric conditions. Pollution of the air by these gases is considerably less on the upper floors of the buildings and in the suburbs. J. GRANT.

Temperature and salinity observations in the Gulf of Aden. D. J. MATTHEWS (Nature, 1927, **121**, 92).—A comparison of published observations. A. A. ELDRIDGE.

Variations in the salinity of estuaries measured *in situ* by electrical conductivity. A. CHAUCHARD and (MME.) CHAUCHARD (Compt. rend., 1927, **185**, 1503—1504).—A modified Kohlrausch conductivity method is described for the determination from a boat of the salinities of rivers and lakes in terms of the electrical conductivity of the water. A correction must be applied for temperature, but for depths of less than 10 m. the pressure has no appreciable effect. J. GRANT.

"Activity" of the best-known iron springs. A. SIMON and K. KOTSCHAU [with G. BUSS] (Z. anorg. Chem., 1927, **168**, 129—144).—Examination of the waters of various German iron springs has shown that, as with the solutions of active iron employed in

previous experiments (A., 1927, 843), the intensity of the benzidine and guaiacum resin reactions is a function of the concentration of ferrous ions. If air is excluded, and the escape of carbon dioxide prevented, the water apparently retains its activity indefinitely. R. CUTHILL.

Acidity of the waters of some Puget Sound bogs. T. G. THOMPSON, J. R. LORAH, and G. B. RIGG (J. Amer. Chem. Soc., 1927, 49, 2981—2988).—The carbon dioxide content of the above waters was measured (cf. Bot. Gaz., 1927, **84**, 264). The acidity is due to an acid (or acids) in addition to, and stronger than, carbonic acid, since the maximum acidity that carbonic acid could produce is less than that observed. Colorimetric and electrometric methods of measuring p_H gave different results. The p_H value is unaffected by boiling, showing that the acid substance is non-volatile, and is unaffected by temperature change; the substance either forms a true solution and is very soluble, or else it is a reversible colloid. The effect of dilution on acidity is similar to that occurring when an acid is buffered by a small quantity of one of its salts. The acidity increases with intensity of colour, *i.e.*, with the stage of plant succession. Water from "wet" bogs (*i.e.*, those surrounding a pond) contains dissolved methane and has a smaller acidity than that from "dry" bogs. The percentage of organic matter in the bogs is a logarithmic function of acidity, indicating that the amount of organic matter is the controlling factor of acidity. S. K. TWEEDY.

Relation between the reducing power of sea water and the distribution of sea-shore organisms. E. FISCHER (Compt. rend., 1927, **185**, 1525—1527).—Dissolved reducing substances in sea water favour the distribution of *Sabella pavonia*, Sav., and *Nassa reticulata*, L. H. BURTON.

Determination of refractive indices of minerals by Becke's immersion method. V. BILLIET (Natuurwetensch. Tijds., 1927, 9, 97—103).—An account of the method and of the practical detail of manipulation, with a discussion of the theoretical basis. S. I. LEVY.

Specific gravities of minerals: index of some recent determinations. L. J. SPENCER (Min. Mag., 1927, **21**, 337—365).—The determination of density by floating in heavy liquids affords a useful "first-aid" in the identification of minerals. A number of crystals of known density act as indicators in a series of tubes containing methylene iodide diluted to different degrees with benzene. The same fragment of the mineral tested can then be used for confirmatory optical and micro-chemical tests. 2277 determined values of density collected from the literature since 1910 are listed numerically from 1·03 (retinite) to 19·0 (native platinum), with a reference to the original literature in each case. A second list gives the minimum and maximum recorded values for each mineral arranged alphabetically. A frequency-curve shows a very pronounced peak at 2·65 for 196 determinations, whilst the arithmetical mean of all the values is 3·62. L. J. SPENCER.

Origin of Chile saltpetre. E. WILKE-DORFURT (Z. anorg. Chem., 1927, **168**, 203—208).—Polemical against Stoklasa (Chem.-Ztg., 1924, **48**, 4, 949). The possible superiority of Chile saltpetre as compared with the synthetic nitrate as a fertiliser for sugar-beet is probably a consequence of the facts that beet, unlike similar cultivated plants, possesses certain inherited halophytic characteristics, and that small amounts of iodine are essential for the life of halophytes. It is considered that Stoklasa's volcanic theory of the origin of the saltpetre is untenable in view of the fact that the iodine content of the nitrate rock as well as the nature and proportions of the other salts present approximate much more closely to what would be expected in a deposit of marine origin than in one produced by volcanic activity. The nitrogen is therefore to be regarded as originating in marine organisms, and the occurrence of iodine, stored up by such organisms, in the nitrate deposits is then in line with its presence in coal, and in phosphate deposits of organic origin. R. CUTHILL.

Composition of two Madagascar minerals: ampangabeite and columbite. G. TSCHERNICK (Bull. Soc. Franç. Min., 1926, **49**, 127—135; Chem. Zentr., 1927, i, 2529).—Ampangabeite, *d* 4·45, almost black, contained Nb_2O_5 50·78, Ta_2O_5 1·80, TiO_2 5·22, SnO_2 0·27, ThO_2 1·65, UO_2 11·98, yttrium earths 4·71, cerium earths 0·67, Fe_2O_3 10·03, CaO 0·87, H_2O 11·04%; lighter-coloured specimens had *d* 4·39 and 3·36, respectively. Columbite contained Nb_2O_5 62·71, Ta_2O_5 12·42, SiO_2 0·65, TiO_2 1·30, SnO_2 0·41, U_3O_8 2·28, FeO 11·02, MnO 8·24, Al_2O_3 0·11, CaO trace, K_2O+Na_2O 0·09%. A. A. ELDRIDGE.

Tourmaline and mica groups. W. KUNITZ (Fortschr. Min. Kryst. Pet., 1927, **11**, 313—314; Chem. Zentr., 1927, i, 2640).—The compositions of the tourmalines, particularly the ratios $SiO_2:B_2O_3:Na_2O:H_2O$, are generally constant. In the magnesium iron tourmalines there is a regular increase in refractive power and decrease in the axial ratio $c:a$ with increase in the iron content. Partial substitution of the magnesium by lithium and aluminium gives a series analogous to the lithium micas. The member $H_5Na(LiAl)_2Al_8Si_8B_8O_{41}$ has ω 1·6401, ϵ 1·6202, $a:c=1:0·4508$; $H_5NaFe_4Al_8Si_8B_8O_{41}$ has ω 1·698, ϵ 1·658, $a:c=1:0·440$. A. A. ELDRIDGE.

Rhyolites and hyperalkaline, quartziferous trachytes, with special reference to those of Korea. A. LACROIX (Compt. rend., 1927, **185**, 1410—1415).—The rhyolites, which are characterised by their richness in alkalis and by the presence of iron and sodium silicates, are divided into two groups, the comendites and the pantellerites. Analyses of samples from Korea show, however, that the members of the groups constitute a continuous series, although two mineralogical types are distinguished throughout the whole independently of the chemical composition. One is produced in a glass-like form by rapid cooling, and the other, which has a membrane structure, may be the result of a transformation of the first. Trachytes containing free silica (hakutoite) are associated with rhyolites and fall into the same mineralogical groups. As with all the hyperalkaline rocks, the types richest in coloured minerals are the richest in quartz. The term hakutoite is applied to all the siliceous α-hyperalkaline trachytes. J. GRANT.

Chemical composition of the lavas of Ahaggar, Central Sahara. M. E. DENAEYER and J. BOURCART (Compt. rend., 1927, **185**, 1492—1494).—Analyses are given of a number of volcanic rocks, and the relationship between the origins of basalts from the valleys, plateaux, and other volcanic centres of the Sahara is indicated. J. GRANT.

Natrojarosite from Kingman, Arizona. E. V. SHANNON and F. A. GONYER (J. Washington Acad. Sci., 1927, **17**, 536—537).—Jarosites are commonly found in the oxidised portions of ore deposits. The formula $(Na,K)_2O,3Fe_2O_3,4SO_3,6H_2O$ has been established by analysis for the earthy, yellowish-brown jarosite described. J. GRANT.

Almandite–spessartite garnet from Gwynns Falls, Baltimore. E. V. SHANNON and F. A. GONYER (J. Washington Acad. Sci., 1927, **17**, 534—536).—Analysis has shown that, like most garnets from granitic pegmatites, the present example is a member of the almandite-spessartite series, but contains the ferrous iron molecule a little in excess of the manganese molecule. The almandite : spessartite ratio is 49·87 : 40·17, and andradite (4·58%), grossularite (2·26%), pyrope (1·62%), and free alumina (1·82%) are also present. The colorimetric determination of manganese is preferable to the basic acetate method in such cases. J. GRANT.

Anthraxolite of Sudbury. A. P. COLEMAN (Amer. J. Sci., 1928, [v], **15**, 25—27).—A material resembling anthracite occurs in some abundance filling veins which cut across the stratification of the pre-Cambrian slates near Chelmsford, Sudbury region, Ontario. It breaks up into lustrous plates and cuboidal fragments, and is much intermixed with quartz and pyrite, showing up to 36·5% of ash. Analysis of selected fragments gave C 94·92, H 0·52, O 1·69, N 1·04, S 0·31, ash 1·52%. The material is referred to anthraxolite and is considered to represent an end-product of the metamorphism of petroleum, which was perhaps of organic origin in the pre-Cambrian seas (cf. A., 1926, 143). L. J. SPENCER.

Vermiculite from the Bare Hills, near Baltimore, Maryland. E. V. SHANNON (Amer. J. Sci., 1928, [v], **15**, 20—24).—A pale-green foliated mineral resembling talc in appearance has been found in the old chromite mines and quarries in serpentine. When heated, it exfoliates like the vermiculites. It encloses some shreds, apparently remnants, of fibrous serpentine or of actinolite. It is optically uniaxial and negative with perfect basal cleavage; ω=1·545, ϵ=1·525. Analysis gave SiO_2 36·12, TiO_2 0·24, Al_2O_3 13·90, Fe_2O_3 4·24, FeO 0·68, NiO 0·28, MnO trace, MgO 24·84, CaO 0·18, H_2O (>130°) 10·74, H_2O (<130°) 8·20, total 99·42, agreeing with the formula $4MgO,Al_2O_3,4SiO_2,6{\cdot}5H_2O$. The analyses and optical data of some other vermiculites are tabulated for comparison. L. J. SPENCER.

Dehydration and optical studies of alunogen, nontronite, and griffithite. E. S. LARSEN and G. STEIGER (Amer. J. Sci., 1928, [v], **15**, 1—19).—The water content of these three minerals is variable, depending on the temperature and on the humidity of the atmosphere, and the optical data show a corresponding variation. Dehydration and rehydration curves are given for each, and optical determinations were made on the partly dehydrated material at different stages. Alunogen from New Mexico consisting of white flattened fibres with n_α 1·460, 1·461, n_γ 1·470 gave on analysis of air-dried material SO_3 37·74, Al_2O_3 16·59, H_2O 44·64, insol. 0·94, total 99·91, agreeing with the formula $Al_2O_3,3SO_3,15{\cdot}5H_2O$. The dehydration curve shows a break at 90°, and the material is then optically isotropic with n 1·502. Nontronite from Woody, California, gave analysis I for dark olive-green material with n_α 1·56, n_β 1·585, n_γ 1·585, d 2·495; and II for citron-green material with n_α 1·57, n_β 1·59, n_γ 1·60.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O (+105°).	H_2O (−105°).	Total.
I.	47·51	0·37	35·17	nil	1·40	2·50	5·90	7·16	100·16*
II.	43·51	2·94	28·62	0·99	0·05	2·22	6·62	14·05	100·02†

* Including Na_2O 0·09, K_2O 0·06. † Including CuO 1·02.

Analysis I agrees with a formula $R^{II}O,3R_2^{III}O_3,10SiO_2,9H_2O$. The published analyses and optical data for nontronite, morencite, hœferite, and müllerite (=zamboninite) are tabulated and compared, and it is concluded that these are all identical, differing mainly in the variable amount of water present. The formula of nontronite may be given as $Fe_2O_3,3SiO_2,nH_2O$, and this shows a gradual passage to the isomorphous mineral beidellite, $Al_2O_3,3SiO_2,nH_2O$ (A., 1926, 143). Data are also given for griffithite (A., 1917, ii, 148). L. J. SPENCER.

South African occurrences of willemite. Fluorescence of willemite and some other zinc minerals in ultra-violet rays. L. J. SPENCER (Min. Mag., 1927, **21**, 388—396).—Willemite (Zn_2SiO_4) is described from Broken Hill and from two other localities in Northern Rhodesia, where it appears to be of abundant occurrence, at one place in association with native silver. Another occurrence is with copper ores at Guchab in South-West Africa. A complete list of localities known for willemite is compiled. The willemite from Franklin Furnace in New Jersey shows a brilliant green fluorescence in ultra-violet rays; that from other localities may show a dark green or a bright yellow, but in most cases no fluorescence at all. Similarly, with some other zinc minerals fluorescence is shown by some specimens and not by others. Of a set of 23 diamonds from British Guiana, a green crystal showed a bright green fluorescence, three colourless crystals a good blue, and the rest gave no effect. Fluorescence in ultra-violet rays is not a constant and essential character of a mineral species, and it evidently depends on the presence of some admixed impurity in the material. L. J. SPENCER.

β-Quartz twins from some Cornish localities. J. DRUGMAN (Min. Mag., 1927, **21**, 366—382).—β-Quartz or high-temperature quartz, stable above 575°, is represented by the porphyritic crystals in quartz-porphyry (the Cornish "elvans"). The twin-laws of this quartz are enumerated, and are distinct from those of α-quartz or low-temperature quartz. L. J. SPENCER.

Occurrence of niccolite and ullmannite in Northumberland, and of serpierite in Killarney,

Ireland. ARTHUR RUSSELL (Min. Mag., 1927, 21, 383—387).—The Settlingstone mine in Northumberland is the largest producer of witherite ($BaCO_3$). Here, in a pipe of galena, the nickel minerals ullmannite (NiSbS) and niccolite (NiAs) have recently been found. Serpierite, as small greenish-blue radial aggregates of minute flattened crystals, has been detected in the waste heaps of the old copper mine on Ross Island in Lough Leane, Killarney. The formula of serpierite given in text-books is based on an error. The only analysis of this mineral (Frenzel, 1894) gives the ratios (Cu,Zn,Ca)O : SO_3 : H_2O = 2·21 : 1 : 3·07. L. J. SPENCER.

Uranium minerals from Lotsmanskaja near Ekaterinoslav and from Khutor Golowin near Shitomit and their radioactivity. N. LESCHENKO (Nachr. Berginst. Ekaterin., 1926, 19, 171—175).—The former (undefined) has radioactivity 50%, and the latter (wiikite) 60%, of that of pitchblende. Both originate from pegmatites. CHEMICAL ABSTRACTS.

Refractive index of becquerelite, curite, kasolite, fourmarierite, parsonite, dumontite, and janthinite. V. BILLIET (Bull. Soc. Franç. Min., 1926, 49, 136—140; Chem. Zentr., 1927, i, 2528).—Values of n_α, n_β, and n_γ, respectively, are: becquerelite, rhombic, 1·750, 1·88, 1·87; schœpite, $UO_3,3H_2O$, rhombic, 1·690, 1·735, 1·714; janthinite, $2UO_2,7H_2O$, rhombic, 1·674, 1·92, 1·90; fourmarierite, $PbO,4UO_3,5H_2O$, rhombic, —, 1·94, 1·92; curite, $2PbO,5UO_3,4H_2O$, rhombic, —, 2·12, 2·07; soddite, $12UO_2,5SiO_2,14H_2O$, rhombic, 1·645, —, 1·662; kasolite, $3PbO,3UO_3,3SiO_2,4H_2O$, monoclinic, 1·89, —, 1·90; sklodowskite, $MgO,2UO_3,2SiO_2,7H_2O$, rhombic, 1·613, 1·657, 1·635; parsonite, $2PbO,UO_3,P_2O_5,H_2O$, monoclinic, 1·85, 1·862, —; dumontite, $2PbO,3UO_3,P_2O_5,5H_2O$, rhombic, 1·88, —, 1·89; dewindite, $3PbO,5UO_3,2P_2O_5,12H_2O$, rhombic, 1·762, —, 1·763. A. A. ELDRIDGE

Villiaumite. T. BARTH and G. LUNDE (Zentr. Min. Geol. Palaont., 1927, A, 57—66; Chem. Zentr., 1927, i, 2529).—*X*-Ray analysis of carmine-red villiaumite shows its identity with pure sodium fluoride; the colour and double refraction are therefore ascribed to the effect of radioactivity. The properties of villiaumite are (incompletely) acquired by sodium fluoride on exposure to *X*-radiation. A. A. ELDRIDGE.

Pleochroic haloes and the age of the earth. F. LOTZE (Nature, 1927, 121, 90).—It is concluded that the coloration of the mineral is accompanied by an alteration in its cohesion properties, with a corresponding increase (revealed especially in the innermost uranium ring) in the range of the α-particles. Hence, it is supposed that with advancing development the outer periphery of the halo advances radially, whereby the part of the ring directed towards the centre is no longer darkened to the same extent as previously. Such a mechanism would explain the discrepancies observed by Joly. The absence of the anomaly in thorium haloes is attributed to the fact that the integral ionisation curve of thorium is less steep than that of uranium, and that no marked maximal absorption of the α-rays coincides with the innermost rings. This explanation invalidates Joly's calculation of geological age. A. A. ELDRIDGE.

Organic Chemistry.

Hydrogen–ethylene reaction in presence of excited mercury atoms. A. R. OLSON and C. H. MEYERS (J. Amer. Chem. Soc., 1927, 49, 3131—3134; cf. A., 1926, 364).—Methane, ethane, propane, and butane are produced when a mixture of hydrogen and ethylene is exposed to ultra-violet light in presence of mercury vapour. Ethane is unaffected under similar conditions. The results obtained appear to indicate the intermediate formation of atomic hydrogen, methylene by fission of the ethylene, and ethylene activated by loss of hydrogen. It is concluded that the energy required for rupture of the carbon–hydrogen linking in ethylene, and the ethylene linking itself, is less than 4·9 volts. F. G. WILLSON.

Hydrogenation of substances with conjugated double linkings. G. VAVON (Bull. Soc. chim., 1927, [iv], 41, 1598—1600).—Gillet's interpretation of the hydrogenation of conjugated double linkings as due to addition of two sodium atoms in the αβ-positions, followed by isomeric change >CNa·CHNa·CH:C< ⟶ >CNa·CNa:CH·CH< (A., 1927, 921) fails to account for hydrogenation of conjugated systems by agents other than sodium which afford nascent hydrogen, *e.g.*, aluminium amalgam and zinc and acetic acid. It is only catalytic methods of hydrogenation that have failed when applied to conjugated systems and any interpretation of the hydrogenation of such systems must account for this difference (cf. A., 1926, 934; 1927, 336). R. BRIGHTMAN.

Ethylenic hydrocarbons obtained by semi-reduction of the corresponding acetylenes. M. BOURGUEL (Bull. Soc. chim., 1927, [iv], 41, 1475—1479).—Δ^α-Olefines boil at lower temperatures than the Δ^β-isomerides, but the difference is less pronounced than with the corresponding acetylenes, being only about 2° with the higher members of the series. With hydrocarbons containing the same number of carbon atoms the Δ^β-acetylene, Δ^α-acetylene, paraffin, Δ^β-olefine, and Δ^α-olefine are in order of decreasing b. p. Similarly differences in density are less pronounced in the olefine series than in the acetylene series, the Δ^α-olefines being the lighter. The following data are recorded: Δ^α-pentene, b. p. 32·5°, d^{20} 0·644, n_D^{20} 1·371; Δ^β-pentene, b. p. 34·5°, d^{19} 0·647, n_D^{19} 1·375; Δ^α-hexene, b. p. 64·5—65°, d^{14} 0·684, n_D^{14} 1·393; Δ^α-heptene, b. p. 94—94·5°, d^{20} 0·705, n_D^{20} 1·404; Δ^α-octene, b. p. 122—122·1°, d^{19} 0·718, 1·408; Δ^β-octene, b. p. 125—126°, d^{20} 0·725, n_D^{20} 1·415; Δ^α-nonene, b. p. 146°, d^{21} 0·721, n_D^{21} 1·414; Δ^β-nonene, b. p. 148·5°, d^{21} 0·738, n_D^{21} 1·420; cyclo*hexyl*-Δ^α-*propene*, b. p. 152°, d^{21} 0·808, n^{21} 1·449; cyclo*hexyl*-Δ^α-*butene*, b. p. 174°/760 mm., 62°/14 mm., d^{21} 0·810,

n_D^{21} 1·450; cyclo*hexyl*-Δ^{β}-*butene*, b. p. 177°/760 mm., 66°/14 mm d^{21} 0·813, n_D^{20} 1·453; cyclo*hexyl*-Δ^{α}-*pentene*, b. p. 196°/760 mm., 83°/14 mm., d^{2} 0·816, n_D^{20} 1·454; cyclo*hexyl*-Δ^{β}-*pentene*, b. p. 198—199°/760 mm., 85°/16 mm., d^{20} 0·822, n_D^{20} 1·458; cyclo*hexyl*-Δ^{α}-*hexene*, b. p. 219°/760 mm., 99°/16 mm., d^{21} 0·820, n_D^{21} 1·457; cyclo*hexyl*-Δ^{β}-*hexene*, b. p. 221°/760 mm., 102°/17 mm., d^{21} 0·823, n_D^{21} 1·459; cyclo*hexylpropane*, b. p. 155°, d^{21} 0·791, n_D^{21} 1·437; cyclo*hexylbutane*, b. p. 177°/760 mm., 68°/16 mm., 0·797, n_D^{20} 1·440; cyclo*hexylpentane*, b. p. 199°/760 mm., 84·85°/16 mm., 0·802, n_D^{20} 1·444; cyclo*hexylhexane*, b. p. 221°/760 mm., 102°/16 mm., d^{20} 0·806, n_D^{20} 1·446. Δ^{α}-Butinene was prepared by catalytic dehydration of *n*-butyl alcohol with alumina, fixation of 2 atoms of bromine on the mixture of Δ^{α}- and Δ^{β}-butenes, treatment of the dibromobutane with alcoholic potassium hydroxide, and finally decomposition of the bromobutene, b. p. 88°, with sodamide in light petroleum at 150—160°. Δ^{β}-Pentinene, b. p. 57°, d^{19} 0·712, n_D^{9} 1·404, is obtained by treatment of Δ^{α}-butinene with sodamide and methyl sulphate.

R. BRIGHTMAN.

Properties of conjugated compounds. III. Bearing of hexatriene chemistry on the reactive form of conjugated hydrocarbons. E. H. FARMER, B. D. LAROIA, T. M. SWITZ, and J. F. THORPE (J.C.S., 1927, 2937—2958).—The addition of bromine to *cis*- and to *trans*-$\Delta^{\alpha\gamma\epsilon}$-hexatriene occurs primarily at the $\alpha\beta$-positions. Since bromine migrates easily in this series, terminal addition, the recorded evidence of which is reviewed, is considered to be probably fallacious and based on phenomena of only a secondary nature. The relation of *cis*-hexatriene to benzene is distant and the electronic formula, $\overset{\cdot}{\mathrm{CH}}\mathrm{:CH:}\overset{\cdot}{\mathrm{CH}}_2{}^{2}$, does not represent any observed fact.

s-Divinylethylene glycol yields two stereoisomeric forms of s-*diethylethylene glycol*, b. p. 87—88°/15 mm., and m. p. 88°, each of which is oxidisable to propionic acid, together with some ethylpropylcarbinol. Bromination of *s*-divinylethylene glycol yields $\gamma\delta$-*dibromo*-$\Delta^{\alpha\epsilon}$-*hexadiene* (*A*), b. p. 94—96°/11 mm., $\alpha\zeta$-*dibromo*-$\Delta^{\beta\delta}$-*hexadiene*, m. p. 85° (*B*), and a *tribromohexene*, b. p. 135—140°/11 mm. All attempts to determine the constitution of the first-named dibromide by oxidative methods or by attempts to prepare the corresponding glycol or diacetate, which afforded complex mixtures, failed. Alcoholic sodium hydroxide yielded $\Delta^{\alpha\epsilon}$-*hexadien-γ-in* (?), b. p. 80—95°, and *γ-bromohexatriene*, b. p. 52—55°/20 mm., both of which rapidly polymerise. Bromination in chloroform solution yields probably $\alpha\beta\gamma\delta$-*tetrabromo*-Δ^{ϵ}-*hexene*, b. p. 155—158°/11 mm., whereas zinc dust and alcohol convert it into cis-*hexatriene*, b. p. 78·5°/760 mm., d_4^{20} 0·7175, n_D^{20} 1·4577, $[R_L]_D$ 30·41° (a lower value than that of the *trans*-), in 30% yield. $\alpha\zeta$-Dibromo-$\Delta^{\beta\delta}$-hexadiene yields the two stereoisomeric forms of $\alpha\beta\epsilon\zeta$-*tetrabromo*-Δ^{γ}-*hexene*, m. p. 111°, and m. p. 46° (the more soluble), which exhibit considerable stability towards ozone and potassium permanganate. On treatment with pyridine the dibromide yields the *dipyridinium* salt, m. p. 212°, and with glacial acetic acid and potassium acetate, $\alpha\zeta$-*diacetoxy*-$\Delta^{\beta\delta}$-*hexadiene*, b. p. 155—160°/14 mm. $\alpha\zeta$-*Diethoxy*-$\Delta^{\beta\delta}$-*hexadiene*, b. p. 116°/20 mm., prepared by the action of alcoholic sodium ethoxide on the dibromide, gives $\alpha\zeta$-*diethoxyhexane*, b. p. 86°/14 mm., on reduction with hydrogen in the presence of colloidal palladium, and α_{ζ}-di-iodohexane by repeated treatment with hydrogen iodide at 100°. The last-named compound may be converted into suberic acid through the dinitrile by the usual methods. $\alpha\delta$-Diethoxy-$\Delta^{\beta\delta}$-hexadiene is oxidised by ozonised oxygen to an *ozonide* (syrup) which decomposes at 85° to give *γ-ethoxycrotonaldehyde*, b. p. 80°/21 mm., and its decomposition products, ethoxyacetic acid and ethoxyacetaldehyde.

Bromination of *cis*-hexatriene in chloroform solution at 0° affords cis-$\alpha\beta$-*dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene*, b. p. 90—96°/11 mm., which, unlike the other dibromides, is colourless. A small amount of $\alpha\zeta$-dibromo-$\Delta^{\beta\delta}$-hexadiene is formed at the same time. Tetrabromohexene, b. p. 155—158°/11 mm., together with a small amount of an *isomeride*, m. p. 91°, may be obtained by the same method using 4 atoms of bromine. By the gradual addition of an alcoholic solution of the dibromide *C* to alcoholic sodium ethoxide, cis-α(or β)-*bromohexatriene*, b. p. 46—65°/20 mm., is obtained.

trans-$\alpha\beta$-*Dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene* (an oil which distils at 1—2 mm.), obtained by the bromination of a glacial acetic acid solution of *trans*-hexatriene with quinoline dibromide at 0°, rapidly isomerises into the dibromide *B*. trans-α(or β)-*Bromohexatriene*, b. p. 53°/22 mm., obtained in the usual way, polymerises very rapidly. Reduction of cinnamaldehyde by Thiele's method (A., 1899, i, 616) yields *s*-distyrylethylene glycol together with an oily residue which on heating gives phenyl-α-naphthylethylene, m. p. 206° (unimolecular in benzene solution and unreduced by hydrogen in the presence of colloidal palladium). *Dibromo*-$\alpha\zeta$-*diphenylhexadiene*, m. p. 124—125°, obtained by the action of phosphorus tribromide on the glycol, affords $\alpha\zeta$-diphenylhexatriene, m. p. 196°, on treatment with zinc dust in chloroform or with diethylamine or pyridine, identical with that obtained by Smedley (J.C.S., 1908, **93**, 376). Addition of bromine to a carbon disulphide solution of the hydrocarbon yields the original dibromide, the *tetrabromide*, m. p. 165°, and the *hexabromide*, m. p. 228—230°. Similarly bromination of *s*-dipropenylethylene glycol affords a mixture of the isomeric dibromides, b. p. 92—100°/14 mm., which in turn may be converted into *methylhexatriene*, b. p. 125—130°, d_4^{18} 0·8394, n_D^{18} 1·45193, and large amounts of polymerides, by treatment with zinc dust and alcohol. $\sigma\eta$-*Dimethyl*-$\Delta^{\gamma\eta}$-*decadiene*-$\epsilon\zeta$-*diol*, b. p. 163—165°/23 mm., d_4^{19} 0·9400, obtained by the reduction of methylethylacraldehyde, affords ϵ_{ζ}-*dibromo*-$\delta\eta$-*dimethyl*-$\Delta^{\gamma\eta}$-*decadiene*, m. p. 99—100°, by treatment with ethereal phosphorus tribromide. Repeated treatment of the latter dibromide affords impure $\beta\epsilon$-*dimethyl*-$\alpha\zeta$-*diethylhexatriene*, b. p. 65—70°/26 mm., together with large amounts of waxy polymerides.

G. A. C. GOUGH.

Preparation of $\Delta^{\alpha\epsilon}$-heptadi-inene and $\Delta^{\beta\zeta}$-octadi-inene. URION (Compt. rend., 1927, **185**, 1286—1287).—Methyl sulphate reacts with the dimagnesium derivative of dipropargyl to form $\Delta^{\alpha\epsilon}$-*heptadi-inene*, b. p. 26—27°/30 mm. d^{21} 0·810, n_D^{21} 1·4521, and

$\Delta^{\beta\zeta}$-*octadi-inene*, m. p. 26·5—27°, b. p. 62°/19 mm., d^{20} 0·828, n_D^{20} 1·4658. Starting with a mixture of diallyl tetrabromides used in the above preparations, an attempt was made to reproduce the dibromodiallyl, b. p. 205—210°, and diallyl hexabromide, m. p. 76—77°, of Henry (cf. A., 1873, 1215). The action of sodium ethoxide on the diallyl tetrabromides yielded a mixture of isomeric dibromides, $C_6H_8Br_2$, giving two fractions, b. p. 85—89° and 89—94°, both of which, on bromination, yielded the same *diallyl hexabromide*, $C_6H_8Br_6$, m. p. 93·5—94°, differing from Henry's product. B. W. ANDERSON.

Preparation of *iso*propyl iodide. A. RÉCSEI (Biochem. Z., 1927, **190**, 57—58).—The method of Markownikoff (Annalen, 1866, **138**, 364) for preparing *iso*propyl iodide from glycerol, iodine, and white phosphorus has been modified by an alteration in the amounts of the reagents and the use of red phosphorus. The redistilled product has a brown colour, probably due to some compound containing iodine; this may be removed by sodium hydroxide but not by sodium thiosulphate solution. A. WORMALL.

Allyl transposition and the mechanism of esterification. C. PRÉVOST (Compt. rend., 1927, **185**, 1283—1285; cf. A., 1927, 851).—Of 13 known reactions in which the allyl ion, (R′CH⁺·CH CH⁺R″), may be involved, the only two which are quite normal are those in which this ion is not necessarily free during the reaction. Conversely, it may be assumed that when normal reactions occur the tripolar ion is not separated. The esterification of substituted allyl alcohols by acetic acid is quite normal, and thus the reaction must be written: (MeCO)(OH)+(RO)(H) (MeCO)(OR)+(H)(OH) (I); esterification by mineral acids, however, is of the type: $(MeCO_2)(H)+(R)(OH)$ $(MeCO_2)(R)+(H)(OH)$ (II), whilst esterification with trichloroacetic acid follows the equation (II), but the reverse process of hydrolysis is of the type (I). B. W. ANDERSON.

Ultra-violet absorption spectra of *cyclo*hexene, ethyl ether, methyl *n*-amyl ether, and ethylene chlorohydrin. A. W. SMITH, C. E. BOORD, C. S. ADAMS, and C. S. PEASE (J. Amer. Chem. Soc., 1927, **49**, 3137—3139; cf. A., 1927, 608, 918).—Re-examination of the materials used for the former experiments has confirmed the presence of benzene as an impurity, which appears to originate from alcohol denatured with benzene which is frequently used for the manufacture of ether, and the use of such ether in Grignard syntheses (*e.g.*, for methyl *n*-amyl ether) will contaminate the products with benzene. Examination of four brands of anæsthetic ether revealed a faint trace of benzene in only one case. The validity of de Laszlo's theoretical criticisms is challenged. F. G. WILLSON.

Interpretation of the acetyl value and ester transformation of glycerides by acetic anhydride. II. D. HOLDE and W. BLEYBERG (Ber., 1927, **60**, [*B*], 2497—2507; cf. A., 1926, 1123).—The saponification values of the products obtained by the action of acetic anhydride on tristearin (Merck or Kahlbaum) are independent of the period of action and of the quantity of acetic anhydride used. Reaction is due to the presence of mono- or di-glycerides and not to ester transformation (cf. Willstatter and Madinaveitia, A., 1912, ii, 1104). Pure tristearin and tripalmitin, prepared by the method of Bellucci (A., 1911, i, 259, 515; 1912, i, 935) with subsequent repeated crystallisation of the products from acetone, after treatment with acetic anhydride are neutral when titrated with 0·1*N*-alcoholic potassium hydroxide in benzene solution and have a saponification value not greater than that of the original material. They therefore do not contain acid anhydride, combined acetic acid, or free fatty acid derived by hydrolysis of the acetylated product. Similar observations with regard to the first point are recorded for ethyl stearate. Tristearin and ethyl stearate when heated with glacial acetic acid under pressure at 200° during several hours suffer ester transformation to the extent of about 14% and 7%, respectively, whereas this change is not effected by acetic anhydride under similar conditions; acetic acid has a scarcely appreciable action on tristearin at atmospheric pressure. Ester transformation is observed to a limited extent when tristearin is boiled with acetic anhydride containing a trace of concentrated sulphuric acid. H. WREN.

Constitution of the glycerides in natural fats. T. P. HILDITCH and C. H. LEA (J.C.S., 1927, 3106—3117).—Oxidation of neutral fats with potassium permanganate in acetone has no action on the saturated glycerides, but converts the mono-, di-, and trioleins into the corresponding acid azelaic esters. Similarly oxidation with an acetic acid solution of hydrogen peroxide gives unaltered saturated glycerides and the dihydroxystearic esters corresponding with the three oleins (A., 1926, 938). Since both methods are almost quantitative and give products which are fairly easily isolated, they may be used to determine the constitution of fats. The vegetable fats contain only small amounts of fully saturated glycerides; the oleic acid is combined chiefly with two molecules of the saturated acid. Cacao butter contains palmitic, stearic, and oleic acids in approximately equal amounts and consists mainly of mono-oleic disaturated glycerides. In cotton-seed oil the palmitic acid is uniformly combined with the saturated fatty acids and the proportion of the saturated to the unsaturated acids is approximately 3 : 1. Mutton tallow contains 25—26% of fully saturated glycerides together with dioleic glycerides. No evidence is obtained for the existence of trioleins in cacao butter or in mutton tallow. G. A. C. GOUGH.

Separation of glycerides. I. Linseed oil. II. Soya-bean oil. B. SUZUKI and Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1927, **3**, 526—528, 529—530).—I. Bromination of linseed oil in light petroleum, and subsequent separation of the bromides by dissolution in various solvents, results in the separation of *dilinoleo-linolenin bromide*, m. p. 78°, yielding, on hydrolysis with hydrochloric acid, tetrabromo-, m. p. 115°, and hexabromo-stearic acids, m. p. 179°, two *linoleo-dilinolenin bromides*, m. p. 117—118° and 158° (hydrolytic products, tetra- and hexa-bromostearic acids), and *dilinoleo-olein bromide* (hydrolytic products, di- and tetra-bromostearic acids).

II. From soya-bean oil, there were obtained, dilinoleo-linolenin bromide, m. p. 78°, linoleo-dilin-

olenin bromide, m. p. 118°, dilinoleo-olein bromide, and *trilinolenin bromide*, m. p. 166° (hydrolytic product, hexabromostearic acid). H. BURTON.

Separation of glycerides. III. Train oil. B. SUZUKI and Y. MASUDA (Proc. Imp. Acad. Tokyo, 1927, 3, 531—532; cf. preceding abstract).—Bromination of train oil affords *arachidono-clupanodono-olein bromide*, m. p. 95° (hydrolytic products, octabromoarachidic acid, m. p. 220° (decomp.), decabromobehenic acid, m. p. 161—162°, and dibromostearic acid), *diclupanodono-olein bromide*, m. p. 132° (hydrolytic products, decabromobehenic and dibromostearic acids), two isomeric *diarachidono-olein bromides*, m. p. 200° (decomp.) and 216° (decomp.) (hydrolytic products, octabromoarachidic and dibromostearic acids), and *dizoomaro-olein bromide*. Treatment of this last bromide with zinc dust and acetic acid, with subsequent oxidation by potassium permanganate, yields dihydroxypalmitic acid, m. p. 115°, and dihydroxystearic acid, m. p. 132—133°. H. BURTON.

Chlorination of ββ'-dichlorodiethyl sulphide. I and II. W. E. LAWSON and T. P. DAWSON (J. Amer. Chem. Soc., 1927, 49, 3119—3125, 3125—3129).—I. Treatment of ββ'-dichlorodiethyl sulphide with chlorine in carbon tetrachloride at −5° to 0° affords *ββ'-dichlorodiethylsulphonium chloride* as a white precipitate, which decomposes at the ordinary temperature with evolution of hydrogen chloride and formation of αββ'-trichlorodiethyl sulphide, this decomposition being apparently autocatalytic. In presence of water it yields ββ'-dichlorodiethyl sulphoxide. -*Trichlorodiethyl sulphide* has d_4^{20} 1·4038, 1·5309, and decomposes on distillation, at ordinary or reduced pressure, with formation of *β-chloroethyl β-chlorovinyl sulphide* (I), b. p. 73·5—74·5°/4 mm., d_4^{20} 1·3280, n_D^{25} 1·5483, and *β-chloroethyl α-chlorovinyl sulphide* (II), b. p. 69·5—70·5°/4 mm., d_4^{20} 1·3193, n_D^{25} 1·550, the former predominating. *ββ'-Dichlorodiethylsulphonium bromide* decomposes when kept in air with formation of *ββ'-dichloro-α-bromodiethyl sulphide*, a yellow liquid, unstable at the ordinary temperature, which yields (I) when distilled. When treated with alcoholic sodium naphthionate, (I) and (II) yield, respectively, *β-naphthoxyethyl β-naphthoxyvinyl sulphide*, m. p. 129·5°, and *α-chlorovinyl β-naphthoxyethyl sulphide*, m. p. 56—57°. Of the above, only (I) and (II) are irritating and slightly vesicant.

II. Treatment of the crude mixture of (I) and (II) in carbon tetrachloride with 1 mol. of chlorine affords *αβββ'-tetrachlorodiethyl sulphide* (III), b. p. 118·5—119°/3 mm., and *β-chloroethyl αβ-dichlorovinyl sulphide*, (IV), b. p. 79·7—80·5°/4 mm., b. p. 108·5—109°/15 mm. The latter is also formed by treatment of ββ'-dichlorodiethyl sulphide with 2 mols. of chlorine in carbon tetrachloride, and is apparently identical with Mann and Pope's supposed αββ'-trichlorodiethyl sulphide (J.C.S., 1922, 121, 594). When oxidised with dilute nitric acid, it yields β-chloroethylsulphonic acid. When heated under reflux at 150—160° for 14 hrs. (III) yields *β-chloroethyl ββ-dichlorovinyl sulphide*, b. p. 90—91°/3·5 mm. Treatment of (IV) with 1 mol. of chlorine in carbon tetrachloride yields *ααβββ'-pentachlorodiethyl sulphide*, liquid, which decomposes on distillation into hydrogen chloride and *β-chloroethyl αββ-trichlorovinyl sulphide*, b. p. 97—98°/4 mm., b. p. 123·5—124·5°/15 mm., apparently identical with Mann and Pope's supposed αβββ'-tetrachlorodiethyl sulphide (*loc. cit.*). Treatment of ββ'-dichlorodiethyl sulphide with excess of chlorine at the ordinary temperature affords hexachlorodiethyl sulphide, together with chlorinated hydrocarbons and the above β-chloroethyl αββ-trichlorovinyl sulphide. ααββ'-Tetrachlorodiethyl sulphide decomposes when distilled, with formation of β-chloroethyl αβ-dichlorovinyl sulphide. None of the above compounds is vesicant. F. G. WILLSON.

Oxidation of certain fatty acids. J. B. RHINE (Plant Physiol., 1926, 1, 349—361).—When the mixed fatty acids from linseed oil are submitted to enzymic hydrolysis at 60—95° in an abundant supply of oxygen, there are formed unidentified volatile and non-volatile aldehydes and short-chain volatile acids fermentable by yeast. CHEMICAL ABSTRACTS.

Simple compounds containing asymmetric carbon. H. J. BACKER (Chem. Weekblad, 1924, 24, 630—633).—A *résumé* of work carried out at Groningen during the past two years. Following the resolution of chlorosulphoacetic acid by crystallisation of alkaloidal salts in the cold, the same method has been applied to the chlorine and bromine substitution products of sulphopropionic acid, and higher sulphocarboxylic acids. The effect of salt formation on the rotation in this series has been systematically studied, as well as the effect of hydrogen-ion concentration on racemisation in this series and with the three sulphopyrotartaric acids. Resolution of sulphonyldipropionic acid and of arsenylpropionic and arsenylbutyric acids, AsO_3H_2·CHMe·CO_2H and AsO_3H_2·CHEt·CO_2H, has also been effected by cold crystallisation. Chlorobromoacetic acid has been resolved in the same way, using the quinine and brucine salts, as well as bromoiodomethanesulphonic acid; a small rotation (1·5°), has also been obtained in aqueous solution with chlorobromomethanesulphonic acid, which had up to now defeated all efforts at resolution. S. I. LEVY.

Interaction of bromine with acetic anhydride. III. Arrest of the reaction. Comparison with bromination of acetone. H. B. WATSON (J.C.S., 1927, 3065—3068).—The inhibitory influence of quinoline on this reaction (A., 1927, 1168) is shown to be removed if 1·6 equivalents of sulphuric acid are concurrently added. The relatively feeble influence of aliphatic primary and secondary amines is ascribed to their inactivation on conversion into the acetyl derivatives and the powerful influence of acetyl nitrate to the oxidation of the hydrogen bromide necessary for the sequence of reactions. Quinoline similarly inhibits the bromination of acetone in carbon tetrachloride until neutralised by the hydrogen bromide liberated by direct substitution of the acetone. After this stage the reaction proceeds rapidly owing to the enolisation of the acetone under the influence of the hydrogen bromide. G. A. C. GOUGH.

Steric series. VIII. Configuration of α-bromopropionic acid. K. FREUDENBERG and L. MARKERT

(Ber., 1927, **60**, [*B*], 2447—2458; cf. A., 1926, 53).—On the assumption that analogous compounds of similar configuration undergo corresponding displacement of rotation when subjected to the same changes, an attempt has been made to elucidate the configuration of α-bromopropionic acid by comparison of the optical behaviour of its esters, chloride, and substituted amides with the similar compounds of *d*-methoxy-, acetoxy-, benzoyloxy-, and *p*-toluenesulphonyloxy-propionic acid. With all four derivatives of *d*-lactic acid a strong displacement in the dextro-direction accompanies the change from dimethylamide to ester. (The esters exhibit irregularities among themselves and the ethyl member is chosen on account of its mean position.) From dimethylamide to chloride dextro-displacement is observed in three instances, whereas the remaining case is doubtful. From chloride to ester dextro-displacement occurs in three instances, lævo-displacement in one. Only the dextrorotatory bromopropionic acid fits into this picture, showing dextro-displacement from dimethylamide to chloride and ester and from chloride to ester. Of the fifteen possible comparisons, thirteen are confirmatory, one is contradictory, and one doubtful. According to these and previous observations inversion occurs during the action of ammonia on bromopropionic acid and its esters, of phosphorus pentabromide on lactic acid and its esters, of potassium hydroxide on bromopropionic acid, and of nitrosyl bromide on alanine esters. Inversion is not observed during the action of nitrous acid on alanine, silver oxide on bromopropionic acid, and nitrosyl bromide on alanine. The following physical data, among others, are recorded: (—)-α-bromopropionic acid, b. p. 80—81°/2 mm., 1·706, $[\alpha]_{578}^{20}$ —30·4°; (—)-α-bromopropionyl chloride, b. p. 47—49°/35—37 mm., d^{0} 1·756, $[\alpha]_{578}^{0}$ —28·7°; *methyl* (—)-*α-bromopropionate*, b. p. 61—63°/32 mm., d^{5} 1·522, $[\alpha]_{578}^{5}$ —59·3°; *ethyl* (—)-*α-bromopropionate*, b. p. 75—77°/38 mm., d^{24} 1·370, $[\alpha]_{578}^{24}$ —40·5°; *propyl* (—)-*α-bromopropionate*, b. p. 92—93°/38 mm., d^{0} 1·321, $[\alpha]_{578}^{5}$ —32·1°; (—)-*α-bromopropionamide*, m. p. 125—126°, $[\alpha]_{578}^{20}$ —24·2° in alcohol (c=10); (—)-*α-bromopropiondimethylamide*, b. p. 44—45°/2 mm., d^{0} 1·336, $[\alpha]_{578}^{0}$ +15·6°; (—)-*α-bromopropiondiethylamide*, b. p. 86—88°/2 mm., d^{20} 1·298, $[\alpha]_{578}$ +5·6°; *d*(+)-*methoxypropionic acid*, b. p. 113—115°/30—32 mm., d^{20} 1·095, $[\alpha]_{578}^{20}$ +74·2° (this and the succeeding values for the optical rotation are probably 4% low); *d*(+)-*α-methoxypropionyl chloride*, b. p. 38—39°/41 mm., d^{20} 1·118, $[\alpha]_{578}^{20}$ +91·8°; methyl *d*(+)-methoxypropionate, b. p. 36—40°/23 mm., d^{0} 1·030, $[\alpha]_{578}$ +96·5°; ethyl *d*(+)-methoxypropionate, b. p. 57—59°/28—30 mm.; *propyl* d(+)-*methoxypropionate*, b. p. 70—71°/25 mm., d^{0} 0·964, $[\alpha]_{78}^{0}$ +87·1°; d(+)-*methoxypropionamide*, m. p. 81°, d^{20} 1·027, $[\alpha]_{578}^{20}$ +38·2°; d(+)-*methoxypropiondimethylamide*, b. p. 90—91°/18—19 mm., d^{0} 1·015, $[\alpha]_{578}^{0}$ +67·9°; d(+)-*acetoxypropionyl chloride*, b. p. 51—53°/11 mm., d^{20} 1·177, $[\alpha]_{s}^{20}$ +51·6° (the optical values of this and the succeeding compounds are probably 10% low); methyl *d*(+)-acetoxypropionate, b. p. 63—65°/10 mm., d^{0} 1·112, $[\alpha]_{578}^{0}$ +50·5°; ethyl *d*(+)-acetoxypropionate, b. p. 73—74°/11—12 mm., d^{2} 1·076, $[\alpha]_{578}^{2}$ +46·7°; *propyl* d(+)-*acetoxypropionate*, b. p. 85—86°/13 mm., d^{0} 1·044, $[\alpha]_{578}^{0}$ +50·9°; d(+)-*acetoxypropionamide*, m. p. 67°, d^{17} 1·117, $[\alpha]_{578}^{17}$ +15·2°; r-*acetoxypropionamide*, m. p. 57°, b. p. 104—105°/2 mm.; r-*acetoxypropiondimethylamide*, m. p. 48°, b. p. 105°/3 mm.; d(+)-*acetoxypropiondimethylamide*, m. p. 57—58°, b. p. 76—78°/0·5 mm., d^{16} 1·083, $[\alpha]_{578}^{6}$ +17·7°; d(—)-*benzoyloxypropionyl chloride*, m. p. 24°, b. p. 135—137°/12 mm., d^{20} 1·213, $[\alpha]_{578}$ —62·7°; *methyl* d(—)-*benzoyloxypropionate*, d^{20} 1·143, $[\alpha]_{s}^{20}$ —17·0°; *propyl* d(—)-*benzoyloxypropionate*, b. p. 157—159°/11—12 mm.; d(—)-*benzoyloxypropiondimethylamide*, m. p. 128°, d^{135} 1·078, $[\alpha]_{578}^{1}$ —37·3°; r-*benzoyloxypropiondimethylamide*, m. p. 106°; d(—)-*benzoyloxypropiondiethylamide*, b. p. 157—160°/2 mm., d^{20} 1·087, $[\alpha]_{s}^{20}$ —37·6°; r-*benzoyloxypropiondiethylamide*, b. p. 157—160°/2 mm.; d(+)-*toluenesulphonyloxypropionyl chloride*, m. p. 42—43°, d^{35} 1·298, $[\alpha]^{35}$ +55·2° (this and the succeeding optical data are probably about 5% low); r-*toluenesulphonyloxypropionyl chloride*, m. p. 59°; d(+)-*toluenesulphonyloxypropionamide*, d^{118} 1·201, $[\alpha]_{5\,8}^{11}$ +33·4°; d(+)-*toluenesulphonyloxypropiondimethylamide*, m. p. 80°, d^{30} 1·222, $[\alpha]_{578}^{30}$ +18·9°; r-*toluenesulphonyloxypropiondimethylamide*, m. p. 80°; d(+)-*toluenesulphonyloxypropiondiethylamide*, m. p. 62—63°, d^{40} 1·148, $[\alpha]_{578}^{40}$ +5·1°, and the corresponding r-*compound*, m. p. 62—63°. H. WREN.

Esters of α-linoleic acid tetrabromide from lumbang oil. (MISS) I. SANTOS and A. P. WEST (Philippine J. Sci., 1927, **34**, 199—203).—The following esters of tetrabromo-α-linoleic acid have been prepared by the general method of interaction of the acid chloride with appropriate alcohols: *methyl*, m. p. 56—60°, *ethyl*, m. p. 58—60°, *propyl*, m. p. 45—50°, iso*propyl*, m. p. 50—52°, and *allyl*, m. p. 72—80°. Qualitative solubilities in the usual organic solvents are given. E. HOLMES.

Constitution of zoomaric acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1927, **30**, 603—607).—Zoomaric acid, a hexadecenoic acid found in cod-liver oil, has also been isolated from humpback whale oil, sei-whale oil, California grey whale oil, and others (cf. B., 1926, 286). On oxidising methyl zoomarate with potassium permanganate in acetone solution, heptoic and azelaic acids were obtained. The ozonide peroxide of zoomaric acid yielded, on boiling with water, heptoic acid, heptaldehyde, and azelaic acid. Therefore the structure of zoomaric acid is $Me\cdot[CH_2]_5\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$, which is the same as that of palmitoleic acid isolated from a specimen of South Georgia whale oil by Armstrong and Hilditch (J.S.C.I., 1925, **44**, 180T). K. KASHIMA.

Constitution of cetoleic acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1927, **30**, 597—602).—Cetoleic acid, $C_{22}H_{42}O_2$ (isomeric with erucic acid), was first discovered by the author in humpback oil and also in sei-whale oil, cod-liver oil, herring oil, and others (cf. B., 1926, 286), and hence is of common occurrence in marine-animal oils. Although the occurrence of erucic acid in certain marine-animal oils has been frequently recorded, no erucic acid could be found in the above-mentioned marine-animal oils. The author suggests that the acid which occurs in marine-animal oils and has been considered as

erucic acid by the earlier authors is in reality cetoleic acid. On oxidising methyl cetoleate isolated from sei-whale oil with potassium permanganate in acetone solution, *n*-undecoic acid and nonane-$\alpha\iota$-dicarboxylic acid were obtained. The ozonide peroxide of cetoleic acid yielded, on boiling with water, *n*-undecoic acid, *n*-undecaldehyde, nonane-$\alpha\iota$-dicarboxylic acid, and possibly also the semi-aldehyde of nonane-$\alpha\iota$-dicarboxylic acid. Therefore cetoleic acid has the constitution $Me\cdot[CH_2]_9\cdot CH{:}CH\cdot[CH_2]_9\cdot CO_2H$.
K. KASHIMA.

Rotatory dispersion of certain derivatives of hydroxy-acids. C. E. WOOD (J.S.C.I., 1927, **46**, 424—427T).—The optical properties of several series of compounds are described with the object of emphasising the differing effects of the alkyl, *cyclo*hexyl, and phenyl groupings when directly attached to the asymmetric centre, the prevailing type of dispersion observed being complex in character. The dispersion curves of typical members of each of these series show how the positive rotations of the lactates change progressively through the *cyclo*hexahydromandelates to the strongly negative rotation of the mandates. The movement in rotation due to the increasing alkyl chain is in the same direction in the *l*-hexahydromandelates as in the *l*-lactates, which is indicative of the configuration relationship of the two acids; two of the higher esters of the former acid exhibit visual anomaly in the positive region. Certain simple cases of compounds containing two centres of optical asymmetry are quoted, and it is concluded that one of the factors in the condition for visual anomaly is that the partial rotations of the two asymmetric centres are of comparable magnitude.

Formation of the hydrazones of ethyl γ-chloroacetoacetate. G. FAVREL (Bull. Soc. chim., 1927, [iv], **41**, 1601—1603).—Ethyl chloroacetate does not behave like monochloroacetone (this vol., 166) with diazonium hydroxides, benzenediazonium chloride in presence of sodium acetate affording about 15% of the phenylhydrazone of ethyl γ-chloroacetoacetate, m. p. 91—92°, and not the expected phenylhydrazone of ethyl chloro-oxalate (cf. Wislicenus, A., 1911, i, 107). It is suggested that the ethyl chloroacetate first condenses with itself to form ethyl γ-chloroacetoacetate.
R. BRIGHTMAN.

Derivatives of ethyl acetoneoxalate. G. FAVREL and J. CHRZ (Bull. Soc. chim., 1927, [iv], **41**, 1603—1607).—Alkyl derivatives of ethyl acetylpyruvate cannot be obtained by the action of alkyl iodides or sulphates on ethyl sodioacetylpyruvate (cf. Kotz and Lemien, A., 1915, i, 247). Acyl derivatives are readily obtained by the action of acyl chlorides on ethyl sodio-acetylpyruvate in ether. Thus acetyl chloride affords the hydrated form of *ethyl diacetylpyruvate*, $CHAc_2\cdot C(OH)_2\cdot CO_2Et$, also obtained by the action of ethyl chloro-oxalate on sodioacetylacetone. Benzenediazonium hydroxide in aqueous acetic acid at 0° converts it into the phenylhydrazone of ethyl acetylpyruvate, m. p. 112—114° (A., 1926, 48). Ethyl acetylpyruvate and 1 mol. of sulphuryl chloride in benzene yield *ethyl β-chloroacetylpyruvate*, b. p. 115—118°/25 mm. (*cupric* derivative), which with benzenediazonium hydroxide in acetic acid at 0° affords the phenylhydrazone of pyruvyl chloride, m. p. 135—136°. With 2 mols. of sulphuryl chloride the reaction affords *ethyl $\beta\delta$-dichloroacetylpyruvate*, b. p. 128—129°/25 mm. (*copper* derivative). These reactions distinguish ethyl acetylpyruvate from the β-diketones generally.
R. BRIGHTMAN.

Mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*. II. T. K. WALKER, V. SUBRAMANIAM, and F. CHALLENGER (J.C.S., 1927, 3044—3054; cf. A., 1927, 228).—Fermentation of dextrose by *A. niger* in the presence of ammonium nitrate and potassium dihydrogen phosphate yielded saccharic acid and traces of citric acid, which may also be formed from the fermentation of calcium gluconate. Dipotassium saccharate yields similarly citric acid. The following fermentations of a similar nature were conducted in order to determine the sequence of reactions in the fermentation of dextrose: citric acid gave acetic acid; ammonium acetonedicarboxylate gave oxalic acid; malonic acid gave glyoxylic acid (isolated as the dixanthylhydrazone) and oxalic acid; calcium glycollate (or the ammonium salt) gave glyoxylic acid and oxalic acid.
G. A. C. GOUGH.

Optical resolution of *dl*-α-*iso*propylglutaric acid. J. READ and W. G. REID (J.S.C.I., 1928, **47**, 11T).—*dl*-α-*iso*Propylglutaric acid, prepared by the oxidation of benzylidene-*dl*-piperitone (Earl and Read, A., 1926, 1040), has been resolved into optically active components by fractionally crystallising the acid brucine salt from absolute alcohol. The less soluble salt, *l*B*d*A, yielded the free *d*-acid with m. p. 88—89° and $[\alpha]^{15}$ +9·35° in absolute alcohol; the corresponding anhydride has m. p. 55—56° and $[\alpha]_D^{15}$ −10·0°, whilst the anilic acid has m. p. 155—156° and $[\alpha]_D^{15}$ +11·5°.

Synthesis of formaldehyde and acetone from oxides of carbon and hydrogen or water by contact substances. T. SABALITSCHKA and C. HARNISCH (Biochem. Z., 1927, **190**, 265—277).—The production of formaldehyde and acetone by passing various gas mixtures (carbon dioxide and hydrogen; carbon dioxide, hydrogen, and water; carbon dioxide and water; carbon monoxide and hydrogen) through a tube at about 300° containing a large number of contact substances is investigated and the results are tabulated.
P. W. CLUTTERBUCK.

Reactions of α-bromoaldehydes. A. KIRRMANN (Compt. rend., 1927, **185**, 1482—1483; cf. A., 1927, 751).—Oxidation of α-bromoheptaldehyde with sulphuric acid and dichromate affords α-bromoheptoic acid, b. p. 147°/12 mm., d^{18} 1·319, n^{18} 1·471, R 44·28 (barium salt). α-Bromoheptaldehyde condenses normally with urethane to form a *compound*, m. p. 112°; it furnishes heptoic acid when boiled with an aqueous suspension of silver oxide and reacts with zinc methyl iodide to give methyl hexyl ketone, b. p. 73°/12 mm., m. p. −20°, d^{20} 0·818. *Heptoyl bromide* has b. p. 80°/12 mm., d^{19} 1·210, n^{19} 1·460. The unsubstituted fatty acid and the ketone are formed, probably through an intermediate keten (cf. Kotz and Rathert, A., 1922, i, 236).
H. BURTON.

Catalytic condensation of methyl ethyl ketone. A. Petrov (Ber., 1927, 60, [*B*], 2548—2551; cf. A., 1926, 1130; 1927, 449).—At the ordinary temperature under the influence of condensing agents such as hydrogen chloride, sulphuric acid, and sodium ethoxide, methyl ethyl ketone yields products analogous to those derived from acetone, but the yield of triethylbenzene is remarkably small. At 380—400° in the presence of aluminium oxide and under a pressure of 80—100 atm., the total yield of hydrocarbons from methyl ethyl ketone is lower than from acetone and attains scarcely 8%; triethylbenzene is produced in very small quantity. Homomesitylene oxide and homo*iso*phorone are obtained. The action of sodamide on methyl ethyl ketone at 0° affords a mixture of the four possible homo*iso*phorones, $C_{12}H_{20}O$, b. p. 129—133°/15 mm., d_{25}^{25} 0·9315, n_{D}^{18} 1·4855, in which the isomerides

$$CH{<}\begin{matrix}CMe{=}CHMe\\CO{-}CHMe\end{matrix}{>}CMeEt$$ and

$$CMe{<}\begin{matrix}CEt{\cdot}CH_2\\CO{-}CH_2\end{matrix}{>}CMeEt$$ appear to predominate. At 220—240° the mixture is hydrogenated under pressure in the presence of nickel oxide to the saturated ketone, $C_{12}H_{22}O$, b. p. 226—236°, d_{25}^{25} 0·9200, n_{D}^{18} 1·4790, whereas at 260—280° in the presence of the oxides of nickel and aluminium it gives a cyclic hydrocarbon, $C_{12}H_{24}$, b. p. 188—198°, d_{25}^{25} 0·8217, n_{D}^{18} 1·4558.

H. Wren.

Relationship of the reduction of cupric oxide by dextrose to the concentration of copper sulphate used. Cupric oxide as a by-product in this reduction. S. Adler (Biochem. Z., 1927, 190, 433—443).—The amount and composition of the reduction product obtained in Bertrand's determination of sugar with varying concentrations of sugar and copper sulphate and times of heating are studied. When the time of heating and the concentration of sugar are constant, the amount of reduction product increases with increasing amount of copper sulphate to a maximum and then decreases. The smaller the excess of copper, the less is the result affected by lengthening the time of heating. If a large excess of copper sulphate is used or if the time of heating is increased, there is formed, besides cuprous oxide, the same hydrated brown cupric oxide as can be obtained by heating together copper sulphate, sodium potassium tartrate, and sodium hydroxide or copper sulphate and sodium hydroxide. Whereas the reduction product when heated for 3 min. is almost entirely cuprous oxide, after 60 min. it consists of about equal amounts of the two oxides. With a small excess of cupric sulphate, cuprous oxide is almost exclusively formed and with increasing concentration of copper sulphate the amount of cuprous oxide decreases and of cupric oxide increases.

P. W. Clutterbuck.

Oxide-ring structure of normal and γ-derivatives of mannose. Preparation and oxidation of γ- and δ-mannonolactones, with an addendum on the formulation of normal and γ-sugars as derivatives of pyran and furan and the suggestion of a new nomenclature. E. H. Goodyear and W. N. Haworth (J.C.S., 1927, 3136—3146).—Methylation of γ-mannonolactone with methyl iodide in the presence of methyl alcohol and silver oxide yields *tetramethyl γ-mannonolactone*, m. p. 108°, $[\alpha]_{D}^{18}$ +65·2° to 61·2° in water (period 9 days; *phenylhydrazide*, m. p. 167°). Treatment of γ-mannonolactone with acetone containing 0·1% of hydrogen chloride yields *γ-mannonolactone* iso*propylidene ether*, m. p. 133°, $[\alpha]_{D}^{20}$ +55·4 in water (*dimethyl* derivative, m. p. 110°), and *γ-mannonolactone di*iso*propylidene ether*, m. p. 126°, $[\alpha]_{D}^{20}$ +50·6 in chloroform, +73·65—45·9° in alcohol (50%; period 20 days). Hydrolysis of the dimethyl compound yields *dimethyl γ-mannonolactone*, m. p. 109—110° $[\alpha]_{D}$ +61·1° to 60·5° in water (period 19 days). *Tetra-acetyl-γ-mannonolactone*, m. p. 120°, prepared by treatment of the lactone with acetic anhydride and pyridine, has $[\alpha]_{D}$ +44·9° in chloroform. Oxidation of tetramethyl-γ-mannonolactone with nitric acid (*d* 1·42), followed by esterification of the product, yields methyl *i*-dimethoxysuccinate (identified by the methylamide). Tetramethyl-δ-mannonolactone yields similarly methyl *i*-dimethoxysuccinate and *d*-arabotrimethoxyglutarate. These results confirm the assignation of the butylene-oxide structure to γ-mannose and the amylene-oxide structure to normal mannose. The similar structural relations of other sugars already established allows the formulation of normal sugars and γ-sugars as pyran and furan derivatives respectively and it is suggested that a new method of naming the sugars, based on this, should be adopted. According to this method the normal sugars would be named pyranoses, *e.g.*, arabinose would become arabopyranose, and the labile sugars furanoses, *e.g.*, γ-fructose would become fructofuranose.

G. A. C. Gough.

Coefficients of diastatic inversion. E. Saillard (Compt. rend., 1927, 185, 1302—1303).—Coefficients of diastatic inversion for solutions of sucrose are given, as calculated from the formula $K=[100(A+B)+0{\cdot}5St]/S$ (cf. A., 1924, ii, 632). The coefficients are lower than those for inversion with hydrochloric acid and show a progressive diminution as the sugar content is lowered. In applying the method to the determination of sugars in beetroot or molasses, a quantity of potassium or sodium chloride equivalent to that in the sample must first be added to the pure sugar solutions.

B. W. Anderson.

Constitution of the disaccharides. XVII. Maltose and melibiose. W. N. Haworth, J. V. Loach, and C. W. Long (J.C.S., 1927, 3146—3155).—Melibionic acid, prepared by the oxidation of melibiose with aqueous bromine, is converted by methylation with methyl sulphate into methyl octamethylmelibionate, b p. 173—175°/0·06 mm., $[\alpha]_{D}^{15}$ +106·4°, n_{D}^{14} 1·4640. Hydrolysis of this ester with hydrochloric acid yields only two products: βγδζ-tetramethylgalactose, m. p. 71—72°, $[\alpha]_{D}^{20}$ +117·8° (equilibrium value), and tetramethylgluconic acid, distilling at 0·05 mm. (bath temperature 164°). The latter acid, on oxidation with nitric acid followed by esterification of the product, affords methyl tetramethylsaccharate, m. p. 77—78°, which may be converted into the diamide, m. p. 237—239°. Repetition of Karrer and Peyer's preparation (A., 1922, i, 809) gave a

product, m. p. 76—77°, identical with the latter ester. These results (see also Charlton, Haworth, and Hickinbottom, A., 1927, 859) confirm the formulation of melibiose as a glucose-α-galactoside. The relation of this formula with the constitutions of the six commonly occurring disaccharides is discussed.

G. A. C. GOUGH.

Optical rotation and atomic dimension. VII. Halogeno-hepta-acetyl derivatives of gentiobiose. D. H. BRAUNS (J. Amer. Chem. Soc., 1927, 49, 3170—3177; cf. A., 1927, 93).—α-Fluorogentiobiose hepta-acetate has m. p. 168—169°, $[\alpha]_D^{20}$ +43·85° (cf. Brauns, A., 1923, i, 441; Helferich, Bäuerlein, and Wiegand, A., 1926, 386). *α-Chlorogentiobiose hepta-acetate*, m. p. 148°, $[\alpha]_D^{20}$ +80·52°, *α-bromogentiobiose hepta-acetate*, m. p. 144°, $[\alpha]_D^{20}$ +101·08°, and *α-iodogentiobiose hepta-acetate*, m. p. 134°, $[\alpha]_D^{20}$ +126·10°, are described, the preparations being given in detail. The specific rotations of the above derivatives show agreement with the regular relationship observed amongst the corresponding derivatives of the monose sugars only if, as in the previous case (*loc. cit.*), the value for the fluoro-derivative is excluded. By modified procedures, β-*chloro*- and β-*iodo-gentiobiose hepta-acetates* were obtained from β-gentiobiose octa-acetate, contaminated with the corresponding α-derivatives, from which it is concluded that the formation of these α-halogeno-derivatives from β-gentiobiose octa-acetate proceeds in at least two stages, the β-halogeno-derivatives being formed intermediately.

F. G. WILLSON.

Acetolysis of mannocellulose. Formation of the new sugars tetramannoholoside and pentamannoholoside. G. BERTRAND and J. LABARRE (Compt. rend., 1927, 185, 1419—1422).—Mannocellulose from *Phytelephas macrocarpa* is acetylated by acetic anhydride and sulphuric acid, then hydrolysed by cold alcoholic potassium hydroxide, and the resulting potassium derivatives are treated with perchloric acid. Fractionation of the syrupy mixture of sugars from various strengths of alcohol yields *tetramannoholoside*, $C_{24}H_{42}O_{21}$, m. p. 278—280°, $[\alpha]_D$ −25° 20′ to +20°, without mutarotation, in 5% aqueous solution (p-*bromophenylosazone*), and *pentamannoholoside*, $C_{30}H_{52}O_{26}$, m. p. 298—300°, $[\alpha]_D$ −31° 40′ to +20°, without mutarotation, in 5% aqueous solution (p-*bromophenylosazone*). The reducing power of these sugars is about one fifth that of mannose. They are hydrolysed by 1% hydrochloric acid at 100°.

H. BURTON.

Oxycelluloses. IV. A. M. NASTUKOFF [with O. P. GOLOFF and A. J. COLLIE] (Ber., 1927, 60, [*B*], 2591—2594).—Oxycellulose, prepared from filter paper by means of bleaching powder, is converted by phenylhydrazine in 10—12% alcoholic solution into the phenylhydrazone; the latter is oxidised, and the product again treated with phenylhydrazine, and the process is repeated until the nitrogen content of the phenylhydrazone is constant at 2·88%. *Oxycellulose*, regenerated from the phenylhydrazone by hydrochloric acid, has the composition $C_6H_{10}O_5,2C_6H_{10}O_6$ or $2C_6H_{10}O_5,4C_6H_{10}O_6$ if the proportion of nitrogen in the phenylhydrazone is taken into account. When freshly prepared it is completely soluble in water, aqueous ammonia, and dilute alkali hydroxides, but the solubility gradually diminishes. It reduces Fehling's solution.

H. WREN.

Complex salts of nickel with aliphatic diamines. F. G. MANN (J.C.S., 1927, 2904—2918).—β-Aminotriethylamine (*A*), prepared by the interaction of phthal-β-bromoethylimide and diethylamine in xylene at 100° followed by hydrolysis with hydrochloric acid, is converted by treatment with nickel succinimide followed by potassium thiocyanate into *bis-β-aminotriethylaminenickelous thiocyanate*, m. p. 213—214° (decomp.) [*chloroplatinate* darkens at 165—168° and shrinks at 179—181°]. Attempts to obtain the *d*-camphor-β-sulphonate resulted in the formation of non-ionic *bis*-d-*camphorsulphonatebis-aminotriethylaminenickel*, m. p. 175—176°; the corresponding d-*α-bromo*-*-camphorsulphonate*, m. p. 165—168°, is formed similarly together with some *β-aminotriethylammonium hydroxide* d-*α-bromocamphorsulphonate*, m. p. 80—82°. *Bis*-d-*camphornitronateaminotriethylaminenickel* has m. p. 258—260° (decomp.), $[\alpha]_{5461}$ +275° in chloroform. β-Bromo-αγ-diaminopropane, prepared by hydrolysis of *αγ-diphthalimidoisopropyl bromide*, m. p. 196—198°, in turn prepared by heating diphthalimido*iso*propyl alcohol with acetic acid and hydrogen bromide at 100°, gives *bis-β-bromo-αγ-diaminopropanenickelous thiocyanate*, m. p. 247—248°. αγ-Diamino*iso*propyl alcohol (*B*) gives with roseocobaltic chloride *dihydroxybis-αγ-diamino-β-hydroxydihydrochloride propane cobaltic monochloride* (corresponding *monothiocyanate*, dark red, decomp. 240—250° after shrinking at about 230°; corresponding *monoiodide*), and with hydrated nickel chloride *bis-αγ-diamino-β-hydroxypropanenickelous thiocyanate*, m. p. 161—163° [corresponding *di-iodide*, m. p. 239—242° (decomp.); d-*camphor-β-sulphonate*, $[\alpha]_{4062}$ +51·5° in water, unresolved by crystallisation]. The latter thiocyanate yields *bis*-d-*camphornitronate-αγ-diamino-β-hydroxypropanenickel*, blackening at 210°, $[\alpha]_{5461}$ +266° in chloroform. β-*Methyltrimethylenediamine dihydrochloride* (*C*), m. p. 195—197° [*dihydrobromide*, m. p. 227—229° (decomp.); *dibenzoyl* derivative, m. p. 92—93° (decomp.; solidifying and remelting at 136—138°)], is prepared by hydrolysis of *αγ-diphthalimido-β-methylpropane*, m. p. 169—171°, which in turn is prepared from potassium phthalimide and αγ-dibromo-β-methylpropane. This amine yields *bis-β-methyltrimethylenediaminenickelous thiocyanate*, m. p. 226—228° (decomp.), converted by silver *d*-camphorsulphonate into *bis-β-methyltrimethylenediaminenickelous* d-*camphor-β-sulphonate*, $[\alpha]_{4063}$ +48·0°, or its *monohydrate*, $[\alpha]_{4062}$ +51·2°, which yields an optically inactive thiocyanate. The *d*-camphorsulphonate combines with ammonium nitrocamphor to afford *bis*-d-*camphornitronate-β-methyltrimethylenediaminenickel*, m. p. 293—295° (decomp.), $[\alpha]_{5461}$ +322° in chloroform (constant). β-Methyltrimethylenediamine also yields *dichloro-β-methyltrimethylenediamineplatinum*, m. p. 273—276° (decomp.), and *bis-β-methyltrimethylenediamineplatinous chloride*, m. p. 266—267° after darkening at 240°, which gives no indication of existing in *cis*- and *trans*-forms. The above co-ordination compounds have been examined in order to determine whether they exhibit *cis-trans*

or optical isomerism. No indication of *cis-trans* isomeric forms could be detected and, owing to experimental difficulties, attempts to resolve the compounds with amines *A*, *B*, and *C* failed. *Cis-trans* isomerism should exist if the four co-ordination valencies of nickel are directed to the corners of a square, whilst if they are directed towards the apices of a tetrahedron optical isomerism should exist. G. A. C. GOUGH.

Reversibility of the oxidative decomposition of amino-acids and its physiological significance. F. KNOOP (XII Int. Cong. Physiol., 1926, 90; Chem. Zentr., 1927, i, 2444).—α-Ketonic acids and ammonia, in presence of molecular hydrogen and palladium, yield 70% of the theoretical quantity of amino-acids. Ferrous salts and cysteine effect the reduction in the absence of free hydrogen and catalysts. A. A. ELDRIDGE.

Chemical constitution and rotatory power. II. Acyl derivatives of *l*-asparagine. S. BERLINGOZZI (Gazzetta, 1927, **57**, 814—819).—Some acyl derivatives of *l*-asparagine have been prepared by the Schotten–Baumann reaction and the rotatory powers of aqueous solutions of their potassium salts have been determined. The m. p. of the acyl-*l*-asparagine, $[\alpha]^{20}$ and $[M]^{20}_{D}$ for the potassium salts are respectively: *anisoyl*-, 190—191°, +15·11°, +40·2°; *benzoyl*-, 189°, +15·35°, +36·2°; m-*nitrobenzoyl*-, 176°, +12·55°, +35·3°; p-*nitrobenzoyl*-, 178°, +10·96°, +30·8°; p-*toluenesulphonyl*-, 175°, +6·83°, +19·5°; chloroacetyl-, 148—149°, +4·71°, +9·8°. The decreasing molecular rotatory power corresponds, except in the case of the chloroacetyl derivative, with increasing dissociation constant of the acid derived from the substituent group (cf. Betti and Bonino, Atti II Congr. Naz. Chim., Palermo, 1926). E. W. WIGNALL.

Condensation of ethyl acetoacetate with sodiomalononitrile. Explanation of similar reactions. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 305—307).—The fact that ethyl sodiocyanoacetate will not condense with ethyl cyanoacetoacetate, as it condenses with ethyl acetoacetate (J.C.S., 1905, **87**, 1685; 1922, **121**, 2216), is explained by the greater affinity of the latter for sodium, which causes an interchange of the metal from one ester to the other. In extension of previous work (this vol., 49), it is found that sodiomalononitrile reacts with ethyl acetoacetate in alcoholic solution to yield a crystalline *sodio*-derivative which, when treated with acids, in turn affords ethyl γγ-dicyano-β-methyl-Δ^{β}-butenoate (an oil), which shows no tendency to combine with water to form the diamide.
G. A. C. GOUGH.

Properties of simple amides. A. PARTS (Ber., 1927, **60**, [*B*], 2520—2522).—Contrary to the observations of Rakshit (J.C.S., 1913, **103**, 1557), the main products of the action of sodium on propionamide and butyramide dissolved in benzene are the sodium amides R·CO·NHNa. The amount of ammonia evolved increases in the sequence butyramide, propionamide, acetamide, but the production of sodium diacetamide is by no means quantitative. Hence there is no sharp distinction between the actions of sodium and potassium. Further evidence in favour of the view that sodium and propionamide yield sodium propionamide is found in the formation of dipropionamide from the latter and propionyl chloride. The formation of triacylamides from acyl chlorides and homogeneous sodium diacylamides is established by the smooth production of tribenzamide from benzoyl chloride and sodium dibenzamide. H. WREN.

Acyl*iso*carbamides. S. BASTERFIELD and M. S. WHELEN (J. Amer. Chem. Soc., 1927, **49**, 3177—3180).—The following acyl *iso*carbamides, NHR·C(OR′):NH, were obtained by treating the appropriate alkyl*iso*carbamide hydrochlorides in ethereal suspension with acyl halides: *phenylacetyl*-, m. p. 207° (decomp.); *chloroacetyl*-, m. p. 183°; *carbo-*n*-propoxy*-, m. p. 36—37°; *carbo-*n*-butoxy*-, m. p. 32°, and *carbo*iso*amyloxy-methyl*iso*carbamide*, m. p. 93°; *phenylacetyl*-, b. p. 160°/20 mm.; p-*nitrobenzoyl*-, m. p. 125°; *bromopropionyl*-, liquid (*polymeride*, m. p. 141°); *chloroacetyl*-, liquid (*hydrochloride*, m. p. 140°); *carbo-*n*-propoxy*-, liquid; *carbo*iso*amyloxy*-, m. p. −10°, and *benzenesulphonylethyl*iso*carbamide*, m. p. 86° when freshly prepared, changing to 101° on keeping. n-*Propyl*iso*carbamide*, liquid (*hydrochloride* of *benzoyl* derivative, m. p. 97°), was obtained through the *hydrochloride* by treatment of cyanamide in *n*-propyl alcohol with hydrogen chloride. n-*Butyl*iso*carbamide hydrochloride* was obtained similarly in an impure condition, and converted into the p-*nitrobenzoyl* derivative, m. p. 118°.
F. G. WILLSON.

Transformation of phenylated azodicarboxylamides into benzotriazines. F. ARNDT and B. EISTERT (Ber., 1927, **60**, [*B*], 2598—2602).—The constitutions $NHPh\cdot CS\cdot N(NH_2)\cdot CO\cdot NH_2$ and $NHPh\cdot CS\cdot NH\cdot NH\cdot CO\cdot NH_2$ have been assigned to the product obtained from phenylthiocarbimide and semicarbazide by Rosenthaler (A., 1927, 451) and Arndt (A., 1922, i, 375), respectively. In favour of the latter formulation it is pointed out that the compound is stable to short treatment with alkali hydroxide and is converted by methyl sulphate in such solution into the non-crystalline *S*-methyl ether, which is oxidised by excess of potassium ferricyanide to the red *azo* compound, $NPh{:}C(SMe)\cdot N{:}N\cdot CO\cdot NH_2$, decomp. 112—113°. The latter substance in boiling ethyl acetate is isomerised to the colourless 3-*methylthiol*-1 : 2-*dihydro*-1 : 2 : 4-*benzotriazine-1-carboxylamide*, m. p. 208—210° after softening and darkening, the constitution of which follows from its oxidation to 3-methylthiol-1 : 2 : 4-benzotriazine (cf. Arndt and Rosenau, A., 1918, i, 40). The azo-compound decomposes at 110—115° into phenylthiourazole methyl ether, m. p. 207—208°. The azo-compound $NPh{:}C(NH_2)\cdot N{:}N\cdot C({:}NH)\cdot SMe$, decomp. 110° (cf. Arndt and Tschenscher, A., 1923, i, 1139), in boiling solvents, however, passes only into the hydrazo-compound and 4-phenylguanazole derived therefrom when heated in suitable solvents; when heated by itself it affords 3-amino-1 : 2 : 4-benzotriazine. H. WREN.

Ureides of bromovaleric acids. Influence of the migration of the halogen on their physicochemical and pharmacodynamic properties. E. FOURNEAU and G. FLORENCE (Bull. Soc. chim.,

1927, [iv], **41**, 1518—1535).—In continuation of earlier work on the ureide of α-bromo*iso*valeric acid (bromural) and the ureide of α-bromo-α-ethylbutyric acid (adaline) the effect of displacement of the bromine atom in the chain and of accumulation of bromine atoms has been examined in relation to the physico-chemical and narcotic properties. The results confirm the relation already observed by Overton between the partition coefficient in oil and water and the hypnotic properties. Tiffeneau's assertion that the parallel holds only within the same series is also supported by the present work. Bromural, containing varying proportions of the ureides of *iso*valeric and α-methylbutyric acids, is a stronger hypnotic than the pure ureide of α-bromo*iso*valeric acid prepared from synthetic *iso*valeric acid. Migration of bromine from the α- to the β-position decreases the hypnotic effect almost to zero, the solubility in water and the partition coefficient decreasing simultaneously. Accumulation of bromine atoms in the molecule exerts a similar influence. The hypnotic effect is thus attributed to the acid chain and not to the bromine atom, the latter decreasing the effect by decreasing the solubility of the ureide. The following data are recorded for the ureides, the percentage figures indicating the solubility in water, plain figures the partition coefficients for olive oil and water: bromural: m. p. 152°, 3·209%, 1·29; ureide of synthetic α-bromo*iso*valeric acid, m. p. 160°, 1·94%, 0·96; *β-bromo*iso*valeric ureide*, m. p. 195°, 1·86%, 0·19; *αβ-dibromo*iso*valeric ureide*, m. p. 172·5° (decomp.), 2·30%, 0·22. *iso*Valeric acid, b. p. 175°, was synthesised from magnesium *iso*butyl chloride in 82% yield. β-Bromo*iso*valeric acid and αβ-dibromo*iso*valeric acid were prepared from dimethylacrylic acid obtained by oxidation of mesityl oxide (Barbier and Léser, A., 1905, i, 628).

R. Brightman.

Action of copper nitrite on thiocarbamide. A. Contardi and A. Dansi (Gazzetta, 1927, **57**, 802—813).—When copper nitrite is treated with thiocarbamide in aqueous solution, a green, gelatinous *product*, $CH_4O_4N_4SCu$, is obtained, which evolves nitric oxide to give a yellowish-white *substance* (I) regarded as $[Cu(CH_4N_2S)(NO_2)_2][Cu(CH_4N_2S)H_2O]$. In presence of carbon dioxide, the action of hydrochloric acid converts this into the additive product of thiocarbamide and cuprous chloride (cf. Rathke, A., 1884, 1017), whilst that of boiling water gives copper sulphide, nitric oxide, and cyanamide. If the initial reaction product is allowed to remain in the mother-liquor it is converted into copper thiocyanate and basic copper nitrate. The compound (I) is also obtained by treating the compound $[Cu(CH_4N_2S)_3]Cl$ with sodium nitrite solution, or the compound $[Cu(CH_4N_2S)Cl_2][Cu(CH_4N_2S)H_2O]$ with thiocarbamide followed by sodium nitrite. Excess of thiocarbamide in the latter reaction, or in reaction with (I), yields the *compound* $[Cu(CH_4N_2S)_2H_2O]NO_2$, converted by washing with water into (I) and the soluble $[Cu(CH_4N_2S)_3]NO_2$.

Aniline and copper nitrite in aqueous solution yield a *compound*, $C_{12}H_{10}O_2N_4Cu$. E. W. Wignall.

Carbolthionic acids and esters. IV. Thioamides and thiohydrazides. Y. Sakurada (Bull. Chem. Soc. Japan, 1927, **2**, 307—310; cf. A., 1926, 950).—The following thioamides are prepared by treatment of the requisite thionester (the eliminated alcohol radical of which is given in parentheses) with ethereal solutions of amines: *thioacetoethylamide*, $CH_3\cdot CS\cdot NHEt$ (oily; propyl), *thiopropioethylamide* (oily; propyl), *thiobenzethylamide* (oily; butyl), *thiophenylacetoethylamide* (oily; *iso*amyl), *thio*-p-*toluethylamide* (oily; propyl), *thioaceto*iso*butylamide* (oily; *iso*amyl), *thiopropio*iso*butylamide* (oily; butyl), *thiobenz*iso*butylamide* (crystalline; methyl), *thiophenylaceto*iso*butylamide* (oily; *iso*butyl), *thio*-p-*tolu*iso*butylamide* (oily; butyl), *thioaceto*iso*amylamide* (oily; *iso*butyl), *thiopropio*iso*amylamide* (oily, *iso*amyl), *thiobenz*iso*amylamide* (crystalline; *iso*amyl), *thiophenylaceto*iso*amylamide* (oily; ethyl), *thio*-p-*tolu*iso*amylamide* (crystalline; methyl). Similarly phenylhydrazine affords the following crystalline *s*-thiophenylhydrazides: *thioacetophenylhydrazide*, *thiopropiophenylhydrazide*, *thiobenzphenylhydrazide*, *thiophenylacetophenylhydrazide*, *thio*-p-*toluphenylhydrazide*.

G. A. C. Gough.

Complex cyanides. G. A. Barbieri and E. Parisi (Ber., 1927, **60**, [*B*], 2418—2421).—Solutions of potassium silver cyanide which, according to electromotive measurements of Bodländer and Eberlein (A., 1904, ii, 401), contain the compound $K_2Ag(CN)_3$, do not give additive compounds with hexamethylenetetramine; if, however, potassium is replaced by sodium, calcium, or magnesium, the *compounds* $Na_2Ag(CN)_3,C_6H_{12}N_4,2H_2O$, $MgAg(CN)_3,2C_6H_{12}N_4,9H_2O$, and $CaAg(CN)_3,C_6H_{12}N_4,3H_2O$ are readily isolated. From suitable solutions of copper cyanide the analogous *compounds* $Na_2Cu(CN)_3,C_6H_{12}N_4,2H_2O$ and $MgCu(CN)_3,2C_6H_{12}N_4,9H_2O$ are similarly derived. If a large excess of hexamethylenetetramine is added to a concentrated solution of vanadyl sulphate and sodium cyanide, the *substance* $Na_3VO(CN)_5,2C_6H_{12}N_4,5H_2O$ crystallises in blue octahedra. H. Wren.

Complex cyanides of molybdenum. W. R. Bucknall and W. Wardlaw (J.C.S., 1927, 2981—2992).—Improved methods for the preparation of tetrapotassium, tetrasilver, tetrathallous, and dicupric molybdenum octacyanide (cf. Rosenheim, A., 1907, i, 688; 1910, i, 101) are given. Treatment of the last-named salt with ammonia (*d* 0·88) yields *hexamminodicupric molybdenum octacyanide*, $Cu[(NH_3)_3]_2Mo(CN)_8$ (dark green), which is converted into the original compound on treatment with acids. By the use of ethylenediamine hydrate *tetramethylenediaminocupric molybdenum octacyanide*, $[Cu(en)_2]_2Mo(CN)_8$ (deep blue), is prepared. Conductivity measurements indicate that it exists as 3 ions (maximum) in very dilute solutions, whilst in more concentrated solutions the values are even less than those required for a binary electrolyte. *Trisilver molybdenum octacyanide* (cf. Olsson, A., 1914, i, i, 504), prepared by the addition of silver nitrate to a dilute solution of the tetrapotassium salt which had been oxidised with potassium permanganate until a faint pink colour persisted, yields *tripotassium molybdenum octacyanide*, $K_3Mo(CN)_8$, when triturated

with potassium chloride in the dark, or *trihydrogen molybdenum octacyanide* ($+3H_2O$) when triturated with hydrochloric acid. The constitution of the new acid, which is very deliquescent, is demonstrated by conversion into the silver salt which may be quantitatively decomposed by hydrochloric acid. The "anomalous" oxidation of molybdenum (Ephraim, "Inorganic Chemistry," English transl., 1926, 280) from the quadri- to the quinque-valent state is explained by the tendency to revert to a compound in which molybdenum exerts its maximum effective atomic number 54.

Electrolysis of a 10% solution of molybdenum trioxide in $3N$-hydrochloric acid in a diaphragm cell followed by concentration and addition of potassium iodide yields a red *cyanide*, $K_4[Mo(OH)_4(CN)_4],H_2O$, the dilute aqueous solutions of which are alkaline and contain more than 5 ions even at 1° [apparent mol. wt. in water (cryoscopic, $c=1{\cdot}517$) 97·9]. A co-ordination number of 8 is indicated since 2 mols. of the associated water are retained at 100° or in a vacuum in the presence of sulphuric acid. Repeated treatment of an aqueous solution of this substance with alcohol yields a blue *cyanide*, $K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O$, which again gives alkaline reaction to phenolphthalein in dilute solutions and is shown by conductivity and mol.-wt. determinations to contain more than 4 ions. By treatment of tetrapotassium molybdenum octacyanide with nitric acid varying amounts of molybdic acid are obtained together with a brick-red, insoluble *molybdenum cyanide*, $H[MoO_2(CN)_2,2H_2O]$, which is shown to contain quinquevalent molybdenum by quantitative oxidation. It is readily soluble in ammonia or alkalis. G. A. C. Gough.

Colour reactions of nitroprusside. N. Tarugi (Annali Chim. Appl., 1927, **17**, 519—524).—Cambi's criticisms (A., 1927, 346) of the author's work (A., 1927, 46) are answered. T. H. Pope.

Reaction of molybdic acid with ferrocyanides. G. A. Barbieri (Ber., 1927, **60**, [*B*], 2415—2418).—If an excess of ammonium or potassium ferrocyanide followed by a large excess of an ammonium salt is added to the solution of a molybdate acidified with acetic acid, a lemon-yellow *precipitate*, $(NH_4)_4Fe(CN)_6,2MoO_3,3H_2O$, is obtained which is so sparingly soluble in concentrated solutions of ammonium salts that the separation of molybdic acid is almost quantitative. The compound is also obtained by dissolving phosphomolybdic acid or its salts in ammonia, addition of potassium ferrocyanide and much ammonium acetate, and acidification with acetic acid. In neutral or alkaline solution the precipitation from polymolybdates is incomplete, but can be made quantitative by addition of a slight excess of an acid. Treatment of the yellow compound with weak acids or with water causes it to become red, whereas strong acids transform it into tile-red powder probably owing to hydrolysis, $(NH_4)_4Fe(CN)_6,2MoO_3+4HX$ $4NH.X+(MoO_2)_2Fe(CN)_6+2H_2O$. The reddish-brown, gelatinous precipitates obtained by the interaction of molybdates and potassium ferrocyanide in the presence of hydrochloric or sulphuric acid are converted by concentrated ammonium acetate into a crystalline *powder* (?), $(NH_4)_4Fe(CN)_6,2MoO_3,2H_2O$, thus indicating that they are probably formed exclusively from molybdenyl ferrocyanide, $(MoO)_2Fe(CN)_6$. Attempts to obtain similar compounds of potassium, sodium, rubidium, or cæsium were unsuccessful. H. Wren.

Catalysts and activated magnesium in the preparation of Grignard reagents. H. Gilman and J. M. Peterson (Proc. Iowa Acad. Sci., 1926, **33**, 173—174).—When a magnesium–copper (12·75%) alloy is heated for 1 hr. in an evacuated tube at 200° with about half its weight of iodine, the activated alloy is superior to that of Baeyer.

Chemical Abstracts.

Qualitative colorimetric reaction for the Grignard reagent. H. Gilman and F. Schulze (Bull. Soc. chim., 1927, [iv], **41**, 1479—1481).—Magnesium *tert.*-butyl chloride, bromide, and iodide, magnesium *tert.*-amyl chloride, and magnesium *tert.*-hexyl chloride give positive results in the colorimetric test for Grignard reagents previously described (A., 1925, ii, 1011), provided 5 min. are allowed for the reaction between the Grignard reagent and Michler's ketone. If the hydrolysis is effected immediately, on account of the lower reactivity of Grignard reagents containing butyl or higher alkyl groups, the coloration may be only faint or negligible, especially if the solutions are not concentrated. R. Brightman.

Apparatus for determining the quantity of gas evolved and the amount of reagent consumed in reactions with magnesium methyl iodide. E. P. Kohler, J. F. Stone, and R. C. Fuson (J. Amer. Chem. Soc., 1927, **49**, 3181—3188).—The apparatus consists essentially of a reservoir for standard Grignard solution, connected through a graduated measuring vessel to a reaction flask of 40 c.c. capacity, the latter being connected in turn through a phosphorus pentoxide tube with a jacketed gas burette. Arrangements are provided for displacing the air in the entire apparatus with nitrogen, for filling the reservoir with filtered Grignard solution without access of air, and for the addition of measured quantities of water to the reaction flask. The Grignard reagent is prepared by adding methyl iodide (40 g.) to a stirred suspension of magnesium (8 g.) in *iso*amyl ether (100 g.) at 0—20°, diluting the resulting solution with *iso*amyl ether (175 g.), and heating the whole at 100° for 1½ hrs., all in an atmosphere of nitrogen. The solution is then filtered into the reservoir, and standarised by measuring the gas evolved when a measured volume of the solution is treated with water in the reaction flask. A sample (about 0·2 g.) of the substance to be studied is then placed in the reaction flask, the apparatus swept out with nitrogen, and a measured volume of the Grignard solution, considerably in excess of that required, added from the reservoir. The mixture is then heated until reaction ceases, and the volume of gas evolved is measured. The amount of Grignard reagent remaining unattacked is then determined by adding water to the reaction flask and measuring the volume of gas generated. Results are accurate to within about 3%, and examples of measurements with 14 substances are listed, including

cases where ketonic and enolic modifications compete for the Grignard reagent (cf. Grignard and Savard, A., 1927. 567). If necessary, the substance under examination may be dissolved in xylene before the Grignard solution is added. F. G. WILLSON.

Cadet's oil. II. Oxidation of cacodyl oxide. A. VALEUR and P. GAILLIOT (Bull. Soc. chim., 1927, [iv], **41**, 1481—1491).—Cacodyl oxide, b. p. 149—151°, d^{15} 1·486, when obtained by the action of sodium carbonate on cacodyl chloride, does not fume in air, and can be distilled without decomposition. When oxidised under water at 15—25° in a current of oxygen, 44·7% of the oxide is converted into cacodylic acid, the remainder being converted by intramolecular change mainly into trimethylarsine, monomethylarsine oxide, and arsenious acid, with a little trimethylarsine oxide and methylarsinic acid. These transformations are regarded as catalytic reactions consecutive on the oxidation, the catalyst being probably a peroxide. R. BRIGHTMAN.

Friedel–Crafts' reaction with non-aromatically combined hydrogen. J. VON BRAUN and M. KÜHN (Ber., 1927, **60**, [*B*], 2557—2566).—Phenyl*cyclo*pentene is only partly and with difficulty reduced by hydrogen in the presence of palladium. It is slowly converted by hydrogen bromide in glacial acetic acid at 100° into 2-*bromophenyl*cyclo*pentane*, b. p. 138—140°/13 mm. The latter substance reacts vigorously with magnesium and the product after treatment with carbon dioxide affords phenyl*cyclo*pentane (see later), *di*(*phenyl*cyclo*pentyl*), and 2-*phenyl*cyclo*pentanecarboxylic acid*, b. p. 190—192°/13 mm. The homogeneity of the acid and consequently of the parent bromide is established by its smooth conversion through 2-*phenyl*cyclo*pentanecarboxyl chloride*, b. p. 150—153°/12 mm., into 2-*phenyl*cyclo*pentanecarboxyanilide*, m. p. 93—95°. The chloride is converted by aluminium chloride in carbon disulphide into the *ketone*, $\begin{matrix}C_6H_4\\C_5H_8\end{matrix}\!\!>\!CO$, b. p. 135—140°/14 mm. (*semicarbazone*, m. p. 170°). Phenyl*cyclo*pentane, as prepared above, is homogeneous, but the yields are poor and the compound is more readily prepared by reduction of 2-bromophenyl*cyclo*pentane by zinc dust and boiling glacial acetic acid. It has b. p. 215°, d_4^{20} 0·9553, n_D^{20} 1·5330, thus agreeing with the data of Borsche and Menz (A., 1908, i, 147); phenyl*cyclo*propane derived from ε-phenyl-*n*-amyl chloride and aluminium chloride has d_4^{20} 0·9385, n_D^{20} 1·5157, in agreement with previous data (von Braun and Deutsch, A., 1912, i, 433). The latter product appears to consist essentially of phenyl*cyclo*pentane, which itself is appreciably modified by aluminium chloride. The *ketones*, b. p. 190—200°/1 mm. and 200 210°/1 mm., obtained from phenyl*cyclo*pentane and benzoyl or anisoyl chloride are ill adapted for its identification; p(?)-cyclo*pentylacetophenone* readily yields a *semicarbazone*, m. p. 212—215° (obtained also from the product from ε-phenyl-*n*-amyl chloride). ε-Phenyl-Δ^{α}-amylene, d_4^{19} 0·8796, n_D^{19} 1·5040, is largely polymerised by aluminium chloride in light petroleum and does not afford phenyl*cyclo*pentane the Friedel–Crafts reaction cannot therefore be due to loss of hydrogen chloride in the side-chain from ε-phenyl-*n*-amyl chloride followed by isomerisation of the hydrocarbon thus produced.

ε-Phenyl-β-methylamyl alcohol is converted with difficulty by the successive action of fuming hydrochloric acid at 125° and phosphorus pentachloride into *ε-phenyl-β-methylamyl chloride*, b. p. 128—130°/12 mm., which is transformed by aluminium chloride in the presence of light petroleum into 3-*phenyl*-1-*methyl*cyclo*pentane*, b. p. 93—94°/12 mm., d_4^{17} 0·9173, n_D^{17} 1·5136, oxidised by permanganate to benzoic acid. *N*-ε-Chloroamylbenzamide, toluene, and aluminium chloride afford ε-p-*tolylamylbenzamide*, b. p. 265—270°/10 mm., hydrolysed to benzoic acid and ε-p-*tolylamylamine*, b. p. 143°/11 mm. The benzoyl compound is converted by phosphorus pentachloride into the corresponding imidochloride, which decomposes when slowly distilled into benzonitrile and ε-p-*tolyl*-n-*amyl chloride*, b. p. 136—138°/11 mm., from which ε-p-*tolyl*-n-*amyl acetate*, b. p. 154—156°/11 mm., and ε-p-*tolyl*-n-*amyl alcohol*, b. p. 158—159°/11 mm., are successively obtained. With aluminium chloride ε-*p*-tolyl-*n*-amyl chloride yields a mixture of *p*-tolyl*cyclo*pentane and (predominatingly) methylbenzosuberane, oxidised by permanganate to a mixture of terephthalic and trimellitic acids. ε-p-*Xylyl*-n-*amylbenzamide*, b. p. 235—238°/1 mm., is hydrolysed to ε-p-*xylyl*-n-*amylamine*, b. p. 146—148°/12 mm. (*picrate*, m. p. 155°; non-crystalline *hydrochloride* and quaternary *methiodide*). ε-p-*Xylyl*-n-*amyl chloride*, b. p. 143—145°/12 mm., from which ε-p-*xylyl*-n-*amyl acetate*, b. p. 162—164°/12 mm., and ε-p-*xylyl*-n-*amyl alcohol*, b. p. 153—155°/14 mm., are successively obtained, is converted by aluminium chloride into 1 : 4-*dimethylsuberane*, b. p. 121—125°/13 mm., d_4^{21} 0·9373, n_D^{21} 1·5330, oxidised to benzene-1 : 2 : 3 : 4-tetracarboxylic acid. Magnesium *p*-xylyl bromide and *cyclo*pentenyl chloride afford a mixture of *p*-xylene, di*cyclo*pentadiene, di-*p*-xylyl, and p-*xylyl*cyclo*pentene*, b. p. 125—127°/14 mm., d_4^{23} 0·9613, n_D^{23} 1·5380. The last-named compound adds hydrogen bromide in glacial acetic acid, giving the *bromo*-derivative, $C_{13}H_{17}Br$, b. p. 163—165°/13 mm., reduced by zinc dust and acetic acid to p-*xylyl*cyclo*pentane*, b. p. 122°/13 mm., $d_4^{20.5}$ 0·9621, $n_D^{20.5}$ 1·5344. The course of the Friedel–Crafts reaction with substituted amyl chlorides is not readily explicable in the light of the work of Wieland and Bettag (A., 1922, i, 1033). H. WREN.

Alkylation of benzene, toluene, and naphthalene. T. M. BERRY and E. E. REID (J. Amer. Chem. Soc., 1927, **49**, 3142—3149; cf. A., 1922, i, 330).—Ethylene is absorbed by benzene in presence of aluminium chloride much more rapidly than is ethyl chloride. Benzene dried with sodium gives better results than when dried with calcium chloride. There is little variation in rate of reaction between 60° and 90°. Absorption is preceded by an induction period which may be shortened by prior refluxing or addition of 10% of ethylated benzenes, and the rate of reaction increases as the products accumulate, until a maximum is reached when about 4 mols. of ethylene have been absorbed. Whilst the reaction cannot be controlled to give a single product, there is preferential formation of triethylbenzene, which has been obtained in

80% yield, and 90% of hexaethylbenzene can be eventually obtained. The optimum molecular ratio of aluminium chloride to benzene appears to be 1 : 13. The reaction product comprises two phases, one of which contains practically all the aluminium chloride associated with an approximately equal weight of hydrocarbons, these latter being always the more highly alkylated, with an especial preference for the pentaethylbenzene. The highest rate of absorption of ethylene observed was 402 c.c. per min. per mol. of benzene. Toluene absorbs ethylene under the same conditions as benzene. The absorption of 0·9 mol. of ethylene by 3·04 mols. of toluene gave a mixture containing toluene, ethylbenzene and xylenes, ethyltoluenes, and higher substitution products of b. p. up to above 207°, the fraction of b. p. 198—203° being highly fluorescent. Bromobenzene affords similarly benzene, ethylbenzenes, brominated ethylbenzenes, and tar. Benzene reacts with propylene under similar conditions, with formation of *iso*propylbenzenes, but the reaction is only about 4% as rapid as that with ethylene, and a higher degree of alkylation than tetra*iso*propylbenzenes could not be obtained on account of tars. Of the di*iso*propylbenzenes formed, the *m*-derivative forms 65%, and the tri*iso*propylbenzenes contain 75% of the 1 : 3 : 5-derivative. 1 : 2 : 4-*Triisopropylbenzene*, b. p. 237—237·5°/752 mm., b. p. 97—97·5°/4 mm., d_{25}^{25} 0·8593, n^{25} 1·4855, was identified by oxidation to the corresponding benzenetricarboxylic acid, and 1 : 2 : 4 : 5-*tetraisopropylbenzene*, m. p. 117°, b. p. 260°/775 mm., was isolated. Propylation of toluene takes place more rapidly than that of benzene, the products being benzene, toluene, xylenes, triethylbenzene, and cymenes (*p*-cymene preponderating) and products of higher b. p. Di*iso*propylbenzene, naphthalene, and aluminium chloride yield, when stirred together at 90° for 4½ hrs., a product, b. p. 264—266°, probably *isopropylnaphthalene*, together with unchanged naphthalene and other unidentified products. *cyclo*-Hexene reacts vigorously with benzene in presence of aluminium chloride, and the mixture boils when rapidly stirred for 30 sec. The product contained a small proportion of *cyclo*hexylbenzene.

F. G. WILLSON.

Derivatives of ethylbenzene. E. L. CLINE and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 3150—3156).—Benzene can be completely converted into ethylbenzene by treatment with ethylene in presence of aluminium chloride with rapid stirring (11,000 r.p.m.; cf. A., 1922, i, 330) if the more highly ethylated benzenes are added to the succeeding batch. Treatment of ethylbenzene (700 g.), stirred at 3000 r.p.m., with a mixture of nitric acid (510 g., *d* 1·42) and concentrated sulphuric acid (675 g.) below 40°, the reaction mixture being subsequently maintained at the ordinary temperature for 3 hrs., then heated to 100° during 4 hrs. and kept at 100° for 2 hrs., affords *o*-nitroethylbenzene, b. p. 135°/37 mm., and *p*-nitroethylbenzene, b. p. 154°/37 mm. (cf. Schultz and Flachslander, A., 1902, i, 751), in the proportion 1·2 : 1 (cf. Behal and Choay, A., 1894, i, 280), together with some 2 : 4-dinitroethylbenzene (cf. Weisweiller, A., 1900, i, 291). Both mononitro-derivatives can be reduced to the corresponding amines by means of tin and hydrochloric acid, but the *o*-nitro-derivative is only slowly reduced by iron and hydrochloric acid or ammonium sulphide. Reduction of the 2 : 4-dinitro-derivative with ammonium sulphide affords mainly the 2-nitro-4-amino-derivative, m. p. 45° (*acetyl* derivative, m. p. 110°), but some 4-nitro-2-aminoethylbenzene is also formed. The *o-aminoethylbenzene* salt, m. p. 237—239°, and *p-aminoethylbenzene* salt, m. p. 247—249°, of anthraquinone-1-butylthiol-5-sulphonic acid were prepared. Sulphonation of *p*-aminoethylbenzene affords 4-*aminoethylbenzene-2-sulphonic acid* (*amide*, m. p. 86°), from which 4-*dimethylamino*-4′-*ethylazobenzene*-3-*sulphonic acid*, closely resembling helianthine, was obtained in the usual manner. Treatment of *p*-aminoethylbenzene hydrochloride in aqueous solution with bromine yields 3 : 5-*dibromo*-4-*aminoethylbenzene*, m. p. 85°. 4-*Ethyldiazoaminobenzene*, yellow, m. p. 75°, is obtained either from diazotised aniline and *p*-aminoethylbenzene or from diazotised *p*-aminoethylbenzene and aniline. *o*-*Ethylphenylhydrazine*, m. p. 49—50°, b. p. 156°/28 mm. (*hydrochloride*), and *p-tolualdehyde-o-ethylphenylhydrazone*, m. p. 102·5—103°, are described. *o*-Ethylphenylhydroxylamine could not be obtained. 4 : 4′-*Diethylazoxybenzene* is obtained by reduction of *p*-nitroethylbenzene with zinc dust and calcium chloride in aqueous alcohol, and yields 4 : 4′-diethylazobenzene, m. p. 63°, when distilled with iron filings. Only a trace of *p*-ethylbenzaldehyde was obtained from ethylbenzene by the Gattermann–Koch reaction. Dyes obtained by coupling diazotised *o*- and *p*-aminoethylbenzenes with 1-naphthol-4 : 8-disulphonic and 1-naphthol-4-sulphonic acid are slightly deeper in colour than the corresponding dyes from *o*- and *p*-toluidines. F. G. WILLSON.

***m*-Diethylbenzene and some of its derivatives.** J. E. COPENHAVER and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 3157—3164).—*m*-Diethylbenzene, b. p. 180·55°, d_{25}^{25} 0·8597, n_D^{25} 1·4926, can be separated from the mixture of isomeric diethylbenzenes, b. p. 180—185°, obtained by condensation of ethylene and benzene in presence of aluminium chloride, by sulphonation of the mixture with 12·5 mols. of sulphuric acid at 15—20°, fractional crystallisation of the barium salts, of which the *m*-isomeride is the least soluble (cf. Voswinkle, A., 1889, 1193), and then hydrolysing the barium *m*-diethylbenzenesulphonate with sulphuric acid (cf. Armstrong and Miller, J.C.S., 1884, 45, 148). Treatment of *m*-diethylbenzene (100 g.) with a mixture of 70% (60 g.) and 90% (40 g.) nitric acids at below 30° affords mainly 4-nitro-*m*-diethylbenzene, b. p. 133°/4 mm., d_{25}^{25} 1·0644, n_D^{25} 1·5300. Reduction of the latter with iron filings and acetic acid yields 4-*amino*-m-*diethylbenzene*, b. p. 116·5°/12 mm., b. p. 141°/30 mm., d_{25}^{25} 0·9545, 1·5395 (*hydrochloride*; *acetyl* derivative, m. p. 112—113·5°; *benzoyl* derivative, m. p. 176·5°), from which the following are obtained by the usual methods: 4-*hydroxy*-, b. p. 124·5—125·5°, d_{25}^{25} 0·9794, n_D^{25} 1·5218; 4-*chloro*-, b. p. 94·5°/12 mm., d_{25}^{25} 1·0119, n_D^{25} 1·5149; 4-*bromo*-, b. p. 106·5°/12 mm., d_{25}^{25} 1·2462, n_D^{25} 1·5359; 4-*iodo*-, b. p. 131·5°/12 mm., 1·4740, n_D^{25} 1·5729 (*iodoso-chloride*, unstable, m. p. 51—53° decomp.); 4-*cyano*-1 : 3-*diethylbenzene*, b. p. 134°/12 mm., d_{25}^{25}

0·9507, n_D^{25} 1·5195, and 2 : 4 : 2′ : 4′-*tetraethylthiocarbanilide*, m. p. 144·5°. Dyes made from this amine by coupling with a series of sulphonic acids have similar but more intense colours than those prepared analogously from aniline and the corresponding xylidine. F. G. WILLSON.

Hydrogenation of tetraphenylmethane and of *p*-hydroxytetraphenylmethane under pressure. V. N. IPATIEV and B. N. DOLGOV (Bull. Soc. chim., 1927, [iv], 41, 1621—1625).—Hydrogenation of tetraphenylmethane at 80—100 atm. and 275—285° in presence of nickel for 5—6 days affords only di*cyclo*hexylmethane, b. p. 251—253°, d^{20} 0·8743, n_D^{21} 1·4755, together with tri*cyclo*hexylmethane, m. p. 48°, d_0^{50} 0·9274, n_D^{50} 1·4967, and probably a little phenyl*cyclo*hexylmethane. Similarly *p*-hydroxytetraphenylmethane affords *cyclo*hexanol, di*cyclo*hexylmethane, and tri*cyclo*hexylmethane. Tetra*cyclo*hexylmethane was not obtained, probably on account of the greater affinity of the central carbon atom for hydrogen than for a fourth *cyclo*hexyl group. (Cf. this vol., 169.) R. BRIGHTMAN.

Reactivity of halogens in various types of naphthalene derivatives. J. B. SHOESMITH and H. RUBLI (J.C.S., 1927, 3098—3106; cf. A., 1926, 389, 1247; 1927, 962).—The halogen in halogenonaphthalene derivatives is found to be more labile than that of the corresponding benzene derivatives. Thus 1-bromo-β-naphthol is more easily reduced by an acetic acid solution of hydrogen iodide than 4-bromo-α-naphthol and, probably owing to quinonoid tautomerisation, either is more easily reduced than the corresponding bromophenol, where the order of reducibility is the reverse. The order of the ease of hydrolysis of the substituted naphthylmethyl bromides is in exact parallel to the corresponding benzene series, although the influence of the second benzene nucleus approximately doubles the rate. Evidence of the transmission of influence from the 1- to the 5-position is obtained by the ease of hydrolysis of the following α-naphthylmethyl bromides which are in the order 5-methoxy->unsubstituted>5-bromo-. 4-*Methoxy-α-naphthylmethyl bromide*, m. p. 119—120° (decomp.), is prepared by the action of a benzene solution of hydrogen bromide on the corresponding carbinol. 3-*Methoxy-α-naphthoyl chloride*, m. p. 79°, obtained by the action of thionyl chloride on the acid, yields 3-*methoxy-α-naphthaldehyde*, m. p. 60° (*oxime*, m. p. 102°; p-*nitrophenylhydrazone*, m. p. 197°; *semicarbazone*, m. p. 200°), which may be converted into 3-*methoxynaphthylcarbinol*, m. p. 88°. 4-*Bromo-α-naphthyl methyl ether*, b. p. 181°/18 mm., is described. 4-*Methyl-α-naphthylcarbinol*, m. p. 75°, prepared by the interaction of the magnesium compound of 4-bromo-1-methylnaphthalene and paraformaldehyde, yields 4-*methyl-α-naphthylmethyl bromide*, m. p. 77 *Aceto-4-bromo-2-methyl-α-naphthalide*, m. p. 223 , obtained by the bromination of the corresponding acetomethylnaphthalide (Lesser, A., 1914, i, 33), yields 4-*bromo-2-methyl-α-naphthylamine*, m. p. 82°, on hydrolysis. 5-Bromo-α-naphthaldehyde (p-*nitrophenylhydrazone*, m. p. 263°) yields similarly 5-*bromo-α-naphthylcarbinol*, m. p. 124°, and 5-*bromo-α-naphthylmethyl bromide*, m. p. 101°. 5-*Methoxy-α-naphthylcarbinol*, m. p. 98°, and 5-*methoxy-α-naphthylmethyl bromide*, m. p. 65°, are also described. G. A. C. GOUGH.

Derivatives of fluorene: 2-chloro-fluorene and -fluorenone. P. CHANUSSOT (Anal. Asoc. Quím. Argentina, 1927, 15, 216—220, and Bull. Soc. chim., 1927, [iv], 41, 1626—1627; cf. A., 1927, 962). —2-Chlorofluorene, m. p. 96—97°, was prepared from 2-diazofluorene by Sandmeyer's reaction and yielded 2-*chlorofluorenone*, m. p. 125—126°, on oxidation. Direct chlorination of fluorene also yields 2-chlorofluorene (cf. Courtot and Vignati, A., 1927, 348, 654). R. K. CALLOW.

2-Iodofluorene. P. CHANUSSOT (Bull. Soc. chim., 1927, [iv], 41, 1625—1626; cf. preceding abstract).—2-Iodofluorene was obtained by the author prior to Korczynski, Karlowska, and Kierzek (A., 1927, 347) in 25—30% yield by the action of potassium iodide on fluorene-2-diazonium chloride (Actas Trab. II. Congr. Quim., 1924, 3, 77). 2-Chloro- and 2-bromofluorene were similarly prepared. R. BRIGHTMAN.

Unsaturated residues in chemical and pharmacological relationship. VI. J. VON BRAUN and M. KÜHN (Ber., 1927, 60, [B], 2551—2557; cf. A., 1926, 850, and previous abstracts).—The outstanding influence of a double linking in the βγ-position is exhibited by the *cyclo*pentenyl group, since *cyclo*pentenyl and allyl derivatives show close analogy in their stabilities and pharmacological action. cyclo*Pentenyldiethylamine*, $NEt_2\cdot CH<\begin{smallmatrix}CH=CH\\ CH_2\cdot CH_2\end{smallmatrix}$, b. p. 164—165° (*hydrochloride*, m. p. 127°; *picrate*, m. p. 124°), is prepared in 70% yield by the action of *cyclo*pentenyl chloride on diethylamine in benzene at 0°; it is converted by cyanogen bromide in ethereal solution exclusively into diethylcyanamide, b. p. 70°/11 mm. *cyclo*Pentenyl chloride and methylamine afford a mixture of cyclo*pentenylmethylamine*, $C_5H_9\cdot NHMe$, b. p. 123° (*hydrochloride*, m. p. 124°; *picrate*, m. p. 136°), and di*cyclopentenylmethylamine*, b. p. 100°/15 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 129°). The tertiary base yields cyclo*pentenylmethylamine*, b. p. about 110°/12 mm., when treated with cyanogen bromide. cyclo*Pentenylmethylbenzylamine*, b. p. 130°/12 mm. (*picrate*, m. p. 115°), and cyanogen bromide yield the hydrobromide of the original base, a quaternary bromide which could not be obtained pure, and a mixture of methylbenzyl- and *cyclo*pentenylmethyl-cyanamides. The *cyclo*pentenyl group is therefore loosely attached to nitrogen, although more firmly than the allyl radical. *cyclo*Pentenyl chloride is converted by ammonium thiocyanate suspended in benzene or toluene into cyclo*pentenylthiocarbimide*, b. p. 80°/14 mm. (cyclo*pentenylphenylthiocarbamide*, non-crystalline; cyclo*pentenyl*-p-*tolylthiocarbamide*, m. p. 186°; cyclo*pentenyl-β-naphthylthiocarbamide*, amorphous). Magnesium phenyl bromide and *cyclo*pentenyl chloride afford cyclo*pentenylbenzene*, b. p. 92—93°/13 mm., d_4^{19} 0·9668, n_D^{19} 1·5396 (*dibromide*, b. p. 130—135°/1 mm.), isomeric or possibly identical with the compound obtained by Borsche and Menz (A., 1908, i, 147). *cyclo*Pentenyl chloride and sodium or potassium phenoxide suspended in toluene give *cyclo*pentadiene,

phenol (derived from primarily formed *cyclo*pentenyl phenyl ether), and *o-cyclopentenylphenol*, b. p. 133—135°/12 mm. (non-crystalline *acetyl* and *benzoyl* derivatives; *methyl ether*, b. p. 125°/15 mm.); the portion insoluble in alkali hydroxide gives analyses indicating a compound of 1 mol. of phenol with 2 mols. of *cyclo*pentadiene or 1 mol. of *cyclo*pentenylphenol with 1 mol. of *cyclo*pentadiene. *cyclo*Pentadiene reacts vigorously with phenols but not with phenolic ethers in presence of a trace of hydrogen chloride. N-cyclo*Pentenylnorcodeine*, m. p. 113° (*hydrochloride*, m. p. 188° after softening at about 180°), prepared from norcodeine and *cyclo*pentenyl chloride in toluene, closely resembles allylnorcodeine in pharmacological behaviour, whilst 5-cyclo*pentenyl*-5-iso*propylbarbituric acid*, m. p. 171—172°, from *cyclo*pentenyl chloride and the sodium derivative of 5-*iso*propylbarbituric acid in toluene, is almost as powerful a soporific as "noctal."

H. WREN.

Alternating effect in carbon chains. XXII. Attempt further to define the probable mechanism of orientation in aromatic substitution. C. K. INGOLD and F. R. SHAW (J.C.S., 1927, 2918—2926).—Experiments on the relative speeds of nitration of aromatic compounds of certain classes are used in an attempt to ascertain the comparative degrees of activation induced by substituents at the *o*-, *m*-, and *p*-positions of the benzene nucleus. The classes of compound investigated are chosen to include cases of simple inductive effect (toluene and benzyltrimethylammonium salts) and of combined inductive and tautomeric effect (halogenobenzenes) (cf. Ann. Reports, 1926, 140). Inductive effects of either sign are shown to operate primarily on the *o*- and *p*-positions, whilst an appreciable second-order effect, always of the same sign as the primary effect, is relayed on to the *m*-position. Tautomeric effects operate powerfully on the *o*- and *p*-positions but no similarly appreciable second-order effect reaches the *m*-position. It is concluded tentatively that, whilst inductive effects give rise to an essentially permanent (not necessarily constant) molecular condition, the tautomeric effect (apart, possibly, from a small permanent residuum) is essentially a temporary phenomenon, of main significance at the moment of attack by a reagent. The mechanism of transmission through the nucleus of the inductive and tautomeric effects is discussed.

M. CLARK.

Sulphonation in basic or neutral media. Arylsulphonanilidosulphonic acids ($Ar\cdot SO_2\cdot NH\cdot C_6H_4\cdot SO_3H$). M. BATTEGAY and A. SCHNEIDER (Bull. Soc. chim., 1927, [iv], **41**, 1491—1494).—Sulphonation of *p*-toluenesulphonanilide with pyridinium anhydrosulphate at 180—190° yields a *sulphonic acid* affording the *calcium* salts $(C_7H_7\cdot SO_2\cdot N\cdot C_6H_4\cdot SO_3)Ca,\frac{1}{2}H_2O$ and $(C_7H_7\cdot SO_2\cdot NH\cdot C_6H_4\cdot SO_3)_2Ca$, the sulphonic group entering the *para*-position. The corresponding derivatives of the three *p*-toluenesulphotoluidides are similarly obtained. In the sulphonation of naphthalene by this method at 140° and 170°, rise of temperature favours the formation of the α-sulphonic acid, which with this method is always formed in greater amount than the β-isomeride.

R. BRIGHTMAN.

Synthesis of substituted carbamides and thiocarbamides. R. M. ROY and J. N. RAY (J. Indian Chem. Soc., 1927, **4**, 339—342).—Carbamide when treated with aniline, *o*-, *m*-, and *p*-toluidines, and *p*-phenetidine in presence of phosphorus pentoxide at 110—125° gives the corresponding monophenylcarbamides. Small quantities of the *s*-diphenylcarbamides are produced also. Thiocarbamide with aniline and *o*- and *p*-toluidines yields the monophenylthiocarbamides. Urethane and thiourethane react with aniline to give *s*-diphenylcarbamide and *s*-diphenylthiocarbamide.

H. BURTON.

Derivatives of *n*-hexylamine with chlorodinitro- and chlorotrinitro-naphthalenes. A. P. J. HOOGEVEEN (Rec. trav. chim., 1927, **46**, 918—924).—*n*-Hexylamine, n_D^{17} 1·4255, is prepared by Frentzel's method (A., 1883, 1075), improved details being given. When heated with the appropriate chloronitronaphthalene in alcohol solution at 100° for 5 hrs. it yields, respectively, 2 : 4-*dinitro*-1-n-*hexylamino*-, m. p. 64°; 2 : 4 : 5-*trinitro*-1-n-*hexylamino*-, m. p. 97°, and 1 : 6 : 8-*trinitro*-2-n-*hexylamino*-, m. p. 164°, -*naphthalenes*. These m. p. are in close agreement with those predicted by Talen (Diss., Leiden, 1927) and by van der Kam (A., 1926, 1240).

J. W. BAKER.

Higher alkyl derivatives of toluene-*p*-sulphonyl-β-naphthylamine. 2-*n*-Butyl-2-toluene-*p*-sulphonyl-1:2-naphthylenediamine. J. REILLY, F. J. DRUMM, and (MISS) K. O'SULLIVAN (J.S.C.I., 1927, **46**, 436—437T; cf. Morgan and Micklethwait, J.C.S., 1912, **101**, 143).—On heating β-naphthylamine with *n*-butyl iodide in *n*-butyl alcohol, β-*naphthyl*-n-*butylamine*, b. p. 348—350°, $d_4^{18.5}$ 1·02, is obtained; it is a colourless oil with a faint violet fluorescence; *hydrochloride*, m. p. 176—178°; p-*bromobenzoyl* derivative, m. p. 125°. When heated with toluene-*p*-sulphonyl chloride in pyridine solution, β-naphthyl-*n*-butylamine yields *toluene*-p-*sulphonyl*-n-*butyl*-β-*naphthylamine*, m. p. 55—56°, which may also be prepared in better yield by butylation of toluene-*p*-sulphonyl-β-naphthylamine. Nitration of this product in glacial acetic acid solution at 40—50° yields 1-*nitro-2-toluene*-p-*sulphonyl*-n-*butylnaphthylamine*, m. p. 129—130°, which is reduced by ammonium chloride and zinc dust to 2-*toluene*-p-*sulphonyl*-n-*butyl*-1 : 2-*naphthylenediamine*, m. p. 119° (*benzoyl* derivative, m. p. 150°). The diazonium salt of this base is comparatively stable in glacial acetic acid solution at the ordinary temperature; it yields with β-naphthol a scarlet *dye*, which with sulphuric acid gives a pure blue solution not changing on dilution, with chromotropic acid a purple and with γ-acid a chocolate-brown *dye*. The diamine couples with diazosulphanilic acid to give a violet *dye*, the sodium salt of which is a scarlet powder giving a purple coloration with sulphuric acid.

W. J. POWELL.

Trypanocidal action and chemical constitution. VII. *s*-Carbamides and arylamides of naphthylamine-di- and -tri-sulphonic acids, with observations on the mesomorphic state. I. E. BALABAN and H. KING (J.C.S., 1927, 3068—3097).—The corresponding *m*-nitrobenzoyl derivatives have

been prepared by the action of *m*-nitrobenzoyl chloride on the sodium salts of 1-naphthylamine-3 : 6-disulphonic acid (I), 2-naphthylamine-6 : 8-disulphonic acid (II), 2-naphthylamine-4 : 8-disulphonic acid (III), 2-naphthylamine-5 : 7-disulphonic acid (IV), 8-hydroxy-1-naphthylamine-3 : 6-disulphonic acid (V), 8-hydroxy-2-naphthylamine-3 : 6-disulphonic acid (VI), and 1-naphthylamine-4 : 6 : 8-trisulphonic acid (VII). The nitro-group has, in each case, been reduced by ferrous hydroxide and the amino-compounds so formed have been converted (*a*) into the *s*-carbamides by the action of carbonyl chloride and (*b*) into the *m*-nitrobenzoyl derivatives. These new nitro-compounds (*b*) have been reduced to the *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives, which have again been phosgenated to give a further series of *s*-carbamides, having the general structure: $CO(NH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}NHR)_2$. *s*-Carbamides have also been prepared from the original amino-acids with the exception of (V), which yields, with carbonyl chloride, I : 8-ON-*carbonylamino-naphthol*-3 : 6-*disulphonic acid* [*disodium* salt $+4H_2O$; *barium* salt). The toxic and trypanocidal action of these substances has been tested on mice and on mice infected with *Trypanosoma equiperdum*. Trypanocidal action appears only at the *s*-carbamide stages of the aminobenzoyl and aminobenzoylaminobenzoyl derivatives and no activity is exhibited by derivatives of (I) and (VI). The substantive dyeing action on cotton was determined for derivatives of (V) and (VI) by measuring the colour intensities developed on immersion in diazotised *p*-nitroaniline of a cotton skein, which had been previously heated at 100° with an aqueous solution of the derivative and sodium chloride. The most pronounced substantive effect appeared at the *s*-carbamide stage in each case and this was confirmed for Bayer 205 (*s*-carbamide of *m'*-aminobenzoyl-*m*-aminotoluoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid), which, at a dilution of 1 in 50,000, gives a precipitate with clupeine sulphate in presence of 20% sodium chloride solution. It is considered that substantivity to cotton is roughly paralleled by the substantivity either to the tissues of the mammalian host or to the trypanosomes or to both. Many of the derivatives of the disulphonic acids exhibit to a pronounced degree the phenomenon of anisotropy in aqueous solution. The following are described: Derivatives of (I): s-*carbamide* ($+14H_2O$); *sodium* m-*nitrobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+5\frac{1}{2}H_2O$); *sodium* m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+5H_2O$) [*sodium hydrogen* salt ($+4\frac{1}{2}H_2O$); *calcium, barium*, and *silver* salts; corresponding *diazo*- and *azoxy*- ($+12H_2O$) compounds; s-*carbamide* ($+14\frac{1}{2}H_2O$)]; *sodium*, m'-*nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+4H_2O$); *sodium hydrogen* m'-*amino-benzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+10H_2O$) [*diazo*-compound; s-*carbamide* ($+14H_2O$) derived from disodium salt (*barium* salt)]. Derivatives of (II): s-*carbamide* ($+10H_2O$) (*barium* salt); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+7H_2O$); *sodium hydrogen* m-*amino-benzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+5\frac{1}{2}H_2O$) [*diazo*-compound; s-*carbamide* ($+13H_2O$) from disodium salt]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+6H_2O$); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* [*sodium hydrogen* ($+5\frac{1}{2}H_2O$), *magnesium, calcium*, and *barium* salts; *diazosulphonate*; s-*carbamide* ($+16\frac{1}{2}H_2O$) (*magnesium, calcium*, and *barium* salts)]. Derivatives of (III): s-*carbamide* ($+5H_2O$); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+5H_2O$); *sodium* m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+7\frac{1}{2}H_2O$) [*sodium hydrogen* salt ($+5\frac{1}{2}H_2O$); *diazosulphonate*; s-*carb-amide* ($+12H_2O$) (*calcium* and *barium* salts)]; m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* [*disodium* salt ($+5H_2O$); *barium, calcium*, and *magnesium* salts]; *sodium hydrogen* m'-*amino-benzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+6\frac{1}{2}H_2O$) [s-*carbamide* ($+14\frac{1}{2}H_2O$) (*magnesium, barium*, and *calcium* salts)]. Derivatives of (IV): s-*carbamide* ($+7H_2O$); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* ($+5\frac{1}{2}H_2O$); *sodium* m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* [*sodium hydrogen* salt ($+4H_2O$); *diazo*-compound; s-*carbamide* ($+15H_2O$) (*barium* salt)]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* ($+9H_2O$); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* [*sodium hydrogen* salt ($+5\frac{1}{2}H_2O$); s-*carbamide* ($+8H_2O$) (calcium and barium salts)]. Derivatives of (V): *sodium* 1-m-*nitrobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7H_2O$) (*barium* salt); *sodium* 1-m-*aminobenz-amido*-8-*naphthol*-3 : 6-*disulphonate* [*sodium hydrogen* salt ($+5H_2O$); *calcium, magnesium*, and barium salts; s-*carbamide* ($+13\frac{1}{2}H_2O$)]; *sodium* 1-m'-*nitro-benzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7\frac{1}{2}H_2O$); *sodium hydrogen* 1-m'-*aminobenz-oyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+6\frac{1}{2}H_2O$) [s-*carbamide* ($+17\frac{1}{2}H_2O$) from disodium salt]. Derivatives of (VI): s-*carbamide* ($+10H_2O$) (*barium* salt); *sodium* 2-m-*nitrobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+4\frac{1}{2}H_2O$) (*barium* salt); *sodium hydrogen* 2-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+4H_2O$) [*barium* salt; *diazosulphonate*; s-*carbamide* ($+8\frac{1}{2}H_2O$) (*calcium* and *barium* salts) from disodium salt]; *sodium* 2-m'-*nitrobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7H_2O$) (*calcium* and *barium* salts); *sodium hydrogen* 2-m'-*aminobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+8\frac{1}{2}H_2O$) [s-*carbamide* ($+9H_2O$) (*magnesium, calcium*, and *barium* salts) from disodium salt]. Derivatives of (VII): s-*carbamide*; *sodium* m-*nitrobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+4\frac{1}{2}H_2O$) (*calcium* and *barium* salts); *sodium* m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* [s-*carbamide* ($+4H_2O$)]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+8H_2O$) (*calcium* and *barium* salts); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+3\frac{1}{2}H_2O$) [*disodium* salt; s-*carb-amide* ($+8H_2O$); *barium* salt]. M. CLARK.

Substitution products of 3-nitro- and 3-amino-diphenyl. W. BLAKEY and H. A. SCARBOROUGH (J.C.S., 1927, 3000—3009; cf. A., 1927, 656).—4'-*Chloro*-3-*nitrodiphenyl* (I), m. p. 89°, 2' : 4'-*dichloro*-3-*nitrodiphenyl* (II), m. p. 115°, (2' : 4' : 5 ?)-*trichloro*-3-*nitrodiphenyl*, m. p. 211°, and (2' : 4' : 5 : 6' ?)-

tetrachloro-3-nitrodiphenyl, m. p. 175°, are obtained by direct chlorination of 3-nitrodiphenyl in presence of ferric chloride under varying conditions of temperature and duration of heating. Reduction of compounds (I) and (II) with alcoholic stannous chloride in presence of concentrated hydrochloric acid, followed by acetylation, gives 4'-*chloro-3-acetamidodiphenyl*, m. p. 184°, and 2' : 4 : 4'-*trichloro-3-acetamidodiphenyl*, m. p. 170°, respectively, converted by hydrolysis into 4'-*chloro-3-aminodiphenyl*, m. p. 82°, and 2' : 4 : 4'-*trichloro-3-aminodiphenyl*, m. p. 105°. Bromination of 3-nitrodiphenyl yields 4'-*bromo-3-nitrodiphenyl*, m. p. 95°, and further bromination does not occur. 4'-*Bromo-3-acetamidodiphenyl* has m. p. 193° and 4'-*bromo-3-aminodiphenyl*, m. p. 105°. Further bromination of the last-named compound gives 2 : 4 : 4' : 6-*tetrabromo-3-aminodiphenyl*, m. p. 104°. Nitration of 3-nitrodiphenyl in fuming nitric acid solution gives a mixture of 3 : 4'-*dinitrodiphenyl*, m. p. 189°, and 2' : 3-dinitrodiphenyl. Further nitration of either compound in sulphuric acid solution yields 2' : 3 : 4 : 4'-*tetranitrodiphenyl*, m. p. 173°, which gives, on treatment with piperidine, 2' : 3 : 4'-trinitro-4-piperidinodiphenyl. Treatment of 3-acetamidodiphenyl with sodium hypochlorite yields N-*chloro-3-acetamidodiphenyl*, m. p. 87°, converted by alcohol and acetic acid into 4-*chloro-3-acetamidodiphenyl* (III), m. p. 148°, alternatively obtained by direct chlorination of 3-acetamidodiphenyl in glacial acetic acid solution. 4-*Chloro-3-aminodiphenyl hydrochloride* has m. p. 247° (decomp.). Treatment of (III) with sodium hypochlorite gives an unstable *N*-chloroamine. Bromination of 3-aminodiphenyl in carbon tetrachloride solution gives 4-*bromo-3-aminodiphenyl hydrobromide*, m. p. 255° (decomp.), and, after prolonged treatment, 2 : 4 : 6-*tribromo-3-aminodiphenyl*, m. p. 141°, which is quantitatively obtained by bromination in acetic acid solution. Deamination gives 2 : 4 : 6-*tribromodiphenyl*, m. p. 64°. Direct bromination of 3-acetamidodiphenyl in glacial acetic acid at the ordinary temperature gives 4-*bromo-3-acetamidodiphenyl*, m. p. 163°, whilst, in the presence of excess of bromine and at 100—120°, 4 : 6-*dibromo-3-acetamidodiphenyl*, m. p. 149°, is obtained. These compounds were converted respectively into 3 : 4-*dibromodiphenyl*, b. p. 215°/15 mm., and 2 : 4-*dibromodiphenyl*, b. p. 235°/15 mm. Nitration of 3-acetamidodiphenyl in a mixture of glacial acetic acid and acetic anhydride at 70° gives 4-*nitro-3-acetamidodiphenyl*, m. p. 115°. 4-*Nitro-3-aminodiphenyl* has m. p. 116°. Nitration of 3-acetamidodiphenyl and of 4-bromo-3-acetamidodiphenyl in fuming nitric acid solution gives 4'-*nitro-3-acetamidodiphenyl*, m. p. 192°, and 4-*bromo-4'-nitro-3-acetamidodiphenyl*, m. p. 158°, respectively. 4'-*Nitro-3-aminodiphenyl* has m. p. 137° and 4-*bromo-4'-nitro-3-aminodiphenyl* has m. p. 145°.

M. CLARK.

Action of chloroacetone on diazonium hydroxides. G. FAVREL (Bull. Soc. chim., 1927, [iv], 41, 1494—1497).—The presence of the electronegative chlorine and carbonyl group confers on chloroacetone properties analogous to those of αγ-diketones. Thus an aqueous solution of benzenediazonium chloride at 0° in presence of sodium acetate gives with chloroacetone a reddish-yellow precipitate, probably the azo-derivative, COMe·CHCl·N:NPh, which is rapidly transformed into the phenylhydrazone of pyruvyl chloride, COMe·CCl:N·NHPh, m. p. 136—137° (yield 30%). The o- and p-*tolylhydrazones* of pyruvyl chloride, m. p. 109—110° and 145—146° respectively, are obtained analogously in yields of 25% and 15%.

R. BRIGHTMAN.

Side-chain derivatives of alkyl*cyclo*pentanes. Tertiary alcohols, unsaturated and saturated hydrocarbons. G. CHAVANNE and P. BECKER (Bull. Soc. chim. Belg., 1927, 36, 591—604).—Magnesium alkyl bromides react with *cyclo*pentanone to form 1-alkyl*cyclo*pentan-1-ols, which are sometimes accompanied by *cyclo*pentanol, thus demonstrating the reducing action of the Grignard reagent. The following data are recorded: ethyl*cyclo*pentanol, b. p. 154·5—155·2°/760 mm., d_4^{15} 0·9225 (*allophanate*, m. p. 169°); *n*-propyl*cyclo*pentanol, b. p. 175·2—175·7°/760 mm., d_4^{15} 0·9083, d_4^{20} 0·9044±0·0005 (*allophanate*, m. p. 178°); n-*butyl*cyclo*pentanol*, b. p. 195·4—195·9°/760 mm., $d_4^{14\cdot95}$ 0·9022, $d_4^{19\cdot8}$ 0·8989 (*allophanate*, m. p. 181°). Dehydration of these tertiary alcohols by passing over alumina at 300°, heating with dry aluminium sulphate at 120—130°, or application of Wuyts' method using *p*-toluenesulphonic acid as catalyst furnishes ethyl*cyclo*pentene, b. p. 106·5—107°/760 mm., m. p. —123·3°, d_4^{15} 0·8041, d_4^{20} 0·8000 (cf. Wallach and von Martius, A., 1909, i, 383), which is oxidised by chromic–acetic acids to propiobutyric acid; n-propyl*cyclo*pentene, b. p. 131·5—132·5°/760 mm., m. p. —100·3°, d_4^{15} 0·8056, d_4^{20} 0·8015 (cf. Eisenlohr, A., 1926, 718), which is oxidised by potassium permanganate, forming mainly butyrobutyric acid and small amounts of glutaric, succinic, propionic, and butyric acids; n-*butyl*cyclo*pentene*, b. p. 157·5—158°/760 mm., m. p. —95·75°, $d_4^{17\cdot8}$ 0·8101. Reduction of these unsaturated hydrocarbons with hydrogen in presence of acetic acid and platinum-black affords ethyl*cyclo*pentane, b. p. 103—103·2°/760 mm., m. p. —137·9°, $d_4^{14\cdot9}$ 0·7711, $d_4^{19\cdot}$ 0·7669; *n*-propyl*cyclo*pentane, b. p. 131·3—131·5°/760 mm., m. p. —120·3°, $d_4^{14\cdot9}$ 0·7814, $d_4^{20\cdot}$ 0·7772; n-*butyl*cyclo*pentane*, b. p. 156·8°±0·1/760 mm., m. p. —108·2°, $d_4^{14\cdot95}$ 0·7887, $d_4^{20\cdot}$ 0·7848. Critical solution temperatures of these last hydrocarbons in aniline are given, together with numerous values of the refractive indices of all the compounds examined.

H. BURTON.

***cis–trans* Isomerism and steric hindrance. VI. 2-Propyl*cyclo*hexanols.** G. VAVON and P. ANZIANI (Bull. Soc. chim., 1927, [iv], 41, 1638—1649).—*o*-Propylphenol, b. p. 100—101°/10 mm., 214—216°/760 mm., obtained by hydrogenation of *o*-allylphenol in acetic acid in presence of platinum, on further hydrogenation affords a mixture of 2-propyl*cyclo*hexanols, b. p. 199—201°, rich in the *cis*-isomeride, and about 25—30% of propyl*cyclo*hexane, b. p. 154°, 2-propyl*cyclo*hexanone forming an intermediate stage. cis-2-*Propyl*cyclo*hexanol* has b. p. 84°/10 mm., d_4^{11} 0·9247, n_D^{11} 1·4688 (*phenylurethane*, m. p. 97—97·5°; *hydrogen phthalate*, m. p. 107—108°; *hydrogen succinate*, m. p. 31—32°; *benzoate*, b. p. 177—178°/14 mm.,

d_4^{16} 1·0262, n_D^{15} 1·5150; *iso*valerate, b. p. 138—139°/18 mm., d_4^{11} 0·914, n_D^{11} 1·450). trans-2-*Propyl*cyclo*hexanol*, b. p. 90°/14 mm., *d* 0·9160, n_D^{11} 1·4668 (*hydrogen phthalate*, m. p. 120—121°; *phenylurethane*, m. p. 69—70°; *hydrogen succinate*, m. p. 48—49°; *benzoate*, b. p. 179—180°/15 mm., d_4^{16} 1·0154, n_D^{16} 1·513; *iso*valerate, b. p. 129—130°/13 mm., *d* 0·9131, n_D^{11} 1·4490), is obtained by heating the sodium derivative of the *cis*-isomeride at 200°, or in 85% yield by hydrogenation of *propyl*cyclo*hexanone*, b. p. 83—84°/13 mm., 198—199°/760 mm., d_4^{13} 0·9145, n_D^{13} 1·4558. The latter is obtained by oxidising the crude mixture of 2-propyl*cyclo*hexanols, b. p. 199—201°. Its *oxime*, m. p. 67—68°, with hydrogen in aqueous hydrochloric acid in presence of platinum-black gives 2-*propyl*cyclo*hexyl*-β-*hydroxylamine*, m. p. 64—65°. The *semicarbazone*, m. p. 133·5—134°, similarly affords 2-*propyl*cyclo*hexylsemicarbazide*, m. p. 103—104° (*hydrochloride*, m. p. 146—148°).

cis-2-Propyl*cyclo*hexanol is esterified only a little more slowly than the *trans*-isomeride, the difference being rather more marked in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed more rapidly than the *cis*-isomeride, the ratio of the velocity coefficients in water being 3·6 at 39° and 2·9 at 69°; in 75% alcohol the corresponding ratios are 2·3 and 2·2. The steric effect of the propyl group is thus much less marked than that of the *iso*propyl group in the corresponding 2-*iso*propyl*cyclo*hexanol derivatives (cf. Vavon and Callier, A., 1927, 455), as the theory of steric hindrance requires. For the hydrogen succinates the ratio of the velocity coefficients for hydrolysis of the *trans*- and *cis*-forms in water at 17° is 4·0; for the benzoates in 75% alcohol at 17°, the ratio is 3·9; and for the *iso*valerates in 75% alcohol at 30°, 2·5. R. BRIGHTMAN.

Dihydroxydiphenylsulphones (hydroxysulphobenzides). J. ZEHENTER and E. FAUSER (J. pr. Chem., 1927, [ii], **117**, 233—244).—Treatment of phenol with fuming sulphuric acid (15—20% SO_3) at 180—190° (cf. Annaheim, A., 1874, 795) yields mainly 4 : 4′-dihydroxydiphenylsulphone, together with a small amount of an isomeric *compound*, m. p. 173—174° (*diacetate*, m. p. 121°; *dibenzoate*, m. p. 205°; *sodium* salt), which is converted by dilute nitric acid into a *dinitrodihydroxydiphenylsulphone*, m. p. 229—230°. Treatment of the sulphone with concentrated sulphuric acid at the ordinary temperature for 24 hrs. gives a water-soluble product, whilst similar treatment of 4 : 4′-dihydroxydiphenylsulphone affords a *disulphonic acid*, $[C_6H_3(OH)(SO_3H)]_2SO_2$, m. p. (anhydrous) 212—214°, m. p. (+8H_2O), 66—68° after previous softening [*potassium*, *barium* (+4H_2O), and *lead* (+2H_2O) salts]. Sulphuric acid at 90—100° converts the sulphone into a *phenoldisulphonic acid* [*barium* salt (+5H_2O), loses 3H_2O at 170°, and decomposes at higher temperatures], and at 180—190° to a *phenoltrisulphonic acid* [*potassium* salt (+4H_2O), loses 2H_2O at 150°]. H. BURTON.

Alcohol additive products of the bromo-derivative of mixed ethers and bromo-derivative of ββ-diphenoxypropane. D. M. BIROSEL (Philippine J. Sci., 1927, **34**, 153—160).—A review of the literature leads to the conclusion that the action of alcohols on bromine derivatives of propenyl compounds, in which the side-chain is directly attached to the benzene ring, is a general reaction for the bromine derivatives of *n*-alkyl compounds. It is now shown to be applicable to compounds in which the side-chain is connected through oxygen to the aromatic nucleus. Direct bromination of *p*-bromophenyl *iso*propyl ether in chloroform solution gives 2 : 4 : 6-*tribromophenyl* β-*bromo*iso*propyl ether*, m. p. 93°, which when boiled with methyl alcohol in the presence of silver nitrate gives 2 : 4 : 6-*tribromophenyl* β-*methoxy*iso*propyl ether*, m. p. 118—120°, and with ethyl alcohol the corresponding *ethoxy*-compound, m. p. 130—132°. Interaction of the foregoing brominated mixed ether and phenol gives a *compound*, m. p. 125—130°, not further characterised, which on bromination gives ββ-*di*-2 : 4 : 6-*tribromophenoxypropane*, m. p. 86·5°. A comprehensive bibliography is included. E. HOLMES.

Replacement of sulphonic groups by nitro-groups in aromatic amino-compounds. R. L. DATTA and P. S. VARMA (J. Indian Chem. Soc., 1927, 4, 321—324).—Nitrous fumes convert sulphanilic acid or anilinedisulphonic acid in aqueous suspension into 2 : 4 : 6-trinitrophenol. Aniline-*m*-sulphonic acid yields 2 : 5-dinitrophenol. Similarly, from *p*-nitroanilinesulphonic acid, dimethylanilinesulphonic acid, *o*-toluidine-5-sulphonic acid, *o*-toluidine-3 : 5-disulphonic acid, *m*-toluidinesulphonic acid, *p*-toluidine-3-sulphonic acid, *p*-toluidine-3 : 5-disulphonic acid, and *m*-xylidinesulphonic acid there were obtained 2 : 4-dinitrophenol, 2 : 3 : 4-trinitrodimethylaniline, 3 : 5-dinitro-*o*-cresol, 3 : 5-dinitro-*o*-cresol, 2 : 4 : 6-trinitro-*m*-cresol, 3 : 5-dinitro-*p*-cresol, oxalic acid, and 5-nitro-1 : 3 : 4-xylenol, respectively. H. BURTON.

Replaceability of the halogen atom in 1-chloro-2 : 4-dinitro-5-ethoxy(methoxy)-benzene by alkoxy groups. H. F. J. LORANG (Rec. trav. chim., 1927, **46**, 891—902).—The velocity of replacement of the chlorine atom in 1-chloro-2 : 4-dinitro- or 1-chloro-2 : 4-dinitro-5-methoxy(and ethoxy)-benzene by a methoxy- or an ethoxy-group by the action of the sodium alkoxide has been measured at various temperatures. The values of the bimolecular reaction coefficients at 0°, 10°, 15°, 20°, and 25° for sodium ethoxide are: with 1-chloro-2 : 4-dinitrobenzene, 0·36, 1·05, 1·80, 2·91, and 4·90 (cf. Luloffs, A., 1902, i, 87, whose values require to be halved); with 1-chloro-2 : 4-dinitro-5-ethoxybenzene, 0·11, 0·22, 0·46, 0·61, and 1·11, respectively. With sodium methoxide and 1-chloro-2 : 4-dinitrobenzene, the values are 0·11, —, 0·59, —, and 1·49, and with 1-chloro-2 : 4-dinitro-5-methoxybenzene, 0·037, 0·091, 0·20, 0·30, and 0·47, respectively. The ratio of the velocities of replacement of the halogen atom in the unsubstituted and in the 5-alkoxy-chlorodinitrobenzenes are therefore 3·4 : 1 and 3 : 1, respectively, in the two series. J. W. BAKER.

Action of light on colouring matters containing the nitro-group. A. SEYEWETZ and D. MOUNIER (Compt. rend., 1927, **185**, 1279—1281).—Textiles of animal or vegetable fibres impregnated with nitrophenols, nitroamines, or even colourless nitro-compounds turn brown when exposed to day-

light or ultra-violet rays. Reduction apparently takes place, as reducing agents hasten, and oxidising agents retard, the effect. The brown *substance* thus formed from picric acid on calico was isolated, by extraction with alkali and precipitation with acid, and found to contain nitro- or nitroso-groups, but no amino-group. This substance may be an azo-compound derived from an azoxy-reduction product of picric acid. B. W. ANDERSON.

Acyl derivatives of o-aminophenol. R. E. NELSON, N. W. SHOCK, and W. H. SOWERS (J. Amer. Chem. Soc., 1927, **49**, 3129—3131; cf. A., 1926, 833).—Treatment of *iso*amyl *o*-hydroxycarbanilate with *n*-butyl chloroformate affords the corresponding *carbo*-n-*butoxy*-derivative, m. p. 77°, the reverse reaction taking place on hydrolysis. Acylation of *n*-butyl *o*-hydroxycarbanilate with *iso*amyl chloroformate affords the same diacyl derivative, indicating the migration of the carbo-*n*-butoxy-group from the nitrogen to the oxygen atom. Treatment of *iso*amyl *o*-hydroxycarbanilate with *iso*butyl chloroformate affords the corresponding *carboisobutoxy*-derivative, m. p. 61·5°, which yields the original *iso*amyl *o*-hydroxycarbanilate on hydrolysis. The same diacyl derivative is obtained from *iso*butyl *o*-hydroxycarbanilate and *iso*amyl chloroformate, indicating the migration of the carbo*iso*butoxy-group. o-*Benzamidophenyl* n-*propyl carbonate*, m. p. 52°, is obtained normally from *o*-benzamidophenol and *n*-propyl chloroformate, and, by rearrangement, from *n*-propyl *o*-hydroxycarbanilate and benzoyl chloride, the carbo-*n*-propoxy-group migrating from nitrogen to oxygen. Acylation of *iso*propyl *o*-hydroxycarbanilate with benzoyl chloride proceeds normally, with formation of the corresponding *benzoate*, m. p. 82°. The latter is also obtained by treatment of *o*-benzamidophenol with *iso*propyl chloroformate, indicating migration of the benzoyl group from nitrogen to oxygen. F. G. WILLSON.

Use of hydrogen peroxide for iodine and other substitutions in aromatic compounds. J. E. MARSH (J.C.S., 1927, 3164).—Examples are given of the use of hydrogen peroxide (30%) in effecting iodination of phenol and β-naphthol; phenol can also be brominated or chlorinated using a bromide or chloride with hydrogen peroxide in acetic acid. The method has also been extended to the introduction of the thiocarbimido-group. The reaction between dimethylaniline and potassium thiocyanate in glacial acetic acid solution followed by the gradual addition of hydrogen peroxide produces a compound, probably a dimethylaminobenzthiazole. R. A. PRATT.

***m*-4-Xylenol and some derivatives.** L. PALFRAY and T. DUBOC (Compt. rend., 1927, **185**, 1479—1481).—*m*-4-Xylenol, b. p. 97—98°/14 mm., d_4^{14} 1·0276, n_D^{14} 1·5420, R_D 37·41 (acetate, b. p. 107·5—108·5°/13 mm., 1·0298, $n_D^{13\cdot5}$ 1·4990, R_D 46·79; *propionate*, b. p. 121·4—121·6°/(corr.)15 mm., d_4^{17} 1·0104, n_D^{17} 1·4944, R_D 51·28; *benzoate*, b. p. 110·5—111°/15 mm., m. p. 37—38°), reacts with ethyl chloroacetate to form *ethyl* m-4-*xylyloxyacetate*, b. p. 150—150·2°/14 mm., d_5^{23} 1·0563, n_D^{23} 1·4942, R_D 57·89 (free *acid*, m. p. 140·5°). Bromination of the xylenol in acetic acid yields the 5-bromo-derivative, b. p. 105·5—106·5°/14 mm., m. p. 8·5—9°, $d_4^{16\cdot5}$ 1·4392, $n_D^{16\cdot5}$ 1·5642, 45·44 (cf. Orton and Coates, J.C.S., 1907, **91**, 53) (*acetate*, b. p. 137·6—137·9°/14 mm., d_4^{23} 1·3684, n_D^{23} 1·53115, 54·97; *propionate*, b. p. 154—154·5°(corr.)/14 mm., d_4^{23} 1·3275, n_D^{23} 1·5246, R_D 59·31; *benzoate*, b. p. 216°(corr.)/15 mm., m. p. 54°). H. BURTON.

Course of oxidation in arylthioarylides [derivatives of Ph·S·NHPh]. E. GEBAUER-FULNEGG and E. RIESZ [with A. LORENZ and R. POLLAK] (Monatsh., 1927, **48**, 645—658).—The oxidation of the compounds formed by the reaction of 4-chloro-2-nitro-1-chlorothiolbenzene with aromatic amines is studied. 4-*Chloro*-2-*nitro*-1-*anilinothiolbenzene*, m. p. 100°, is oxidised by peracetic acid to a brownish-violet *nitro*-compound, $C_{21}H_{16\,(or\,14)}O_4N_4Cl_2S_2$, decomp. 135—137°, reduced by zinc and acetic acid to the corresponding *amine*, decomp. 115—116°, and unaffected by the Claasz reaction (A., 1912, i, 851). Reduction of the original anilide causes decomposition with formation of acetanilide. The action of chlorine yields 4-chloro-2-nitrobenzenesulphonyl chloride and ammonium chloride, and the same compounds are obtained from the oxidised product.

4-*Chloro*-2-*nitro*-1-*diphenylaminothiolbenzene*, m. p. 127°, is oxidised slowly by peracetic or chromic acid to unidentified products. Nitric acid in acetic acid nitrates the two phenyl groups, yielding thus a *trinitro*-compound, decomp. 140—176°.

Hydrazobenzene with the chlorothiolbenzene gives equal amounts of benzidine and azobenzene, with a large amount of 4 : 4′-dichloro-2 : 2′-dinitrodiphenyldisulphide. Benzidine yields *bis*-(4-*chloro*-2-*nitrophenylthiol*)-pp′-*diaminodiphenyl*, m. p. 235°; oxidation products could not be isolated. Dihydrophenazine yields the hydrophenazine hydrochloride double salt (Hinsberg and Garfunkel, A., 1897, i, 123), phenazine, and 4 : 4′-dichloro-2 : 2′-dinitrodiphenyldisulphide. *o*-Chloroaniline yields 4-*chloro*-2-*nitro*-1-o-*chloroanilinothiolbenzene*, m. p. 112°, which is oxidised by peracetic acid to a *substance*, $C_{24}H_{14}O_4N_4S_2Cl_4$, decomp. 170°. E. W. WIGNALL.

Direct methylthiolation. Application in the preparation of substituted thioanisoles. H. H. HODGSON and F. W. HANDLEY (J.S.C.I., 1927, **46**, 435—436T).—The process, which is of general application for chloronitrobenzenes with labile chloro- or nitro-groups, consists in passing the gases evolved from a warm mixture of methyl sulphate and a 10% aqueous solution of sodium hydrosulphide into an alcoholic solution or suspension of the chloronitrobenzene in the presence of sodium hydroxide, or, in certain cases, of potassium carbonate. By this means 3-chloro-6-nitrothioanisole was obtained in excellent yield from 1-chloro-3 : 4-dinitrobenzene, as also were 2-nitro-, 4-chloro-2-nitro-, 2-nitro- and 4-nitro-5-methoxy-, and 2 : 4-dinitro-thioanisoles from 2-chloro- and 2 : 5-dichloro-nitrobenzenes, 3-chloro-4- and -6-nitro-anisoles, and 1-chloro-2 : 4-dinitrobenzene, respectively. An exception occurred with 4-chloronitrobenzene, which was mainly converted into 4 : 4′-dichloroazoxybenzene.

Action of aminosulphonic acid on diphenols. A. QUILICO (Gazzetta, 1927, **57**, 793—802).—When

aminosulphonic acid is heated with pyrocatechol, *ammonium pyrocatechol-4-sulphonate*, m. p. 260° (decomp.), is obtained, and with excess of aminosulphonic acid, the same product. Resorcinol yields similarly *ammonium resorcinol-4-sulphonate*, m. p. 190° (decomp.), identified by conversion by ammonia and ammonium chloride in a sealed tube into *ammonium* m-*phenylenediamine-4-sulphonate*, from which m-*dichlorobenzene-4-sulphonyl chloride*, m. p. 35°, is obtained, and finally, by the action of thionyl chloride, 1 : 3 : 4-trichlorobenzene. With excess of aminosulphonic acid, *ammonium resorcinol-4 : 6-disulphonate* (carbonises at 305°) is obtained; the *potassium* salt is converted into resorcinol-4 : 6-disulphonyl chloride (*-disulphonamide*, m. p. 263°, decomp.), and thence into *s*-tetrachlorobenzene. Quinol yields similarly *ammonium quinol-2-sulphonate*, m. p. 200—205°, and *-2 : 5-disulphonate* (carbonises at about 300°), converted into the *disulphonyl chloride*, m. p. 100°, and by thionyl chloride into *s*-tetrachlorobenzene.

E. W. WIGNALL.

Synthesis of some aralkylamines containing phenolic hydroxyl groups in the benzene nucleus. S. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 149—165).—Vanillin and benzyl chloride react in presence of alcohol and anhydrous potassium carbonate to form 4-benzyloxy-3-methoxybenzaldehyde, b. p. 213—214°/5 mm., m. p. 63—64°, which condenses with nitromethane in presence of methylamine to give *ω-nitro-4-benzyloxy-3-methoxystyrene*, m. p. 122—123°. Reduction of this compound with zinc dust and alcoholic acetic acid at 5—10° affords *4-benzyloxy-3-methoxyphenylacetaldoxime*, m. p. 118—119°, which on further reduction with sodium amalgam and alcoholic acetic acid yields *β-4-benzyloxy-3-methoxyphenylethylamine*, b. p. 201—202°/4 mm., m. p. 67—69° [*hydrochloride*, m. p. 173—175°; *picrate*, m. p. 171—172°; *chloroplatinate*, m. p. 211° (decomp.); *chloroaurate*, m. p. 220—221° (decomp.)]. This amine hydrochloride is hydrolysed by concentrated hydrochloric acid, forming *β-4-hydroxy-3-methoxyphenylethylamine*, m. p. 156—157° [*hydrochloride*, m. p. 210—211°; *picrate*, m. p. 194—196; *chloroplatinate*, m. p. 211° (decomp.)]. *ω-Nitro-4-acetoxy-3-methoxystyrene* and *ω-nitro-3-methoxy-4-methoxymethoxystyrene* have m. p. 161—162° and 102—103°, respectively. Condensation of 4-benzyloxy-3-methoxybenzaldehyde with ethyl cyanoacetate gives *ethyl α-cyano-4-benzyloxy-3-methoxycinnamate*, m. p. 127—129°, hydrolysed by alcoholic potassium hydroxide to the corresponding *cyano-acid*, m. p. 202—203° (*potassium* and *silver* salts). Reduction of this acid with sodium amalgam and water gives *α-cyano-β-4-benzyloxy-3-methoxyphenylpropionic acid*, m. p. 125—126·5°, which when heated with pyridine at 130—140° furnishes *β-4-benzyloxy-3-methoxyphenylpropionitrile*, m. p. 78—79°. Reduction of this compound with sodium and alcohol affords *γ-4-hydroxy-3-methoxyphenylpropylamine*, m. p. 105—107° [*hydrochloride*, m. p. 154·5—155·5°; *picrate*, m. p. 165—166°; *chloroplatinate*, m. p. 198—199° (decomp.)], together with a small amount of *β-4-benzyloxy-3-methoxyphenylpropionic acid*, m. p. 98·5—99·5° (*amide*, m. p. 119—120°), also obtained by reducing *4-benzyloxy-3-methoxycinnamic acid*, m. p. 188—190°. An improved method of isolating vanillylamine [*hydrochloride*, m. p. 212—214°; *picrate*, m. p. 198—200° (decomp.)] is given (cf. Nelson, A., 1919, i, 543). *Di-(4-hydroxy-3-methoxybenzyl)amine*, m. p. 134° [*hydrochloride*, m. p. 235—236°; *picrate*, m. p. 205° (decomp.)], is obtained by the reduction of vanillinoxime with zinc dust and approx. 80% acetic acid. *4-Benzyloxy-3-methoxybenzaldoxime*, m. p. 113—115°, on reduction yields *4-benzyloxy-3-methoxybenzylamine* [*hydrochloride*, m. p. 207—208°; *picrate*, m. p. 173—175°; *chloroplatinate*, m. p. 211—212° (decomp.); *chloroaurate*, m. p. 143—144°].

3 : 4-Methylenedioxybenzyl chloride reacts with potassium and mercuric cyanides in presence of water to form 3 : 4-methylenedioxyphenylacetonitrile, m. p. 43—44° (cf. A., 1906, i, 421); in aqueous alcohol the nitrile and *3 : 4-methylenedioxybenzyl ethyl ether*, b. p. 118—120°/8 mm., were produced. Reduction of the nitrile with sodium and boiling alcohol gives β-3 : 4-methylenedioxyphenylethylamine (*hydrochloride*, m. p. 208—209°) together with 3 : 4-methylenedioxytoluene, b. p. 193—195°, 83/14 mm. (cf. Schepss, A., 1913, i, 1154).

H. BURTON.

[Nuclear condensation of phenols with nitriles.] K. HOESCH (Ber., 1927, **60**, [*B*], 2537; cf. A., 1927, 353).—A reply to Houben (A., 1927, 870).

H. WREN.

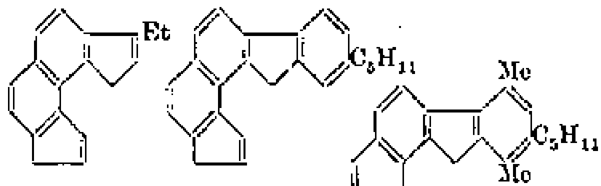
Catalytic hydrogenation under pressure of *p*-hydroxytriphenylcarbinol and *p*-hydroxydiphenylmethane. V. IPATIEV and B. DOLGOV (Compt. rend., 1927, **185**, 1484—1486).—Hydrogenation of *p*-hydroxytriphenylcarbinol in *cyclo*hexanol, in presence of nickel oxide, at 220° and an initial pressure of 80—100 atm., affords phenol, diphenylmethane, and p-*hydroxytriphenylmethane*, b. p. 250—253°/25 mm., m. p. 107—108°. Hydrogenation of this last substance at 270—275° gives *tri*cyclo*hexylmethane*, m. p. 48°, d_0^{50} 0·9265, n^{50} 1·4976. Hydrogenation of the carbinol at 280° yields mainly *di*cyclo*hexylmethane*, d_{20}^{19} 0·8776, n_{D}^{22} 1·4752, whilst at 320° a small amount of tri*cyclo*hexylmethane, some methane, and mainly di*cyclo*hexylmethane are produced.

Hydrogenation of *p*-hydroxydiphenylmethane, at 250—260° and 100 atm., gives di*cyclo*hexylmethane, dehydrogenated by sulphur at 280° to diphenylmethane.

H. BURTON.

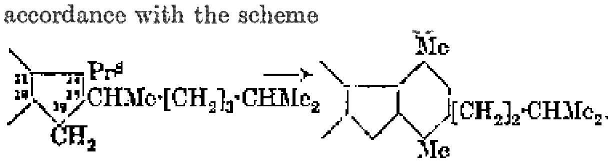
Dehydrogenation of cholesterol. III. O. DIELS, W. GADKE, and P. KORDING (Annalen, 1927, **459**, 1—26).—Dehydrogenation of cholesterol and some of its derivatives is smoothly effected at a lower temperature by the use of selenium instead of sulphur or palladised charcoal and the danger of alteration in the cholesterol skeleton is thus minimised. Dehydrogenation of the hydrocarbon $C_{19}H_{28}$ obtained by the thermal decomposition of cholesteryl chloride (Mauthner and Suida, A., 1896, i, 425) with palladised charcoal yields chrysene together with methane, ethane, propane, and octane. Similar dehydrogenation of cholesterol itself (Diels and Gadke, A., 1927, 241) yields hexane and *iso*octane in addition. Dehydrogenation of cholesteryl chloride with selenium at 240—310° yields an aromatic *hydrocarbon*, $C_{18}H_{16}$,

m. p. 123—124° (*picrate*, m. p. 117—118°), and a *hydrocarbon*, $C_{25}H_{24}$, m. p. 219—220° (*dinitro*-derivative, m. p. 261—262°), to which the structures (I) and (II) are respectively assigned. When the hydro-



(I.) (II.) (III.)

carbon (I) is treated with nitrous gases in ether and the product is heated with pyridine, formic or acetic acids, a *compound*, $C_{18}H_{13}O_2N$, m. p. 231—232° (decomp.) on slow heating, 238—240° on rapid heating, is obtained. The hydrocarbon (II) when oxidised with sodium dichromate and glacial acetic acid yields a *ketone*, m. p. 191—192°, which by reduction with magnesium and acetic acid yields an *alcohol*, m. p. 250—252°. When the acid $C_{26}H_{44}O_3$ obtained by the oxidation of cholesterone (Windaus, A., 1906, i, 579) is reduced by Clemmensen's method it yields a monobasic *acid*, $C_{26}H_{46}O_2$, m. p. 138°, which is dehydrogenated by selenium at 330° for 25 hrs. to yield a hydrocarbon, $C_{24}H_{26}$ (III), m. p. 171° (*dinitro*-derivative, m. p. 210), very similar to the hydrocarbon $C_{25}H_{24}$ (above), but readily oxidised by sodium dichromate and acetic acid directly to a *ketone*, $C_{24}H_{24}O$, m. p. 131°. Cholesterol itself by dehydrogenation with selenium for 30 hrs. yields the two hydrocarbons (I) and (II). On the basis of these results the authors consider that the existence of two five-membered rings in the cholesterol molecule is confirmed, in agreement with the conclusions of Wieland, Schlichting, and Jacobi (A., 1927, 247), the *iso*propyl and *iso*octyl groups being attached to the five-membered ring in positions 14 and 18, respectively. Six-membered ring formation during hydrogenation thus involves the interaction of the side-chains in accordance with the scheme



The formation of chrysene at the higher temperature results from the fission of the five-membered ring systems and subsequent ring closure to yield the six-rings present in this hydrocarbon. J. W. Baker.

Walden inversion. XI. Oxidation of secondary mercaptans to sulphonic acids; Walden inversion in series of secondary carbinols. P. A. Levene and L. A. Mikeska (J. Biol. Chem., 1927, **75**, 587—605).—α-Naphthylethyl alcohol and *cyclo*hexylphenylcarbinol form exceptions to the compounds previously investigated (A., 1927, 53) in that the sign of rotation of their thio-derivatives is unaltered on oxidation to the sulphonic acids. However, in the former case a great increase in lævorotation is observed on passing from *l*-thiol to *l*-sulphonic acid, so that it is concluded that the *l*-carbinol and *l*-halide are configuratively related, whilst in the latter case the change of rotation from thiol to sulphonic acid is opposite in direction from that between carbinol and halide when the latter conversion is brought about by phosphorus pentachloride, so that in this case the carbinols are regarded as configuratively related to the halides of the opposite rotation. With this assumption it is possible to conclude in general that simple aliphatic carbinols and phenylbenzylcarbinol are converted into the halogen derivatives without Walden inversion, regardless of the halogenating reagent; with α-phenylethyl alcohol and α-phenyl-*n*-propyl alcohol and with *cyclo*hexylphenylcarbinol inversion takes place only when thionyl chloride is used; with α-phenyl-*n*-butyl, α-phenyl-β-methylpropyl, α-phenyl-*n*-amyl, and α-naphthylethyl alcohols inversion always occurs.

d-α-*Methyl*-n-*butyl alcohol* has $[\alpha]_D^{20}$ +18·5° in ether; l-α-*methyl*-n-*butyl alcohol*, $[\alpha]^{20}$ −9·06°, gave, with hydrobromic acid, *d*-β-bromo-*n*-pentane, b. p. 115—118°, $[\alpha]_D$ +9·14° in ether; with thionyl chloride it gave *di*-α-*methyl*-n-*butyl sulphite*, b. p. 113—119°, $[\alpha]_D$ +5·58°; *d*-β-*bromo*-n-*pentane*, $[\alpha]_D^{20}$ +6·8° in ether, gave l-β-*thiol*-n-*pentane*, b. p. 112°, $[\alpha]_D^{20}$ −4·66° in ether; d-β-*thiol*-n-*pentane*, $[\alpha]_D^{20}$ +7·92° in ether, yielded l-n-*pentane*-β-*sulphonic acid*, −3·25° (*barium* salt, $[\alpha]_D^{20}$ −2·51°). d-cyclo*Hexylphenylcarbinol* has $[\alpha]_D^{20}$ +37·6° in ether; l-cyclo*hexylphenylcarbinol*, $[\alpha]_D$ −21·4° in ether, gave, with thionyl chloride, *chloro*-l-cyclo*hexylphenylmethane*, b. p. 105—107°/0·7 mm., $[\alpha]_D^{20}$ −29·4° in ether, and, with phosphorus pentachloride, the same compound, b. p. 112—113°/1·3 mm., $[\alpha]_D^{20}$ −3·43° in ether; d-cyclo*hexylphenylmethyl mercaptan*, $[\alpha]_D$ +27·7° in ether, yields d-cyclo*hexylphenylmethylsulphonic acid*, $[\alpha]^{20}$ +4·79° (*potassium* salt, $[\alpha]_D^{20}$ +4·10°). d-α-*Naphthylethyl alcohol*, $[\alpha]^{20}$ +11·06° in ether, gave, with thionyl chloride, l-α-*naphthylethyl chloride*, $[\alpha]_D^{20}$ −36·4° in ether, whilst l-α-*naphthylethyl alcohol*, $[\alpha]_D^{20}$ −35·2° in alcohol, gave, with phosphorus pentachloride, d-α-*naphthylethyl chloride*, $[\alpha]_D^{20}$ +5·42° in ether; the *l*-chloride, $[\alpha]_D^{20}$ −12·1°, gave d-α-*naphthylethyl mercaptan*, $[\alpha]_D^{20}$ +9·2°; the l-*mercaptan*, $[\alpha]^{20}$ −24·8° in ether, gave l-α-*naphthylethylsulphonic acid*, $[\alpha]_D^{20}$ −66·9°. d-α-cyclo*Hexylethyl alcohol*, $[\alpha]_D^{20}$ +7·40° in ether, gave, with phosphorus pentachloride, l-α-cyclo*hexylethyl chloride*, b. p. 70—72°/16 mm., $[\alpha]_D^{20}$ −5·02° in ether; the d-*chloride*, $[\alpha]_D^{20}$ +3·83°, gave *l*-α-cyclo*hexylethyl mercaptan*, $[\alpha]_D^{20}$ −3·60° in ether, which yielded d-α-cyclo*hexylethylsulphonic acid*, $[\alpha]^{20}$ +9·1° (*potassium* salt, $[\alpha]_D$ +7·4°). d-α-cyclo*Hexyl*-n-*propyl alcohol*, $[\alpha]_D^{20}$ +8·95° in ether, gave, with phosphorus pentachloride, l-α-cyclo*hexyl*-n-*propyl chloride*, b. p. 88—93°/16 mm., $[\alpha]_D^{20}$ −1·20° in ether, and, with thionyl chloride, the same compound, $[\alpha]_D^{20}$ −2·97°; this gave d-α-cyclo*hexyl*-n-*propyl mercaptan*, b. p. 95—100°/16 mm., $[\alpha]_D^{20}$ +0·64°, which yielded d-α-cyclo*hexyl*-n-*propylsulphonic acid*, $[\alpha]_D^{20}$ +2·97° (*barium* salt, $[\alpha]_D^{20}$ +1·79°). C. R. Harington.

Molecular migrations. [Mme.] P. Ramart and [Mlle.] P. Amagat (Ann. chim., 1927, [x], 8, 263—328; cf. A., 1926, 710; 1927, 241).—A large number of primary alcohols of the types $CHArR{\cdot}CH_2{\cdot}OH$ (I), $CHAr_2{\cdot}CH_2{\cdot}OH$ (II), and $CAr_2R{\cdot}CH_2{\cdot}OH$ (III) have been prepared and the action of dehydrating agents

on them has been investigated. In case (I) the corresponding amides were first prepared by hydrolysis of the alkylated benzyl cyanide with either 85% sulphuric acid or concentrated alcoholic potassium hydroxide and thus are obtained *α-phenyl-γ-methyl-*n*-valeramide*, b. p. 195—196°/15 mm., m. p. 80—82° (*acid*, m. p. 75°, b. p. 178—180°/30 mm.); *α-phenyl-Δ^γ-pentenamide*, m. p. 60°. In cases II and III the benzyl esters of the corresponding acids (obtained by alkylation of the diarylacetic esters) were first prepared by the silver salt method and thus are obtained *benzyl α-phenyl-α-tolylacetate*, b. p. 252°/12 mm.; *benzyl α-phenyl-α-*p*-anisylacetate*, m. p. 68—69°, b. p. 275—280°/20 mm.; *α-phenyl-α-tolylpropionic acid*, m. p. 128—129° (*amide*, m. p. 85—86°; *benzyl* ester, b. p. 252°/12 mm.); *benzyl α-phenyl-α-tolyl-Δ^γ-pentenoate*, b. p. 252°/10 mm. (*acid*, m. p. 91°); *benzyl αβ-diphenyl-α-*p*-tolylpropionate*, m. p. 83—84°, b. p. 255°/5 mm. (*acid*, m. p. 145—146°). When reduced with sodium and boiling alcohol with the addition of toluene these amides or esters yield the corresponding primary alcohols, the reaction being accompanied by a secondary reaction which results in the formation of the amine or the saturated hydrocarbon, and thus are obtained α-phenylethyl alcohol (*benzoate*, b. p. 198—200°/20 mm.) together with α-phenylpropylamine; β-phenyl-*n*-butyl alcohol (*benzoate*, b. p. 202—203°/18 mm.; *phenylurethane*, m. p. 58—59°), together with β-phenyl-*n*-butylamine (chloroplatinate); β-phenyl-γ-methylbutyl alcohol (*benzoate*, b. p. 212°/22 mm.; *phenylurethane*, m. p. 70°), together with *β-phenyl-γ-methylbutylamine*, b. p. 155—156°/24 mm. (*chloroplatinate*); *β-phenyl-δ-methyl-*n*-amyl alcohol*, b. p. 138—139°/14 mm. (*phenylurethane*, m. p. 78°); *β-phenyl-Δ^δ-penten-α-ol*, b. p. 130—135°/15 mm. (*phenylurethane*, m. p. 78°); βγ-diphenylpropyl alcohol (*phenylurethane*, m. p. 92—93°); *ββ-diphenylethyl alcohol*, m. p. 62°, b. p. 190—195°/20 mm. (*phenylurethane*, m. p. 138—139°; *benzoate*, m. p. 90—91°); *β-phenyl-β-*p*-tolylethyl alcohol*, m. p. 45—46°, b. p. 192—193°/12 mm. (*phenylurethane*, m. p. 79—80°); ββ-diphenylpropyl alcohol (*phenylurethane*, m. p. 148—149°; *benzoate*, m. p. 94—95°). β-Phenyl-β-tolylpropyl alcohol and βγ-diphenyl-β-tolylpropyl alcohol could only be obtained contaminated with the saturated hydrocarbon, from which they cannot be separated by distillation. Dehydration of the carbinols of type I was effected by passing the vapour of the alcohol over infusorial earth as a catalyst at 300—400°, the mixture of ethylenic hydrocarbons obtained being identified by conversion into their crystalline dibromides and by oxidation with chromic oxide in acetic acid, the various isomerides being synthesised for purposes of comparison. In this class of carbinols dehydration occurs mainly in accordance with the scheme $CHArR{\cdot}CH_2{\cdot}OH \longrightarrow CHAr{:}CHR$ (A) and only slightly in the direction $CHArR{\cdot}CH_2{\cdot}OH \longrightarrow CArR.CH_2$ (B), the amount of the hydrocarbon B produced decreasing as the mol. wt. of the alkyl radical increases, so that in the case of βγ-diphenylpropyl alcohol the product consists almost entirely of αγ-diphenyl-Δ^α-propene (*dibromide*, m. p. 112°). Dehydration of the diaryl alcohols (II) was effected by heating with phosphoric oxide in benzene. Migration of an aryl radical occurs in each case, ββ-diphenylethyl alcohol yielding stilbene and β-phenyl-β-tolylethyl alcohol yielding *ω-tolylstyrene*, m. p. 119—120°, b. p. 175—180°, as the sole products. In the dehydration of the diarylalkyl alcohols (III) by phosphoric oxide migration of the phenyl group always occurs.

J. W. BAKER.

Amino-substituted tetraphenylethylenes, benzpinacols, and benzpinacolins. W. MADELUNG and M. OBERWEGNER (Ber., 1927, 60, [*B*], 2469—2491; cf. A., 1925, i, 1459).—Criticism is directed against the proposals of Wizinger and Fontaine (A., 1927, 764). It appears inadvisable simply to re-name Witt's chromophors and to contrast them as negative auxochromes or antiauxochromes with the positive auxochromes previously termed simply auxochromes. Further, the co-ordinatively unsaturated, electrically charged central atom of a coloured ion cannot be regarded as a chromophor, since there is no evidence that the electronic vibrations which may be regarded as responsible for selective absorption are exclusively or predominatingly proper to the central atom. Selective absorption is observed whenever a sufficient number of carbon atoms of co-ordination 3 or nitrogen atoms of co-ordination 2 form a continuous open chain or ring; a single atom cannot therefore be regarded as a chromophor, but rather a sequence of such atoms. In the triphenylmethane series, the whole triphenylmethyl residue and not the central carbon atom is to be regarded as chromophor.

Benzpinacol dissolved in benzene or carbon tetrachloride is converted by hydrogen chloride into *s*-tetraphenylethylene chloride; under similar conditions hydrogen bromide affords tetraphenylethylene and bromine.

Octamethyltetra-aminotetraphenylethylene, m. p. 318° after softening at 312°, is converted by saturation of its solution in benzene with hydrogen chloride into the colourless *tetrahydrochloride*, $C_{34}H_{40}N_4,4HCl$, immediately hydrolysed by water to the ethylene; the corresponding *tetraperchlorate*, *tetramethiodide*, and tetramethoperchlorate are described. The base adds acid chlorides in benzene solutions, giving the *compounds* $C_{34}H_{40}N_4,4AcCl$ and $C_{34}H_{40}N_4,2COCl_2$. Symmetrical coloured salts are produced by the action of oxidising agents on the ethylene under conditions such that an anion of the salt is produced from the oxidising agent; they are quantitatively reconverted into the ethylene by alkalis, ammonia, alkali cyanide, sulphite, or sulphide, or by reducing agents. Thus chlorine gives the dichloride (cf. Wizinger, *loc. cit.*), whereas ferric chloride in glacial acetic acid affords the double *salt*, $C_{34}H_{40}N_4Cl_2,2FeCl_3$. The *dibromide* and *di-iodide* are described; with excess of halogen the perbromide or periodide is produced. Nitrogen peroxide gives the *dinitrite*, whilst potassium ferricyanide in acetic acid solution affords the *ferrocyanide*; the *disulphate* and *dibenzoate* are obtained by means of potassium persulphate and benzoyl peroxide, respectively, and the *diperchlorate* by addition of the acid to a solution of the ethylene oxidised by sodium nitrite.

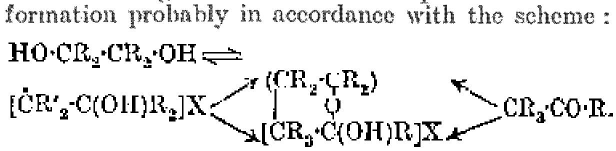
The resistance of benzpinacols to the exchange of two hydroxyl groups for ionic residues is remarkable. Octamethyltetra-aminobenzpinacol in acetic acid and

in mineral acid if not used in excess readily yields coloured monoacidic salts, whereas tetramethyldiaminobenzpinacol is stable in acetic acid and the solutions contain normal di- or tetra-acid salts such as *tetramethyldiaminobenzpinacol dihydrochloride*. With octamethyltetra-aminobenzpinacol, hydrogen chloride and carbonyl chloride afford the additive *compounds*, $C_{34}H_{42}O_2N_4,4HCl$ and $C_{34}H_{42}O_2N_4,2COCl_2$. With phosphorus chlorides or highly concentrated acids dye salts are produced which readily lose their colour owing to formation of pinacolins; nuclear substitution is not thereby observed.

Reconversion of the symmetrical coloured salts into ethylenes can frequently be effected simply by heating; thus octamethyltetra-aminotetraphenylethylene dichloride is converted into the base at 120°, nuclear substitution not being observed. Similarly, in hot concentrated hydrochloric acid the salt is gradually decomposed into the ethylene hydrochloride, whereas the corresponding tetramethyldiamino-derivative affords mainly the pinacolin which in both cases is produced exclusively in concentrated sulphuric acid. Although it appears impossible to oxidise the aminated tetraphenylethylenes to benzpinacols through their coloured salts, this can be effected readily by treatment with permanganate in acetone solution.

Unsymmetrically constituted coloured salts can be obtained from octamethyltetra-aminotetraphenylethylene by the use of less than 4 mols. of mineral acid, but their isolation as individuals has not been accomplished. The *compound* $[(NMe_2{\cdot}C_6H_4)_2C{\cdot}C(OH)(C_6H_4{\cdot}NMe_2)_2]ClO_4$, obtained by the regulated addition of ammonia to an alcoholic solution of the colourless tetraperchlorate, behaves as a coloured salt of the di- or tri-phenylmethane series and has high electrical conductivity. Alkalis convert it into the pinacol, whilst with potassium cyanide it affords the *cyanohydrin*, $C_{35}H_{41}ON_5$, m. p. 229°, and with ammonia the *amino-alcohol*, $C_{34}H_{43}ON_5$. If, however, the temperature is somewhat raised during these reactions, octamethyltetra-aminobenzpinacolin is produced. The formation of pinacolin is also observed when the pinacol is boiled with absolute alcohol in the absence of acids, a coloured base appearing to be produced. Similarly, production of pinacolin occurs when the coloured salt is treated with boiling aqueous alcohol (but not with absolute alcohol) in the absence of alkali; the reaction is greatly facilitated by sodium acetate. The observations are considered to give experimental support to Meerwein's theory of the pinacolin transformation.

Octamethyltetra-aminobenzpinacolin is converted by treatment with boiling glacial acetic acid or with alcohol containing not more than 1 mol. of mineral acid into the monoacid coloured salt of the pinacol, thus realising a "direct" retro-pinacolin transformation probably in accordance with the scheme:



The initially colourless solution of octamethyltetra-aminobenzpinacolin in glacial acetic acid gradually becomes violet when preserved, a similar change being observed when the absolute-alcoholic solution of the blue pinacol monoperchlorate is boiled during several hours; the solution then contains the perchlorate of crystal-violet and dimethylaminobenzaldehyde in addition to unchanged pinacol salt. Tetramethyldiaminobenzpinacol appears to undergo similar fission with production of malachite-green in boiling glacial acetic acid or alcohol containing a little perchloric acid.

Tetramethyldiaminobenzpinacol is converted by very protracted treatment with boiling alcohol into *tetrabenzoylmethyldiaminotriphenylmethane*, m. p. 221° (*hydrochloride*), the constitution of which is established by its fission by alcoholic potassium hydroxide into benzoic acid and leuco-malachite-green. If, however, the solution of the pinacol in concentrated sulphuric acid is preserved or, preferably, heated at 100° the isomeric *p*-dimethylaminobenzoyldimethylaminotriphenylmethane, m. p. 255—256°, is produced; it converted by alkali into *p*-dimethylaminobenzoic acid and *p*-dimethylaminotriphenylmethane. H. WREN.

Photochemical reaction between bromine and cinnamic acid or stilbene. II. R. PURKAYASTHA and J. C. GHOSH (J. Indian Chem. Soc., 1927, 4, 409—422; cf. A., 1926, 366).—The photobromination of cinnamic acid and stilbene has been studied in carbon tetrachloride and carbon disulphide solutions in blue and green light, and it is found that the value of the unimolecular velocity coefficient diminishes regularly with increase of time. The velocity coefficient varies as the square root of the intensity of incident radiation for blue light, but the increase is greater for green light. The rate of reaction depends on the concentration of the cinnamic acid and stilbene. The temperature coefficient of the reaction between cinnamic acid and bromine increases with the wave-length of the light. The number of mols. of cinnamic acid transformed per quantum of light absorbed varies from 22 (533 $\mu\mu$) to 43 (488 $\mu\mu$) in carbon tetrachloride solution and from 101 to 156 in carbon disulphide. For stilbene, the values are 16 to 34 in carbon tetrachloride and 52 to 99 in carbon disulphide. The molecular extinction coefficient of bromine in carbon disulphide solution for different wave-lengths is 1·5—2 times as great as in carbon tetrachloride. H. BURTON.

Catalytic hydrogenations with platinum oxide. II. Mechanism of the process. F. DIAZ AGUIRRECHE (Anal. Fís. Quím., 1927, 25, 411—420; cf. A., 1927, 1188).—Examination of the course of hydrogenation of salicylic acid and phthalic anhydride in presence of platinum oxide shows that after an induction period the velocity rises to a maximum as the platinum oxide is reduced, and then falls slowly as the reaction proceeds. The platinum is actually found in colloidal form at the end of the reaction in decahydronaphthalene.

The great activity of colloidal noble metals is illustrated by measurements of the decomposition of hydrogen peroxide in the presence of colloidal gold, and compared with the smaller activity in the presence of a protective colloid.

In acetic acid the reduction of the platinum oxide is rapid, but the catalyst is soon fatigued. In decahydronaphthalene the reduction is slower and the activity lasts longer. In alcohol the behaviour is intermediate. This is consistent with an influence by the solvent, among other factors, on the formation of finely-divided platinum, followed by coagulation. The results are closely analogous to those obtained in catalysis with colloidal solutions (Madinaveitia and Aguirreche, A., 1921, ii, 390), when a maximum activity precedes coagulation, and are related to observations of the change of physical state of catalysts, demonstrating the close connexion between the change of state and catalytic activity.

The reactivation of platinum catalysts by oxygen is discussed and the literature reviewed. Reactivation is regarded as a superficial oxidation, followed by reduction, producing change in the surface or state of subdivision of the catalyst.

R. K. CALLOW.

Isomeric derivatives of α- and β-naphthoic acids obtained by catalytic hydrogenation. J. RANEDO and A. LEÓN (Anal. Fis. Quim., 1927, 25, 421—433).—Hydrogenation was carried out in presence of platinum oxide. α-Naphthoic acid gave Δ^1-dihydro-α-naphthoic acid (*chloride*, b. p. 206°/64 mm.; *amide*, m. p. 186°), and *Δ^3-dihydro-α-naphthoic acid*, m. p. 138° (*chloride*, b. p. 205—206°/64 mm.; *amide*, m. p. 200°). Further hydrogenation gave *ar*-tetrahydro-α-naphthoic acid, m. p. 134—135° (*amide*, m. p. 176—177°), and (?)-*tetrahydro-α-naphthoic acid*, m. p. 146° (*chloride*, b. p. 190°/55 mm.; *amide*, m. p. 181—182°). Complete hydrogenation of α-naphthoic acid or of *ac*-tetrahydro-α-naphthoic acid (*chloride*, b. p. 182—183°/50 mm.; *amide*, m. p. 165°) gave *decahydro-α-naphthoic acid*, m. p. 127° (*chloride*, b. p. 200°/120 mm.; *amide*, m. p. 198—199°). β-Naphthoic acid gave decahydro-β-naphthoic acid, m. p. 76—79° (*chloride*, b. p. 210°/180 mm.; *amide*, m. p. 145°). The calcium, strontium, and barium salts are soluble, with the exception of the *calcium* salt of *decahydro-α-naphthoic acid*. The dihydro- and tetrahydro-acids, but not the decahydro-acids, give an intense red coloration in sulphuric acid on the addition of a drop of nitric acid.

R. K. CALLOW.

Intermediate products for dyes [derivatives of β-naphthylthioglycollyl chloride]. SOC. CHEM. IND. IN BASLE.—See B., 1928, 8.

Derivatives of methyl 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylate. C. S. GIBSON, K. V. HARIHARAN, and J. L. SIMONSEN (J.C.S., 1927, 3009—3015).—An improved method for the preparation of 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylic acid (J.C.S., 1904, **85**, 138) is described. The *methyl* ester, b. p. 158°/100 mm., yields, on bromination in acetic acid solution, a dibromo-ester regarded as *methyl* 4 : 4-*dibromo*-2 : 2-*dimethyl*cyclo*pentan*-3-*one*-1-*carboxylate*, m. p. 76—77°. This ester, on treatment with barium hydroxide, yields 4-*hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid* (I), m. p. 150—152° (slight decomp.) (*acetyl* derivative), oxidised by dilute nitric acid to dimethylmalonic and oxalic acids, and 4-*hydroxy*-2 : 2-*dimethyl*-Δ^4-cyclo*penten*-3-*one*-1-*carboxylic acid* (II), an oil, oxidised by nitric acid to *as*-dimethylsuccinic acid. On treatment with semicarbazide acetate or with *o*-phenylenediamine, the hydroxy-acid (I) reacts as the tautomeric diketo-acid, yielding respectively the *disemicarbazone* of 2 : 2-*dimethyl*cyclo*pentane*-3 : 4-*dione*-1-*carboxylic acid*, decomp. 200—201°, and a *quinoxaline* derivative, m. p. 175—177°, alternatively obtained from the acid (II). When the compound (I) is distilled under reduced pressure, a small quantity of an oil, probably 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione*, b. p. 80—100°/4 mm., is obtained together with unchanged starting material. The following are described: *ethyl* βγ-*dicyano*-β-*methylpentane*-γε-*dicarboxylate*, b. p. 184°/5 mm.; *ethyl* 3 : 3-*dimethyl*cyclo*pentan*-2-*one*-1 : 4-*dicarboxylate*, b. p. 145°/4 mm.

M. CLARK.

Preparation of phenyl salicylate. F. CHEMNITIUS (Pharm. Zentr., 1927, 68, 795—797).—The details of a laboratory preparation from phenol and salicylic acid, in presence of phosphoryl chloride, are given.

S. I. LEVY.

Action of iodine in alkaline media on phenyl*iso*crotonic acid: some new mixed anhydride derivatives of benzoylacrylic acid. E. CATTELAIN (Bull. Soc. chim., 1927, [iv] **41**, 1500—1507; cf. A., 1927, 458).—For the preparation of mixed anhydride derivatives of benzoylacrylic acid by Bougault's method (A., 1908, i, 791, 983) the organic acid must be sparingly soluble in water. Thus, *o*-aminobenzoic acid gives no mixed anhydride, and β-phenylpropionic acid (solubility, 1 part in 168 parts) gives poor yields. Acids of high mol. wt., such as *o*-benzoylbenzoic acid or *o*-benzoyl-*p*-toluic acid, give no mixed anhydride or only indifferent yields. The purity of the acid is important; traces of salicylic acid in *o*-methoxybenzoic acid prevent the formation of the mixed anhydride; the presence of *m*-hydroxybenzoic acid in *m*-methoxybenzoic acid, or of cinnamic acid in hydrocinnamic acid, acts similarly. The iodine is added gradually to avoid the formation of the iodolactone of phenyl*iso*crotonic acid. The following *mixed anhydrides* of benzoylacrylic acid are new: o-*methoxybenzoic*, m. p. 91—92°; m-*methoxybenzoic*, m. p. 104°; o-*chlorobenzoic*, m. p. 106°; m-*chlorobenzoic*, m. p. 112°; o-*bromobenzoic*, m. p. 110°; p-*bromobenzoic*, m. p. 138°; o-*iodobenzoic*, m. p. 103°, m-*iodobenzoic*, m. p. 126°, and p-*iodobenzoic*, m. p. 163°; β-*phenylpropionic*.

R. BRIGHTMAN.

Preparation of *m*-iodobenzoic acid. Purification of *o*-iodobenzoic acid. E. CATTELAIN (Bull. Soc. chim., 1927, [iv], **41**, 1546—1548).—*m*-Iodobenzoic acid is obtained pure, m. p. 186·5°, by decomposing diazotised *m*-aminobenzoic acid with potassium iodide in 20% sulphuric acid; *o*-iodobenzoic acid obtained by the same method requires purification by crystallisation from 50% alcohol; the cumbersome purification method of Cohen and Raper is unnecessary.

R. BRIGHTMAN.

Action of carbon tetrachloride on certain mercaptans. S. KRISHNA and S. SINGH (J. Indian Chem. Soc., 1927, **4**, 291—296).—Thiophenol when heated with carbon tetrachloride in presence of

potassium hydroxide solution at 100—110° for 24 hrs., yields *o*-thiolbenzoic acid (12%), m. p. 177° (lit. 165°). *p*-Chlorothiophenol, under similar conditions, yields 4 : 4′-*dichloro*-6′(?)-*carboxydiphenyl disulphide*, m. p. 210—212°, which when reduced with zinc and hydrochloric acid gives *p*-chlorothiophenol and 5-*chloro*-o(?)-*thiolbenzoic acid*, m. p. 110°. 2 : 2′ : 5 : 5′-*Tetrachloro*-6′(?)-*carboxydiphenyl disulphide*, m. p. 176°, is obtained from 2 : 5-dichlorothiophenol, and on careful reduction with zinc dust and acetic acid yields 3 : 6-*dichloro*-o(?)-*thiolbenzoic acid*, m. p. 122°. *p*-Tolylmercaptan, *p*-nitrothiophenol, and *p*-bromothiophenol yield 4 : 4′-*dimethyl*-3′(?)-*carboxydiphenyl disulphide*, m. p. 156°, 4 : 4′-*diamino*-3′(?)-*carboxydiphenyl disulphide dihydrochloride*, chars at 280°, and 4 : 4′-*dibromo*-6′(?)-*carboxydiphenyl disulphide*, m. p. 241—242°, which on reduction furnish 6-*methyl*-m(?)-*thiolbenzoic acid*, m. p. 82°, 6-*amino*-m(?)-*thiolbenzoic acid hydrochloride*, and 6-*bromo*-m(?)-*thiolbenzoic acid* [5-*bromo*-o(?)-*thiolbenzoic acid* (?)], m. p. 210°, respectively.

H. BURTON.

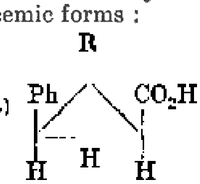
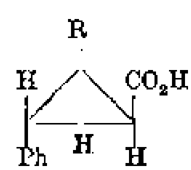
Relative ease of formation of rings. I. J. VON BRAUN, O. BAYER, and L. CASSEL (Ber., 1927, **60**, [*B*], 2602—2609).—The comparison is based on the exclusive or predominating formation of one ring from a compound from which two similar ring closures are theoretically possible. It is essential that the active groups should be identical.

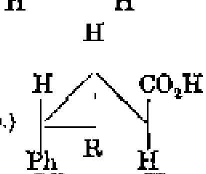
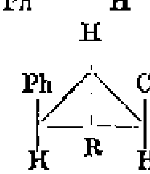
p-Benzylphenol is very readily reduced by hydrogen at somewhat above 200° under pressure in the presence of nickel to 4-*benzyl*cyclo*hexanol* (mixture of two stereoisomerides), b. p. 171°/14 mm. (*phenylurethane*, m. p. 154—157°), oxidised by chromic acid in glacial acetic acid to 4-*benzyl*cyclo*hexanone*, b. p. 165—166°/14 mm., m. p. 46—47° (*semicarbazone*, m. p. 145—147°). 4-*Hexahydrobenzyl*cyclo*hexanol*, b. p. 158°/14 mm. (*phenylurethane*, m. p. 153—155°), similarly prepared from 4-benzyl-phenol or -*cyclo*-hexanol, is oxidised to 4-*hexahydrobenzyl*cyclo*hexanone*, b. p. 155°/14 mm. Oxidation of 4-benzyl*cyclo*hexanol by very dilute, alkaline permanganate at 0° gives β-*benzyladipic acid*, m. p. 110—111° (*anhydride*, b. p. 245—250°/16 mm., m. p. about 90°; *ethyl* ester, b. p. 220°/14 mm.); at higher temperatures, β-benzylglutaric acid is mainly produced. β-Benzyladipic acid is converted by successive treatment with phosphorus pentachloride in nitrobenzene and aluminium chloride into β-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-3-*propionic acid*, m. p. 136—137°, in 55% yield; the corresponding *semicarbazone*, m. p. 260°, *oxime*, m. p. 148°, and *phenylhydrazone*, m. p. 152°, are described. Reduction by Clemmensen's method converts the ketonic acid into β-1 : 2 : 3 : 4-*tetrahydronaphthyl*-2-*propionic acid*, b. p. 73° (*ethyl* ester, b. p. 188—190°/14 mm., d_4^{22} 1·040, n_D^{22} 1·5153; *amide*, m. p. 130°). Naphthalene is formed when the ethyl ester is passed over heated lead oxide–pumice in an atmosphere of carbon dioxide. The four-membered carbon chain is therefore more readily attached to the benzene nucleus as a ring than the five-membered.

βγ-Diphenylpropylamine, b. p. 182°/18 mm., is obtained in poor yield by the reduction of α-phenylcinnamonitrile with sodium and alcohol, in 60% yield (accompanied by small amounts of the corresponding secondary *amine*, b. p. about 282°/18 mm.) by treatment with hydrogen in the presence of nickel at about 210°, preferably in the absence of solvent; its *benzoyl* derivative, b. p. about 280°/11 mm., is converted by phosphorus pentachloride into benzonitrile and βγ-*diphenylpropyl chloride*, b. p. 150°/11 mm. The base is converted by treatment with ethyl bromoacetate and hydrolysis of the ester thus produced followed by the action of *p*-toluenesulphonyl chloride on the portion soluble in alkali hydroxide into N-p-*toluenesulphonyl*-βγ-*diphenylpropylaminoacetic acid*, m. p. 135° (the corresponding *benzenesulphonyl* derivative is non-crystalline). Ring closure is effected by treating the glycine derivative with phosphoric oxide in boiling xylene, whereby carbon monoxide and 2-p-*toluenesulphonyl*-4-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 158—160°, are produced in almost 100% yield. The sulphonyl compound is hydrolysed by hydrochloric acid at 160° to 4-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, b. p. 204—205°/15 mm., m. p. 49—50° (*hydrochloride*, m. p. 155°; *picrate*, m. p. 150°; non-crystalline *acetyl* derivative; *nitroso*-compound, m. p. 100°; *phenylthiocarbamide*, m. p. 166°; quaternary *methiodide*, m. p. 186°). Dehydrogenation to 4-benzyl*iso*quinoline, m. p. 119°, is effected by reduced nickel. The tendency towards the formation of the tetrahydro*iso*quinoline ring is therefore greater than that towards the homotetrahydro*iso*quinoline complex.

H. WREN.

Degradation of truxillic and truxinic acids. XIII. R. STOERMER and F. SCHENCK [in part, with E. PANSEGRAU] (Ber., 1927, **60**, [*B*], 2566—2591).—Revision of the attempted decarboxylation of a truxillic acid to a diphenyl*cyclo*butanemonocarboxylic acid (Stoermer and Schmidt, A., 1926, 290) has been rendered necessary by the observation that four different anhydrides of *cis*-hydroxy-acids can be derived from a single truxillic acid, whereas only three such compounds are theoretically derivable from hydroxydiphenyl*cyclo*butanemonocarboxylic acids. An explanation is found in the contraction of the ring during the replacement of the amino- by the hydroxyl group in the aminodiphenyl*cyclo*butanemonocarboxylic acids so that these acids are phenyl-α-hydroxybenzyl*cyclo*propanecarboxylic acids. Since they contain four dissimilar asymmetric carbon atoms they exist theoretically in four pairs of racemic forms :

(I *a*, *b*.)   (II *a*, *b*.)

(III *a*, *b*.)   (IV *a*, *b*.)

(R=Ph·CH·OH), the isomerism within each pair being due to the spatial arrangement around the

carbinol carbon atom. If the isomerism in this position is destroyed, four keto-acids (R=PhCO·) are produced. The constitution of the ketonic acids is established by the identity of two of them with the acids obtained in a completely different manner by Kohler (A., 1917, i, 566, 568; 1919, i, 530) and by the isolation from them of compounds in which the phenyl groups are separated from one another by a chain of four carbon atoms and not by two or three as in the *cyclo*butane formulation of the truxinic and truxillic acids. The configuration of the hydroxy-acids is tentatively based on that of the corresponding truxillic and truxinic acids on the supposition that if the phenyl and carboxyl groups maintain their relative positions after the action of nitrous acid it is possible that they also do so, at any rate as far as the main products of the change are concerned, when the ring contracts.

Degradation of γ-truxillic acid. γ-Truxillamic acid is converted by sodium hypochlorite at 35—37° into *3^c-amino-2^c : 4^t-diphenyl*cyclo*butane-1^c-carboxylic acid*, decomp. 195—196° (*trihydrate*; *methyl* ester, m. p. 83·5—84°; *monoacetyl* derivative, m. p. 236—237°). The action of nitrosyl bromide on the amino-acid yields small amounts of diphenylbutadiene tetrabromide and a mixture of lactones (see later), mainly *2^c-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylactone* (cf. I*a*), m. p. 133·5—134°, obtained also by Barbels (Diss., Rostock, 1924) from α-truxillamic acid. When distilled in a vacuum the lactone yields *trans-trans*-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene. With piperidine at 160—170° it affords the *piperidide* of the corresponding hydroxy-acid, m. p. 162·5—163°, whilst it is transformed by boiling alcoholic potassium hydroxide into *2^c-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylic acid* (I*a*), m. p. 145—146° (decomp.) when rapidly heated (*methyl* ester, m. p. 124—125°, prepared by means of diazomethane). The latter ester is oxidised by an excess of chromium trioxide in glacial acetic acid to *methyl 3^c-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylate* (cf. I), m. p. 115—116°, which is stable towards Fehling's solution and ammoniacal silver solution, moderately stable to alkaline permanganate and bromine in chloroform; the corresponding *oxime*, m. p. 201—202°, and *semicarbazone*, m. p. 253—255°, are described. Hydrolysis of the ester by acids affords *3^c-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylic acid*, m. p. 157—157·5°, isomerised by alcoholic potassium hydroxide to 3^t-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylic acid (see later), and reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid. The isomeric *2^c-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylactone* (cf. I*b*), m. p. about 167°, is obtained in very small amount from the mixture of lactones described above; the corresponding hydroxy-acid (I*b*) could not be investigated completely but its oxidation to the ketonic acid I is established.

*Phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylactone*, m. p. 120—121° (cf. II*a*), is most readily separated from lactone I*a* by isomerisation of the latter to the hydroxy-acid II*a* by alkali and preservation of the acidified mixture in which the lactone II*a* is slowly regenerated. Unlike lactone I*a* it can be distilled unchanged in a vacuum. It is hydrolysed to *2^t-phenyl-3^c-hydroxylbenzyl*cyclo*propane-1^c-carboxylic acid* (II*a*), m. p. 122° (decomp.) (*methyl* ester, m. p. 73—74°; *piperidide*, m. p. 132—133°). The methyl ester is oxidised to *methyl 3^c-benzoyl-2^t-phenyl*cyclo*propane-1-carboxylate*, m. p. 93°, hydrolysed by acids to 3^c-benzoyl-2^t-phenyl*cyclo*propane-1^c-carboxylic acid, m. p. 174—175° (ethyl ester, m. p. 103°), identical with the product described by Kohler and Steele (*loc. cit.*). The isomeric *2^t-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylic acid* (II*b*), m. p. 170° (decomp.) when rapidly heated (*methyl* ester, m. p. 86—87°), is identical with the compound obtained by Stoermer and Schmidt (*loc. cit.*) from ε-truxillamic acid and regarded as hydroxydiphenyl*cyclo*butanecarboxylic acid; the corresponding *lactone*, m. p. 112°, is obtained by the action of acetic anhydride on the acid and also from β-truxinic acid (see later). *2^t-Phenyl-3^t-hydroxybenzyl*cyclo*propane-1^c-carboxylic acid* (III*a*), decomp. 185—186°, is obtained by isomerisation of lactone I*a* by very concentrated alcoholic potassium hydroxide or from α-truxillamic acid through the corresponding amino-acid; the *methyl* ester, m. p. 75—76°, and the *potassium* salt are described. It is oxidised to 3^t-benzoyl-2^t-phenyl*cyclo*propane-1^c-carboxylic acid, m. p. 153—154° (*methyl* ester, m. p. 66—67°; ethyl ester, m. p. 93—94°), identified with the compound described by Kohler (*loc. cit.*); the keto-acid is reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid, whereas the ethyl ester is converted by zinc dust and boiling acetic acid into a mixture of α-phenacyl-β-phenylpropionic and γ-benzoyl-β-phenyl-*n*-butyric acids.

Methyl 3^c-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylate is converted by boiling alcoholic potassium hydroxide into *3^t-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylic acid* (cf. IV), m. p. 136—137° (*methyl* ester, m. p. 66—67·5°; *oxime*, m. p. 166—167°), reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid. *trans-trans-αδ-Diphenyl-$\Delta^{\alpha\gamma}$-butadiene*, m. p. 152—153°, is obtained by the distillation of lactones I*a* and II*b*, by heating the methyl ester of hydroxy-acid I*a*, when the hydroxy-acid III*a* is melted, and during the preparation of its bromo-ester. The non-crystallisable residues obtained during the preparation of lactone I*a* are converted by distillation into *trans-trans*-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene and γ-phenyl-α-benzylidene-*iso*crotonolactone, m. p. 152°. Treatment of methyl 2^c-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylate with phosphorus pentabromide in the presence of ether affords the *compound* $C_{18}H_{17}O_2Br$, m. p. 131—132° [? CHPh:CH·CH(CO_2H)·CHPhBr], hydrolysed by alcoholic potassium hydroxide to α-benzylidene-γ-phenyl*iso*crotonic acid, m. p. 169—170°, and converted by successive reduction by aluminium amalgam and hydrolysis into γ-phenyl-α-benzyl*iso*crotonic acid, m. p. 125—126°. Treatment of the bromo-ester with hydrogen in the presence of palladised barium sulphate affords αδ-diphenylbutane-β-carboxylic acid, m. p. 55—57°.

Degradation of β-truxinic acid. β-Truxinamic acid is converted by sodium hypochlorite solution at 38—40° into *4^c-amino-2^t : 3^t-diphenyl*cyclo*butane-1^c-*

carboxylic acid, m. p. 161° (decomp.) [*hydrochloride*; *hydrobromide*; *sulphate*; *monoacetyl* derivative, m. p. 194°, and its *methyl* ester, m. p. 127—128°; *methyl* ester, m. p. 64°; *compound*, $C_{34}H_{29}O_3N$, m. p. 161°, possibly a mixed anhydride of the amino- and corresponding hydroxy-acid). The amino-acid is transformed by nitrosyl bromide into 2^t-phenyl-3^c-hydroxylbenzy*cyclo*propane-1^c-carboxylactone (cf. II*b*), the corresponding hydroxy-acid (II*b*), and *2-phenyl-3-α-bromobenzyl*cyclo*propanecarboxylic acid*, m. p. 167° (*methyl* ester, m. p. 112°, obtained also from phosphorus pentabromide and the methyl ester of the hydroxy-acid). Reduction of the bromo-acid by zinc dust and acetic acid, hydriodic acid, aluminium, or sodium amalgam or catalytic hydrogenation in the presence of palladised barium sulphate yields the unsaturated *acid*, $C_{17}H_{14}O_2$, m. p. 125—126°. *Methyl 2^t-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylate*, m. p. 86—87°, and *2^t-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylamide*, m. p. 142°, are described.

β-Truxinic anhydride is converted by an excess of hydrazine hydrate at 0° into the *hydrazine* salt of β-truxinhydrazidic acid, hydrolysed by much boiling water to *β-truxinhydrazidic acid*, $C_{18}H_{18}O_3N_2$, m. p. 182° (*sodium* salt; *benzylidene* derivative, $C_{25}H_{22}O_3N_2$, m. p. 214°, and its *methyl* ester, $C_{26}H_{24}O_3N_2$, m. p. 142°). The acid is converted by hot 5% hydrochloric acid into the unimolecular *hydrazide*, $C_{18}H_{16}O_2N_2$, m. p. 106—107° (from which it is regenerated by boiling alkali hydroxide), and (?) a bimolecular, secondary hydrazide, m. p. 250—260°. Attempts to convert the hydrazidic acid into the azidic acid were unsuccessful, resulting apparently in the production of a carbamide *derivative*, $CO(NH{\cdot}C_{16}H_{14}{\cdot}CO_2H)_2$, m. p. 224°. H. WREN.

Photobromination of ethyl *m*-nitrobenzylidenemalonate. I. J. C. GHOSH and K. BASU (J. Indian Chem. Soc., 1927, 4, 375—386).—The photobromination of ethyl *m*-nitrobenzylidenemalonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light, and the ratio of the equilibrium constants measured equals the square root of the ratio of intensities of incident light. The equilibrium constant is slightly affected by temperature, rise of temperature causing an increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentration of ester, bromine, or dibromide. The temperature coefficient of *k* for 10° is 2·4. Application of Einstein's law of photochemical equivalence shows that more than one quantum of energy is necessary for the production of 1 mol. of the dibromide. H. BURTON.

Relation between chemical constitution and pungency in acid amides. S. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 166—184; cf. Jones and Pyman, A., 1926, 60).—The following acid amides have been prepared and their pungencies compared with that of undecenovanillylmethylamide (=1000), m. p. 60—61° (Nelson, A., 1920, i, 154, gives m. p. 53—55°; cf. Ott and Zimmermann, A., 1922, i, 137); undecovanillylmethylamide, m. p. 73—74° (Nelson, *loc. cit.*, gives m. p. 54—56°) (pungency 1000); *undeceno-β-vanillylethylamide*, m. p. 80—81° (O-*benzyl* derivative, m. p. 102—103°), *undeceno-γ-vanillylpropylamide*, m. p. 59—60°, *undecenopiperonylmethylamide*, m. p. 87—88°, and *undeceno-β-piperonylethylamide*, m. p. 81—82°, are all non-pungent. The pungencies of *δ-piperonylvinylacrylovanillylmethylamide*, m. p. 165—167°, and *δ-piperonyl-*n*-valerovanillylmethylamide*, m. p. 90—91°, are both 100, whilst the *piperonylmethylamide*, m. p. 187—189°, and *β-piperonylethylamide*, m. p. 198—200°, of δ-piperonylvinylacrylic acid are non-pungent, thus demonstrating the necessity of a hydroxyl group in the amine residue. Cinnamovanillylmethylamide, m. p. 146—147° (Ott and Zimmermann, *loc. cit.*, give m. p. 138°), *β-phenylpropiovanillylmethylamide*, m. p. 91—92°, and *β-piperonylacrylovanillylmethylamide*, m. p. 189—190°, have pungencies of 50; n-*valerovanillylmethylamide* has a value of 20, and *β-veratrylacrylovanillylmethylamide*, m. p. 145·5—147°, a value of 1. *β-Vanillylacrylobenzylamide*, m. p. 128·5—130° (O-*acetyl* derivative, m. p. 132—134°), *β-vanillylacrylopiperonylmethylamide*, m. p. 161—163° (O-*acetyl* derivative, m. p. 154·5—155·5°), and the *vanillylmethylamides* of β-vanillylacrylic, m. p. 179—181°, 4-hydroxycinnamic, m. p. 192—193°, and β-vanillylpropionic acids, m. p. 128—130°, are all non-pungent. The *carbethoxy*-derivative (*chloride*) of β-4-hydroxy-3-methoxyphenylpropionic acid has m. p. 88—90°.

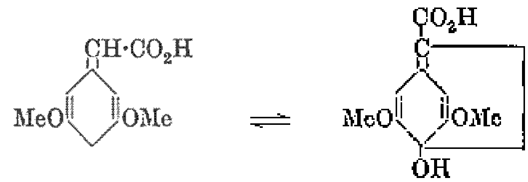
4-Benzyloxy-3-methoxybenzaldehyde condenses with acetaldehyde to form *4-benzyloxy-3-methoxycinnamaldehyde*, m. p. 89—90° (*phenylhydrazone*, m. p. 144—146°). An improved method of preparing 3-methoxy-4-methoxymethoxycinnamaldehyde, m. p. 78—79° (cf. Pauly and Wascher, A., 1923, i, 342), is given. Application of the Perkin reaction to this substance yields *3-methoxy-4-methoxymethoxyphenylvinylacrylic acid*, m. p. 145·5—146·5°, which is hydrolysed by dilute hydrochloric acid to the corresponding *4-hydroxy-acid*, m. p. 193—194° (decomp.) (*carbethoxy*-derivative, m. p. 143—145°). 3 : 4-Methylenedioxybenzylamine (hydrochloride, m. p. 238—239°; cf. A., 1912, i, 217) has b. p. 135—137°/12 mm., and *di-(3 : 4-methylenedioxybenzyl)amine hydrochloride* has m. p. 257—258° (decomp.). H. BURTON.

Double compounds of α-unsaturated acid amides with acid and ammonia. S. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 185—195).—Treatment of a solution of β-*O*-acetylvanillylacrylobenzylamide in acetic acid with concentrated sulphuric acid gives a *compound*, m. p. 147—150°, consisting of 1 mol. of β-vanillylacrylobenzylamide and 1 mol. of sulphuric acid, which on exposure to air loses 0·5 mol. of sulphuric acid forming a *compound*, m. p. 170—173°. β-Vanillylacrylobenzylamide and hydrochloric acid or ammonia yield the additive *compounds*, $C_{17}H_{17}O_3N,HCl$, m. p. 106° (decomp.), and $C_{17}H_{17}O_3N,NH_3$, m. p. 126° (decomp.). The hydrochloric acid *compound* of the *O*-acetyl derivative has m. p. 163° (decomp.). The following additive compounds have been isolated and, except where stated, contain 1 mol. of the amide and

1 mol. of the reagent: β-vanillylacrylopiperonylmethylamide [*sulphuric acid*, $+0{\cdot}5H_2SO_4$, m. p. 201° (decomp.); *hydrochloric acid*, m. p. 134° (decomp.); *ammonia*, m. p. 161—163°; O-*acetyl hydrochloric acid*, m. p. 118—142°]; β-vanillylacrylovanillylmethylamide [*sulphuric acid*, m. p. 161—162° (decomp.); *hydrochloric acid*, m. p. 132° (decomp.)]; β-O-*acetylvanillylacryloanilide*, m. p. 146—147° [*sulphuric acid*, m. p. 138° (decomp.); *hydrochloric acid*, m. p. 107° (decomp.)]; β-*vanillylacryloanilide*, m. p. 141—143° [*sulphuric acid* $+0{\cdot}5H_2SO_4$, m. p. 185° (decomp.); *hydrochloric acid*, m. p. 121° (decomp.); *ammonia*, m. p. 141°]; β-*vanillylacryloamide*, m. p. 150—151° [*ammonia*, m. p. 156°; *sulphuric acid*, m. p. 184° (decomp.); *hydrochloric acid*, m. p. 172° (decomp.)]; δ-piperonylvinylacrylo-β-piperonylethylamide (*sulphuric acid*, m. p. 140—141°, $+0{\cdot}5H_2SO_4$, m. p. 169—170°; *hydrochloric acid*, m. p. 198—200°); δ-piperonylvinylacrylopiperonylmethylamide [*sulphuric acid*, m. p. 142—145° (decomp.); *hydrochloric acid*, m. p. 187—189°]; δ-piperonylvinylacrylovanillylmethylamide [*hydrochloric acid*, m. p. 180° (decomp.)]; *p*-hydroxycinnamamide [*hydrochloric acid*, m. p. 202° (decomp.); *ammonia*, m. p. 188°]; 3 : 4-methylenedioxycinnamamide and cinnamamide yield hydrochloric acid *compounds* having m. p. 178° (decomp.) and 147° (decomp.), respectively. Most of these additive compounds are coloured, and the ammonia additive products generally lose ammonia when heated. H. BURTON.

Perylene and its derivatives. XV. A. PONGRATZ (Monatsh., 1927, **48**, 639—643).—The yield of perylene-3 : 9-dicarboxylic acid is increased to 90% by modifying the conditions of hydrolysis of the dinitrile (cf. A., 1927, 1190). If hydrolysis by heating with concentrated sulphuric acid is attempted, the solution deposits orange-red crystals of 9-*carboxyperylene-4-sulphon-3-carboxylimide*. Similarly, the action of concentrated sulphuric acid on perylene-3 : 9-dicarboxylic acid yields orange-red 9-*carboxyperylene-4-sulpho-3-carboxylic anhydride*. The action of concentrated sulphuric acid followed by manganese dioxide on 3 : 9-dibenzoylperylene yields a vat dye, *hydroxyisoviolanthrone* (cf. Zinke, A., 1925, i, 819; F.P. 612338; B., 1927, 698). E. W. WIGNALL.

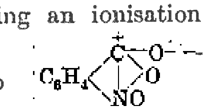
Bios. III. B. SUZUKI and Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1927, **3**, 521—525).—Treatment of crude bios with boiling 30% sodium hydroxide solution and an excess of alcohol yields resinous products, together with "*γ-acid*," $C_{10}H_{10}O_5$, m. p. 187—189° (decomp.) (*benzoyl* derivative, m. p. 216°; *ethyl* ester, m. p. 86°), which is methylated by methyl sulphate to a *methyl-γ-acid*, m. p. 130°, and its *methyl* ester, m. p. 100°. Oxidation of the methylated acid with potassium permanganate furnishes 3 : 4 : 5-*trimethoxybenzoic acid*, m. p. 169°. Ethylation of the acid yields *ethyl-γ-acid*, oxidised by potassium permanganate to 3 : 5-*dimethoxy-4-ethoxybenzoic acid*, m. p. 123°, also obtained by ethylation of syringic acid. Reduction of γ-acid by Willstatter's method affords *dihydro-γ-acid*, m. p. 102°, which yields a *methyl* derivative, m. p. 105° (*dibromo*-derivative, m. p. 122°). The original acid furnishes an *oxime*, decomp. 199—201°, in acid solution only. The acid, which is a colouring matter, is represented as



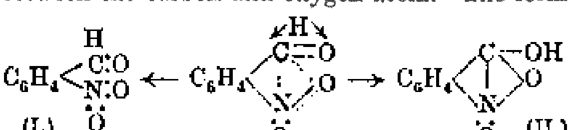
H. BURTON.

Salicylsulphonephthalein and its tetrabromo- and monomercury derivatives. W. C. HARDEN (J. Amer. Chem. Soc., 1927, **49**, 3139—3142).—*Salicylsulphonephthalein*, red, amorphous, is obtained by heating together salicylic acid (50 g.), *o*-sulphobenzoic anhydride (24 g.), sulphuric acid (2 c.c.), and stannic chloride (10 c.c.) at 120—130° for 4 hrs., then at 160—180° for several hrs., and pouring the mass into 4 litres of hot water, purification being effected by repeated dissolution in, and reprecipitation with hydrochloric acid from, aqueous sodium carbonate. It forms an excellent indicator, being yellow at p_H below 6·6, brown at p_H 7·0—7·2, and bluish-red at p_H 8·2. Bromination in hot glacial acetic acid affords a *tetrabromo*-derivative, yellow, amorphous, which is yellow at p_H below 3·2, changing through a brownish-purple to clear purple at p_H 4·6. Colour standards prepared with these indicators showed no appreciable fading after several months' exposure to daylight; the names "salicyl-red" and "salicyl-purple" are suggested. Treatment of the disodium salt of salicylsulphonephthalein in aqueous solution with mercuric acetate and acetic acid, with subsequent boiling until an ammonium sulphide test indicates absence of mercury ion, filtration, and acidification, affords *monohydroxymercurisalicylsulphonephthalein*, a brown powder. In 1% solution, the latter kills *B. typhosus* and *Staph. aureus* in 1 min. At 1 : 2000, it kills the former in 15 min. *S. aureus* is killed at 1 : 500 in 5 min., but not in 15 min. at 1 : 1000. F. G. WILLSON.

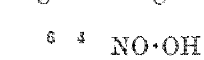
Explanation of the mechanism of isomerisations and spontaneous reactions in organic chemistry with the aid of the theory of polar valencies. I. TANASESCU (Bull. Soc. chim., 1927, [iv], **41**, 1468—1475).—It is suggested that organic molecules which do not form ions in the usual sense can be regarded as virtually divided into atomic groups, consisting either of atoms or radicals which carry equal and opposite electric charges. These electronegative and electropositive radicals represent the first phase in the division of the molecule. They are not necessarily ionised, but can become true ions in certain cases. Groupings in which the polar valencies are not perfectly neutralised are unstable and may undergo transformation into arrangements possessing a more pronounced positive or negative character, and representing the most stable configuration under given conditions. This theory is used to interpret a number of isomerisations effected by light. Thus the isomerisation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid is interpreted

by assuming an ionisation of the *o*-nitrobenzaldehyde into  and H^+ (cf. following abstract). The isomerisation of *o*-nitrobenzylideneglycol and of *o*-nitrotriphenylmethane are similarly interpreted and the theory affords a simple explanation of the absence of photochemical isomerisation with hexanitrotriphenylmethane. Similarly in the isomerisation of *o*-nitro-*p'p''*-diaminotriphenylmethane into *o*-nitroso-*p'p''*-diaminotriphenylcarbinol it is suggested that the unstable ions $[-C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NO_2]^+$ and H^- are first formed which are rapidly transformed into $[-C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NO]^+$ and OH^-, an interpretation which accords with increase of basic properties in the carbonium bases with the accumulation of electropositive groups in the molecule observed by Bayer. Similarly, the stability of the "ions" $[-C(C_6H_4{\cdot}OH)_3]$ (1)(4) and H^+ accounts for the non-existence of the corresponding carbinol. *cis*- and *trans*-Isomerisations and the behaviour of *αγ*-diketones are similarly interpreted. R. BRIGHTMAN.

Tautomerism of *o*-nitrobenzaldehyde. I. TANASESCU (Bull. Soc. chim., 1927, [iv], **41**, 1497—1499).—To account for the existence of a mobile hydrogen atom in *o*-nitrobenzaldehyde, the weak but appreciable acidity, and the readiness with which this substance isomerises in light, it is now suggested (cf. A., 1926, 1247) that the molecule of *o*-nitrobenzaldehyde represents an equilibrium between (I) and (II), determined by oscillation of a hydrogen atom between the carbon and oxygen atom. The formula



(I.) (II.)

(II) allows of a ready interpretation of the formation of arylanthranils by the action of aromatic hydrocarbons in presence of sulphuric acid, and of the appearance of the direct carbon–nitrogen linking in similar reactions. The structure  previously advanced is now abandoned, as it indicates much more pronounced acidic properties than *o*-nitrobenzaldehyde possesses. R. BRIGHTMAN.

Isomerism of the oximes. XXXII. Sulphates. O. L. BRADY and A. D. WHITEHEAD (J.C.S., 1927, 2933—2937).—Treatment of certain α-aldoximes (A) with concentrated sulphuric acid provides a convenient method of conversion into the β-aldoxime (cf. Luxmoore, J.C.S., 1896, **69**, 180) if only small quantities are used. The sulphates of a number of oximes have been prepared and, in general, the α-form of these compounds is more stable than the corresponding hydrochloride. Sulphuric acid did not bring about isomeric change in those oximes (B) the α-hydrochlorides of which fail to change or change with difficulty to the β-form, nor was it possible to convert those α-oximes (C) which did not form hydrochlorides although the sulphates were isolated. Prolonged heating of aldoximes at 100° with concentrated sulphuric acid resulted in the formation of the corresponding amides. The following are described: (A) α-m-*nitrobenzaldoxime sulphate*, m. p. 71—76°, p-*nitrobenzaldoxime sulphate*, deliquescent, and α-p-*methoxybenzaldoxime sulphate*, m. p. 79—80°; (B) α-o-*methoxybenzaldoxime sulphate*, m. p. 143°, and α-o-*chlorobenzaldoxime sulphate*; (C) α-6-*bromo*-3 : 4-*dimethoxybenzaldoxime sulphate*, m. p. 105°, and α-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime sulphate*, m. p. 110—135°; and α-3 : 4-*methylenedioxybenzaldoxime sulphate*, unstable. M. CLARK.

Reimer–Tiemann reaction with *m*-bromo- and *m*-iodo-phenol. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1927, 3041—3044).—A mixture of 4-bromo-2-hydroxybenzaldehyde (I) [*sodium*, *potassium*, and *copper* salts; oxime, m. p. 168° (lit. 151°); p-*nitrophenylhydrazone*, m. p. 258° (decomp.); *semicarbazone*, m. p. 212°; *benzoate*, m. p. 115°] and 2-bromo-4-hydroxybenzaldehyde [p-*nitrophenylhydrazone*, m. p. 274° (decomp.); *semicarbazone*, m. p. 212°; oxime, m. p. 184° (lit. 128·5°)] in almost equal proportions is obtained from *m*-bromophenol by the Reimer–Tiemann reaction. *m*-Iodophenol yields in like manner approximately equal quantities of 4-*iodo-2-hydroxybenzaldehyde*, m. p. 87° [*alkali-metal*, *ammonium*, *silver*, and *copper* salts; *oxime*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 242° (decomp.); *semicarbazone*, m. p. 252°; *benzoate*, m. p. 62°], and 2-*iodo-4-hydroxybenzaldehyde*, m. p. 163° [*alkali-metal* and *copper* salts; p-*nitrophenylhydrazone*, m. p. 265° (decomp.); *semicarbazone*, m. p. 232° (decomp.); *oxime*, m. p. 155°; *benzoate*, m. p. 112°]. The constitutions of the aldehydes are determined by the method already described for the corresponding chlorohydroxybenzaldehydes (A., 1927, 877). The following are also described: 4-*bromo-2-methoxybenzaldehyde*, m. p. 71° (*oxime*, m. p. 132°; p-*nitrophenylhydrazone*, m. p. 215°; *semicarbazone*, m. p. 224°); 4-*bromo-2-methoxybenzoic acid*, m. p. 155°; 4-*bromo-2-hydroxybenzoic acid*, m. p. 214°; 2-*bromo-4-methoxybenzaldehyde*, m. p. 77° [*oxime*, m. p. 93°; p-*nitrophenylhydrazone*, m. p. 250° (decomp.); *semicarbazone*, m. p. 232°]; 2-*bromo-4-methoxybenzoic acid*, m. p. 199°; 2-*bromo-4-hydroxybenzoic acid*, m. p. 151°; 4-*iodo-2-methoxybenzaldehyde*, m. p. 85° [*oxime*, m. p. 138°; p-*nitrophenylhydrazone*, m. p. 238° (decomp.); *semicarbazone*, m. p. 228°]; 4-*iodo-2-methoxybenzoic acid*, m. p. 150°; 4-*iodo-2-hydroxybenzoic acid*, m. p. 230° (decomp.); 2-*iodo-4-methoxybenzaldehyde*, m. p. 115° [p-*nitrophenylhydrazone*, m. p. 247° (decomp.); *semicarbazone*, m. p. 211°; *oxime*, m. p. 101°]; 2-*iodo-4-methoxybenzoic acid*, m. p. 184°; 2-*iodo-4-hydroxybenzoic acid*, m. p. 179° (decomp.). M. CLARK.

Vanillin derivatives. G. C. HILMAN and O. H. ALDERKS (Proc. Iowa Acad. Sci., 1926, **33**, 175).—A dibromovanillin (under investigation) gives an oxime which exists in but one form, and the nitrile derived from it is very resistant to hydrolysis. CHEMICAL ABSTRACTS.

Mechanism of the catalytic hydrogenation of phenols. V. GRIGNARD and G. MINGASSON (Compt. rend., 1927, **185**, 1552—1556).—Catalytic reduction

of phenol in *cyclo*hexanol solution (the critical temperatures above which dehydrogenation of the latter to *cyclo*hexanone occurs being 155°/18—22 mm., 157°/30 mm., 160°/50 mm., 170°/100 mm., 175°/200 mm., and 180°/760 mm.) at 150°/18—22 mm. with a nickel catalyst yields only the *enol* form, b. p. 55°/12 mm., of *cyclo*hexanone (12—15% yield), since the active hydrogen in the product, determined by the method of Job and Reich (A., 1924, i, 24), is 100%. Fractional distillation of the product obtained by treating the reduction mixture with acetic anhydride and fused sodium acetate yields *cyclo*hexyl acetate, phenyl acetate, and the *acetate*, b. p. 75—77°/17 mm., d_{15}^{4} 1·0237, n_D^{23} 1·4732, of the enol, which is stable to boiling water but is hydrolysed to the free enol by boiling with a 10% solution of oxalic acid for 5 hrs. By similar reductions of the appropriate phenols are obtained the *enols* of *p*-methyl*cyclo*hexanone, n_D^{1} 1·45507 for a mixture containing 80% of enol (*acetate*, b. p. 92—93°/12 mm., 191—192°/760 mm., 0·9813; n_D^{14} 1·46086), and carvomenthone, b. p. 104—106°/11 mm., n^{20} 1·4624 (75% enol) (*acetate*, b. p. 103—105°/11 mm., d_{13}^{4} 0·947, n_D^{13} 1·46196). Reduction of phenols therefore occurs by direct addition of hydrogen to the two double linkings in the Kekulé formula not contiguous to the hydroxyl group, the resulting enol of the cyclic ketone then either ketonising or being further reduced to the secondary alcohol. J. W. BAKER.

Odour and molecular asymmetry. IV. The three 3 : 5-dimethyl*cyclo*hexanones and the four 3 : 5-dimethyl*cyclo*hexanols. J. VON BRAUN and E. ANTON (Ber., 1927, 60, [*B*], 2438—2446; cf. A., 1926, 1142).—*s*-*m*-Xylenol is hydrogenated to a mixture of 3 : 5-dimethyl*cyclo*hexanols, which is oxidised to a mixture of 3 : 5-dimethyl*cyclo*hexanones. Oximation of the latter gives a crystalline and a liquid oxime. Reduction of the liquid compound affords *r*-3 : 5-dimethyl*cyclo*hexylamine, which cannot be satisfactorily resolved by camphorsulphonic, bromocamphorsulphonic, or mandelic acids, but from which by means of *d*-tartaric acid in aqueous solution l-3 : 5-*dimethyl*cyclo*hexylamine* is obtained. Lack of material prevented the preparation of the homogeneous *d*-base by means of *l*-tartaric acid. The bases are converted by sodium nitrite in cold, dilute acetic acid solution into l-3 : 5-*dimethyl*cyclo*hexanol*, b. p. 89—90°/17 mm., d_4^{20} 0·9166, $[\alpha]_D^{18}$ −7·74°, and non-homogeneous d-3 : 5-*dimethyl*cyclo*hexanol*, b. p. 89—90°/17 mm., d_4^{20} 0·9146, $[\alpha]_D^{20}$ +4·55°, which are oxidised by potassium dichromate and sulphuric acid to l-3 : 5-*dimethyl*cyclo*hexanone*, b. p. 67—68°/16 mm., d_4^{20} 0·9074, $[\alpha]_D^{23}$ −7·91° (*semicarbazone*, m. p. 189°), and d-3 : 5-*dimethyl*cyclo*hexanone*, b. p. 67—68°/16 mm., d_4^{20} 0·9083, $[\alpha]_D^{20}$ +4·65° (*semicarbazone*, m. p. 187—189°).

The two inactive 3^c : 5^c-dimethyl*cyclo*hexylamines obtained by reduction of the crystalline oxime, m. p. 73° (see above), are separated from one another by crystallisation of their benzoyl derivatives from 96% alcohol. Hydrolysis of the homogeneous derivatives with concentrated hydrochloric acid affords 3^c : 5^c-*dimethyl*cyclo*hexylamine* A, b. p. 167° (*hydrochloride*, m. p. 235—237°; *picrate*, m. p. 205°; *acetyl* compound, m. p. 137°; *phenylthiocarbamate*, m. p. 181°; *benzoyl* derivative, m. p. 162—163°), and 3^c : 5^c-*dimethyl*cyclo*hexylamine* B, b. p. 167° (*hydrochloride*, m. p. 211—213°; *picrate*, m. p. 194—195°; *acetyl* compound, m. p. 125°; *phenylthiocarbamate*, m. p. 165°; *benzoyl* derivative, m. p. 116—117°). The base *A* is transformed by sodium nitrite in acetic acid solution into 3^c : 5^c-*dimethyl*cyclo*hexanol* A, m. p. 41° (non-crystalline *hydrogen phthalate*; *phenylurethane*, m. p. 96°), whereas the base *B* yields 3^c : 5^c-*dimethyl*cyclo*hexanol* B, m. p. 16—17° (*hydrogen phthalate*, m. p. 105—106°). The alcohol *A* appears to undergo partial isomerisation to alcohol *B* when distilled. The crystals which separate from the mixture of dimethyl*cyclo*hexanols derived from xylenol consist of a mixture of alcohols *A* and *B*, which can be separated into its components by conversion by the successive action of sodium in ether and phthalic anhydride into the corresponding hydrogen phthalates and crystallisation of the latter from dilute alcohol; treatment with phthalic anhydride at 140° results in the production of much dimethyl*cyclo*hexene. Oxidation of either alcohol affords 3^c : 5^c-dimethyl*cyclo*hexanone (oxime, m. p. 73°). The alcohol of m. p. 17° has a pronounced odour of mint, whereas that of m. p. 41° more closely resembles stored acetone. The optically active alcohols have sweeter odours analogous to those of certain amyl esters; the odour of the *d*-form is fresher and more powerful than the milder and heavier odour of the *l*-variety. Similar differences in odour are observed among the ketones.

The mixture of the two optically inactive dimethyl*cyclo*hexanols is converted by phosphorus tribromide at 0° into a mixture of the corresponding *bromides*, b. p. 81—82°/14 mm., which with magnesium and carbon dioxide affords a readily separable mixture of the 3^c : 5^c-*dimethyl*cyclo*hexylcarboxylic acids*, m. p. 68° (corresponding *amide*, m. p. 160°), and non-crystalline, d_4^{20} 0·9776 (corresponding *amide*, m. p. 148—149°). Probably other compounds of the 3 : 5-dimethyl*cyclo*hexane series containing a pseudo-asymmetric carbon atom in position 1 may be separated with comparative ease. H. WREN.

Pyrogenic decomposition of cyclic ketones. V. IPATIEV and A. PETROV (Ber., 1927, 60, [*B*], 2545—2548; cf. A., 1927, 1076).—Homo*iso*phorone, in the form of a mixture of four possible isomerides obtained by condensation of methyl ethyl ketone under the influence of sodamide, is decomposed when heated under high pressure at 470—480° in the presence of ferric oxide into gases, carbon, phenols approximating to xylenol in composition, and comparatively small amounts of hydrocarbons, b. p. 60—240°. 2-Methyl*cyclo*hexanone decomposes at 470—490°, giving a mixture of hydrocarbons closely analogous to that obtained from *cyclo*hexanone; toluene is present in traces, whereas phenols are completely absent. Condensation products of high b. p. are formed in small amount. At 380—400° pulegone affords phenols, cyclic and unsaturated hydrocarbons, and cymene. The absence of thymol is due to its conversion under these conditions into a complex mixture of phenols. H. WREN.

Azomethine derivatives of fluorene. A. Novelli (Anal. Asoc. Quím. Argentina, 1927, **15**, 187—209).—The formation of azomethines by the reaction of fluorene derivatives with nitroso-compounds is discussed in relation to the activation of methylene groups and the relation between colour and constitution. Although dibenzo*cyclo*pentadiene-imine is colourless, the substituted phenylimines (azomethines) are deep red. Condensation of 2 : 7-dibromofluorene with *p*-nitrosoalkylanilines takes place in boiling alcoholic solution, readily on the addition of alcoholic sodium ethoxide, less readily with potassium cyanide. The following *2 : 7-dibromodibenzo*cyclo*pentadiene-imines* were prepared : p-*dimethylaminophenyl*-, m. p. 205—206°; p-*diethylaminophenyl*-, m. p. 176° (*hydrochloride*, m. p. 185—186°); p-*methylaminophenyl*-, m. p. 201—202°; p-*ethylaminophenyl*-, m. p. 171°, and p-*methylethylaminophenyl*-, m. p. 168°. These compounds are rapidly hydrolysed by dilute mineral acids to 2 : 7-dibromofluorenone and the corresponding amine.

R. K. Callow.

Isomeric relationships in the chalkone series. V. Dibenzoylmethane, *p*-bromodibenzoylmethane, and *p*-methylchalkone [phenyl *p*-methylstyryl ketone]. C. Weygand [with H. Hennig] (Ber., 1927, **60**, [*B*], 2428—2432; cf. A., 1926, 1248).—Hydrolysis of the α-form of phenyl β-ethoxystyryl ketone with alcoholic hydrogen chloride affords the phenyl β-hydroxystyryl ketone, m. p. 80—81°, of von Baeyer and Perkin. The known isomeric forms of phenyl β-ethoxystyryl ketone have m. p. 63°, 73—74°, 77—78°, and 80—81°, respectively. The varieties of phenyl β-methoxystyryl ketone have m. p. 65°, 77—78°, and 80—81°, and those of phenyl β-hydroxystyryl ketone have m. p. 72—73°, 77—78°, and 80—81°, respectively. In all cases the varieties of highest m. p. are unstable (cf. Dufraisse and Gillet, A., 1927, 58). The enolic form of *p*-bromodibenzoylmethane exists in two *varieties*, m. p. 94° and 86·5°, the latter being obtained by solidification of the undercooled melt of the former under certain conditions. Phenyl *p*-methylstyryl ketone exists in an unstable *α-variety*, m. p. 99°, a stable β-form, m. p. 96·5°, and a metastable γ-variety, m. p. 90°. The α- is obtained from the β-variety by cautious crystallisation from hot methyl alcohol. Contrary to Dufraisse and Gillet (*loc. cit.*), the authors propose to designate the form of highest m. p. as the α-variety until a reasonable explanation of the isomerism is forthcoming. Since the isomerides are not distinguished from one another by visible difference in colour, it is considered improbable that the isomerism is of the *cis–trans* type and all the isomerides are regarded as *cis*-forms in analogy with *cis*-dibenzoylethylene and *cis*-cinnamic acid. H. Wren.

Tautomerism of α-diketones. C. Dufraisse and H. Moureu (Bull. Soc. chim., 1927, [iv], **41**, 1607—1621).—The dimorphism of phenylbenzylglyoxal (cf. Widman, A., 1916, i, 406; Jorlander, A., 1907, i, 343) is attributed to the two stereoisomerides of the enolic form, COPh·C(OH)⁚CHPh, the α-form, m. p. 67°, being the unstable form. The β-form has m. p. 90°. The appearance of either form in the preparation of phenylbenzylglyoxal is not to be attributed to differences in the technique of preparation (cf. Jorlander, *loc. cit.*). In support of the enolic structure is advanced the existence of the following coloured salts: *potassium*, *copper*, ferric, *uranium*, *zinc*, *lead*, *antimony*. The antimony salt, $COPh·C(OSbCl_2)⁚CHPh$, m. p. 179—180°, is obtained in 75% yield by the action of antimony trichloride on either the α- or β-form. On exposure to the atmosphere for a year phenylbenzylglyoxal yields benzoic acid, a substance, m. p. 235—236°, insoluble in ether and in alkali, and a substance, m. p. 193—194°, soluble in ether and alkali. With crystalline phenylbenzylglyoxal in the cold, magnesium methyl iodide affords 93% of the theoretical amount of methane. Hydroxylamine in aqueous alcohol yields mainly an *oxime*, $C_{15}H_{13}O_2N$, m. p. 114—115°, together with some oximinobenzylacetophenone, and, probably, a little dioxime, m. p. 220°. Attempts to obtain this oxime from α-piperidinobenzylideneacetophenone failed, the latter giving piperidine and oximinobenzylacetophenone when treated with hydroxylamine. When distilled at 192—193°/15 mm. crystalline phenylmethylglyoxal is converted (yield 90%) into a liquid *isomeride*, b. p. 137—138°/0·3 mm., n_D^1 1·5881, $d_4^{18.5}$ 1·1333, which affords the same monoxime, m. p. 114—115°, and metallic derivatives, the latter on decomposition with acids yielding the crystalline form. Magnesium methyl iodide yields only about 50% of the theoretical amount of methane, a result indicating that whilst the crystalline form consists almost entirely of the enolic form, a large amount of the liquid isomeride is ketonic. Some of the enol present in the latter case may be due to enolisation by the Grignard reagent. Conversion of the liquid into the crystalline form is best effected through the antimony salt, the latter being decomposed with hydrogen sulphide or 40% tartaric acid. The liquid form on keeping (10 months) in a sealed tube changes to the β-form, m. p. 89°. Hydrolysis of oximinobenzylacetophenone with 25% sulphuric acid gives a little crystalline phenylbenzylglyoxal.

Similarly, phenylanisylglyoxal, m. p. 70°, gives coloured sodium, potassium, and ferric salts; the orange-yellow *antimony* salt has m. p. 199—200°. When distilled at 211—213°/8 mm. the crystalline form is converted into a liquid *isomeride*, n^{23} 1·5932, d_4 1·1656, giving the same metallic derivatives from which the crystalline form is regenerated. The crystalline form of benzylmethylglyoxal, m. p. 69—70°, is obtained by the action of piperidine on dibromobenzylideneacetophenone and cold hydrolysis of the piperidino-compound. The yellow *antimony* salt has m. p. 184—185°. When heated the crystalline form is converted into the liquid isomeride, b. p. 107°/17 mm. The crystalline form is regenerated by decomposition of the sodium salt.

R. Brightman.

Heteropolar carbon compounds. V. Influence of phenoxy- and substituted phenoxy-groups on the halochromy of chromogens. W. Dilthey, E. Bach, H. Grutering, and E. Hausdorfer (J. pr. Chem., 1927, [ii], **117**, 337—368).—p-*Phenoxyphenyl β-phenylvinyl ketone*, m. p. 85—86° (with previous sintering; *dibromo*-additive compound,

m. p. 137°), and p-*phenoxyphenyl* β-p-*methoxyphenylvinyl ketone*, m. p. 97°, are prepared by condensation of *p*-phenoxyacetophenone with the appropriate aldehyde. 4 : 4'-*Diacetyldiphenyl ether*, m. p. 100—101° (*dioxime*, m. p. 182—183°), prepared either by the interaction of diphenyl ether and acetyl chloride in carbon disulphide solution in the presence of aluminium chloride or from the potassium salt of *p*-hydroxyacetophenone and *p*-bromoacetophenone by Ullmann's method, yields pp'-*dicinnamoyldiphenyl ether*, m. p. 170° [*tetrabromo*-additive compound, m. p. 224° (decomp.)], and pp'-*di*-β-*anisylacrylyldiphenyl ether*, m. p. 207—208° [*tetrabromo*-additive compound, m. p. 198° (decomp.)]. pp'-*Dibenzoyldiphenyl ether*, m. p. 163—164° [*dioxime*, m. p. 215—216° (decomp.)], prepared by both the above methods from the suitable components, reacts with magnesium phenyl bromide to give finally pp'-*dichlorodiphenylmethyldiphenyl ether*, decomp. at 120° (melting and frothing at 165°), or pp'-*dibromodiphenylmethyldiphenyl ether*, m. p. 193° (decomp.). pp'-*Di*(*hydroxydiphenylmethyl*)*diphenyl ether*, m. p. 90—95° (frothing; *dimethoxy*-derivative, m. p. 138—139°), gives on reduction with acetic acid and zinc dust pp'-*di*(*diphenylmethyl*)*diphenyl ether*, m. p. 167—168° (darkening; when crystallising with $2C_6H_6$, m. p. 85—90°). p-*Phenoxytriphenylmethane*, m. p. 138—140°, is prepared by the interaction of *p*-phenoxvbenzophenone and magnesium phenyl bromide. 4-p-*Tolyloxybenzophenone*, m. p. 68°, 4-p-*tolyloxyacetophenone*, m. p. 53—54° (*oxime*, m. p. 138°), 4-p-*nitrophenoxybenzophenone*, m. p. 126° (*oxime*, m. p. 162°; *phenylhydrazone*, m. p. 167°), and 4-p-*nitrophenoxyacetophenone*, m. p. 82—83°, are prepared from the ethers by the Friedel–Crafts method. p-*Tolyl* p-*cinnamoylphenyl ether*, m. p. 84°, p-*tolyl* β-p-*anisylacrylylphenyl ether*; m. p. 109—110°, p-*nitrophenyl* p-*cinnamoylphenyl ether*, m. p. 165—166°, p-*nitrophenyl* 4-β-p-*anisylacrylylphenyl ether*, m. p. 135°, and p-*nitrophenyl* p-*cinnamylideneacetylphenyl ether*, m. p. 138° [*chlorostannate* of corresponding amine, m. p. 263° (decomp.)], are prepared by condensation of the aldehydes with the acetophenone derivatives. 4-p-*Aminophenoxybenzophenone*, m. p. 85° (*acetyl* derivative, m. p. 156°; *benzoyl* derivative, m. p. 172°), and 4-p-*aminophenoxyacetophenone*, m. p. 123° (*compound* with benzaldehyde, m. p. 144—145°), are obtained by reduction of the corresponding nitro-compounds with stannous chloride in saturated hydrogen chloride solution. p-*Aminophenyl* 4-β-p-*anisylacrylylphenyl ether*, m. p. 148° [*chlorostannate*, m. p. 246° (decomp.); *hydrochloride*, m. p. 198—200° (decomp.); *picrate*, m. p. 207° (yellow); *monoperchlorate*, m. p. 218—220°; *diperchlorate*, m. p. indef.], and p-*aminophenyl* p-*cinnamoylphenyl ether*, m. p. 104° (*chlorostannate*, m. p. 239—240°; *acetyl* derivative, m. p. 171°; *monoperchlorate*, m. p. 223°; *diperchlorate*, m. p. indef.), are obtained similarly. The colours given when these compounds are treated with sulphuric acid or with sulphuric acid and glacial acetic acid are recorded and are found to confirm the theory previously published (A., 1926, 727).

G. A. C. GOUGH.

Action of primary amines on nitroso-β-naphthol. R. LANTZ and A. WAHL (Compt. rend., 1927, 185, 1489—1491).—2-Hydroxy-α-naphthaquinone-1-imine-4-anil (A., 1926, 617) is obtained by heating a mixture of nitroso-β-naphthol, aniline, and benzene for 12—15 min. The reaction is catalysed by copper, and when copper is used there is formed some phenyldinaphthoxazime, presumably from the above anil and α-amino-β-naphthol produced during the reaction. H. BURTON.

Preparation of anthraquinone. P. S. VARMA and J. L. D. GUPTA (J. Indian Chem. Soc., 1927, 4, 297—298).—Eleven methods of preparing anthraquinone are compared. The use of nitrous oxides in water or alcohol as oxidising agent is described. The highest yield, 4·3 g. from 5·0 g. of anthracene, is obtained using chromium trioxide and glacial acetic acid (Fischer's method). H. BURTON.

Catalytic action of mercury in the sulphonation of anthraquinone. A. MEYER (Bull. Soc. chim., 1927, [iv], 41, 1627—1638).—A more detailed account of work already published (A., 1927, 463). The transformation of anthraquinone-α-sulphonic acid into the β-sulphonic acid observed by Martinet and Roux (A., 1921, i, 257) is attributed to the presence of traces of mercury as impurity (cf. also Coppens, A., 1925, i, 1432; Clough, A., 1923, i, 46; Fierz-David, A., 1927, 463; Wibaut, A., 1927, 566). If the mercuric sulphate or oxide used is not ground up with the anthraquinone before charging into the sulphuric acid, erratic results may be obtained. Sulphonation of anthraquinone at 160° with 50% oleum in presence of 1% of mercuric sulphate affords 56·8% of anthraquinone-α-sulphonate, 20% of the 1 : 5- and 1 : 8-disulphonic acids, and 3·5% of trisulphonic acid, 19·6% of the anthraquinone being unattacked. R. BRIGHTMAN.

Aromatic thionyl and chlorothionyl derivatives. III. Reactions of thionylalizarin. A. GREEN (J.C.S., 1927, 2930—2932).—Thionylalizarin reacts with the corresponding free weak organic acids to give the following 2-monoacyl derivatives of alizarin: 2-*monobenzoyl*-, m. p. 208—210° (lit. 214—216°); 2-*phenylacetyl*-, m. p. 165°; 2-*phenoxyacetyl*-, m. p. 179°; 2-*cinnamoyl*-, m. p. 209°; 2-o-*toluoyl*-, m. p. 192°; 2-m-*bromobenzoyl*-, m. p. 214°, and 2-p-*bromobenzoyl-alizarin*, m. p. 195°. With dichloro-, trichloro-, and dibromo-acetic acids, thionylalizarin yields alizarin only, whilst with chloroacetic acid it yields a mixture of alizarin and a substance assumed to be the chloroacetyl derivative. Benzoic anhydride condenses with thionylalizarin giving dibenzoylalizarin, isolated in a new labile *modification*, m. p. 160°, as well as in the ordinary modification, m. p. 187°. Only the latter is obtained when benzoyl chloride is used. When thionylalizarin is heated under pressure with acetyl chloride, diacetylalizarin is obtained. With succinic or phthalic anhydrides, and with alkyl halides or sulphates, no reaction occurs. With boiling absolute alcohol or hot phenol, sulphur dioxide is evolved with formation of alizarin. With hot primary aromatic amines the alizarin first formed undergoes further slow reaction with formation of secondary amines. M. CLARK.

Nuclear hydrogenation of quinones in non-acidic media. A. SKITA [with F. KEIL and H.

WITTE] (Ber., 1927, 60, [*B*], 2522—2527).—Acenaphthenequinone, suspended in aqueous sodium hydroxide or ammonia, is converted by hydrogen in the presence of colloidal platinum into the tetrahydric *alcohol*, $C_{10}H_{14}<\begin{matrix}C(OH)\cdot(OH)C\\ C(OH)\cdot(OH)C\end{matrix}>C_{10}H_{14}$, m. p. 207—208° (*tetra-acetate*, m. p. 138°), which is not identical with the tetrahydroxy-alcohol, m. p. 206° (now formulated $C_{24}H_{26}O_4$; *tetra-acetate*, m. p. 102—103°), obtained by hydrogenation of acenaphthenequinone in acid solution (cf. A., 1926, 173). Anthraquinone dissolved in decahydronaphthalene in the presence of a nickel catalyst is converted by hydrogen at 75° and 50 atm. almost exclusively into tetrahydroanthraquinol, which readily passes by atmospheric oxidation into tetrahydroanthraquinone, m. p. 158°. At 90° and 50 atm., hexahydroanthraquinol (*diacetate*, m. p. 215—216°), readily oxidised to hexahydroanthraquinone, m. p. 175°, is produced. At 150° and 50 atm., anthraquinone affords octahydroanthraquinone, m. p. 184°, mixed with about 30% of octahydroanthranol. If the temperature is reduced to 130°, the production of octahydroanthranol falls to 15% without any appreciable change in the rate of the reaction. At 130° and 25 atm., anthranol formation occurs only to the extent of 10%, whereas the yield of octahydroanthraquinone is proportionately increased. H. WREN.

Dyes and intermediates [dibenzanthronyls]. R. F. THOMSON, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1928, 9.

1-Diazoanthraquinone-2-carboxylic acids. I. G. FARBENIND. A.-G.—See B., 1928, 45.

Determination of santonin in *Flores cinæ*. H. BECKURTS (Festschr. A. Tschirch, 1926, 6—12; Chem. Zentr., 1927, i, 2586).—Loss of santonin on purification takes place as follows: with potassium permanganate solution, 6—10%; through the lead compound, 7·2—8·3%; by coagulation of the impurities with potassium alum (2·1—2·3%) or ferric chloride (1·3—1·5%); by using Pukall filters, 1·9—2·4%. Pure santonin may be obtained, although not quantitatively, by ultra-filtration.

A. A. ELDRIDGE.

Structure of methyl*iso*borneol from α-methylcamphene, of β-methylcamphenilone, and of their derivatives. S. NAMETKIN and L. BRUSSOV (Annalen, 1927, 459, 144—171).—The compound previously regarded as 6(β)-methyl*iso*borneol (cf. A., 1926, 619; Bredt, A., 1919, i, 125) has now been shown to be the 4-methyl derivative (I) as follows: (*a*) The hydrazone of the corresponding methylcamphor is converted by sodium ethoxide at 200° into 4-*methylcamphane*, m. p. 138—139°, b p. 170—170·5°/752 mm. This yields as main product of nitration by Konovalov's method a sec.-*nitro*-derivative, m. p. 144—146°, which is oxidised by permanganate to the original methylcamphor. (*b*) Attempts to brominate the corresponding methylcamphoric acid using bromine and red phosphorus result only in anhydride formation. These reactions indicate the absence of hydrogen from the 4-position. By applying the usual pinacolin-type transformation to 4-methyl*iso*borneol, formulæ (II) [R—(*a*) :CH_2, (*b*) :O,

$$\text{(I.)}\quad \begin{array}{l} CH_2\cdot CMe\cdot CH_2 \\ |\qquad CMe_2 \quad | \\ CH_2\cdot CMe\cdot CH\cdot OH \end{array} \qquad\qquad \begin{array}{l} CH_2\cdot CMe\cdot CMe_2 \\ |\qquad CH_2 \quad | \\ CH_2\cdot CH{-}C{:}R \end{array}\quad\text{(II.)}$$

(*c*) :H_2] are obtained for (*a*) β-methylcamphene, (*b*) β-methylcamphenilone, and (*c*) β-methylcamphenilan. These are confirmed in the following ways: (1) When β-methylcamphenilan is nitrated by Konovalov's method it gives 4-*methylapofenchocamphoric acid* (3 : 3 : 4-*trimethyl*cyclo*pentane*-1 : 4-*dicarboxylic acid*), m. p. 187—188°, and a sec.-*nitro*-derivative, m. p. 110—114°, the constitution of which follows from its oxidation by permanganate to 4-*methyl*iso*camphenilone* (III), m. p. 146—147° (*semicarbazone*, m. p. 202—204°). The accepted formula required the formation of a *tert*.-nitro-derivative and of an acid, $C_7H_{12}(CO_2H)_2$. (2) When β-methylcamphenilonehydrazone is oxidised by freshly-precipitated mercuric oxide, *iso*cyclene, m. p. 119° (cf. Bredt, A., 1917, i, 655), not fenchocyclene, is obtained. (3) Free β-*methylcamphenylic* (camphenilolic) *acid* (1 : 1-*methyl*iso*propyl*cyclo*pentane* 3-*carboxylic acid*), b. p. 143—143·5°/10 mm., d_4^{20} 0·9853, n_{20} 1·4641, prepared from the amide (A., 1923,

$$\text{(III.)}\quad \begin{array}{l} CO{-}CMe\cdot CMe_2 \\ |\qquad CH_2 \quad | \\ CH_2\cdot CH{-}CH_2 \end{array} \qquad\qquad \begin{array}{l} CH_2\cdot CH{-}CMe_2 \\ |\qquad CH_2 \\ CH_2\cdot CMe\cdot C{:}CH_2 \end{array}\quad\text{(IV.)}$$

i, 690), has been treated with red phosphorus and bromine and the product hydrolysed by calcium carbonate to *calcium 3-hydroxy*-1 : 1-*methyl*iso*propyl*cyclo*pentane-3-carboxylate* (+18H_2O). The free acid is oxidised by lead dioxide and sulphuric acid to a new *ketone* [(?) 1 : 1-*methyl*iso*propyl*cyclo*pentan*-3-*one*], b. p. 195—196°/756 mm. (*semicarbazone*, m. p. 198—199°), which is not identical with 1-methyl-3-*iso*propyl*cyclo*pentan-5-one (Wallach, A., 1918, i, 442). Thus, the hydration of α-methylcamphene (IV) to 4-methyl*iso*borneol (I) must involve, first, hydration and simultaneous migration of a methyl group from the 3- to the 2-position, followed by ring-isomerisation, whilst the formation of the same compound from β-methylcamphene (II) is not accompanied by methyl-wandering. This apparently dissimilar behaviour of two closely-related substances is explained by the tendency of the hydroxyl group to enter such a position in the molecule (adjacent to a :CH group) that by ring-isomerisation a secondary alcohol is formed. The reverse change, dehydration of methyl*iso*borneol, appears to proceed in both directions and both schemes are applicable to the formation of *iso*borneol from camphene. H. E. F. NOTTON.

Derivatives of camphorquinone. J. PALMEN (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 9).—Magnesium phenyl bromide converts camphorquinone into hydroxyphenylcamphor, m. p. 78—80°; magnesium benzyl chloride gives hydroxybenzylcamphor (not isolated in a state of purity); magnesium ethyl bromide gives a product which may contain some dihydroxydiethylcamphane.

G. A. C. GOUGH.

Decomposition of the ozonides of semicyclic unsaturated systems. Ozonisation of sabinol. T. HASSELSTROM (Annal. Acad. Sci. Fennicæ, 1927,

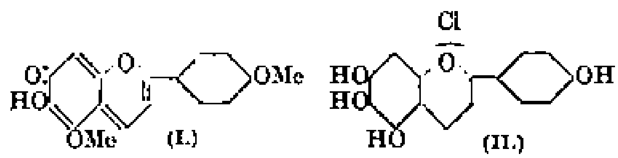
A, 29, No. 5).—A glacial acetic acid solution of sabinol ozonide, prepared by the action of ozone on a solution of sabinol in that solvent, decomposes when heated for 3 hrs. at 100° to give formaldehyde, α-tanacetogendicarboxylic acid, α-tanacetogen acid aldehyde, and α-oxysabina ketone. G. A. C. GOUGH.

Furfuryl and furfurylidene compounds of menthone. E. BOEDTKER, B. WIGER, and T. AAGAARD (J. Pharm. Chim., 1927, [viii], 5, 193—204).—Menthone condenses with furfuraldehyde in presence of sodium ethoxide to give *furfurylidenementhone*, yellow, b. p. 181°/12 mm., $[\alpha]_D^{15}$ −190° 51′, 1·5649, which, by the action of magnesium alkyl halides is converted into the following alkyl (R) substituted furfurylmenthones, $C_{10}H_{17}O{\cdot}CHR{\cdot}C_4H_3O$; *methyl-*, b. p. 149—150°/9 mm., $[\alpha]_D^{15}$ −19° 7′, n_D^{15} 1·4986; *ethyl-*, b. p. 165°/12 mm., $[\alpha]_D$ nil, n_D^{15} 1·4941; n-*propyl-*, b. p. 164°/9 mm., $[\alpha]_D$ nil, n_D^{15} 1·4929; iso*propyl-*, b. p. 162°/9 mm., $[\alpha]_D^{15}$ +49° 58′, n_D^{15} 1·4938; n-*butyl-*, b. p. 174°/10 mm., $[\alpha]_D^{15}$ +13° 22′, n_D^{15} 1·4905; iso*butyl-*, b. p. 169—170°/10 mm., $[\alpha]_D^{15}$ +19° 33′, n_D^{15} 1·4911; iso*amyl-*, b. p. 181°/10 mm., $[\alpha]_D^{15}$ +21° 46′, 1·4915; *phenyl-*, m. p. 93·5—94°, $[\alpha]_D^{18\cdot5}$ +22° 45′, n_D^{15} 1·5415. Furfurylidenementhone reacts with hydroxylamine, giving a *compound*, $C_{11}H_{20}O_2N$, m. p. 139—140°. 2 : 6-Difurfurylidene-*cyclo*hexanone, m. p. 145°, has been prepared by a slight modification of the method of Wolff (A., 1922, i, 668). It gives a violet colour with concentrated sulphuric acid. E. H. SHARPLES.

Reduction of furan derivatives. N. WILLIAMS (Ber., 1927, 60, [*B*], 2509—2514).—*Tetrahydrofurfuraldoxime*, b. p. 110°/8 mm., d^{18} 1·1314, n_D^{18} 1·4845, is prepared from the aldehyde or from its diacetate after treatment with sulphuric acid. It is reduced by sodium and alcohol to a mixture of *tetrahydro-2-furylmethylamine*, b. p. 54—56°/30 mm., 154°/750 mm., d^{17} 0·9792, n_D^{17} 1·4580 (*hydrochloride*; *chloroplatinate*; *chloroaurate*), and ε-hydroxy-*n*-amylamine, b. p. 110—112°/10 mm., n_D^{17} 1·4619 (chloroplatinate). *Tetrahydrofuran-2-carboxylonitrile*, b. p. 80—82°/23 mm., d^{23} 1·0295, n_D^{23} 1·4351, prepared by the action of acetic anhydride and sodium acetate on the corresponding oxime, gives only very small amounts of tetrahydro-2-furylmethylamine when treated with sodium and alcohol. Di-2-furylmethylamine (*hydrochloride*, $C_{10}H_{11}O_2N,HCl$, m. p. 170—172°) is obtained by the catalytic reduction of furfuraldoxime in the presence of palladised charcoal. 2-Furylmethylamine is not reduced by hydrogen in ethereal solution, but in glacial acetic acid in the presence of palladised charcoal affords tetrahydro-2-furylmethylamine. H. WREN.

Derivatives of furfuraldehyde. V. Action of organo-magnesium compounds on furyl ketones; constitution of furylidenemethyl ethyl ketone. I. KASIWAGI (Bull. Chem. Soc. Japan, 1927, 2, 310—319).—The condensation product of furfuraldehyde with methyl ethyl ketone, previously described as α-furyl-Δ^α-penten-γ-one (A., 1926, 842), is shown to be actually α-furyl-β-methyl-Δ^α-buten-γ-one. α-Furyl-β-methylbutan-γ-one (previously described as α-furyl-γ-pentanone), prepared by the hydrogenation of the last-named, reacts with magnesium methyl iodide to give *α-furyl-βγ-dimethylbutan-γ-ol*, b. p. 82·5°/3·5 mm., d_4^{23} 0·9923, 1·4779, and with magnesium ethyl iodide to give α-furyl-βγ-dimethylpentan-γ-ol, b. p. 90—91°/3 mm., d_4^{23} 0·9892, n_D^{23} 1·4800. Both these tertiary alcohols are dehydrated by phenylcarbimide and the alternative synthesis of the second from magnesium methyl iodide and α-furyl-β-methylpentan-γ-one indicates the actual structure of the furylidenemethyl ethyl ketone. Additional evidence is obtained by the oxidation of this ketone with sodium hypochlorite to *β-furyl-α-methylacrylic acid*, m. p. 110·5—111°, which may also be obtained (with m. p. 116°) by hydrolysis of the *ethyl* ester, b. p. 103—104°/4·5 mm., d_4^{23} 1·0800, n_D^{23} 1·5418, obtained by condensation of furfuraldehyde with ethyl acetate by Claisen's method. The following compounds are incidentally described: *α-furyl-γ-methylbutan-γ-ol*, b. p. 93·5—94°/8 mm., d_4^{23} 0·9972, n_D^{23} 1·4745 (*phenylcarbamate*, m. p. 126·5—127°; *acetate*, b. p. 83—85°/3 mm., d_4^{23} 1·0188, n_D^{23} 1·4583); *α-furyl-γ-methylpentan-γ-ol*, b. p. 83·5—84·5°/2 mm., d_4^{23} 0·9926, n_D^{23} 1·4780 (*phenylcarbamate*, m. p. 84·5—85°); *β-furylacrylic acid*, m. p. 139·5—140°; *αε-difuryl-β-methylpentan-γ-one*, m. p. 61°. G. A. C. GOUGH.

Colouring matters of carajura. E. CHAPMAN, A. G. PERKIN, and R. ROBINSON (J.C.S., 1927, 3015—3041; cf. Perkin, Proc. C.S., 1914, 30, 212).—Extraction of carajura with benzene and other suitable reagents affords the red substances *carajurin* (I), m. p. 205—207° (*hydrogen sulphate*; *hydrochloride*, blackens at 196° with partial fusion), and *carajurone*, m. p. 183—186° (decomp.). Bromination



(I.) (II.)

of (I) in acetic acid yields a *tetrabromide*, $C_{17}H_{14}O_5Br_4$, darkens at 195° and becomes black at 300°, which is converted by hot acetone into a *dibromocarajurin*, $C_{17}H_{12}O_5Br_2$, decomp. 300°. Fission of (I) with alcoholic potassium hydroxide affords *p*-acetylanisole, whilst acetylation with acetic anhydride in pyridine yields colourless O-*triacetyldihydrocarajurinol*, $C_{23}H_{22}O_9$, m. p. 142°. Reduction of (I) with hydriodic acid gives *carajuretin*, blackens at 330° (*hydriodide*; *hydrogen sulphate*; *hydrogen perchlorate*), which is acetylated in pyridine, forming O-*penta-acetyldihydrocarajuretinol*, $C_{25}H_{22}O_{11}$, m. p. 156—157°. *Carajuretin hydrochloride* (II), is obtained by decomposition of the hydriodide with silver chloride. Methylation of 2 : 6-dimethoxyquinol yields 1 : 2 : 3 : 5-tetramethoxybenzene and antiarol (3 : 4 : 5-trimethoxyphenol) (*sodium* salt; *acetyl* derivative, m. p. 74°). 3 : 6-*Dihydroxy-2 : 4-dimethoxybenzaldehyde*, m. p. 135—136°, and *antiarolaldehyde* (*2-hydroxy-4 : 5 : 6-trimethoxybenzaldehyde*), m. p. 65° [*semicarbazone*, m. p. 245° (decomp.)], are obtained by the Gattermann method from the corresponding phenols. 4 : 5-*Dimethoxyresorcinol*, m. p. 115—116°, is prepared by prolonged boiling of an aqueous solution of 3 : 5-diaminoveratrole hydrochloride containing a little stannous chloride. Antiarol reacts with acetyl chloride in presence of aluminium chloride and nitro-

benzene to form 4 : ω-*dimethoxy*-2 : 6-*diacetylresorcinol*, m. p. 92—93°, a small amount of 4 : 5-*dimethoxy-2-acetylresorcinol*(?), m. p. 160—161°, and a trace of a *substance*, m. p. 78—84°. 4 : 5-Dimethoxyresorcinol reacts with methoxyacetonitrile in ethereal hydrogen chloride to yield ω : 5 : 6-*trimethoxyresacetophenone*, m. p. 129—130°.

Condensation of anisoylacetone, m. p. 57° (previously recorded m. p. 54·5°), best obtained by condensing *p*-acetylanisole and ethyl acetate in presence of sodamide, with 2 : 6-dimethoxyquinol in formic acid in presence of hydrogen chloride affords 6-*hydroxy*-5 : 7 : 4′-*trimethoxy*-4-*methylflavylium chloride*, $+1{\cdot}5H_2O$, (III), m. p. 139—145° (decomp.) (*ferrichloride*, m. p. 205°). Anisoylacetone and iretol yield similarly 5 : 7-*dihydroxy*-6 : 4′-*dimethoxy*-4-*methylflavylium chloride*, $+0{\cdot}5H_2O$, (IV), m. p. 208° (decomp.) after darkening at 100—105° (*ferrichloride*, m. p. 180—181° with previous darkening), whilst anisoylacetone and antiarol afford 5 : 6 : 7 : 4′-*tetramethoxy*-4-*methylflavylium chloride*, m. p. 143—144° (decomp.) after darkening (*ferrichloride*, m. p. 176°). Demethylation of (III) and (IV) with a mixture of phenol and hydriodic acid gives 5 : 6 : 7 : 4′-*tetrahydroxy*-4-*methylflavylium iodide*, m. p. 290° (decomp.) after darkening at 278° (*chloride*, darkens at 200—270° without melting). Condensation of antiarolaldehyde and *p*-acetylanisole in acetic acid by hydrogen chloride gives 5 : 6 : 7 : 4′-*tetramethoxyflavylium chloride*, m. p. 145—146° (decomp.) (*ferrichloride*, m. p. 170°), which is demethylated by phenol and hydriodic acid to 5 : 6 : 7 : 4′-*tetrahydroxyflavylium iodide*. Conversion of this iodide into the chloride (scutellareinidin chloride) showed this substance to be identical with carajuretin hydrochloride. *Scutellareinidin chloride monomethyl ether* does not melt below 285°.

Condensation of iretol with *p*-anisyl β-hydroxyvinyl ketone gives 5 : 7-*dihydroxy*-6 : 4′-*dimethoxyflavylium chloride*, m. p. above 260°, which is also demethylated to carajuretin hydrochloride. Antiarolaldehyde and acetophenone yield 5 : 6 : 7-*trimethoxyflavylium chloride*, m. p. 124—125° (decomp.) (*ferrichloride*, m. p. 151°), which on demethylation affords 5 : 6 : 7-*trihydroxyflavylium chloride* (*baicaleinidin chloride*), decomp. 250—252° after darkening above 220° [*iodide*, m. p. 254° (decomp.) after sintering].

The dyeing properties of carajurin, carajurone, and carajuretin towards mordanted wool are recorded.

H. BURTON.

South African flowers. J. MOIR (J.S. African Chem. Inst., 1927, **10**, 36—47).—The absorption spectra of dilute extracts of the colouring matter of various flowers were studied, using a modified direct-vision spectroscope. In order to find the pigment causing colour, the spectra of the oxonium salts of the following substances were examined: pelargonidin, cyanidin, delphinidin, myricetin, apigeninidin, and luteolinidin. Glucosides of pelargonidin were detected in Barberton daisy, brown nasturtium, scarlet salvia, and *Chelone barbata*. Other red flowers in which glucosides of other members of the class are regarded as contaminating the pelargonin or which are possibly glucosides of a methyl ether of pelargonidin are scarlet protea, bramble, eendagsbloem lily, and the red canna lily. Glucosides of cyanidin were found in scarlet zinnia, pink convolvulus, purple convolvulus, deep red Ards rose, pink hydrangea, blue hydrangea, crimson verbena, *Lychnis coronaria*, scarlet geum, puce-coloured hollyhock, and the anthers of the agapanthus lily. Glucosides of delphinidin are present in nearly all bright blue flowers.

Delphinin was detected in blue agapanthus lily, azure plumbago, blue jacaranda, scarlet pointsettia, royal-blue convolvulus, and common larkspur.

Petunin was found in the petunia, bramble, and habrothamnus. The yellow sunflower is coloured with a mixture of xanthophyll and quercitrin. The alkali-soluble pigment of sunflower is probably a quercetin glucoside. The common orange marigold probably contains glucosides of kæmpferol and myricetin. The brown Japanese sunflower probably contains lycopin and kæmpferol glucoside. Flowers yielding indefinite results were: the sulphur-yellow chrysanthemum, the yellow coreopsis, and the *Montbretia* lily. Every stage in the origin of flower colours can be followed by examining all the intermediate substances in concentrated sulphuric acid solution.

R. A. PRATT.

Pinacolin transformation in *N*-ring pinacones. L. ORTHNER (Annalen, 1927, **459**, 217—233).—Ditertiary glycols which have one hydroxyl group attached to a piperidine ring are dehydrated, but not converted into pinacolins, by boiling with acids. This is probably due to the positive charge on the piperidinium ion inhibiting the formation of the carbonium ion through which the pinacolin transformation proceeds (cf. Meerwein, A., 1923, i, 324). Methyl 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine-4-carboxylate (cf. D.R.-PP., 90245, 91122), prepared from triacetonamine, is converted by magnesium ethyl bromide into 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-γ-*hydroxy*-γ-*amylpiperidine* (I), m. p. 68—69°, b. p. 131°/0·3 mm. (*picrate*, m. p. 135°), with some 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-α-*hydroxy*-α-*propylpiperidine*, m. p. 131·5° (*picrate*, m. p. 179—180°), and ethylene, and by magnesium iodide into 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-β-*hydroxy*isopropyl*piperidine* (II), m. p. 120·5°, b. p. 132—133°/13 mm. (*picrate*, m. p. 185·5—186°). The pinacone (I) is converted by boiling 20% sulphuric acid into a mixture containing no ketonic substances, from which 2 : 2 : 6 : 6-*tetramethyl*-4-γ-Δ^{γ}-*pentenyl*-1 : 2 : 3 : 6-*tetrahydropyridine*, b. p. 109—110°/13 mm. (*picrate*, m. p. 136—137°); 2 : 2 : 6 : 6-*tetramethyl*-4-γ-Δ^{γ}-*pentenylpiperidine*, b. p. 110—112°/11 mm. (*picrate*, m. p. 163°), and a little of the *ethylene oxide* (III) ($R=Et_2$), $\begin{array}{l}\text{CMe}_2{\cdot}\text{CH}_2{\cdot}\text{C}\!\!\underset{\text{O}}{\frown}\!\!\text{CR}\\ \text{NH-CMe}_2{\cdot}\text{CH}_2\end{array}$, m. p. 62·5° (*picrate*, m. p. 170·5°), are separated through the picrates. The oxide (III) forms the main product when (I) is boiled with 15% hydrochloric acid. Similarly, the glycol (II) affords with acids a mixture from which 2 : 2 : 6 : 6-*tetramethyl*-4-isopropenyl-1 : 2 : 3 : 6-*tetrahydropyridine picrate*, m. p. 179—180°, 2 : 2 : 6 : 6-*tetramethyl*-4-isopropenyl*piperidine picrate*, m. p. 253° [free *base* (IV) (?), m. p. 77—77·5°], and the *ethylene oxide* (III) ($R=Me_2$), m. p. 62° (*picrate*, m. p. 195—196°), are isolated. The constitution of the ethylene oxides (III) is established by their oxidation by

chromic and sulphuric acids to αα′α′-trimethyldiethylamine-αβ-dicarboxylic acid, identified as the *ethyl ester picrate*, m. p. 127—128°. This is also obtained in this way from 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine-4-carboxylic acid, but the base (IV) gives an *ethyl ester picrate*, m. p. 193—194°.

H. E. F. NOTTON.

Syntheses by means of magnesylpyrroles. [II.] XI. α- and β-Ketonic acids. B. ODDO and A. ALBANESE (Gazzetta, 1927, **57**, 827—835).—Ethoxalyl chloride reacts with magnesylindole to give *ethyl indolyl-3-glyoxylate*, (I), m. p. 186°, which is hydrolysed to the *acid*, m. p. 215° (decomp.) (*silver*, *lead*, *copper*, and *ferric* salts insoluble, *mercuric*, *barium*, *cobalt*, *nickel*, *cadmium*, and *manganese* salts soluble); this forms an *amide*, m. p. 248°, and on heating yields indole-3-aldehyde. With magnesylmethylindole, *ethyl 2-methylindolyl-3-glyoxylate* (II), m. p. 129·5°, is obtained; the *acid* has m. p. 186° (decomp.).

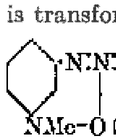
Ethmalonyl chloride (obtained from thionyl chloride and ethyl potassium malonate) reacts with magnesylpyrrole to give a mixture of *ethyl 3-acetylindole-ω-carboxylate*, $NH<{C_6H_4 \atop -CH}>C{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (III), m. p. 121°, hydrolysed to the *acid*, m. p. 192° (with decomposition to 3-acetylindole), and (probably) *ethyl 2-acetylindole-ω-carboxylate* (IV), m. p. 116°, hydrolysed to an *acid*, m. p. 315° (decomp.). (I) and (II) do not give silver derivatives with an ammoniacal silver nitrate solution; (III) and (IV) give a reaction, so that the former pair can probably assume an enolic and (?) quaternary basic form.

E. W. WIGNALL.

Oxidation of pyridine and the pyridine nucleus by sodium persulphate. J. DORRONSORO (Anal. Fís. Quim., 1927, **25**, 409—410).—Pyridine and its derivatives are easily oxidised by sodium persulphate, as they are by potassium permanganate (cf. Delépine, A., 1927, 254). When pyridine was treated with 20% aqueous sodium persulphate in the amount required by the equation $2C_5H_5N+11O_2=10CO_2+2NH_3+2H_2O$, a small quantity of pyridine was recovered unchanged, and some nitric acid was found, formed by further oxidation of the nitrogen. α-Picoline behaved similarly, acetic acid being also formed.

R. K. CALLOW.

Nitroamines of the pyridine series; 3-nitroaminopyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (Ber., 1927, **60**, [*B*], 2433—2438).—3-Aminopyridine, dissolved in sulphuric acid (*d* 1·84), is converted by nitric acid (*d* 1·5) into *3-nitroaminopyridine*, decomp. 170—175° (*barium*, *potassium*, and *sodium* salts; *sulphate*). Unlike the corresponding compounds of the 2- and 4-series it does not suffer isomerisation when treated with acids, but (preferably under the influence of acetic anhydride in acetic acid) loses nitrous oxide and gives 3-hydroxypyridine. It is transformed by methyl sulphate into the *substance*


(I.)

(I), m. p. 189° after darkening at 185°. Reduction of 3-nitroaminopyridine by zinc dust in alkaline solution yields mainly 3-aminopyridine with small amounts of 3-hydrazinopyridine, identified as *benzaldehyde-3-pyridylhydrazone*, m. p. 163—165°. The isomerisation of 2-nitroaminopyridine by concentrated sulphuric acid is accompanied by the production of pyrid-2-one, which is obtained in 60% yield if acetic acid is used.

H. WREN.

Reaction of diazonium salts with hydroxymethylene*cyclo*hexanones and cyclic β-diketones. H. K. SEN and S. K. GHOSH (J. Indian Chem. Soc., 1927, **4**, 477—491; cf. Coffey, A., 1923, i, 803).—2-Hydroxymethylene*cyclo*hexanone reacts with benzenediazonium chloride to give *cyclo*hexane-1 : 2-dionemonophenylhydrazone, m. p. 181—185° (osazone, m. p. 153—154°), which is transformed in boiling acetic acid to 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole, m. p. 168°. From the hydroxymethylene*cyclo*hexanone and the requisite diazonium chlorides there were prepared cyclo*hexane*-1 : 2-*dione*-p-*tolylhydrazone*, m. p. 190° (p-*tolylhydrazonephenylhydrazone*, m. p. 150° after sintering at 145°), and cyclo*hexane*-1 : 2-*dione*-p-*nitrophenylhydrazone*, m. p. 228—230° after darkening at 223° (p-*nitrophenylhydrazonephenylhydrazone*, m. p. 215—217°). The monohydrazones yield 1-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 194°, and 6-*nitro*-1-*keto*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 212° after sintering at 209°. 6-Methyl-2-hydroxymethylene*cyclo*hexanone and benzenediazonium chloride yield a *product*, sintering at 88°, becoming turbid and partly melting at 91°, and becoming clear at 131°, which is probably a mixture of two isomeric 6-methyl*cyclo*hexane-1 : 2-dionemonophenylhydrazones (*osazone*, m. p. 151—153°), and furnishes 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 171—173°. 6-*Methyl*cyclo*hexane*-1 : 2-*dione*-p-*tolylhydrazone* occurs in two modifications, m. p. 117—118° and 91—93° (p-*tolylhydrazone-phenylhydrazone*, m. p. 158—159°), and affords 1-*keto*-2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 195°. 6-*Methyl*cyclo*hexane*-1 : 2-*dione*-β-*naphthylhydrazone*, m. p. 85—88°, yields 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthcarbazole*, m. p. 225° after blackening at 212°. 2-Acetyl*cyclo*hexanone with benzene- and toluene-*p*-diazonium chlorides yields cyclo*hexane*-1 : 2-*dione-acetylphenylhydrazone*, m. p. 159—161°, and -*acetyl*-p-*tolylhydrazone*, m. p. 151—153°. From 2-acetyl-6-methyl*cyclo*hexanone there are obtained the *acetylphenylhydrazone*, m. p. 137—140°, and the *acetyl*-p-*tolylhydrazone*, m. p. 117—120°, of 6-methyl*cyclo*hexane-1 : 2-dione. 2-Carbethoxy*cyclo*hexanone with benzene- and toluene-*p*-diazonium chlorides affords the *carbethoxyphenylhydrazone*, m. p. 90—92°, and the *carbethoxy*-p-*tolylhydrazone*, m. p. 97—99°, of *cyclo*hexane-1 : 2-dione.

H. BURTON.

Action of the Grignard reagent on alkylbarbituric acids. A. W. DOX (J. Amer. Chem. Soc., 1927, **49**, 3189—3190; cf. A., 1927, 1087).—In view of the results of Bauer (A., 1904, i, 417) and Houben (A., 1904, i, 302) on the formation of cyclic derivatives from a single carbonyl group and a Grignard reagent, the compounds to which the endo-ether structure was previously ascribed (*loc. cit.*) may, alternatively, have a structure analogous to that represented in the annexed formula.

$$CR_1R_2<{CR_3(OH){\cdot}NPh \atop CR_3R_4{-}NPh}>CO$$

F. G. WILLSON.

Mechanism of the oxidation of pyrazolines. R. Locquin and R. Heilmann (Compt. rend., 1927, **185**, 1477—1479; cf. 1925, i. 1185).—The products formed during the oxidation of 3-methyl-5-*iso*-propylpyrazoline are 3-methyl-5-*iso*propylpyrazole, a mixture of the ketazines of *iso*butylideneacetone and *iso*heptanone, hydrolysed by sulphuric acid to hydrazine and the corresponding ketones, and high-boiling pyrazoline-like compounds. Similar results are obtained with 3-methyl-5-*iso*butylpyrazoline. The mechanism of the oxidation is discussed.

H. Burton.

Reactions of hydrazines with hydroxymethylene-ketones and their derivatives. II. K. von Auwers and H. Mauss (J. pr. Chem., 1927, [ii], **117**, 311—336; cf. A., 1927, 361).—*s*-Benzoylphenylhydrazine reacts with phenyl β-hydroxyvinyl ketone in ethereal solution to give 2-*benzoyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 155—155·5°, which is converted on long keeping into an *isomeride*, m. p. 188°. The substance of m. p. 155—155·5° is transformed into *s*-benzoylphenylhydrazine by boiling with alcoholic alkalis or by heating with glacial acetic acid and zinc dust; treatment with benzoyl chloride and pyridine affords *dibenzoyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 163—164°. Methylation yields 2-*benzoyl*-1-*phenyl*-1-β-*benzoylvinyl*-2-*methylhydrazine*, m. p. 158·5—159°, which is converted by hydrolysis into 2-benzoyl-1-phenyl-2-methylhydrazine, m. p. 135—136°. *as*-Benzoylphenylhydrazine reacts with phenyl β-hydroxyvinyl ketone to give β-*benzoylacetaldehydebenzoylphenylhydrazone*, m. p. 132—133°, which is converted into benzanilide by zinc dust and acetic acid and by benzoylation into 1 : 2-dibenzoyl-1-phenyl-2-benzoylvinylhydrazine (benzoyl derivative of the tautomeric form), m. p. 162·5—163°. By heating an alcoholic sodium hydroxide solution of the hydrazone, 4-*benzoyl*-1 : 5-*diphenylpyrazole*, m. p. 144—145°, identical with a specimen synthesised by heating 1 : 5-diphenylpyrazole with benzoyl chloride at 250°, is produced. β-p-*Toluoylacetaldehydebenzoylphenylhydrazone*, m. p. 132·5—134° (cf. A., 1926, 272), prepared from *as*-benzoylphenylhydrazine and *p*-tolyl β-hydroxyvinyl ketone, yields 4-p-*toluoyl*-1 : 5-*diphenylpyrazole*, m. p. 151—152°, which may also be prepared from *p*-toluoyl chloride and 1 : 5-diphenylpyrazole. 2-*Toluoyl*-1-*acetyl*-2-*phenylhydrazine*, m. p. 165—166°, from *s*-acetylphenylhydrazine and *p*-toluoyl chloride, affords *as*-p-*toluoylphenylhydrazine*, m. p. 80—82°, on boiling with 2*N*-sulphuric acid. The last-named condenses with phenyl β-hydroxyvinyl ketone to give, after treatment of the product with sodium hydroxide, 4-*benzoyl*-5-p-*toluoyl*-1-*phenylpyrazole*, m. p. 172—173°, which was also prepared by the alternative method. 1-*Phenyl*-2-β-p-*toluoylvinylhydrazine*, m. p. 124—125°, prepared from *p*-tolyl β-hydroxyvinyl ketone, yields on heating 5-p-*toluoyl*-1-*phenylpyrazole*, b. p. 220—240°, m. p. 61·5—62·5°, which may be converted into the 4-*benzoyl* derivative, m. p. 178·5°, by heating with benzoyl chloride at 220°. *p*-Tolyl β-hydroxyvinyl ketone and *s*-formylphenylhydrazine yield 1-*formyl*-2-*phenyl*-2-β-p-*toluoylvinylhydrazine*, m. p. 180·5°, which affords 3-*p*-toluoyl-1-phenylpyrazole, m. p. 95·5°, when heated with 2*N*-hydrochloric acid. The action of phenylhydrazine on p-*tolyl* β-*benzyloxyvinyl ketone*, m. p. 86—87°, yields 1-*phenyl*-1-β-p-*toluoylvinylhydrazine*, m. p. 172·5—173·5° (p-*nitrobenzylidene* derivative, m. p. 181·5°). 2-*Acetyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 169—170°, prepared from *s*-acetylphenylhydrazine and phenyl β-hydroxyvinyl ketone, yields a *methyl* derivative, m. p. 135·5—136·5°, which gives 1-acetyl-2-phenyl-1-methylhydrazine, m. p. 91—92°, and a *benzoyl* derivative, m. p. 161·5—162·5°. Phenyl β-hydroxyvinyl ketone and benzoylhydrazine react to afford 2-*benzoyl*-1-β-*benzoylvinylhydrazine*, m. p. 145—146°, which gives acetophenonebenzoylhydrazone on hydrolysis, and a *dimethyl* derivative, m. p. 147—148°.

G. A. C. Gough.

Condensation of glyoxalines with formaldehyde. R. Grindley and F. L. Pyman (J.C.S., 1927, 3128—3136; cf. A., 1924, i, 1111).—4(5)-Bromoglyoxaline is converted by formaldehyde at 150° into 4(5)-*bromo*-5(4)-*hydroxymethylglyoxaline*, $+\frac{1}{2}H_2O$, m. p. 116—117° (all m. p. are corr.) [*hydrochloride*, m. p. 157° (decomp.); *picrate*, $+H_2O$, m. p. anhydrous 180°], which is reduced by hydriodic acid and phosphorus to 4(5)-methylglyoxaline. 1 : 4-Dimethylglyoxaline yields similarly 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline*, m. p. 126—127° (*hydrochloride*, m. p. 145°; *hydrogen oxalate*, m. p. 106—107°; *picrate*, m. p. 167—168°), which on reduction affords 1 : 4 : 5-trimethylglyoxaline. 1 : 5-Dimethylglyoxaline furnishes 1 : 5-*dimethyl*-2-*hydroxymethylglyoxaline*, $+\frac{1}{2}H_2O$, m. p. 126—127° (*picrate*, m. p. 174°), reduced to 1 : 2 : 5-*trimethylglyoxaline* (*picrate*, m. p. 208—209°; *chloroaurate*, m. p. 186—187°). 1 : 5-*Dimethyl*-4-*hydroxymethylglyoxaline* (*picrate*, m. p. 178—179°) is obtained by methylation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline and has m. p. 164—165°. 5-Chloro-1-methyl- and 1-methyl-glyoxaline yield the corresponding 2-hydroxymethyl derivatives (cf. Sarasin, A., 1923, i, 711; 1924, i, 1114; Sonn, Hotes, and Sieg, A., 1924, i, 877; 1925, i, 157). The nitroglyoxalines studied do not condense with formaldehyde. The above results show that glyoxalines containing a free imino-group yield 4(5)-hydroxymethyl derivatives, whilst *N*-methylglyoxalines yield either the 2- or 5-derivatives.

H. Burton.

5 : 6 : 8-Trihydroxybenzo-1 : 10-naphthyridine, and its oxidation to 1 : 8-naphthyridine derivatives. E. Sucharda (Kosmos, 1920, 15 pp.; Chem. Zentr., 1927, i, 2831).—5 : 6 : 8-*Trihydroxybenzo*-1 : 10-*naphthyridine* (*sodium* derivative; *acetyl* derivative; *hydrochloride*), yellow, m. p. 348°, obtained by heating 2-aminopyridine-3-carboxylic acid and phloroglucinol at 210—220°, is oxidised by permanganate to 5-*hydroxy*-1 : 8-*naphthyridine*-6 : 7-*dicarboxylic acid*, light yellow, m. p. 304° (decomp.), which, when heated at 120° or boiled with 20% hydrochloric acid, affords 1 : 8-*naphthyridine*-6-*carboxylic acid*, white, m. p. 304° (decomp.). At 304°, both acids give 5-*hydroxy*-1 : 8-*naphthyridine*, white, m. p. 239°.

A. A. Eldridge.

Manufacture of vat dyes of the [phen]anthraquinone series [complex carbazoles]. I. G. Farbenind.—See B., 1928, 9.

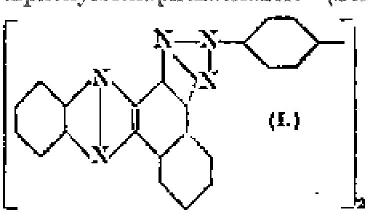
2-Aryl-αβ-naphtha-1 : 2 : 3-triazoles. G. Charrier and M. Gallotti (with J. M. Casaletto,

L. Masciadri, and E. Greppi) (Gazzetta, 1927, **57**, 754—760).—By diazotising 2-*p*-aminophenyl-αβ-naphtha-1 : 2 : 3-triazole (A., 1924, i, 335), and treating the product with potassium iodide, the corresponding 2-p-*iodophenyl* compound, m. p. 218°, is obtained. When in the diazotisation concentrated solutions are used, the 2-*phenylnaphthatriazole*-p-*diazonium sulphate* can be isolated; when this is suspended in water and treated with potassium arsenite solution in the presence of copper powder, 2-*phenyl*-4 : 5-αβ-*naphtha*-1 : 2 : 3-*triazole*-4′-*arsinic acid* (decomp. before m. p.) is obtained, with a large proportion of the phenylnaphthatriazole itself.

By the action of benzenediazonium chloride on 4-nitro-1-naphthylamine, 4-*nitro*-1-*amino*-2-*benzeneazonaphthalene*, m. p. 226°, is obtained, which on heating with copper in nitrobenzene yields 5-*nitro*-2-*phenyl*-αβ-*naphthatriazole*, m. p. 191°.

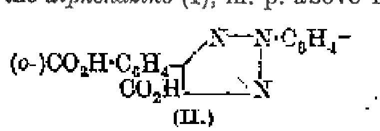
E. W. Wignall.

Polynuclear 1 : 2 : 3-triazoles and their oxidation products. G. Charrier and G. B. Crippa [with C. Pagani, E. Rovida, and C. Azimonti] (Gazzetta, 1927, **57**, 749—754).—The di-ψ-azimide, diphenylbisnaphthatriazole (Schmidt and Hagenbocker, A., 1921, i, 898), is oxidised by chromic acid to a *bis*-o-*quinone*, m. p. 390° (decomp.), which with phenylhydrazine yields a *bis*-(α-*hydroxy*-β-*benzeneazo*) derivative, m. p. 306°, and with *o*-phenylenediamine the *diphenazine* (I), m. p. above 435°



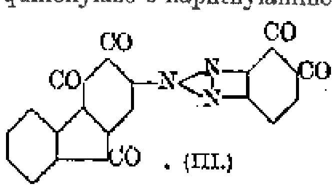
(I.)

Oxidation of the original triazole by alkaline potassium permanganate yields the *tetracarboxylic acid* (II), m. p. 330°



(II.)

Similarly, 2-β-anthraquinonyl-αβ-naphthatriazole, m. p. 305°, obtained by dehydrogenating β-anthraquinonylazo-β-naphthylamine by copper powder in nitrobenzene, yields a *bis*-o-*quinone*, m. p. 350° (decomp.), an orange-red substantive dye to cotton. By the action of fluorene-2-diazonium sulphate on β-naphthylamine, 2-*fluoreneazo*-β-*naphthylamine*, decomp. from 360°, is formed; this is dehydrogenated to the *triazole*, $\begin{matrix}CH_2\\C_6H_4\end{matrix}\!\!>\!C_6H_3{\cdot}N_3{:}C_{10}H_6$, unchanged at 360°, which oxidises to the *keto-bis*-o-*quinone* (III), unchanged at 360°.



(III.)

E. W. Wignall.

Reaction of hydroxylamine with enol ethers and acetylenic ketones; new constitutionally unambiguous *iso*oxazole synthesis. C. Weygand and E. Bauer [with W. Heynemann] (Annalen, 1927, **459**, 123—143).—Since it has been shown that the first stage in the formation of an *iso*oxazole from an unsaturated ketone and hydroxylamine may be either oximation or addition to the multiple linking (A., 1925, i, 1288), further evidence for the constitution of 3 : 5-disubstituted *iso*oxazoles is required (cf. Moureu, A., 1904, i, 95; Ruhemann and Watson, J.C.S., 1904, **85**, 1319; Jörlander, A., 1917, i, 222). This is afforded by their synthesis from chloroaldoximes (hydroxamic chlorides) and sodium arylacetylides in ethereal solution. Thus, ω-chloroanisaldoxime, m. p. 89—90° (cf. Rheinboldt, A., 1927, 245), and sodium phenylacetylide yield 5-phenyl-3-anisyl*iso*oxazole (I), m. p. 120—121°, whilst ω-chlorobenzaldoxime and sodium anisylacetylide yield 3-phenyl-5-anisyl*iso*oxazole (II), m. p. 127—128° (cf. Pond and Shoffstall, A., 1901, i, 35). When phenyl α-4-dimethoxystyryl ketone and hydroxylamine react in presence of acid or alkali, the compound (I) is obtained, but in neutral solution alkali-insoluble *phenyl* α-*hydroxylamino*-4-*methoxystyryl ketone* (III), m. p. 134°, is formed by addition of hydroxylamine to the double linking and elimination of methyl alcohol. This is precipitated by addition of water in an alkali-soluble enolic form which is converted by acids into the *iso*oxazole (I). Anisyl α-methoxystyryl ketone and hydroxylamine yield isomeride (I) in presence of hydrochloric acid, (II) in acetic acid or alkaline solution, and *anisyl* α-*hydroxylaminostyryl ketone*, m. p. 155—157°, in neutral solution. This resembles (III), being converted by acids into (II). When, however, (*a*) phenyl β-bromo-*p*-methoxystyryl ketone, (*b*) *p*-anisyl β-bromostyryl ketone, and the dibromides of (*c*) phenyl *p*-methoxystyryl ketone and (*d*) *p*-anisyl styryl ketone are treated with hydroxylamine and alkali, (*a*) and (*c*) yield (II), and (*b*) and (*d*), (I). This is attributed to the intermediate formation of a dimethylacetal oxime. Crude phenyl α-bromo-β-methoxy-β-anisylethyl ketone yields with hydroxylamine and alkali (II) and a little 4(?5)-hydroxy-3-phenyl-5-anisyl-4 : 5-dihydro*iso*oxazole (Jörlander, *loc. cit.*). By analogy, the products from phenyl α-methoxy-*p*-methylstyryl ketone and *p*-tolyl α-methoxystyryl ketone and this reagent are 5-*phenyl*-3-p-*tolyl*-, m. p. 125—126°, and 3-*phenyl*-5-p-*tolyl*-, m. p. 136—137°, -iso*oxazoles*, respectively. Benzoyl-*p*-anisylacetylene and hydroxylamine afford (*a*) with acetic acid or alkali the substance (I), (*b*) with hydrochloric acid (II), whilst p-*anisoylphenylacetylene*, m. p. 90—91°, from sodium phenylacetylide and anisoyl chloride gives (*a*) (II), (*b*) (I). Thus in (*a*) the reaction probably proceeds through a hydroxylamino-derivative similar to (III) and in (*b*) through an oxime.

H. E. F. Notton.

Hydroxythiazoles or thiazolones. A. Hantzsch [with H. Schwedler and H. Schwaneberg] (Ber., 1927, **60**, [*B*], 2537—2545).—Mainly a reply to Tcherniac (J.C.S., 1919, **115**, 1071).—Thiocyanoacetone is converted slowly by cold, rapidly by hot concentrated hydrochloric acid without resinification into methylthiazolone, $NH\!<\!\begin{matrix}CMe{:}CH\\CO{-}S\end{matrix}$ (formerly considered to be hydroxymethylthiazole); under the influence of alkalis, even hydrogen carbonates, the production of the thiazolone is accompanied by extensive resinification. 2-Hydroxy-4-methylthiazole is very readily obtained by the action of methylxanthamide on chloroacetone; if, however, the hydrolysing action of the liberated hydrogen chloride

is inhibited by the addition of potassium acetate and the use of alcohol is avoided, 4-*methoxy*-2-*methylthiazole*, b. p. 59—60°/18 mm. (additive *compound* with mercuric chloride, m. p. 123—124°), and, analogously, 4-*ethoxy*-2-*methylthiazole*, b. p. 71—72°/15 mm., are readily prepared. The methyl ether is also obtained by the action of diazomethane on methylthiazolone dissolved in alcohol, ether, chloroform, or benzene. It gives a *hydrochloride*, m. p. 78° with evolution of methyl chloride and production of methylthiazolone, thus differing from the isomeric *N*-ether *hydrochloride*, m. p. 109° with evolution of hydrogen chloride. Methylthiazolone and its *N*-methyl ether give additive *compounds* with mercuric chloride, m. p. about 180° (decomp.). This behaviour cannot be reconciled with Tcherniac's formulation of methylthiazolone as "methylrhodim,"

$O<\begin{matrix}CMe:CH\\C(:NH)\cdot S\end{matrix}$, which could not give rise to *O*-ethers

and the *N*-ethers of which must yield methylamine when hydrolysed. Contrary to Tcherniac's observation, homogeneous hydroxymethylthiazole and thiocyanoacetone are converted into methylthiazole (and resinous substances) when distilled with zinc dust. Comparison of hydroxymethylthiazole with its *O*- and *N*-ethers shows that it is to be regarded as methylthiazolone when solid. Optical analysis shows it to be a mixture of hydroxymethylthiazole and methylthiazolone in alcoholic solution, whereas in chloroform and, particularly, in benzene and ether the hydroxy-form appears present only in traces. Methylthiazolone dissolved in phosphoryl chloride is converted by a slight excess of phosphorus pentachloride in the presence of boiling ether into 5-*chloro*-4-*methylthiazol*-2-*one*, m. p. 140°, regarded by Tcherniac as "methylchlororhodim," which dissolves in solutions of alkali or sodium hydrogen carbonate and is precipitated unchanged from these solutions by immediate addition of acid. Boiling phosphoryl chloride transforms 4-methylthiazol-2-one into 2-chloro-4-methylthiazole, b. p. 164—165°, identical with the substance obtained by Tcherniac from thiocyanoacetone and hydrogen chloride. H. WREN.

Thiazoles. XIV. Synthesis of 2-*o*- and -*m*-aminophenyl-6-methylbenzthiazoles; new isomerides of dehydrothio-*p*-toluidine, and incidental compounds. M. T. BOGERT and L. SMITH (J. Amer. Chem. Soc., 1927, **49**, 3135—3137; cf. A., 1927, 680).—Condensation of zinc 4-aminothio-*m*-tolyloxide with *m*-nitrobenzoyl chloride affords 1-m-*nitrophenyl*-5-*methylbenzthiazole*, yellow, m. p. 166°. The latter, on reduction with tin and hydrochloric acid, yields 1-m-*aminophenyl*-5-*methylbenzthiazole*, m. p. 181°, and this affords a *sulphonic acid*, dark brown, which is converted into a *dye*, analogous to chloramine-yellow, on treatment with alkaline hypochlorite. 1-o-*Nitrophenyl*-5-*methylbenzthiazole*, yellow, non-crystalline, and 1-o-*aminophenyl*-5-*methylbenzthiazole*, m. p. 137° (*acetyl* derivative, m. p. 150°), are obtained analogously, but sulphonation of the latter and subsequent treatment with hypochlorite does not yield a dye. F. G. WILLSON.

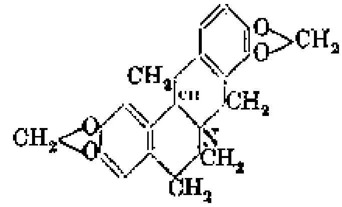
Benzidine rearrangement in heterocyclic series. I. P. K. BOSE (J. Indian Chem. Soc., 1927, **4**, 331—338).—Phenacyl bromide and phenylthiosemicarbazide react in alcohol to form 2-*phenylhydrazino*-4-*phenylthiazole*, m. p. 191° (*hydrobromide*; *acetyl* derivative, m. p. 161°). Boiling dilute hydrochloric acid converts the thiazole into 2-*amino*-4-*phenyl*-5-p-*aminophenylthiazole*, m. p. 193—194° [*dihydrochloride*, $+H_2O$, decomp. above 260°; *picrate*, m. p. 134—135° (decomp.); *chloroplatinate*; *diacetyl* derivative, m. p. 285—286°], due to a benzidine rearrangement (cf. Fargher and Pyman, J.C.S., 1919, **115**, 222; Pyman and Ravald, *ibid.*, 1920, **117**, 1426). 2-*Phenylhydrazino*-4-p-*tolylthiazole*, m. p. 186° (*hydrobromide*; *acetyl* derivative, m. p. 146°), yields similarly 2-*amino*-4-p-*tolyl*-5-p-*aminophenylthiazole*, m. p. 182° [*diacetyl* derivative, m. p. 290°; *dihydrochloride*; *chloroplatinate*; *picrate*, m. p. 215° (decomp.)]. 2-*Phenylhydrazino*-4-*methylthiazole*, m. p. 179° (*acetyl* derivative, m. p. 232°), yields 2-*amino*-4-*methyl*-5-p-*aminophenylthiazole*, m. p. 181° [*dihydrochloride*, $+2H_2O$, decomp. above 240°; *chloroplatinate*; *picrate*, m. p. 214° (decomp.); *benzylidene* derivative, m. p. 177°]. Oxidation of 2-*acetamido*-4-*methyl*-5-p-*acetamidophenylthiazole*, m. p. 292°, with potassium permanganate gives *p*-acetamidobenzoic acid, thus affording further proof of the constitution. H. BURTON.

Manufacture of thiazole derivatives of α-naphthaquinone. I. G. FARBENIND.—See B., 1928, 8.

Simple homologues of codeine. A. E. TSCHITSCHIBABIN and A. KIRSSANOV (Bull. Soc. chim., 1927, [iv], **41**, 1649—1652).—With propyl *p*-toluenesulphonate in boiling *n*-propyl alcohol morphine affords the n-*propyl ether*, m. p. 69—72° ($+\frac{1}{2}H_2O$) [*hydrochloride*, m. p. 146—153° (decomp.) ($+H_2O$, m. p. 111—114°)]. The n-*butyl ether hydrochloride*, $+H_2O$, m. p. 101—104° (anhydrous, m. p. 119—122°), is similarly prepared. R. BRIGHTMAN.

Synthesis of oxypalmatine. Dehydronoroxy-ψ-corydaline. J. N. RAY (J. Indian Chem. Soc., 1927, 4, 403—408).—Homoveratrylamine and meconinecarboxyl chloride react, giving *meconinecarboxy*-β-*veratrylethylamide*, m. p. 185°, which is converted by prolonged treatment with phosphorus oxychloride, followed by reduction with zinc dust and acetic acid, into oxypalmatine, m. p. 194—196° (Haworth, Koepfli, and Perkin, A., 1927, 472, give m. p. 183°). A small quantity of a chloro-compound is produced at the same time, probably similar to chloro*nor*oxyberberine, m. p. 229—230° (cf. Perkin, Ray, and Robinson, A., 1925, i, 695). H. BURTON.

How do alkaloids originate? J. GADAMER (Festschr. A. Tschirch, 1926, 36—41; Chem. Zentr., 1927, i, 2558—2559).—A discussion. [With WACHSMUTH.]—From *Corydalis cava* tops an *alkaloid*, to which the annexed formula is ascribed, has been obtained, and has been resolved by means of bromocamphorsulphonic acid. A. A. ELDRIDGE.



Silicon organic compounds. I. Phenol esters of silicic acid. H. JORG and J. STETTER

(J. pr. Chem., 1927, [ii], **117**, 305—310).—Silicon tetrachloride reacts with phenol (2 mols.) at 100° to give *dichlorodiphenoxysilicane*, b. p. 167—171°/13 mm., *chlorotriphenoxysilicane*, b. p. 229—230°/14 mm., and tetraphenoxysilicane, b. p. 280°/14 mm. In a similar manner *chlorotri*-p-*bromophenoxysilicane*, b. p. 310—320°/12 mm., *trichlorothiophenoxysilicane*, b. p. 110°/12 mm., and *tetra*-o-*methoxyphenoxysilicane*, b. p. 317—323°/12 mm., are prepared. By the interaction of magnesium phenyl bromide and dichlorodiphenoxysilicane in ethereal solution diphenylsilicanediol, m. p. 116° (cf. Martin, A., 1912, i, 1014), is prepared. Chlorotriphenoxysilicane yields similarly *triphenoxyphenylsilicane*, m. p. 40°, b. p. 250°/13 mm.

G. A. C. Gough.

Isomerism of *p*-hydroxyphenylarsinic acid. G. Gilta (Compt. rend., 1927, **184**, 1073—1075).—*p*-Hydroxyphenylarsinic acid, its 3-nitro-derivative, and its barium salt all occur in two different crystalline forms, which are regarded as possessing the benzenoid and quinonoid structure, respectively. The 3 : 5-dinitro-derivative of the acid is obtained in one form only. Isomerism analogous to the above is found in 4-hydroxy-3-methylphenylarsinic acid.

B. W. Anderson.

Dicarboxyphenylarsinic acids. II. 3 : 4-Dicarboxyphenylarsinic acid and some of its derivatives. C. S. Hamilton and V. C. Jelinek (J. Amer. Chem. Soc., 1927, **49**, 3165—3169; cf. A., 1926, 1162).—Methyl 4-aminophthalate is converted by the normal process into 3 : 4-*dicarbomethoxyphenylarsinic acid*, which is hydrolysed by absolute-alcoholic sodium ethoxide to the *tetrasodium* salt of 3 : 4-*dicarboxyphenylarsinic acid*, yellow, m. p. 180° (decomp.) (*trisodium* salt; *ethyl* ester), the latter being isolated by treatment of the *silver* salt in aqueous suspension with hydrochloric acid, and evaporation after removal of the silver chloride. The *acid anhydride* is obtained by heating the acid for 3 days under reduced pressure at 160° in presence of phosphorus pentoxide.

F. G. Willson.

Organo-antimony compounds. I. S. C. Niyogy (J. Indian Chem. Soc., 1927, **4**, 397—402).—2 : 6-*Di-iodo-4-nitroacetanilide*, m. p. 245—246°, is reduced by ammonium sulphide in alcoholic solution to 2 : 6-*di-iodo-4-aminoacetanilide* (*di-iodo-acetyl*-p-*phenylenediamine*), m. p. 247—248°, which is converted by the usual method into 3 : 5-*di-iodo-4-acetamidophenylstibinic acid* (*sodium* salt). Similarly, from 2 : 6-*dichloro-4-aminoacetanilide*, m. p. 209—210°, 2-*bromo-4-aminoacetanilide*, m. p. 120—121°, 2 : 6-*dibromo-4-aminoacetanilide*, m. p. 235—236°, and 2-*iodo-4-aminoacetanilide*, m. p. 134—135°, there were prepared the *sodium* salts of 3 : 5-*dichloro-4-acetamidophenyl*-, 3-*bromo-4-acetamidophenyl*-, 3:5-*dibromo-4-acetamidophenyl*-, and 3-*iodo-4-acetamidophenyl-stibinic acids*. 2-*Iodo-4-nitroacetanilide* has m. p. 138—139°.

H. Burton.

Derivatives of bismuth di- and tri-phenyl. S. Rozenblumówna and S. Weil (Viadomosci farm., 1927, **54**, 25—28; Chem. Zentr., 1927, ii, 1251).—Diphenyliodobismuthine yielded bismuth triphenyl, not bismuth diphenyl; diphenylhalogenobismuthines, when treated in alcoholic solution with sodium hydroxide, yielded diphenylhydroxybismuthine (cf. Challenger and Allpress, J.C.S., 1921, **119**, 913).

A. A. Eldridge.

Hydrolysis of egg-albumin by pepsin in relation to the formation of diketopiperazines. A. Blanchetière (Compt. rend., 1927, **185**, 1321—1323; cf. A., 1927, 474).—Egg-albumin was hydrolysed at 45° in aqueous solutions containing 0·1N-hydrochloric acid, 0·1 g. of pepsin, and some toluene, for 1—82 days, and the diketopiperazine-nitrogen content was determined in each case. With raw albumin this figure decreased rapidly at first, reaching a constant value after 30 days. The reverse occurred with albumin previously denatured at 100°, an increase to a constant value being observed. The formation and hydrolysis of diketopiperazines indicated by these results is discussed.

B. W. Anderson.

Anhydrides of amino-acids from gelatin: hydrolysis by the method of Zelinski and Sadikov. N. Gavrilov and K. Lavrovski (Biochem. Z., 1927, **190**, 278—285).—From the solution obtained by heating gelatin in an autoclave with 1·5% sulphuric acid, *l*-prolylglycine anhydride and *l*-leucylglycine anhydride are isolated and together form 10% of the gelatin used.

P. W. Clutterbuck.

Hydrolysis of proteins by acids and alkalis. J. S. Jaitschnikov (Biochem. Z., 1927, **190**, 114—121).—The kinetics of the hydrolysis of 2 : 5-diketopiperazine, glycylglycine, peptone, and proteins (albumin, caseinogen, edestin, glutin, elastin, keratin, and silk) by varying concentrations of sodium hydroxide and hydrochloric acid at different temperatures have been determined. With the 2 : 5-diketopiperazine and the dipeptide the hydrolysis is a unimolecular reaction, whilst for peptones and proteins the formula of Schütz and Borisoff ($K=x/\sqrt{t}$, where K is the coefficient, x the amount of protein hydrolysed, and t the time) is applicable. The amount of hydrolysis has been measured by formol titration (Sørensen) after neutralisation.

A. Wormall.

Formation of metal-albumin compounds. A. Benedicenti and G. B. Bonino (Arch. sci. biol., 1926, **8**, 241—247; Chem. Zentr., 1927, i, 2521—2522).—The ratio of the *P.D.* between cobalt and egg-albumin treated with powdered cobalt to the temperature has a maximum value at the coagulation temperature of the protein. The effect of dilution with water and of variation in p_H around the isoelectric point was investigated.

A. A. Eldridge.

Protein-metal compounds. I. G. B. Bonino and M. Bottini. **II—IV.** G. B. Bonino and A. Grandi (Arch. sci. biol., 1926, **8**, 248—257, 258—276, 277—288, 289—292; Chem. Zentr., 1927, i, 2522—2523).—I. The potential of cobalt towards water is —0·708 volt, and towards a cobalt-protein solution of p_H 6·4 —0·648 volt.

II. With hydrogen-ion concentrations greater than that of the isoelectric point, the fixation of cobalt to gelatin and the decrease in the conductivity and viscosity are parallel.

III. Gelatin solutions (1%) of p_H 2—7 were treated with cobalt and placed in Malfitano's collodion sacs,

the exterior liquid being $0\cdot002N$-cobalt chloride solution, and the p_H and total cobalt content were determined after 5—6 days. Parallel experiments were performed with gelatin solution against distilled water containing powdered cobalt, and also with exterior liquids of hydrogen-ion concentration greater than that of the isoelectric point, or N with respect to potassium chloride. In solutions of the same composition, qualitatively and quantitatively, values of ε in the relation $(1/\varepsilon)([Co_{total}]_2/[Co_{total}]_1)^{\frac{1}{2}} = ([Co^{\cdot\cdot}]_2/[Co^{\cdot\cdot}]_1)^{\frac{1}{2}}$ are highly concordant or identical. Increase of the total cobalt content is accompanied by decrease of the quotients $[H^{\cdot}]_1/[H^{\cdot}]_2$ and $\varepsilon([Co_{total}]_2/[Co_{total}]_1)^{\frac{1}{2}}$. If the metal–protein is brought into equilibrium with an acid solution, so that the p_H of the protein is less than 4·7, the values at equilibrium are less than unity.

IV. Varying quantities of sodium hydroxide were added to pure gelatin, and a portion was brought into equilibrium with cobalt. The conductivity increases at $p_H>7$, and on further increase of p_H becomes zero, although combined cobalt is still present. It is supposed that at $p_H>7$ tervalent cobalt is present in a complex form corresponding with the cobaltammines.

A. A. ELDRIDGE.

Combination of gelatin with organic bases. A. PETRUNKIN and M. PETRUNKIN (J. Gen. Physiol., 1927, **12**, 101—110).—Alkaloids (atropine, strychnine, and quinine) and organic bases (guanidine and adrenaline) combine with gelatin on the basic side of the isoelectric point of the protein, but very little, if at all, on the acid side. W. O. KERMACK.

Irradiated proteins. II. Absorption in the ultra-violet of light-denatured serum-albumin. M. SPIEGEL-ADOLF and O. KRUMPEL (Biochem. Z., 1927, **190**, 28—41).—Absorption spectra and curves have been determined for electrolyte-free serum-albumin solutions and for irradiated and non-irradiated serum-albumin in acid and alkaline solutions. The irradiated solutions show a stronger power of absorption for short waves in the region of 400 μμ to 267·5 compared with the non-irradiated solutions, but there is no apparent displacement of the absorption maxima and minima. The absorption spectra of non-irradiated acid and alkaline serum-albumin solutions show slight differences only, whilst those of the irradiated solutions are practically identical. The results are discussed in relation to the absorption curves of the aromatic amino-acids and the behaviour of these acids on irradiation, and also in relation to the stronger absorption powers of 2 : 5-diketopiperazines compared with the corresponding dipeptides. A. WORMALL.

Separation of ovalbumin from conalbumin. H. WU and S. M. LING (Chinese J. Physiol., 1927, **1**, 431—434).—A method is described for the separation of the ovalbumin from the conalbumin in egg-white based on the fact that ovalbumin undergoes coagulation by shaking whilst conalbumin does not. Of the total albumin of egg-white 10% is conalbumin.

E. A. LUNT.

Denaturation of proteins. V. Factors controlling coagulation of proteins by shaking. H. WU and S. M. LING (Chinese J. Physiol., 1927, **1**, 407—430).—The conditions relating to the mechanical coagulation of solutions of egg-albumin, oxyhæmoglobin, and methæmoglobin have been investigated and show that, in contrast to the coagulation of albumin by alcohol, mechanical coagulation is not separable into the two stages of denaturation and agglutination. Whilst the rate of coagulation of hæmoglobin is increased by the addition of neutral alkali salts, the increase being approximately proportional to the concentration of the added salt, the coagulation of egg-albumin is not appreciably affected in this way. Non-electrolytes increase the rate of coagulation of both these substances. The p_H at which maximum coagulation takes place in the absence of electrolytes corresponds with the isoelectric point of the proteins examined, and the amount of coagulation is independent of the concentration of the protein solution used and is a linear function of time. No evidence of the liberation of any non-protein substance as a result of mechanical coagulation was obtained. It is concluded that mechanical coagulation is an irreversible surface reaction.

E. A. LUNT.

Determination of complex proteins by means of their "protein-error." R. GOIFFON and HAUDIQUET (Compt. rend. Soc. Biol., 1927, **97**, 311—313; Chem. Zentr., 1927, ii, 1288).—Disturbance in colorimetric hydrogen-ion determinations caused by the presence of proteins (Sørensen's "protein-error") is employed for the determination of the proteins, by measuring (using a 0·02% solution of orange-IV) the increased buffer action of a solution on addition of a strong acid. A. A. ELDRIDGE.

Pregl's universal filling applied to macro-combustions. W. DAVIES (J.C.S., 1927, 3161—3162).—The universal filling devised by Pregl ("Die Quantitative Organische Mikroanalyse," 1923) for carbon and hydrogen determination has been successfully applied on a macro-scale. Details are given regarding the filling of the combustion tube and the special precautions to be taken in drying the lead peroxide asbestos plug. The lead peroxide in the combustion tube is heated by a hollow copper boiler, which itself is heated by *o*-dichlorobenzene. The procedure is normal, and representative analyses gave excellent results. R. A. PRATT.

Simultaneous determination of sulphur and chlorine in organic compounds. E. GEBAUER-FÜLNEGG and E. PETERTIL (Monatsh., 1927, **48**, 619—625).—The method of Asbóth (A., 1896, ii, 448) for the determination of sulphur in organic compounds is adapted so that chlorine when also present may also be determined. The substance is heated with excess of sodium carbonate and sodium peroxide in a nickel crucible, which while still hot is plunged into water in a porcelain dish. The solution is acidified with nitric acid and is evaporated to dryness to render insoluble the silica which has been removed from the porcelain, and the sulphur in the soluble product is determined as barium sulphate. After the latter is precipitated, the solution is boiled with sodium sulphite and the chlorine determined as silver chloride.

E. W. WIGNALL.

Biochemistry.

Application of the oil turbine type of ultracentrifuge to the study of the stability region of carbon monoxide–hæmoglobin. T. SVEDBERG and J. B. NICHOLS (J. Amer. Chem. Soc., 1927, **49**, 2920—2934).—Experiments with an oil turbine ultracentrifuge show that over the range p_H 6·0—7·56 the diffusion constant (0·071 cm.^{2}/day) and specific sedimentation velocity ($5{\cdot}46\times10^{-13}$ cm./sec.) of carbon monoxide–hæmoglobin are normal, whilst the mol. wt., 68,000, is normal from p_H 6·0 to p_H 9·05. At p_H 9·05, the carbon monoxide–hæmoglobin molecule appears to hold a unimolecular layer of water at its surface. F. G. WILLSON.

Metabolism of blood platelets. G. ENDRES and F. KUBOWITZ (Biochem. Z., 1927, **191**, 395—397).—The respiration and anaerobic glycolysis of the platelets of human and dog's blood are determined and tabulated. P. W. CLUTTERBUCK.

Biological test for blood. W. WILLCOX (Analyst, 1928, **53**, 2—5).—The value of the precipitin test is emphasised. The complement fixation test is regarded only as a confirmatory test. D. G. HEWER.

Technique of the precipitin test and its forensic value. G. R. LYNCH (Analyst, 1928, **53**, 5—13).—For the detection of blood stains by the precipitin test it is necessary to prepare an antiserum (best from rabbits) capable of precipitin formation with at least a 1—5000 dilution of human serum in normal saline. The unknown extract is prepared by incubating the stained area in saline at 37°, testing for protein concentration, and diluting to give a concentration not greater than 1 in 1000, thus avoiding negative reactions due to zone reactions or false positive results from group reactions. The test is then made, either by layering, by dropping the antiserum on to the unknown extract, by running the antiserum down the side of the tube previously moistened with the unknown extract, or by Collés' tube method. The complete test requires 10 control tubes and is useful for the detection of occult blood in fæces and of the addition of egg-albumin to urine to simulate disease. It may also be used in cattle-maiming cases and is likely to find increased scope in food examination, for the blood of any animal may be immunised against a protein foreign to that animal. Difficulties due to group reactions of sera of closely-related animals may be overcome by the absorption method, by cross-immunisation, by dilution of the antiserum beyond the group reaction point, or by taking account of precipitation from similar dilutions of the antigen and related antigens. D. G. HEWER.

Use of blood-grouping reactions in forensic investigations. F. C. MARTLEY (Analyst, 1928, **53**, 14—18).—Bloods may be divided into 4 groups according as to whether the blood-cells agglutinate when mixed with the sera or not. A blood may be placed in its correct group by mixing its corpuscles with sera of two known groups and observing presence or absence of clumping, and if necessary mixing the unknown serum with corpuscles from the known groups. Such tests are necessary before blood transfusion can be safely undertaken. Extent of agglutination varies within rather wide limits and is finite. Dried blood stains may be placed by using a known test serum of dilutions from 0·5, 0·25, down to 1 in 500 or 1000, and 1% agglutinable washed corpuscles added to an equal volume of each, and dilutions at which clumping occurs noted. The process is repeated with the same serum incubated with a piece of the same material free from stain, when clumping may not extend so far down the series. Incubation of the same serum with the blood stain is then carried out, when either the serum will cease to clump the test corpuscles or its power will be extinguished several places sooner than in the last test. D. G. HEWER.

Different sulphur contents of hæmoglobins from different sources. J. VALER (Biochem. Z., 1927, **190**, 444—455).—A series of careful determinations of the sulphur and iron contents of recrystallised samples of the oxyhæmoglobin of the horse, ox, dog, and cat showed that whereas in cat and ox consistent values for the sulphur content could be obtained, this was not the case for horse, whilst with dog no sample contained the same amount of sulphur as any other, the preparation containing most having almost half as much again as that having least. With cat's oxyhæmoglobin, the minimal mol. wt. calculated from the iron content was 1690 and from the sulphur content 3299, *i.e.*, the iron and sulphur are in the proportion FeS_5. For ox blood, the proportions are FeS_3, and for horse, whilst several preparations correspond with the proportion FeS_3, others agree with Fe_2S_5. It is concluded that the supposed uniformity of samples of oxyhæmoglobin from different sources (previously concluded from identical iron determinations) does not exist. P. W. CLUTTERBUCK.

Nature of the blood-sugar. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1927, **96**, 414—416; Chem. Zentr., 1927, i, 2565).—Deproteinisation by zinc hydroxide in Hagedørn and Jensen's method for the determination of dextrose yields for the non-fermentable residue values which fluctuate around 0·23 g. per 1000. The non-fermentable residue is almost equally great in normal glycæmia for dogs, rabbits, and man, and is not augmented in hyperglycæmia. The origin of variations in the values obtained by various investigators is discussed. A. A. ELDRIDGE.

Protein-blood-sugar. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1927, **96**, 417—421; Chem. Zentr., 1927, i, 2565).—The yeast method for the determination of blood-sugar reveals no so-called "protein-sugar," although traces, if present, could scarcely be detected. A. A. ELDRIDGE.

Ability of human blood to form lactic acid in presence of monosaccharides. A. ABRAHAM (Z. Klin. Med., 1926, **104**, 609—618; Chem. Zentr., 1927, i, 2439).—The production of lactic acid by defibrinated human blood is increased in presence of dextrose, mannose, or (less markedly) lævulose. A. A. ELDRIDGE.

Fermentation of dextrose in blood-plasma by yeast. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, **96**, 410—413; Chem. Zentr. 1927, i, 2562).—A mixture of 1 c.c. of serum or 0·2% oxalated blood, 1 c.c. of a suspension of fresh yeast (5 g.) in 0·9% sodium chloride solution (10 c.c.), and 8 c.c. of 0·9% sodium chloride solution is shaken for 30 min. at 38°, cooled, filtered, freed from protein with zinc hydroxide, and the dextrose determined by Hagedørn and Jensen's method. The autoreduction error is inconsiderable when the duration of the fermentation is brief. A. A. Eldridge.

Serum-globulin. L. Reiner (Biochem. Z., 1927, **191**, 158—174).—The precipitate corresponding with euglobulin may be prepared from sera by electrodialysis after repeated and thorough extraction with ether–alcohol. Euglobulin is not a lipoid–protein complex. By fractionation and purification, it changes in physical properties, particularly in solubility, becoming denatured in the process. The chief constituent of the globulin fraction is a protein practically insoluble in water and in physiological saline. By dialysis, the compound of globulin and protective colloid dissociates and the euglobulin precipitates. After the first precipitation, the precipitate still contains considerable amounts of protective colloid and it may still be dispersed as a cloudy solution in saline. After repeated precipitation, the protective colloid content and the dispersibility of the globulin decrease. The protective colloid also protects the globulin from the denaturing action of ether–alcohol. That the globulin has a wide isoelectric zone is evident from the course of the dissociation curve obtained by cataphoretic measurements, dissociation taking place at p_H 5·9 and between 4 6 and 4·1. Globulins with different isoelectric points could not be isolated. P. W. Clutterbuck.

Physico-chemical characteristics of normal and pathologically altered blood-serum. G. Lasch and J. Reitstotter (Biochem. Z., 1927, **190**, 84—94).—The methods employed previously (Reitstotter, A., 1921, ii, 176; 1923, i, 393) and the apparatus used are described fully, and it is considered that uniform, well-defined, and electrolyte-free protein fractions can be obtained in this way. The serum (*e.g.*, diphtheritic serum), contained in the centre portion of a cell which is divided into three chambers by two membranes, is freed from electrolytes and "extractive" substances (protein decomposition products) by electrodialysis. Euglobulin and a small fraction of the antitoxic substance are precipitated and are removed by centrifuging. The albumin and fatty substances which are still present can be removed by modifications of the process, and finally a water-clear solution, which contains the pseudoglobulin and the specific substance (antitoxin) associated with it, is obtained. The previous findings of Reitstotter (*loc. cit.*) on the sensitising action of protein fractions of normal and immune sera on ferric hydroxide sols, and the confirmatory experiments of Freundlich and Beck (A., 1926, 316), are discussed. A. Wormall.

Action of ultra-violet light on serum colloids. W. Gobel (Biochem. Z., 1927, **190**, 95—100).—Irradiation of human serum *in vitro* results in a lowering of the surface tension, but *in vivo* irradiation may lead to a rise or a fall. Subjects who have lived at high altitudes for a short period only (1—3 months) show a rise in the surface tension of the serum after irradiation, whilst those tested after a longer period (5—21 months) show a fall. This difference is probably due to an adaptation process, but no relationship between the type and the magnitude of the alteration in surface tension and the pigmentation of the irradiated skin can be observed. It is suggested that the results support the view that protein therapy and ray therapy have many common features and may be analogous. A. Wormall.

Loosely-combined copper and iron in blood-serum. O. Warburg and H. A. Krebs (Biochem. Z., 1927, **190**, 143—149).—The cysteine method for the determination of loosely-combined copper and iron in serum is described (cf. Warburg, A., 1927, 985). The values obtained for human serum give an average of $1{\cdot}7\times10^{-3}$ mg. of copper and $0{\cdot}7\times10^{-3}$ mg. of iron per c.c. of serum. Whereas the sera of the frog, dog, rabbit, guinea-pig, and rat contain about the same amount of copper as human serum, the sera of birds give lower values, although birds rendered anæmic by bleeding show an increase in serum-copper of three- to six-fold. The amount of loosely-bound iron in the sera of these different animals is generally greater than that in human serum. The loosely-bound copper of four different sera (horse and man) determined by this method is found to be equal to the total copper of the ashed serum. The copper content of the serum of rats which have received an intravenous injection of copper sulphate (0·5 mg. Cu per 160 g. rat) dissolved in physiological saline falls rapidly from its immediate high level and in about 6 hrs. has become normal. A. Wormall.

Chemical composition and properties of blood before and after food. I. Hydrogen-ion concentration of blood and its chloride, sugar, and calcium content. S. E. Sewerin. **II. Changes of the alkali reserve of the blood and of its chloride content during the digestion process.** G. W. Derwies and S. E. Sewerin (Biochem. Z., 1927, **190**, 326—329; 330—335).—I. Determinations of p_H on a number of rabbits after 1·5—2·5 days' fasting and on the same animals 3 hrs. after feeding with cabbage are tabulated and show that the blood is more acid during starvation. The chloride and calcium content of the blood is the same in the two conditions. The sugar content of the different rabbits varies greatly, but is higher in the fed than in the starving animals.

II. During digestion the alkaline reserve of the blood increases and the chloride content is only insignificantly changed, generally suggesting a slight rise. P. W. Clutterbuck.

Preservation of blood for chemical analysis by means of sodium fluoride. J. H. Roe, O. J. Irish, and J. I. Boyd (J. Biol. Chem., 1927, **75**, 685—695).—Under sterile conditions 1% of sodium fluoride will preserve blood for 10 days with respect to its content of non-protein nitrogen, uric acid,

creatinine, sugar, and cholesterol; in the absence of aseptic precautions 2% of sodium fluoride is necessary to prevent marked changes in the blood. For the determination of carbamide by the urease method in blood preserved by fluoride, the blood must be diluted until the concentration of fluoride is 0·3% or less. C. R. HARINGTON.

Simultaneous protease and residual nitrogen determination for blood. F. HIMMERICH (Biochem. Z., 1927, **191**, 74—82).—A micro-method for the simultaneous determination of protease and residual nitrogen of whole blood is described. Addition of sodium fluoride to hæmolysed blood in amount sufficient to act as antiseptic does not disturb the precipitation of protein and the action of blood-proteases. Shaking hæmolysed blood with chloroform accelerates the subsequent precipitation of protein with trichloroacetic acid, without having any effect on the residual nitrogen values obtained. The protein is also quantitatively precipitated by keeping for a long time with chloroform. Trichloroacetic acid is recommended as precipitant in protease determinations since it does not precipitate peptide nitrogen as do phosphotungstic acid and colloidal ferric hydroxide. P. W. CLUTTERBUCK.

Gasometric nitrogen determination in small amounts of blood and urine by sodium hypobromite, using Borodin's apparatus. L. SOLOWJEW (Biochem. Z., 1927, **190**, 199—216).—1—2 c.c. of urine or 0·3—1·0 c.c. of blood is heated with concentrated sulphuric acid and 30% hydrogen peroxide until the fluid is decolorised. The liquid is diluted with water to 30—50 c.c. and the ammonia in an aliquot portion (15—30 c.c.) is determined in the Borodin nitrometer by treatment with alkaline sodium hypobromite solution and measurement of the nitrogen evolved. The error under these conditions is less than $\pm 3{\cdot}0\%$. Solutions of sodium hypobromite which have been kept for some time give higher but more consistent results. The chief error is due to the liberation of small amounts of oxygen with the nitrogen, and when sodium hypobromite solution which has been kept for 2—5 days and then filtered is used, and the oxygen evolved in the determination removed by pyrogallol, the error is reduced to ± 1—2·5% for quantities of nitrogen between 5 and 30 mg. A. WORMALL.

Determination of minimal quantities of nicotine in blood. A. S. SOKOLOV and V. D. LYUBOVTZEVA (Trans. Sci. Chem. Pharm. Inst., 1923, No. 3, 69—77).—Blood (5 c.c.) is added to boiling water (25—30 c.c.) containing 2—3 drops of 10% acetic acid solution; 0·5 g. of sodium hydroxide and 4 g. of sodium chloride are added, and the mixture is distilled with steam. Nicotine (to 1 in 5×10^5) is determined in 150 c.c. of distillate (evaporated to 25 c.c.) with Lugol's solution.

CHEMICAL ABSTRACTS.

Formation of ammonia from cyanic acid. C. ARTOM (XII Int. Cong. Physiol., 1926, 9—10; Chem. Zentr., 1927, i, 2408).—The amount of ammonia formed when alkali cyanates at various p_H values are heated at 38° for 2—96 hrs. increases with rise of hydrogen-ion concentration, particularly between p_H 5 and 7. Cyanates may be present in the blood, and it may be possible to correlate spontaneous increase in the acidity of blood with extravascular and renal ammonia formation. A. A. ELDRIDGE.

Determination of inorganic phosphorus in small amounts of blood. J. WARKANY (Biochem. Z., 1927, **190**, 336—339).—The Briggs' modification of the Bell-Doisy method for the determination of phosphorus is adapted for micro-determinations, inorganic phosphorus being determined in 0·2 c.c. of serum. The method gives good agreement with the macro-method and is used for serum, serum of rachitic children, and for diluted serum after addition of known amounts of phosphate.

P. W. CLUTTERBUCK.

Blood coagulation. H. DE WAELE (XII Int. Cong. Physiol., 1926, 165—166; Chem. Zentr., 1927, i, 2439).—The properties of fibrinogen and its compounds are described. Blood fibrinogen has solubility minima at p_H 4 and 7—9. Defatted fibrinogen does not coagulate. A. A. ELDRIDGE.

Blood coagulation. XVI. Glycolysis in an artificial clotting mixture (fibrinogen+thrombin). XVII. Displacement of p_H during clotting. XVIII. Influence of hypo- and hyperpnea on clotting. B. STUBER and K. LANG (Biochem. Z., 1927, **191**, 374—377, 378—385, 386—394).—XVI. Whereas in the clotting of fibrinogen-serum or in the spontaneous clotting of whole blood and plasma a considerable amount of glycolysis occurs, the velocity of which is proportional to the clotting time, in the clotting of fibrinogen with the thrombin of Schmidt, no such glycolysis takes place, the difference being regarded as evidence of the artificial nature of this thrombin (cf. A., 1927, 68).

XVII. A double electrode is used to determine the changes of hydrogen-ion concentration in various clotting systems from the beginning of clotting at short intervals. During the clotting of both blood and milk, a displacement of the p_H to the alkaline side occurs.

XVIII. During hypo- and hyper-pnea, the clotting power of blood is greatly increased, glycolysis is considerably accelerated, and an increase in thrombocytes occurs. P. W. CLUTTERBUCK.

Glycolysis and blood coagulation. B. STUBER and K. LANG (Verh. deut. Ges. inn. Med., 1926, 369—370; Chem. Zentr., 1927, i, 2439).—The glycolysis of blood rendered uncoagulable by oxalate, citrate, fluoride, etc. is subnormal. Coagulation of native plasma is associated with absorption of oxygen and production of carbon dioxide.

A. A. ELDRIDGE.

Fibrinogen. R. NORDBO (Biochem. Z., 1927, **190**, 150—156).—From potentiometric titrations the isoelectric point of fibrinogen is found to be about p_H 5·5 and the acid-binding power in 0·85% sodium chloride solution is equal to 0·06 mg. of hydrogen chloride per mg. of fibrinogen. The flocculation zone differs with varying concentrations of fibrinogen and is broader with higher concentrations of the protein. A. WORMALL.

Amount of fibrinogen and its relation to lability in plasma. K. SAMSON (Biochem. Z.,

1927, **191**, 220—233).—The method of Leendertz (A., 1922, ii, 798) for the determination of fibrinogen gives results 15—20% lower than that of Starlinger (A., 1925, i, 716). In most cases the sinking velocity runs parallel to the determination of the amount of fibrinogen, the parallelism being least when the fibrinogen content is high. The method of Georgi (Klin. Woch., 1925, No. 43, 2053) for determination of the lability of the plasma by salting out with 26% sodium chloride and that of Gerloczy (Klin. Woch., 1922, No. 43) by inhibition of coagulation are based on quantitative processes and the parallelism with fibrinogen content is always clear. Refractometric determination of fibrinogen by salting out with sodium chloride is not possible. P. W. CLUTTERBUCK.

Highly active anticoagulant from tissue. M. DOYON (XII Int. Cong. Physiol., 1926, 41; Chem. Zentr., 1927, i, 2566).—The filtrate from organs which had been incubated for months in sodium chloride solution was treated with alcohol, the precipitate redissolved in water and the constituents containing phosphorus precipitated at 100°. The nitrogenous, highly active substance was precipitated with acetic acid and alcohol, washed with alcohol and ether, and dried in a vacuum. A. A. ELDRIDGE.

Composition of living organisms. I. Inorganic elements contained in cats. V. S. SADIKOV and M. K. SHCHEGL'SKA (Bull. Acad. Sci. U.R.S.S. [Russia], 1926, 1619—1646).—The animals were heated in an autoclave for 6 hrs. at 180—200°, and the product was resolved into an aqueous, an ethereal, an alcoholic, and a residual fraction. The percentage of carbon, hydrogen, and nitrogen in the aqueous fraction is identical for cats of all ages; chlorides, phosphates, and sulphates decrease with age, but the phosphorus content is constant. The carbon content of the ethereal fraction decreases somewhat with age. The carbon content of the alcoholic fraction increases with age; the nitrogen content is largest in old cats, and smallest in well-nourished cats. The residual fraction is chiefly inorganic; it is rather rich in phosphorus.

CHEMICAL ABSTRACTS.

Composition of living organisms. II. Inorganic elements contained in frogs. V. S. SADIKOV and R. A. GUTNER (Bull. Acad. Sci. U.R.S.S. [Russia], 1927, 95—116; cf. preceding abstract).—Analytical data are given for frogs in various conditions of age and nourishment. CHEMICAL ABSTRACTS.

Influence of feeding on the quantitative composition of hens' eggs. E. F. TERROINE and P. ELIN (Bull. Soc. Chim. biol., 1927, 9, 1074—1084).—The relative weights of white and yolk in eggs vary widely but independently of the food administered. The composition both of the white and of the yolk is very constant and independent of the food. In particular, the fatty substances remain constant whether or not fat is given in the food, provided ample carbohydrate is administered.

W. O. KERMACK.

Relation of the sterols to other substances of animal and plant origin. A. WINDAUS (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 24).—A summary of present knowledge of the sterols with special reference to their biological significance.

G. A. C. GOUGH.

Cholesterol and nitrogen content of the cartilage at various ages and its significance in the physiology of age. M. BÜRGER (Verh. deutsch. Ges. inn. Med., 1926, 352—358; Chem. Zentr., 1927, i, 2662).—With increasing age, the cholesterol and nitrogen content and the dry matter of costal cartilage increase. A. A. ELDRIDGE.

Characterisation of fats. P. BAMBERGER (Biochem. Z., 1927, **190**, 247—250).—The usual characteristic values (acid, saponification, Reichert–Meissl, Polenske, iodine) are expressed in such a way that from them an idea of the molecular composition of the fat can be obtained; *e.g.*, the number of c.c. of *N*-potassium hydroxide used for hydrolysis is found and gives the millimols. of fatty acid (free and esterified) in 1 g. of fat; the number of c.c. of *N*-sodium hydroxide needed to neutralise the free fatty acid in 1 g. of fat is found and gives the millimols. of free fatty acid in 1 g. of fat; the number of c.c. of 2*N*-iodine (2*N* since one double linking adds two iodine atoms) required for 1 g. of fat gives the new iodine value, etc.

P. W. CLUTTERBUCK.

Determination of the fat of animal organs. P. BAMBERGER (Biochem. Z., 1927, **190**, 251—260).—A method is described for determining the fat of organs, designed to eliminate possibility of change in its composition during the process, in which the carefully minced organ is dried in a vacuum at 80—90° for 10—12 hrs., most of the fat separated by continuous ether extraction of the powder for 6 hrs., and the rest obtained by transferring the residue to a collodion sac and treating in a special apparatus under sterile conditions with pepsin–hydrogen chloride for 6—8 days and then with trypsin (lipase-free) for 2—3 days with subsequent ether extraction of the residue after washing and drying in a vacuum. The fatty extracts are worked up in the usual way and the light petroleum extracts evaporated and dried, and the fat is weighed. The fat may be kept for months without change, out of contact with air and more particularly with light.

P. W. CLUTTERBUCK.

Glycerophosphatase of the central nervous system. Glycerophosphatase in men and animals. V. VONDRÁČEK (Biochem. Z., 1927, **191**, 88—94).—The enzyme is present in greatest amount in the cerebellum, less in the cerebrum, and least in the spinal cord in man. Comparative examination also in the case of rabbit, dog, ox, pig, and sheep shows also that the intensity of the action of phosphatase runs parallel neither to the phosphorus content nor to the phylogenetic development of the animal.

P. W. CLUTTERBUCK.

Mineral content of human skin. H. BROWN (J. Biol. Chem., 1927, **75**, 789—794).—Figures are given for the concentrations of the inorganic constituents of human skin at various ages. C. R. HARINGTON.

Fluorine content of teeth. F. TREBITSCH (Biochem. Z., 1927, **191**, 234—240).—The method of Gabriel (A., 1893, ii, 81) is unsuitable for determination of fluorine in teeth. The fluorine content

determined by the lanthanum method of Meyer and Schulz (A., 1925, ii, 598) is 0·29—0·59% of the dry weight. P. W. CLUTTERBUCK.

Occurrence of trimethylamine oxide [in fish muscle]. F. A. HOPPE-SEYLER and W. SCHMIDT (Z. Biol., 1927, **87**, 59—68).—Disintegrated muscle from various sea and river fish has been extracted with boiling water and the extract examined for trimethylamine oxide. This substance is more widely distributed than was previously thought and it has been isolated in appreciable amounts from the extracts of the sea fish, but in no case from the extracts of fresh-water fish. This difference is possibly due to differences in the food supply. No evidence has been obtained that spawning time or the season has any influence on the formation of this base. A. WORMALL.

γ-Butyrobetaine [in fish muscle]. F. A. HOPPE-SEYLER and W. SCHMIDT (Z. Biol., 1927, **87**, 69—71).—γ-Butyrobetaine has been isolated from aqueous extracts of river-eel (*Anguilla vulgaris*), the yield of gold salt being 2·42 g. from 9·8 kg. of moist muscle. A. WORMALL.

Sex differences of proteins in animals and plants. I. Sex differences of muscle- and serum-proteins. T. TADOKORO, M. ABE, and S. WATANABE (Proc. Imp. Acad. Tokyo, 1927, **3**, 543—546).—The ash and phosphorus contents of myosin and myogen, obtained from the muscles of various male and female animals, is appreciably greater in the female specimens. Titration of an alkaline solution of myosin and myogen (rotatory power lower for female specimen) with hydrochloric acid to determine the maximum point of the surface tension and turbidity of the solution shows that the female specimens require a smaller quantity of the acid. The free amino-nitrogen content of the female protein is also lower than that of the male. Arginine and lysine are in excess in the male protein, whilst histidine is in excess in the female.

Extension of the above work to male and female serum-globulin from different mammalian sources shows similar results. H. BURTON.

Composition of the sexual organs. II. Amino-acids of the ovary of *Strongylocentrotus lividus* in various stages of the function cycle of the organ. G. RUSSO (Arch. sci. biol., 1926, **8**, 293—309; Chem. Zentr., 1927, i, 2662).—During development of the ovaries the protein-nitrogen increases, the non-protein-nitrogen remaining constant. The lysine increases and the histidine and cystine diminish. The amino-acids of the non-coagulable nitrogen increase during the development, but decrease at the beginning of the cycle. A. A. ELDRIDGE.

Composition of the sexual organs. III. Free and combined amino-acids in the testicles of *Bos taurus*. G. RUSSO (Boll. soc. biol. sperim., 1926, **1**, 210—212; Chem. Zentr., 1927, i, 2662; cf. preceding abstract).—A comparison of the composition of the testicles of the ox and the sea-urchin. A. A. ELDRIDGE.

Salivary secretions of blood-sucking insects in relation to blood-coagulation. L. LLOYD (Nature, 1928, **121**, 13).—A discussion of the action of coagulin and anti-coagulin. A. A. ELDRIDGE.

Occurrence of acetaldehyde in cerebrospinal fluid. P. THOMAS and E. MAFTEI (XII Int. Cong. Physiol., 1926, 158—159; Chem. Zentr., 1927, i, 2441).—Normal cerebrospinal fluid contains traces of acetaldehyde; larger quantities are observed in diabetes, paralysis, and dementia præcox. A. A. ELDRIDGE.

Effect of inanition on yield and composition of cow's milk. O. R. OVERMAN and K. E. WRIGHT (J. Agric. Res., 1927, **35**, 637—664).—Comparative data are given for the quantity and composition of the milk from **3** cows, giving a positive reaction to the tuberculin test, but otherwise in apparently good physical condition, during an inanition period of 5 days. As the period of inanition progresses the milk flow decreases together with the total fat, protein, lactose, and ash contents, whilst the percentages of fat, protein, and ash increase. There is a continual decrease in the specific gravity of the milk, and in the percentage of lactose. These changes were not so marked in one cow which was at the beginning of its lactation period, as in the other two which were in the later stages of lactation. E. A. LUNT.

Elimination of iodine in milk. W. RASCHE (Z. Kinderheilk., 1926, **42**, 124—132; Chem. Zentr., 1927, i, 2441).—After ingestion by cows and goats of potassium iodide (0·5—1 g. 3—4 times at 48 hr. intervals), 11% of the iodine was recovered from the milk, irrespective of its volume or fat content. A. A. ELDRIDGE.

Amino-acid content of milk. F. SPIRITO (Pediatria riv., 1926, **34**, 921—929; Chem. Zentr., 1927, i, 2663).—Amino-acids were determined (mg. per 100 c.c.) as follows: cow's milk 10·17—14·68, asses' milk 16·03, goat's milk 10·53, human milk (3—4 months) 12·82, (9—12 months) 8·50, colostrum 17·48. A. A. ELDRIDGE.

Creatinuria in children and its dependence on the thyroid gland. A. PALLADIN and E. SSAWRON (Biochem. Z., 1927, **191**, 1—12).—Creatinuria, as found in children, also occurs in various other young mammals, but does not depend on the thyroid gland. Both creatine and creatinine are present in the urine of growing guinea-pigs, white mice, dogs (under 4—5 months), and rabbits (3—6 weeks). In young animals showing creatinuria, the creatine coefficient is greater than in adults. Extirpation of the thyroid gland in dogs during the period of creatinuria does not stop creatinuria, but results first in a transient decrease and after some time in a slightly lower creatinuria than in the control animals. P. W. CLUTTERBUCK.

Iodometric determination of homogentisic acid in urine. E. METZ (Biochem. Z., 1927, **190**, 261—264).—A method is described depending on the oxidation of the homogentisic acid in alkaline (hydrogen carbonate or borax) solution to the quinone by adding iodine until a blue colour is obtained with starch, and the reversion of the reaction on acidification with the setting free quantitatively of the amount of iodine used, with titration by thiosulphate. P. W. CLUTTERBUCK.

Conversion of Ronchese's method for the determination of urinary uric acid into a micro-method. R. Danet (J. Pharm. Chim., 1927, [viii], 6, 405—407).—In a conical centrifuge tube are placed 10 c.c. of urine, 1·5 g. of ammonium chloride, and 1·5 c.c. of ammonia solution. After at least ½ hr., the liquid is centrifuged and decanted, the precipitate treated with 2 c.c. of Ronchese's ammoniacal solution, and after centrifuging the liquid is decanted. The ammonium urate is treated with 30 c.c. of water, dissolved by means of a few drops of dilute acetic acid, treated with 2 c.c. of saturated sodium hydrogen carbonate solution, and titrated with 0·02*N*-iodine.

B. Fullman.

Serum-lipase, its determination by the stalagmometric method, significance, and clinical value. S. Katzenelbogen and H. Wohlers (Ann. med., 1926, 20, 373—391; Chem. Zentr., 1927, i, 2557).—Rona and Michaelis' method was employed. Blood-serum gives velocity coefficients of 0·006—0·008; turbid serum gives higher values, but hæmolysis produces no change. The lipase titre falls in general cachexia. A. A. Eldridge.

Anæmia among troops in Bombay. P. N. Basu (Indian J. Med. Res., 1927, 15, 107—116).—The gastric juice was deficient in hydrochloric acid, and there is a slight diminution in blood-lipins. The ratio of neutral fat to free fatty acids in the fæces is 1 : 8·8 instead of 1 : 2·9. Chemical Abstracts.

Epidemic dropsy: its blood picture. C. Ray (Indian J. Med. Res., 1927, 15, 67—79).—Values (mg. per 100 c.c. of whole blood) were: total nitrogen 1400—2520, non-protein-nitrogen 22·4—42, urea 18—30, creatinine 1·2—1·4, uric acid 2·8—5·0, dextrose 95—135, chlorides 490—677, calcium 6·1—15, cholesterol 89—185. Chemical Abstracts.

Distribution of electrolytes in intestinal obstruction. D. W. Atchley and E. M. Benedict (J. Biol. Chem., 1927, 75, 697—702).—In intestinal obstruction there was observed in the blood-serum a decrease in total base, chlorides, and water, and an increase in carbonates, protein anions, phosphates, and sulphates; the last three account for the increase in undetermined acid observed by Gamble and Ross (A., 1925, i, 1352). The decrease of chlorides is due to their loss in the vomitus, the chlorine in the blood being replaced by phosphate and sulphate.

C. R. Harington.

Form of organic phosphorus in neoplasms. J. Enselme and [Mme.] J. Enselme (Bull. Soc. Chim. biol., 1927, 9, 1017—1026).—The phosphorus has been determined in normal and tumour tissue, by the method of Javillier and Allaire (A., 1925, i, 996). In cancerous tissue there is an increase of nucleic and of lipoid phosphorus. Radium treatment increases the lipoid phosphorus but decreases the nucleic phosphorus below the normal level.

W. O. Kermack.

Content in reduced glutathione of animal tissues during tuberculosis and various intoxications. P. Delore (Bull. Soc. Chim. biol., 1927, 9, 1070—1073).—The organs of tuberculous guinea-pigs and oxen contain the same quantity of reduced glutathione as do those of normal animals of the same species. Administration of phosphorus, arsenic, or of "novarsenobenzol" to a guinea-pig does not appreciably influence the content of its liver in reduced glutathione. W. O. Kermack.

Preparation and properties of glutathione. J. M. Johnson and C. Voegtlin (J. Biol. Chem., 1927, 75, 703—713).—A slight modification of the method of Hopkins (A., 1921, i, 635) is described by which 0·1 g. of reduced glutathione may be obtained from 1 kg. of baker's yeast. Copper, gold, and lead compounds of reduced glutathione have been prepared, in all of which the hydrogen of the thiol group appears to have been substituted by the metal; the yield of all these derivatives is small, owing, apparently, to oxidation of part of the glutathione with simultaneous reduction of the metallic salt employed. The criticism of Hopkins (A., 1927, 478) of the work of Hunter and Eagles (*ibid.*) is supported.

C. R. Harington.

Physiological study of glutathione by liver perfusion. R. Fabre and H. Simonnet (Compt. rend., 1927, 185, 1528—1530).—The amount of reduced glutathione found in Ringer's solution which has been perfused through the rabbit's liver for about 3 hrs. is remarkably small (5—8 mg. per 100 c.c.), whilst the liver loses all its glycogen. Destruction of the physico-chemical equilibrium of the cells, by circulation of water, or Ringer's solution containing 0·1% of potassium cyanide, or chloroform, causes the reduced glutathione of the liver to pass into the perfusate. H. Burton.

Relation of rate of growth to diet. II. L. B. Mendel and H. C. Cannon (J. Biol. Chem., 1927, 75, 779—787).—The conclusions of Osborne and Mendel (A., 1926, 1180), that the optimum rate of growth for rats at present accepted is too low, are supported by growth records of numerous animals in which daily increments of 3—5 g. were observed. These increments are comparable with those obtained on transferring an animal from a deficient to a complete diet, and with those observed by Evans (Harvey lectures, 1923—1924, 19, 212) to follow administration of pituitary extract to growing rats.

C. R. Harington.

Carbohydrate metabolism of the central nervous system. Glycogen and cerebroside content of the brain and the glycogen content of the heart in the normal condition and during deficiency of oxygen. Y. Kojima (Biochem. Z., 1927, 190, 379—387).—The glycogen content of the central nervous system and the cerebroside sugar content of rats are determined and, like the carbohydrate content of the heart, are shown to be very resistant during deficiency of oxygen. In 17 normal animals, the mean glycogen content of the brain was 0·2266% and of the heart 0·0829%, whilst in 7, kept in an atmosphere deficient in oxygen until symptoms supervened, they were respectively 0·2498 and 0·0816%. The heart and brain behave therefore differently from skeletal muscle.

P. W. Clutterbuck.

Absorption and utilisation of inulin in the white rat. M. G. Bodey, H. B. Lewis, and J. F. Huber (J. Biol. Chem., 1927, 75, 715—723).—Young

white rats, on a basal carbohydrate-free diet, deposited considerable amounts of liver glycogen on addition of lævulose, and smaller but definite amounts after addition of inulin to the diet. C. R. HARINGTON.

Alimentary hyperglycæmia with lævulose feeding. F. KRONENBERGER and P. RADT (Biochem. Z., 1927, **190**, 161—167).—Lævulose (5—10 g.) has been administered to rabbits to determine whether the hyperglycæmia which is quickly produced after sugar administration is due to rapid absorption of the sugar or to a reflex stimulation of the liver by the sugar in the alimentary tract. Before, and after varying intervals following, the administration of lævulose, the total blood-sugar and the blood-lævulose have been determined, the latter by a modification of Selivanov's reaction and later by the diphenylamine method of van Creveld (Klin. Woch., 1927, 6, 697). The increases in total sugar and lævulose of the blood do not run parallel, although in some cases the amount of lævulose absorbed into the blood-stream is sufficient to account for the hyperglycæmia. In the majority of cases, however, evidence that hyperglycæmia may be produced by a reflex action is obtained. A. WORMALL.

Intermediary carbohydrate metabolism. IV. Reaction of normal dogs to continuous intravenous injection of dextrose. M. WIERZUCHOWSKI and H. GADOMSKA (Biochem. Z., 1927, **191**, 198—219; cf. A., 1926, 979; 1927, 790).—When dextrose is injected intravenously into dogs at the rate of 2 g. per kg. per hr., reaction may be "assimilative" (glycosuria approaches nil, blood-sugar 200 mg.-%) or "subassimilative (glycosuria about 20% of the injected quantity, blood-sugar 300 mg.-%), or anything between these two extremes. In long experiments, deterioration of the power to assimilate dextrose was obtained in both types, but particularly in the assimilative type. The mean lactic acid content of the blood of a fasting dog is 15·7 mg.-%. By intravenous injection of sugar, the blood lactic acid follows a characteristic curve, increasing in the second and third hours by 6—28·7 mg.-% over the original values, the curve then either falling or remaining steady. The lactic acid values do not show differences with the different types of assimilation. Insulin injected during dextrose infusion generally has no effect on the blood lactic acid content, but when administered before dextrose injection affects the lactic acid values during the first hour after injection. P. W. CLUTTERBUCK.

Production of sugar from fat. Y. KOJIMA (Biochem. Z., 1927, **190**, 352—378).—When glycerol is added to the diet of rats rendered carbohydrate-free by feeding with peptone and thyroid tablets, sugar is formed from it. P. W. CLUTTERBUCK.

Utilisation of sodium *dl*-lactate administered intravenously. I. Excretion by kidneys and intestines. II. Changes in acid-base equilibrium. H. A. ABRAMSON and P. EGGLETON. **III. Glycogen synthesis by the liver. Blood-sugar. Oxygen consumption.** H. A. ABRAMSON, M. G. EGGLETON, and P. EGGLETON (J. Biol. Chem., 1927, 75, 745—752, 753—761, 763—778).—I. After intravenous administration of sodium *dl*-lactate to fasting anæsthetised dogs in doses of 0·5—4·0 g. per kg., 7—40% of the *dl*-lactic acid was excreted in the urine within 3 hrs.; practically none was excreted into the intestine; the concentrating power of the kidney for lactic acid was about 10-fold.

II. Injection of sodium lactate was followed by an alkalosis, indicating utilisation of the lactic acid.

III. Injection of sodium lactate caused a slight fall in the blood-sugar, and in the glycogen in the liver (cf. Jansson and Jost, A., 1925, i, 1354; Elias and Schubert, A., 1919, i, 54); the oxygen consumption was but little increased; the rate of utilisation of lactic acid by dogs under these conditions was about 0·5 g. per kg. per hr.

C. R. HARINGTON.

Metabolism of alcohol in man. A. BORNSTEIN and A. LOEWY (Biochem. Z., 1927, **191**, 271—292).—The alcohol content of the blood of four persons, to whom 25—30 g. of alcohol was administered by mouth, increased within 30 min. from nil to 0·05—0·075% and then decreased, the blood becoming alcohol-free again after 4 hrs. The alcohol did not appear to have any specific dynamic action and the respiratory exchange was unaffected. If a large amount of carbohydrate in hourly doses for 7 hrs. was ingested before administration of alcohol, then, after taking alcohol, the R.Q. immediately began to fall, remained at this low level for 3 hrs., and then slowly increased. During these 3 hrs. the R.Q. remained unchanged in spite of the fact that the alcohol content of the blood decreased from 0·06 to 0·004%. Although no specific dynamic action was found on administration of alcohol either alone or after carbohydrate, yet a slight action was obtained when the two were administered simultaneously.

P. W. CLUTTERBUCK.

Active substances of striped muscle and the chemistry of muscular contraction. G. EMBDEN (Klin. Woch., 1927, **6**, 628—631; Chem. Zentr., 1927, i, 2844).—Contraction of muscle is accompanied by liberation of ammonia, rapidly followed by recombination. Adenosinephosphoric acid and lactacidogen are considered active substances of striped muscle; their function is discussed. A. A. ELDRIDGE.

Heat measurements of the chemical reactions in muscle. O. MEYERHOF and J. SURANYI (Biochem. Z., 1927, **191**, 106—124).—The heat of hydrolysis of glycogen to reducing sugar, per 1 g. of sugar, amounts to 12—14 g.-cal. and the heat of esterification of glycogen with phosphate to 10—30 g.-cal., the amount being covered by the increase of acidity and the de-ionisation of muscle protein. The heat of conversion of hexosemono- into hexosediphosphoric acid is about 30 g.-cal., and this is explainable almost entirely in terms of increase of acidity. The heat of conversion of hexosediphosphate into lactic acid and phosphate is about 220 g.-cal. per g. of lactic acid. The average heat of breakdown of glycogen is 204 g.-cal., and deducting 25—30 g.-cal. for the increase in acidity, the heat of breakdown itself is 176 g.-cal. Finally, the hydrolysis of creatinephosphoric acid is 150—160 g.-cal. per g. of phosphoric acid. P. W. CLUTTERBUCK.

Can lactic acid disappear anaerobically from muscle? F. Lipmann (Biochem. Z., 1927, **191**, 442—449).—In presence of sodium fluoride, lactic acid never disappears anaerobically from minced muscle, the loss found by other authors being due to the methods used. P. W. Clutterbuck.

Ammonia content of and ammonia formation in muscle and its relationship to function and changes of condition. IV. W. Mozołowski and W. Lewiński (Biochem. Z., 1927, **190**, 388—398).—The formation of ammonia in frog's muscle depends on its size and on the time of the year, being much higher in the summer than in the winter. In the muscle of the intact normal frog the ammonia accumulated during work slowly decreases. Movement of the animal affects the resting value very considerably within 30—60 min. In nervous tissues, the ammonia content is not altered by mincing. In the curarised animal, stimulation of the nerves yields no increase of ammonia in the muscle, but direct stimulation gives the same result as in the non-curarised state. Sodium fluoride inhibits ammonia formation in muscle pulp, but in the intact muscle similar liberation of ammonia occurs as in mincing, heat rigor, or after caffeine. P. W. Clutterbuck.

Quantitative variations of urinary creatinine during muscular work and physical exercise. G. Carpentier and M. Brigaudet (Bull. Soc. Chim. biol., 1927, **9**, 1085—1094).—Physical exercise is followed promptly by an increase of creatinine in the urine and the amount of this increase does not appear to depend on the condition of training of the individual. W. O. Kermack.

Metabolism of nerves. III. Chemistry and intermediate processes. R. W. Gerard and O. Meyerhof (Biochem. Z., 1927, **191**, 125—146; cf. Amer. J. Physiol., 1927, **82**, 381; J. Physiol., 1927, **63**, 280).—Isolated resting nerve does not form lactic acid in oxygen, but does in nitrogen. The velocity of anaerobic lactic acid formation increases for the first 2 hrs. and then gradually falls away, amounting in the maximal period to 7·4 mg.-% per hr., and the total yield in 20 hrs. is 50—100 mg.-% at 25°. This decrease is caused by lack of carbohydrate. On suspending the nerve in Ringer's solution containing dextrose, the velocity remains constant at 12·5 mg.-% per hr. for more than 30 hrs., *i.e.*, a 60% increase over the maximal velocity without sugar. Accumulation of lactic acid does not itself inhibit glycolysis. On the other hand, lactic acid, once formed, does not disappear in oxygen. By stimulating in nitrogen, the formation of lactic acid is either not increased or only slightly. The total yield of lactic acid in sugar-free solutions corresponds approximately with the carbohydrate content of the nerves. Ammonia formation in resting nerves in oxygen is very small, in nitrogen is still smaller, but is considerably increased by stimulating the nerves in oxygen. The R.Q. of nerve at rest is 0·8 and is not affected by adding sugar, but increases to 1·0 on stimulating. Anaerobic formation of lactic acid is not inhibited by $4\times10^{-2}N$-potassium cyanide, but $2\times10^{-2}-1\times10^{-3}N$-potassium cyanide inhibits it to the extent of 80—90%. P. W. Clutterbuck.

Fat and lipin metabolism. VI. Role of the lungs in fat and lipin metabolism. S. Leites (Biochem. Z., 1927, **190**, 286—303).—Emulsions of olive oil and oleic acid injected into the jugular vein of normal dogs do not appear in the arterial blood as cholesterol or lecithin sols. After previous " blockade " with colloidal silver or colloidal ferric hydroxide, the injection of olive oil or fatty acid emulsions results in an increase of neutral fat or fatty acid in arterial blood. With parenteral injection of oleic acid or of sodium oleate, its retention in the lung is accompanied by an increase of cholesterol and of neutral fat in the arterial blood. In control experiments, the injection of oleic acid in the femoral artery does not bring about any increase in the cholesterol content of the blood of the femoral vein. With parenteral injection of lecithin sols, an increase of cholesterol and neutral fat is obtained in the arterial blood, along with the absorption in the lung. When (after " blockade ") the amount of fatty acid in the arterial blood is increased by retention of lecithin in the lung, the cholesterol content does not increase. By administration of olive oil by mouth, the neutral fat content of the arterial blood increases parallel to the retention of fatty acids in the lungs. These results support the assumption of cholesterol and neutral fat synthesis in the lungs from the absorbed oleic acid. In splenectomised dogs the cholesterol content of the arterial blood increases with enteral and parenteral injection of olive oil. By injection of cholesterol sols into the jugular vein an increase of neutral fat in the arterial blood is obtained which runs parallel to the retention of cholesterol in the lungs. P. W. Clutterbuck.

Fat metabolism. IX. Formation of acetone substances. R. Mancke and P. Serbescu (Z. Biol., 1927, **87**, 1—7; cf. A., 1927, 275).—Young pigs weighing about 35 kg. have been kept for 8—17 days on a purely fat diet and the amount of fat absorbed has been determined. No alterations in the blood-sugar or blood-lactic acid occurred and no acetone could be detected in the blood and urine. With a diet containing oleic acid only, with no antiketogenic glycerol present, and also with a diet consisting of oleic acid, olive oil, cod-liver oil, and butyric acid (as a ketogenic substance), similar results were obtained, and even in the latter case traces only of acetone were found in the urine. From these experiments it has been calculated that the pig is capable of oxidising completely per day nearly 2 g.-mol. of fatty acid which is not accompanied by antiketogenic substances. No evidence has been obtained that carbohydrate has been synthesised from fat in these experiments. A. Wormall.

Effect of administration of flesh on the respiratory exchange of rats after preliminary treatment in different ways, in respect to the function of the liver. T. Honda (Biochem. Z., 1927, **191**, 13—33).—After abundant administration of flesh and peptone to rats, further feeding with flesh shows a very decided specific dynamic action and this is even more pronounced when phloridzin is injected after several days' feeding. The effect is possibly due to

a stimulated condition of the liver being set up during the preliminary treatment. P. W. CLUTTERBUCK.

Effect of administration of flesh in respect to the preliminary condition of nutrition. T. HONDA (Biochem. Z., 1927, **191**, 34—60).—The specific dynamic action of flesh, in rats, is considerably increased by previous administration of bread and milk. If a considerable amount of sucrose is added to this diet, the specific dynamic action of the flesh is even further increased. By feeding with fat, the specific dynamic action of flesh more or less disappears. P. W. CLUTTERBUCK.

Nitrogen retention on feeding with ammonium salts. E. SCHLIEPHAKE (Biochem. Z., 1927, **190**, 59—66).—The nitrogen loss of guinea-pigs fed on a nitrogen-deficient diet is converted into a retention of nitrogen by the addition of ammonium chloride or citrate to the diet. The added ammonium salt has no significant influence on the total nitrogen, ammonia-nitrogen, or amino-nitrogen of the liver. A. WORMALL.

Nitrogen distribution in the paunch of ruminants during feeding and starvation and its relationship to paunch infusoria. E. MANGOLD and C. SCHMITT-KRAHMER (Biochem. Z., 1927, **191**, 411—422).—The utilisation of micro-organisms as a source of protein in the nutrition of ruminants is investigated. The bacterial nitrogen is 10% of the total nitrogen of the paunch content of sheep receiving normal food. The paunch infusoria provide only a small part of the total paunch nitrogen. The total nitrogen of the paunch content in normally nourished sheep is 0·2—0·3%, and decreases quickly on starvation, amounting after 7 days to 0·05%. P. W. CLUTTERBUCK.

Iron reserve. C. S. WILLIAMSON and H. N. ETS (Arch. Int. Med., 1927, **40**, 668—675).—Comparative experiments have been carried out on 126 rats to determine the effect on the iron reserve of a diet containing liver. Half the young animals were given a standard caseinogen diet, the other half received a similar diet with the caseinogen replaced by dried beef liver. The latter group after 3 months contained 141% more iron in the spleen and 57% more iron in the liver than the former group. That this iron can be used in the formation of hæmoglobin was shown by comparing the rates of hæmoglobin regeneration in each set of animals when anæmia induced by bleeding was followed by feeding both groups on the caseinogen diet. The former group showed no appreciable hæmoglobin regeneration in 28 days; the hæmoglobin concentration in the latter group was practically normal after the same period. E. A. LUNT.

Electromotive action of drugs as cause of their toxicity. II. Chemical nature of the tissue constituents which produce bioelectricity. III. Electromotive action of alkaloids on tissues compared with that on proteins, lipins, and "oils." R. BEUTNER (J. Pharm. Exp. Ther., 1927, **32**, 101—113, 115—120).—II. In support of the view that lipins play an important role in the phenomena of bioelectricity, it is found that the electromotive force of the system $0·1M$-potassium chloride|lecithin|$x+$ is positive when x is a solution of propylamine hydrochloride, tetramethylammonium chloride, methylene-blue, rhodamine-$3B$, cocaine, or strychnine, and that the system $0·1M$-potassium chloride|animal or plant tissue|x gives similar results. The effect of water, alcohol, and ether mixtures on the electrical potentials given by tissues also supports this conclusion. The results obtained by Hober (cf. A., 1925, ii, 131) with proteins are probably to be regarded as an effect of the water in the material.

III. The electromotive force of the system $0·1M$-potassium chloride|R|$x+$ is positive in the sense indicated when x represents a solution of an alkaloidal salt and R represents a colloid and is very slightly positive or zero when R is lecithin, but is negative when R is an ordinary oil immiscible with water. When R represents a frog's muscle the system may be positive or negative according to the exact conditions, from which it appears that both types of material play a part in the electrical phenomena of tissues. W. O. KERMACK.

Relationship between chemical reactivity and biological activity of iron compounds. L. ROSENFELD (Biochem. Z., 1927, **190**, 17—27).—The biological effects of oral administration to rabbits of a non-magnetic ferrosoferric carbonate which has a strong benzidine activity (with hydrogen peroxide) and a strongly magnetic iron oxide with a weak benzidine activity have been measured by determinations of the urinary C : N ratio. No increases in this ratio similar to those obtained with active iron oxide (Wada, A., 1926, 1057) have been observed. Thus neither the magnetic property nor the power to give the benzidine reaction is a measure of the biological activity or the therapeutic value of an iron compound. A. WORMALL.

Hypoglycæmic action of ergotamine in diabetes. H. MORETTI (Compt. rend. Soc. Biol., 1927, **97**, 320—324; Chem. Zentr., 1927, ii, 1278).—The mechanism of the hypoglycæmic action of ergotamin is discussed. A. A. ELDRIDGE.

Hypoglycæmic properties of galegine sulphate. H. SIMONNET and G. TANRET (Compt. rend., 1927, **185**, 1616—1617; cf. A., 1927, 991).—Galegine sulphate, in doses of the order of 4 mg./kg., causes a fall in the blood-sugar of both dogs and human beings in amounts varying up to 20%, a figure lower than that obtained by Muller and Reinwein (A., 1927, 1109). The same result is obtained with depancreatised dogs. J. W. BAKER.

Effects of synthalin on metabolism. N. R. BLATHERWICK, M. SAHYUN, and E. HILL (J. Biol. Chem., 1927, **75**, 671—683).—Administration of synthalin to rabbits by stomach tube caused no hypoglycæmia, but subcutaneous and intravenous injections produced this effect. Synthalin caused acute nephritis and damaged the liver in such a way as to interfere with the deamination of glycine after injection of the latter. The toxic effects of synthalin bear a general resemblance to those of hydrazine, and part of its power to reduce the blood-sugar apparently depends on the damage to the liver interfering with gluconeogenesis. C. R. HARINGTON.

Physiology of the pyrimidines. L. R. Cerecedo (J. Biol. Chem., 1927, **75**, 661—670).—Uracil, thymine, and 4 : 5-dihydroxyhydrothymine, when administered to dogs, gave rise to increased excretion of carbamide; this indicates a possible similarity between the physiological oxidation of thymine and its oxidation *in vitro* (cf. Baudisch and Davidson, A., 1925, i, 1100). Cytosine and 5-methylcytosine were excreted partly unchanged, and partly as uracil and thymine, respectively. C. R. Harington.

Effect of some fractions of Liebig's meat-extract, obtained by the methods of Gulewitsch and Krimberg, on gastric secretion. A. Korchov (Biochem. Z., 1927, **190**, 188—198).—The carnosine fraction of meat extract, and carnosine itself, stimulate gastric secretion in dogs when injected subcutaneously or intravenously. The carnitine fraction has a similar action and the effect is proportional to the amount of carnitine present. The maximum rate of secretion occurs about the first half hour with intravenous and subcutaneous injections, but administration of either fraction *per os* produces a smaller effect, with a maximum rate of secretion 1½—2½ hrs. later. The stimulation is effected through the circulatory system. A. Wormall.

Comparative physiological action of phenylethanolamine. G. A. Alles (J. Pharm. Exp. Ther., 1927, **32**, 121—133).—β-Hydroxy-β-phenylethylamine is less toxic to guinea-pigs and has a more marked effect on the blood-pressure of rabbits than phenylethylamine. The conclusion of Barger and Dale (J. Physiol., 1910, **41**, 19) that the introduction of a hydroxyl group into the side-chain of phenylethylamine does not increase the activity unless there is at least one hydroxyl group in the nucleus does not appear to be true. W. O. Kermack.

Anomalies in the regulation of blood-sugar under Röntgen irradiation. J. Hisamoto and M. Takeshima (Okayama Ig. Zasshi, 1927, **39**, 315—331).—Röntgen irradiation of rabbit's liver proportionally increases the blood-sugar when the liver-glycogen is high, and decreases it when the glycogen is low. Irradiation of the thorax or abdomen causes considerable variations in the blood-sugar. Irradiation of the liver of the normal fasting dog is followed by a persistent decrease in blood-sugar.
Chemical Abstracts.

Biochemistry of irradiation. VI. Influence of X-rays on the permeability of the surviving frog's skin. VII. Influence of X-rays on the composition of an artificially introduced peritoneal fluid. C. Kroetz (Biochem. Z., 1927, **191**, 250—262, 263—270; cf. A., 1925, i, 178; 1927, 589). —VI. X-Rays increase the permeability to chlorine and dextrose of the surviving skin of the frog (the mean increase is 198%), the effect being greater by irradiation of the membrane *in vivo* than *in vitro*. Irradiated sera and hæmoglobin solutions have no effect on the permeability to chlorine of unirradiated membranes.

VII. The globulin, amino-acid, and phosphate content of normal saline or Ringer's solution which has been introduced into the abdominal cavity of rabbits is greatly increased by irradiation of the abdomen with X-rays for some time. Since this increase is much greater than the increase of these substances in the blood, it is suggested that the permeability of the endothelial cells of the abdominal wall must become increased. P. W. Clutterbuck.

Biological effect of light. L. Pincussen (XII Int. Cong. Physiol., 1926, 134; Chem. Zentr., 1927, i, 2559).—The injurious or protective effect of alkali, alkaline-earth, or magnesium salts, and of halides and fatty acids, when dissolved in water in which tadpoles were exposed to radiation from a quartz lamp, was investigated. A. A. Eldridge.

Formation and constitution [and anti-tubercular action] of sodium aurosulphite. B. Oddo and Q. Mingoia.—See this vol., 140.

Chronic methyl alcohol poisoning. A. Leo (Biochem. Z., 1927, **191**, 423—438).—In dogs, it is possible in a short time to produce a tolerance to lethal doses of methyl alcohol, 1 litre of methyl alcohol being administered in 2 months. The excretion of formate in the urine decreases parallel with this increase in tolerance, but the decrease in excretion is not due to its increased combustion.
P. W. Clutterbuck.

Fatty degeneration of embryonic cells. G. Rosenfeld (Biochem. Z., 1927, **190**, 101—108).—Phloridzin, and in other cases phosphorus, have been administered to pregnant dogs, the dogs killed, and the fat contents of the livers of the mother and fœtal dogs determined. The livers of the fœtal dogs from the phloridzinised mother gave normal values for fat (mean value 2·91% of the dried weight), but with the phosphorus-treated dog the fat content of the fœtal liver was 3—4½ times the normal value. Similarly, the liver of a new-born dog to which small amounts of phloridzin were administered for 3 days had an abnormally high fat content. These increases in liver-fat are real and are not relative increases due to the disappearance of glycogen, and thus definite evidence of fat infiltration into embryonic livers has been obtained. The question of fat infiltration into embryonic and tumour cells is discussed.
A. Wormall.

Changes in oxygen capacity of the blood of rabbits following administration of nitrobenzene. B. B. Stimson (J. Biol. Chem., 1927, **75**, 741—744).—Following oral administration to rabbits of 0·1 c.c. per kg. of nitrobenzene, 2·2—14·7% of the total hæmoglobin was converted into a substance similar to but not identical with methæmoglobin.
C. R. Harington.

Multiphase action of potassium cyanide on the living cell. M. S. Resnitschenko (Biochem. Z., 1927, **191**, 345—354).—The amount of oxygen used by normal eggs of *Ascaris megalocephala* increases slowly in the first hour by 1·5% and in 16 hrs. by 22%, an increase related to the development of the egg. The respiration is only slightly decreased by concentrations of cyanide up to 2*M*, due to the physico-chemical properties of the egg membrane, but with 3·2*M*-solutions, the eggs use 60% more oxygen ("paradox phase") in the first 30 min. after addition than in the same time before addition. The oxygen utilisation then falls fairly quickly and reaches a

minimal value in 7—8 hrs. The amount of this minimal value is different for different concentrations of cyanide, the increased oxygen utilisation being directly proportional and the minimal oxygen usage inversely proportional to the cyanide concentration. Eggs placed in $3 \cdot 2M$-cyanide continue to use some oxygen up to the seventh day. The increased utilisation of oxygen is not conditioned by the reagent, but is due to reaction of the protoplasm itself.

P. W. CLUTTERBUCK.

Zymosthenic action of mineral waters on liver catalase. A. MOUGEOT and V. AUBERTOT (Compt. rend. Soc. Biol., 1927, **96**, 399—400; Chem. Zentr., 1927, i, 2554).—Carbonated mineral waters activate the catalase in consequence of the bivalent ions, particularly in presence of calcium ions. Sulphur waters arrest the activity on account of the hydrogen sulphide content. The sulphate ion is antagonistic to the activating cations. A. A. ELDRIDGE.

Endocrine glands and enzymes of the blood. I. Influence of potassium iodide, iodine, and "iodated albumin" on the catalase of the blood. O. A. STEPPUN and A. M. TIMOFEEVA (Trans. Sci. Chem. Pharm. Inst., 1923, No. 3, 3—18).—Under the conditions employed, iodine and "iodated albumin," when added to rabbit's blood, decreased the catalase index (Bach); potassium iodide was without effect.

CHEMICAL ABSTRACTS.

Role of the catalase–anticatalase system in the animal organism. L. STERN and F. BATTELLI (XII Int. Cong. Physiol., 1926, 157; Chem. Zentr., 1927, i, 2554).—Catalase is often accompanied in animal tissues by anticatalase, the activity of which is concealed by the philocatalase. Anticatalase is active only in presence of oxygen or a hydrogen-acceptor; the optimal p_H is 6—7, and temperature 38—40°. A. A. ELDRIDGE.

Decomposition of dextrose in the animal organism. A. ALEKSEEV (Bull. Univ. Asie Cent., 1926, **10**, 39—49).—The presence of reductase and carboxylase in animal tissues was demonstrated by measurement of the carbon dioxide evolved in the reaction: $CHMe(OH) \cdot CO_2H \longrightarrow CH_3 \cdot CO \cdot CO_2H + CH_3 \cdot CHO + CO_2$. The activity of an extract is greatly diminished by boiling, but increased by addition of methylene-blue. The aqueous extract of ox liver and muscle is most active at p_H 7·0.

CHEMICAL ABSTRACTS.

Acceleration of sugar formation in the excised frog's liver by destruction of its structure. E. J. LESSER (Biochem. Z., 1927, **191**, 175—180).—The amount of sugar found in the frog's liver, which has been ground after washing out with buffer solution at p_H 7·5 for removal of blood-diastase, is always about 4·5 times as high as the sugar content of the intact liver. The view of Bang (A., 1913, i, 552, 553, 1267) that this is due to the greater action of blood-diastase in the ground material is incorrect, and his inability to show that disintegration of structure was responsible for the increase in sugar is explained by the fact that the intact and ground lobes of liver were not examined under comparable conditions (cf. A., 1913, i, 931).

P. W. CLUTTERBUCK.

Partial hydrolysis of populin to saligenin and benzoylglucose by an enzyme in taka-diastase. T. KITASATO (Biochem. Z., 1927, **190**, 109—113).—Populin (monobenzoylsalicin) is hydrolysed by an enzyme of taka-diastase into saligenin and a *benzoylglucose* which appears to differ from the natural compound (vacciniin). Some free benzoic acid and dextrose are also formed by partial hydrolysis of the benzoylglucose and the last-named has not been obtained pure. A. WORMALL.

Biochemical synthesis of β-5-bromosalicylglucoside. Attempt to synthesise β-3 : 5-dichlorosalicylglucoside. P. DELAUNEY (Compt. rend., 1927, **185**, 1530—1532; cf. A., 1927, 174).—5-Bromosaligenol and dextrose, dissolved in aqueous acetone, are treated with emulsin, when β-5-bromosalicylglucoside (lævorotatory) is formed. Using 3 : 5-dichlorosaligenol, the initial rotation shows a large increase during 15 days, presumably due to the formation of the glucoside. H. BURTON.

Reversibility of enzyme action. I. B. SUZUKI and T. MARUYAMA (Proc. Imp. Acad. Tokyo, 1927, **3**, 533—535).—A solution of β-glucosidase has no action on maltose or α-methylglucoside. With β-methylglucoside a reducing sugar is produced. *iso*Maltose develops an increased reducing power, whilst *iso*maltosazone develops a slight reducing action after 3 days. A concentrated dextrose solution shows a decrease in its reducing power when treated with β-glucosidase, owing to the formation of *iso*maltose (cf. Armstrong, A., 1906, i, 127), isolated after removal of the dextrose with *S. marxianus* as the osazone, m. p. 155°. H. BURTON.

Extraction of amygdalin and emulsin from bitter almond cake. M. BRIDEL and (MLLE.) M. DESMAREST (Compt. rend., 1927, **185**, 1514—1515).—Details are given for the extraction of amygdalin by 70% alcohol, and emulsin by water, from the same material. The emulsin preparation contains also β-glucosidase, lactase, and invertase. H. BURTON.

Enzymic liberation of methyl alcohol from pectin by an enzyme of tobacco. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, **190**, 232—240).—Autolysis of tobacco leaves results in the liberation of 60% of the loosely-combined methyl alcohol, which presumably comes from the pectin-like constituents of the leaves (cf. A., 1927, 385). A pectase solution can be obtained by pressing fresh tobacco leaves, and keeping the juice for 24 hrs. under chloroform, followed by filtration. The enzyme in the filtrate can be purified by precipitating with alcohol and dissolving in water, and these solutions, as well as the impure filtrates, have a very powerful pectase activity; the optimum p_H for the coagulation of solutions of lemon pectin is about 5·5, which is the p_H of the natural juice. This coagulation of lemon pectin by tobacco-leaf extracts is accompanied by an almost complete liberation of methyl alcohol, since 80—90% of the pectic methyl alcohol is liberated in less than 1 hr. Heated extracts of tobacco leaves have no action on pectin. A. WORMALL.

Arsenate activation and the specificity of phosphatase. C. NEUBERG and J. LEIBOWITZ

(Biochem. Z., 1927, **191**, 460—465).—The effect of arsenate on the hydrolysis of zymodiphosphate by yeast in presence of chloroform and toluene is investigated under conditions which exclude fermentation. Very great acceleration of hydrolysis is obtained, the phosphatase action being increased five times. Arsenate also activates taka-phosphatase in its action on hexosediphosphate. Kidney phosphatase, although indifferent to small concentration of arsenate, is inhibited by the higher concentrations which activate yeast. Many organisms possess two specifically different phosphatases. Kidney phosphatase acts differently from the muscle enzyme.

P. W. CLUTTERBUCK.

Decomposition of zymodiphosphate by means of animal phosphatase to hexosemonophosphoric ester. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1927, **191**, 456—459).—Magnesium hexosediphosphate is treated with the clear maceration juice of horse kidney and the monophosphate isolated as the barium salt; yield 30%.

P. W. CLUTTERBUCK.

Action of suprarenal tissue on lecithin. H. C. W. VINES (Endocrinol., 1927, **11**, 224—228).—The lipolysis of lecithin by suprarenal tissue in a saline medium at p_H 7·4 and 37° is increased in the presence of cholesterol. Choline is probably attacked. The side-chain of the adrenaline molecule may be derived from choline. CHEMICAL ABSTRACTS.

Adsorption of urease by cholesterol. M. JACOBY (Biochem. Z., 1927, **190**, 157—160).—Cholesterol adsorbs urease from solution (cf. Jacoby and Shimizu, A., 1922, i, 481). The activity of the adsorbed enzyme is greatly increased by the addition of "auxo-bodies" (potassium cyanide) and is decreased when the adsorption precipitate is washed with a phosphate solution of p_H 9·18. A. WORMALL.

Comparative sensitiveness of the active and inactive forms of enzymes to ultra-violet rays and to heat. E. F. TERROINE and R. BONNET (Bull. Soc. Chem. biol., 1927, **9**, 982—1000).—The amylases of the dog's pancreatic fluid and of the gastro-intestinal juice of *Helix pomatia* and intestinal invertase are more easily destroyed by the action of ultra-violet rays when they are activated by the presence of sodium chloride. Pepsin, lipase, and trypsin, on the other hand, are not more sensitive to the action of these rays when activated by their respective co-enzymes, hydrochloric acid, or sodium chloride, bile salts, and enterokinase. Pepsin and snail amylase are, but pancreatic amylase, lipase, trypsin, and intestinal invertase are not more sensitive to heat when activated. W. O. KERMACK.

Proteolytic activity of pancreatic extracts. I. A. SMORODINCEV and A. N. ADOVA (Bull. Acad. Sci. U.R.S.S. [Russia], 1926, **20**, 1491—1502).—Dog's pancreatic juice, obtained by Pavlov's method, is 1·5—2 times as active as the best tryptic preparations; the proteolytic activity of the latter is weakened by treatment involved in Wittich's, and in Frankel's modification of Danilevski's method. Wittich's preparation is 10 times as active as Danilevski's. Treatment of aqueous pancreatic extracts with phosphoric acid and milk of lime reduces the proteolytic activity by nearly 50%. Prolonged evaporation of extracts in a vacuum causes reduction of proteolytic activity by 14%. Filtration of aqueous glycerol pancreatic extract through paper leaves a residue which possesses considerable digestive properties; the filtrate yields with alcohol a precipitate which is easily soluble in alkalis and possesses a high proteolytic activity, whereas the residual liquid has no proteolytic properties. CHEMICAL ABSTRACTS.

Determination of protease and p_H optimum. A. N. ADOVA (XII Int. Cong. Physiol., 1926, 4—5; Chem. Zentr., 1927, i, 2457).—In Gross' method, the p_H of the medium deviates from the optimum value for pepsin and caseinogen. In the determination of α-proteases by Mett and Fuld's method, and in that of β-proteases by Gross and Robertson's method, the protein is prepared in nearly optimal medium.

A. A. ELDRIDGE.

Pepsin. H. ELBLINGER and C. FUNK (Biochem. Z., 1927, **191**, 186—197).—Aqueous pepsin solutions are very unstable, being inactivated by too great dilution and by shaking with air. Addition of alcohol or acetone in presence of mineral acids converts pepsin into an insoluble compound from which it cannot be regenerated. Pepsin can be precipitated from concentrated solutions by picrates etc. (cf. Funk, this vol., 208) and by this method it may be concentrated 2—5 times. Pepsin gives two fractions, either of which has only feeble activity but recombined has the original peptic power. The view that these precipitates are compounds and not adsorbates is favoured by the greater stability and by the fact that many reagents give only inactive precipitates. The solubility of the sodium and barium salts and the insolubility of the heavy metal salts possibly indicate the presence of acidic groups in the pepsin molecule.

P. W. CLUTTERBUCK.

Action of tyrosinase on phenols. Classification of oxidases. C. E. M. PUGH and H. S. RAPER (Biochem. J., 1927, **21**, 1370—1383).—Anilino-*o*-quinones produced by the action of tyrosinase on several phenols in presence of aniline have been isolated. From phenol or pyrocatechol dianilino-*o*-benzoquinone was obtained, whilst in the case of *m*-cresol, *p*-cresol, or homocatechol dianilinohomoquinoneanil was produced. The *o*-quinones are therefore produced by the enzyme from the phenols, but owing to their transient existence they can be isolated only when removed from the sphere of action. Peroxidase and hydrogen peroxide, acting on pyrocatechol or homocatechol, also produce *o*-quinones. Further evidence indicating the formation of *o*-quinones is offered by the isolation of a sulphinic acid derivative of *o*-benzoquinone by the action of tyrosinase on pyrocatechol in presence of benzenesulphinic acid.

The isolated anilinoquinones have been identified by synthesis. 4 : 5-Dianilino-*o*-benzoquinone, m. p. 193·5° (cf. Kehrmann and Cordone, A., 1913, i, 1396), was prepared by treating an ethereal solution of *o*-benzoquinone with aniline in water. *Dianilinohomoquinoneanil*, $C_{25}H_{21}ON_3$, brownish-red, m. p. 202·5°, was obtained by treating homoquinone with aniline in water or by oxidising homocatechol with

silver oxide in glacial acetic acid in presence of aniline.

Not all phenolic substances which are attacked by tyrosinase give rise to anilinoquinones when the enzyme acts on them in the presence of aniline, but *m*- and *p*-methoxyhydroxybenzenes do so. Tyrosine and pyrogallol, although oxidised by the enzyme, do not yield anilino-compounds under these conditions.

Homoquinone deaminates glycine in the same manner as does *o*-benzoquinone (cf. Happold and Raper, A., 1925, i, 474; Robinson and McCance, *ibid.*, 745). The oxygen absorbed during the oxidation by tyrosinase of several phenols has been measured and indications have been obtained with those phenols giving rise to anilinoquinones that, in absence of aniline, some further reaction involving oxidation occurs beyond formation of the *o*-quinone. The " direct oxidase " theory of Bach and Chodat is criticised in the light of the above results, and a new classification of oxidases into aerobic and anaerobic oxidases is suggested. S. S. ZILVA.

Purification of rennin. H. LUERS and J. BADER (Biochem. Z., 1927, **190**, 122—142).—Rennin preparations have been purified by the application of adsorption methods involving the use of alumina and kaolin as adsorbents and a phosphate buffer of p_H 6·97 for elution. The most active preparation obtained has an activity of 1 in $16{\cdot}44 \times 10^6$ calculated on the dry weight, compared with values of 1 in 20,000 to 1 in 100,000 for commercial rennet preparations. The salt-free dried substance contains 0·687% of nitrogen, gives weak biuret and xanthoproteic reactions, and negative ninhydrin and Millon's tests. The preparation does not reduce Fehling's solution either before or after hydrolysis with hydrochloric acid. The rennin and peptic activities of the preparation do not run parallel throughout the process of purification, but the differences are not significant enough to prove that the two enzymes are different. A. WORMALL.

Biological sugar degradation. H. VON EULER, K. MYRBACK, and R. NILSSON (Annal. Acad. Sci. Fennicæ, 1927, *A*, **29**, No. 3).—Dried yeast, free from co-zymase, has little action on an aqueous solution of acetaldehyde containing a phosphate buffer (p_H 6·12), but rapidly attacks it when co-zymase is added. Dried *B. casei* ε behaves similarly to co-zymase-free yeast. The extracts of the muscle and the liver of the rat decolorise methylene-blue at p_H 8·3 in aqueous solution and more rapidly if solutions glycogen, zymophosphate, or sodium succinate are added. G. A. C. GOUGH.

Influence of colloids on fermentation. R. GRIEG-SMITH (Proc. Linn. Soc. N.S. Wales, 1927, **52**, ii, 17—24).—Fermentation, but not inversion, of sucrose by heated yeast is accelerated by mineral colloids, which adsorb the invertase of normal yeast. Fermentation of dextrose by normal yeast is accelerated by fuller's earth. Small quantities of agar depress, and large quantities accelerate, the fermentation of invert-sugar. CHEMICAL ABSTRACTS.

Modifications produced in the course of alcoholic fermentation by the action of an oscillating electromagnetic field on the yeast. II. E. BENEDETTI (Atti R. Accad. Lincei, 1927, [vi], **6**, 331—335; cf. A., 1927, 1221).—Fermentation of dextrose solution containing inorganic nutrient materials is accelerated considerably if the yeast used is previously exposed to the action of an oscillating electromagnetic field of 272·7 kilocycles for 35—40 min., and slightly if the frequency is 400 or 500. The fermentation is, however, retarded if the frequency is as high as 1200. T. H. POPE.

Apparatus for graphic registration of fermentation. G. JOACHIMOGLU (Biochem. Z., 1927, **190**, 399—401). P. W. CLUTTERBUCK.

Partial dephosphorylation of hexosediphosphoric acid by yeast. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1927, **191**, 450—455).—Magnesium hexosediphosphate is treated with bottom yeast and the hexosemonophosphate isolated as the barium salt; yield 17% of theory.

P. W. CLUTTERBUCK.

Structure of hexosephosphoric esters and methylglyoxal from their spectrographic behaviour. C. NEUBERG and S. A. SCHOU (Biochem. Z., 1927, **191**, 466—471).—The spectrographic behaviour of magnesium hexosediphosphate, calcium hexosemonophosphate (Neuberg's), and barium hexosemonophosphate (Robison's) is investigated. All these esters show, besides general absorption, an absorption band with a maximum at about 2630 Å., the position of which corresponds with the absorption maximum of acetone. The molecular extinction coefficient ε is 10—100 times as high for the sugar phosphoric esters as for the free sugars. For methylglyoxal, absorption began at 3200 Å. and attained a maximum at 2780 Å. (ε=13·2). At shorter wave-lengths, the absorption decreases and shows a minimum at 2415 Å. (ε=2·7) followed by a further increase in the extreme ultra-violet. The course of absorption corresponded entirely with that of aliphatic substances which contain only one carbonyl group, as is seen by comparison with the absorption of propaldehyde. It is therefore suggested that one carbonyl group of methylglyoxal, probably the ketone group, is hydrated, its absorption effect being thus lost. P. W. CLUTTERBUCK.

Supposed separation of methylglyoxal in alcoholic fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, **191**, 472—477).—It was not found possible to isolate any methylglyoxal by means of semicarbazide during alcoholic fermentation, the sparingly soluble substance obtained being shown to be hydrazodicarbonamide, resulting from decomposition of semicarbazide itself.

P. W. CLUTTERBUCK.

Carbohydrate and fat metabolism of yeast. IV. Nature of the phospholipins. C. G. DAUBNEY and I. S. MACLEAN (Biochem. J., 1927, **21**, 373—385).—The total amount of ether-soluble substances in yeast increases to five times its original amount and that of the phospholipins to three times its original value after incubation in dextrose–phosphate medium. The lipin fraction was investigated in the following way. Pressed yeast was grown in a sugar–phosphate medium for 28 hrs., while a current

of air was blown through the solution. After collecting the yeast, it was ground with sand and extracted with alcohol. The ethereal solution of this extract was then precipitated with acetone. The lecithin–kephalin ratio of the lipin fraction (the precipitate) was examined by hydrolysing, removing the fatty acids by extraction, and determining the total and amino-nitrogen. The examination of the degree of unsaturation by determining the iodine value and by bromination of the acids of the ether-soluble lead salts of the lipin fraction established the presence of oleic acid only. Palmitic acid was also present. From the quantitative data obtained, it is computed that yeast kephalin is a mixture of 82% of dioleylkephalin and 18% of oleylpalmitylkephalin, and the lecithin a mixture of 75% of oleylpalmityl-lecithin and 25% of dioleyl-lecithin.

The analysis of the acetone-soluble fraction of the alcoholic extract of the yeast revealed the presence of dibromostearic and tetrabromostearic acids, from which the existence of oleic and linoleic acids in the original fat is deduced. Palmitic acid was also isolated. The unsaponifiable fraction consisted of about 50% of sterols, including ergosterol and some unidentified compounds. S. S. ZILVA.

Sulphur metabolism of yeast. H. SUGATA and F. C. KOCH (Plant Physiol., 1926, **1**, 337—347).—Sulphate is the form of sulphur most available to yeast; it is converted into yeast-protein, and probably partly into cystine. Cystine, cysteine, and hydrogen sulphide stimulate yeast growth at low, and retard it at higher, concentrations. Cystine is converted partly into yeast protoplasm and partly into sulphate. CHEMICAL ABSTRACTS.

Phytochemical reduction by bacteria. C. NEUBERG and E. SIMON (Biochem. Z., 1927, **190**, 226—231).—*p*-Xyloquinone is reduced practically quantitatively to *p*-xyloquinol and valeraldehyde to amyl alcohol (yield 73%) by *B. coli* which is fermenting a nutrient solution containing dextrose, whilst sodium thiosulphate with *B. lactis aerogenes* yields hydrogen sulphide, but only to the extent of 1—2%. The high yields in the first two cases indicate that the reduction is a true hydrogenation and is not a dismutation process in which two molecules of substrate are concerned. A. WORMALL.

Action of *B. lactis aerogenes* and *B. coli* on hexosemonophosphoric acid. N. KAGEURA (Biochem. Z., 1927, **190**, 181—187).—*B. lactis aerogenes* and *B. coli* produce appreciable amounts of lactic acid from the sodium and calcium salts of the hexosemonophosphoric acid prepared by the method of Neuberg and Leibowitz (A., 1927, 993). The yield of lactic acid is always less than the theoretical amount calculated from the amount of inorganic phosphate liberated. A. WORMALL.

Formation of succinic acid by fermentation of sugars by *B. coli*. A. I. VIRTANEN (Annal. Acad. Sci. Fennicæ, 1927, *A*, **29**, No. 26).—Anaerobic fermentation of dextrose by a strain of *B. coli* isolated from fæces, in an atmosphere of carbon dioxide, yielded after 18 days about 39·1% of lactic acid, 19·8% of succinic acid, 11·0% of acetic acid, and 4·8% of formic acid. In a similar way aerobic fermentation yields after 24 days 34·0% of lactic acid, 20·6% of succinic acid, 11·3% of acetic acid, and 1·1% of formic acid. It is suggested that dextrose breaks down in two ways during this fermentation: first to succinic acid and acetaldehyde (which gives alcohol and acetic acid) and second through a hexosephosphate to methylglyoxal, which in turn gives lactic acid, acetaldehyde, and formic acid (see also A., 1927, 701). G. A. C. GOUGH.

Applications of the polarographic method. M. SHIKATA.—See this vol., 136.

Fission of sugar by *Bacillus propionicus*. K. MAURER (Biochem. Z., 1927, **191**, 83—87).—The result of Virtanen (Soc. sci. Ferm., 1923, **1**, 36; 1925, **2**, 20) that by the fermentation of sugar with *B. propionicus* there are produced by a subsidiary reaction acetaldehyde and succinic acid, was not confirmed. P. W. CLUTTERBUCK.

Influence of active and inactive serum on the bacterial formation of nitrite. O. WELTMANN, O. BSTEH, and K. NEUMAYER (Z. Hyg. Infekt.-Krankh., 1927, **107**, 126—129; Chem. Zentr., 1927, i, 2440).—Bacterial reduction of nitrate to nitrite is arrested by serum diluted with physiological sodium chloride solution. Inactive serum has no inhibitory effect. A. A. ELDRIDGE.

Alcohol-soluble specific substances of *Bacillus diphtheriæ* and of *Streptothrix*. J. FREUND (J. Immunol., 1927, **13**, 161—169).—The alcohol-soluble specific substance of *B. diphtheriæ* contains 5·6—5·7% N; after hydrolysis the biuret reaction is negative and the ninhydrin reaction positive. It is probably not of protein nature. An alcohol-soluble specific substance was present in a *Streptothrix* strain, but not in *B. xerosis*, *Trichophyton*, *Actinomyces*, or yeast. CHEMICAL ABSTRACTS.

Urea-splitting bacterium in the human intestinal tract. J. V. COOKE and H. R. KEITH (J. Bact., 1927, **13**, 315—319).—"*B. ammoniagenes*" is exceptionally active in producing ammonia from urea. CHEMICAL ABSTRACTS.

Formation of indigotin from indole by soil bacteria. P. H. H. GRAY (Proc. Roy. Soc., 1927, B, **102**, 263—280).—A soil organism, *Pseudomonas indoloxidans*, has been isolated, which will oxidise indole to indigotin. It is probable that the oxidation does not take place within the organism but is brought about in the surrounding medium by an exo-enzyme which diffuses from the growth. The organism cannot use indole as a sole source of energy, but given a source of carbon and no nitrogen other than indole it can oxidise indole to indigotin. A high ratio of carbon to hydrogen in the energy source favours indigotin formation.

Mycobacterium globerulum and *Micrococcus piltonensis* produce small amounts of indigotin on indole agar only. E. A. LUNT.

Antiseptic action of phenol and *p*-chlorophenol in solvents with different dielectric constants. W. E. ENGELHARDT (Biochem. Z., 1927, **190**, 217—225).—The antiseptic action against *Staphylococcus aureus* and anthrax spores of phenol

dissolved in different solvents shows no relationship to the dielectric constant of the solvent, but *p*-chlorophenol has an antiseptic action in solvents of high dielectric constant only (water, glycerol, and nitrobenzene). This difference between phenol and *p*-chlorophenol cannot be explained on the basis of lipoid-solubility, but is attributed to the greater dissociation of *p*-chlorophenol. These results support the hypothesis of Hellenbrand and Joachimoglu (A., 1925, i, 466) that dissociated substances have an antiseptic action which is related to the degree of dissociation, and therefore to the dielectric constant, of the solvent. A. WORMALL.

Amount of carbohydrate in antitubercular vaccine B.C.G. of Calmette and Guerin. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1027, **9**, 1095—1096).—*B. tuberculosis* bovine type when boiled with sulphuric acid yields 22·6% of its weight as hexose and pentose (calculated as dextrose), of which 11% is pentose (calculated as arabinose). The corresponding figures for the bacillus prepared for use as a vaccine by Calmette and Guérin's process are 26·8 and 9·6%, respectively. W. O. KERMACK.

Influence of electrolytes on the phenomena of agglutination. M. PIETTRE and A. CHRETIEN (Compt. rend., 1927, **185**, 1319—1321).—Dilute solutions of sodium chloride and similar electrolytes exert little influence on the agglutination of paratyphoid bacilli. Maximum agglutination of these bacilli, cultivated in peptone water, is obtained in faintly acid solution, whilst, if the peptone water also contains dextrose, the fermentation of which produces an acid reaction, maximum agglutination is observed in faintly alkaline solution. Chemical neutrality of the bacillary substance is the most favourable condition for its combination with agglutinin.

B. W. ANDERSON.

Insulin-like substances in higher plants and micro-organisms. P. E. SIMOLA (Annal. Acad. Sci. Fennicæ, 1927, *A*, **29**, No. 15).—Extraction of potatoes, rhubarb leaves, yeast, and bacteria (*B. casei* ε and *B. subtilis*) with alcohol containing hydrochloric acid (but not with aqueous acids) yields insulin-like substances, which may also be obtained by the extraction of a mixture of the cells and picric acid with acetone. Whilst the crude products sometimes exert hyperglycæmic action, the purified extracts all produce hypoglycæmia, a state which is often accompanied by considerable toxic symptoms when the extracts are purified by the picrate method.

G. A. C. GOUGH.

Structure-fixation of dextrose and its significance in the fate of dextrose. O. LOEWI (Naturwiss., 1927, **15**, 93—94; Chem. Zentr., 1927, i, 2565—2566).—Human erythrocytes in sodium fluoride plasma fix dextrose, which is not attacked, but in serum the same erythrocytes convert a portion into lactic acid. The effect of insulin is to make greater quantities of dextrose available for decomposition by causing greater fixation. In diabetic plasma the dextrose-fixing power is reduced by a thermostable, dialysable substance, which can be extracted from the dialysate with alcohol; it appears in blood when excess of insulin is given. A. A. ELDRIDGE.

Distribution of reducing substances between blood-plasma and striped muscle. Effect of insulin. B. S. CUENCA (Biochem. Z., 1927, **190**, 1—16).—The reducing substances have been determined (as dextrose) in blood-plasma and voluntary muscle of starved and fed mice and the effect on these values of injection of insulin, dextrose, and adrenaline has been noted. The ratio, reducing substances in 100 g. of muscle to reducing substances in 100 c.c. of blood-plasma, is $0·72\pm0·05$ for mice previously starved for 18 hrs. and $0·77\pm0·06$ for fed mice. The plasma-sugar figures 5 min. after intravenous injection of a 10% solution of dextrose (0·2 g. of dextrose per 100 g. weight) are 551 mg. (as dextrose) per 100 c.c. for the starved mouse, 477 mg. for the insulin-treated starved mouse, and 453 mg. for the fed mouse. The corresponding distribution coefficients (muscle-sugar/plasma-sugar) are 0·28, 0·26, and 0·48, respectively, and normal coefficients are attained after more than 30 min., in 10 min., and in 23 min., respectively. These results are interpreted as indicating that the sugar penetrates into the muscle most rapidly with the insulin mouse and least with the starved mouse, and it is suggested that the number of open muscle capillaries is greatest in the former case and least with the starved animal. A. WORMALL.

Action of insulin on dextrose *in vitro*. T. J. C. COMBES (Compt. rend, Soc. Biol., 1927, **97**, 268—270; Chem. Zentr., 1927, ii, 1278). No action was detected.

A. A. ELDRIDGE.

Insulin reactions. L. FOSHAY (Arch. Int. Med., 1927, **40**, 661—667).—Data are given for the serum and corpuscular dextrose in the blood in the case of five diabetic patients on insulin treatment. In all cases the insulin reaction occurred where the corpuscular dextrose concentration was low, even although the serum-dextrose concentration was high, thus showing that the whole blood-sugar concentration bears no relation to the occurrence of insulin reactions. The author believes that the insulin reaction is due to a lack of available dextrose in the cells of the fixed tissues and regards the corpuscular dextrose concentration as an index of this quantity. E. A. LUNT.

Glycæmia, glycogen, and insulin action with decapsulated rats. A. ARTUNDO (Compt. rend. Soc. Biol., 1927, **97**, 411—413; Chem. Zentr., 1927, ii, 1278).—Resistance or sensitivity towards insulin cannot be ascribed only to glycogen changes.

A. A. ELDRIDGE.

Effect of insulin on the decomposition of pyruvic acid in mammalian muscle. E. TOENNIESSEN (Verh. deut. Ges. inn. Med., 1926, 454—456; Chem. Zentr., 1927, i, 2445).—The decomposition of pyruvic acid to acetic acid by the abdominal muscles of the rabbit, suspended in Ringer solution of p_H 6·8—7·3, is almost completely inhibited by the addition of small quantities of insulin; with larger quantities, the pyruvic acid disappears by synthesis of carbohydrate.

A. A. ELDRIDGE.

Influence of insulin on phosphorus metabolism. Z. KOŁODZIEJSKA and K. FUNK (Med. dośw. spol., 1926, **6**, 83—90; Chem. Zentr., 1927, i, 2564).—Insulin appears to have no influence on the phosphorus elimination or content of rats. A. A. ELDRIDGE.

Influence of nickel and cobalt on the hypoglycæmic action of insulin in the rabbit. M. Labbé, Roubeau, and F. Nepreux (Compt. rend., 1927, 185, 1532—1534).—Traces of nickel and cobalt salts prolong the hypoglycæmic effect of insulin (cf. Bertrand and Mâchebœuf, A., 1926, 869).

H. Burton.

Antagonism of insulin and "thyreodin" in carbohydrate metabolism. M. Rosenberg (Klin. Wochschr., 1927, 6, 631—634; Chem. Zentr., 1927, i, 2841).—In diabetes, insulin and "thyreodin" are antagonistic. Glycosuria in non-diabetics is not markedly affected by insulin. A. A. Eldridge.

Influence of the thyroid hormone on protein metabolism. L. Lichtwitz and L. Conitzer (Z. ges. exp. Med., 1927, 56, 527—534; Chem. Zentr., 1927, ii, 1277).—Loss of weight following treatment of myxœdema with "thyreodin" is not simply correlated with loss of nitrogen. The negative nitrogen-balance is due to the removal of the supply-protein, and is accompanied by a reduction of the plasma-protein. A. A. Eldridge.

Methylating function of the thyroid. B. Stuber and F. Stern (Biochem. Z., 1927, 191, 363—373).—Further work (see A., 1924, i, 239) on the methylation of guanidineacetic acid to creatine shows that in dogs, rabbits, and cats this methylation is a specific function of the thyroid and is not shared by either the pituitary or the sex glands. Methylation of pyridine in dogs, however, proceeds quite independently of these glands. P. W. Clutterbuck.

Female sexual hormones. Bencan, C. Champy, and T. Keller (Compt. rend. Soc. Biol., 1927, 97, 229—232; Chem. Zentr., 1927, ii, 1277).—The placenta contains the hormone of the follicles and the hormone of the corpus luteum; thus the secretion of sexual hormones is not confined to a definite class of histological elements. A. A. Eldridge.

Blood-gases and their relations to the internal secretions of animals kept on a diet deficient in vitamin-*A* and -*B*. E. Miyake (Fol. endocrinol. japon., 1926, 2, 23—24, 593—641).

Chemical Abstracts.

Avitaminosis and metabolism. A. Palladin (XII Int. Cong. Physiol., 1926, 123—124; Chem. Zentr., 1927, i, 2443).—Metabolic disturbances due to avitaminosis and hunger, respectively, are distinct; the differences observed are described.

A. A. Eldridge.

Glutathione and avitaminosis-*B* in the pigeon. L. Randoin and R. Fabre (Bull. Soc. Chim. biol., 1927, 9, 1027—1069).—Various tissue extracts from pigeons have been titrated with iodine, using as end-point (1) ammonium nitroprusside to determine the free sulphydryl groups (G) and (2) a starch reagent to determine the total power of the tissue to reduce iodine (G_1). The G values of the various organs of pigeons decrease as the result of starvation simultaneously with the decrease in body temperature. Pigeons on a diet deficient in vitamin-*B* show a decrease of G in the skeletal and heart muscles after the tenth or fifteenth day. With normal pigeons the ratio G_1/G remains comparatively constant, being 1·65 for the pectoral muscle, 1·77 for the leg muscles, 1·92 for the heart muscle, 1·49 for the liver, and 1·38 for the blood. When the pigeons are deprived of vitamin-*B* the ratios for the skeletal and heart muscles markedly increase. During starvation the ratios for the muscles also increase, but to a smaller extent. The increase in G_1/G occasioned by lack of vitamin-*B* results partly from the decrease of the free sulphydryl groups in the tissues, G, and partly from the simultaneous increase in reducing substances other than those containing the sulphydryl group.

W. O. Kermack.

Vitamin-*B*. C. Funk (XII Int. Cong. Physiol., 1926, 58; Chem. Zentr., 1927, i, 2443).—A mixture of naphthol-yellow-*S* and silver picrate precipitates the greater part of vitamin-*B*, most of the other nitrogenous substances remaining in solution. Vitamin-*B* appears to be separable into two fractions.

A. A. Eldridge.

Chemical composition of the bones of scorbutic guinea-pigs. E. Brouwer (Biochem. Z., 1927, 190, 402—410).—The bones (tibia) of guinea-pigs fed on a diet free from vitamin-*C* contain 10% less calcium and phosphorus and 19% less dry substance (but the ratio CaO/P_2O_5 is unchanged) than those of animals on practically the same diet to which is added 1—2 g. of fresh grass per day. A similar result is obtained by adding 0·5 g. of cod-liver oil daily. The brittleness of scorbutic bones is caused less by the deficiency of calcium and phosphorus than by changes in microscopic structure.

P. W. Clutterbuck.

Isolation of the antirachitic factor from irradiated cholesterol. I. I. Nitzescu and G. Popoviciu (XII Int. Cong. Physiol., 1926, 118; Chem. Zentr., 1927, i, 2443).—Concentration of the antirachitic factor can be effected with alcohol.

A. A. Eldridge.

Reproductive failure of white rats on synthetic diets. U. Suzuki, W. Nakahara, and N. Hashimoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 143—151).—White rats fed on a synthetic diet of meat protein, sucrose, starch, mineral salts, oryzanin, and biosterin proved sterile. The addition of cholesterol or synthetic triolein to the diet, or the ultra-violet irradiation of the rats, did not affect this condition, which is attributed to absence of vitamin-*E* in the diet. E. A. Lunt.

Food requirements of the growing rat. II. Effect of variation in proportion and quality of recognised nutrients. L. S. Palmer and C. Kennedy (J. Biol. Chem., 1927, 75, 619—657).—Young rats were kept, out of access to their fæces, on a basal diet of dextrin, purified caseinogen, butter fat, agar, salts, and wheat embryo extract, which, according to views at present accepted, should have been sufficient for normal growth; the growth obtained was, however, always less than that obtainable on a full natural diet. The deficiency was not affected by increasing the supplies of any known vitamin. Improved growth was obtained by addition to the diet of fat-free wheat embryo, or of commercial lactose, or by substitution of a crude animal protein for the purified caseinogen. The effect of the wheat embryo

was not due to vitamin-*B*, since yeast had no influence on growth. Butter fat of summer origin gave better results than that obtained in winter. It appears therefore that hitherto unrecognised factors essential to growth may have been associated with the lactose and the crude proteins which gave good results.

C. R. HARINGTON.

Vitamin "D_m" [bios] in fermentation vinegar. A. JANKE and H. LACROIX (Biochem. Z., 1927, **190**, 67—74).—The growth factor responsible for the stimulation of yeast growth is present in fermentation vinegar but not in vinegar essence, and that present in the former is derived from the metabolism of the acetic acid bacteria. The growth factor is resistant to heat and can be adsorbed by fuller's earth, from which it is eluted with 1% ammonia. No activation of the growth of yeast by this growth factor occurs in the absence of the salt solution used. A. WORMALL.

Respiration and fermentation in green plants. II. Metabolism of phanerogams. L. GENEVOIS (Biochem. Z., 1927, **191**, 147—157; cf. A., 1927, 905).—Measurements of the respiratory and fermentative activities of the parts of plants (*Lathyrus odorata*, *Caltha palustris*, *Aquilegia vulgaris*, *Elodea canadensis*, etc.) at different stages of growth are described and an attempt is made to trace a connexion between the amount of their metabolism and their condition of growth and development, and to compare these activities in plant and animal cells. Fermentation is increased during the growth of the embryo, but both respiration and fermentation decrease with increasing age. Both respiration and fermentation are also equally high during the formation of seed. Whereas there is no difference in fermentation in the intact and the minced seeds, respiration increases considerably on mincing, the oxygen supply being, in the intact seed, insufficient to attain maximal respiration. The sensitivity to cyanide of the respiration of embryos decreases with age. The respiration of older embryos, however, can be increased with sugar, and this increased respiration is then inhibited, in the same way as the high respiration of the younger embryos, by cyanide. P. W. CLUTTERBUCK.

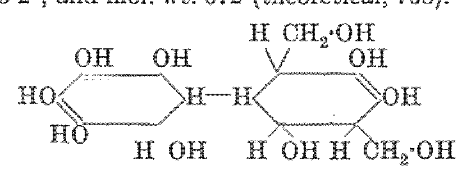
Formation of pigments in plants. H. SCHMALFUSS and H. BARTHMEYER [with H. BRANDES] (Biochem. Z., 1927, **190**, 424—432).—The conditions for darkening of the fruit-cases of the horse-chestnut, of the pulp of apples and pears, and of the tissues of many fungi correspond with those for the pods of the broom (*Sarothamnus scoparius*, Wimm.). With the Sarothamnus type, the scratched part reacts more acid and darkens under the influence of atmospheric oxygen in 30 min. at 20°. This type is different from the bean type (*Vicia faba*, L.) in that, with the latter, the scratched part becomes more acid but does not darken in 30 min. but only slowly on keeping. In the intact bean pod, formation of melanin is but little affected by the concentration of oxygen, chromogen, and acidity within wide limits, but is greatly affected by concentration of enzyme. The formation of melanin is inhibited by various secondary products present, but darkening may be artificially brought about by treating with ammonia, chloroform, and ether, crushing, and drying. P. W. CLUTTERBUCK.

I. Assimilation of formaldehyde. II. Enzymic condensation of formaldehyde to sugar. J. BODNAR, L. E. RÓTH, and C. BERNAUER (Biochem. Z., 1927, **190**, 304—325).—The changes of dry substance and sugar contents of leaves of *Tropæolum majus* when grown in normal air and in atmospheres containing formaldehyde, acetaldehyde, and toluene, in presence and in absence of sunlight, are determined. The dry substance and sugar contents of the formaldehyde-treated leaves are greater than that of the control and of the original leaves, the leaves therefore having synthesised sugar from formaldehyde. No starch could be detected in leaves grown in formaldehyde with the exclusion of light and it is assumed that formaldehyde inhibits the condensation of sugar to starch. Acetaldehyde, however, cannot increase the dry substance and sugar contents of the leaves, but both acetaldehyde and toluene are injurious to respiration. P. W. CLUTTERBUCK.

Anthocyanins in the pigment of Isabella grapes. R. J. ANDERSON and F. P. NABENHAUER (N.Y. Agric. Exp. Sta. Tech. Bull., 1926, No. 123, 1—13). —The pigment is a monoglucoside, $C_{23}H_{25}O_{12}Cl,4H_2O$, apparently identical with œnin. Œnidin chloride is 3 : 5 : 7-trihydroxy - 2 - (4 - hydroxy - 3 : 5-dimethoxyphenyl)benzopyrylium chloride.

CHEMICAL ABSTRACTS.

Bergenin. I. V. S. SADIKOV and R. GUTHNER (Biochem. Z., 1927, **190**, 340—351).—The "glucoside" bergenin, extracted in 1850 by Garreau from Siberian saxifrage (*Bergenia Siberica*) and renamed bergenitol by Morelle (A., 1882, 159), on account of its resemblance to mannitol, is re-examined. By extraction with cold (0—5°) water (Morelle extracted at 80°) a crystalline sample of bergenin was obtained the prismatic angle of which was 88° 45′ (Morelle's bergenitol, 91° 15′), which showed the phenomenon of double m. p. at 138° and 230° (Morelle's bergenitol, 130° and 230°), the mol. wt., 348, and the analytical composition of which agreed with the formula $C_{14}H_{20}O_{10}$ (Morelle's bergenitol, $C_8H_{12}O_6$). Two samples of this bergenin had rotations α_D +47·2°, +51·3°, whereas Morelle's bergenin had α_D −51·36°. This bergenin contained two methoxy-groups and when heated with sodium acetate and acetic anhydride gave a deca-acetyl derivative, $C_{14}H_{10}(OAc)_{10}$, m. p. 192·5—193·5°, α_D +25·2°, and mol. wt. 672 (theoretical, 768). Berg-



enin is not hydrolysed by heating with 5% sulphuric or hydrochloric acid and is not a glucoside. The above formula is suggested and discussed.

P. W. CLUTTERBUCK.

Preparation of sinigrin. H. HÉRISSEY and R. BOIVIN (Bull. Soc. Chim. biol., 1927, **9**, 947—949).—Black mustard seed (1 kg.) is extracted for 20 min. with boiling acetone (10 litres containing 2·5 litres of water). The mixture is cooled and filtered and the filtrate is distilled until the residue is reduced to about 2 litres, which, after being separated from oil and

filtered, is fermented by fresh baker's yeast for 2—3 days. The product is neutralised by adding calcium carbonate to the hot solution, filtered, and concentrated under reduced pressure to a syrup which is taken up in 85% alcohol (3 litres). After 24 hrs. the alcoholic solution is filtered and concentrated under reduced pressure. The residue is extracted with boiling 95% alcohol (300 c.c.), kept for 24 hrs., filtered, and seeded, when almost pure sinigrin slowly crystallises. The extraction of the residue is repeated six or seven times. The yield is 11—12 g.

W. O. KERMACK.

Chemical nature of the sulphur-containing glucoside of *Alliaria officinalis*. H. HERISSEY and R. BOIVIN (Bull. Soc. Chim. biol., 1927, 9, 950—952).—By the use of the authors' method (cf. preceding abstract) for the separation of sinigrin 1·4 g. of this compound have been isolated from 400 g. of seeds of *A. officinalis*.

W. O. KERMACK.

Cortex of *Byrsonima crassifolia*. G. HEYL and H. HEIL (Festschr. A. Tschirch, 1926, 62—71; Chem. Zentr., 1927, i, 2668).—The cortex of *Byrsonima crassifolia* contains *byrsonimol*, $C_{29}H_{52}O$, m. p. 197·5°, $[\alpha]$ +96·94° (*acetyl* derivative, m. p. 242°; *benzoyl* derivative, m. p. 232°), giving in concentrated sulphuric acid a yellow solution becoming brown on addition of acetic anhydride or reddish-yellow to dull red when warmed. The substance, when treated with acetic anhydride and (dropwise) with concentrated sulphuric acid, gives a deep violet-red solution. These and other colour reactions are given by naturally occurring higher alcohols of the character of phytosterols.

A. A. ELDRIDGE.

Gossypol. I. Preparation and properties. E. P. CLARK (J. Biol. Chem., 1927, 75, 725—739).—Gossypol was obtained from cotton seed as the acetate by the method of Carruth (A., 1918, i, 266), freed from acetic acid, and crystallised from a mixture of ether and light petroleum; it had the formula $C_{30}H_{30}O_8$, mol. wt. 572, m. p. 214° (decomp.); on titration with potassium hydroxide it neutralised 2 molecules of the latter. On treatment in ethereal solution with acetic acid it yielded the *substance* $C_{30}H_{30}O_8$,AcOH, m. p. 189—190° (decomp.), which was decomposed by water; on heating at 215° it lost $2H_2O$ to give *anhydrogossypol*, m. p. 268° (softening at 229—230°). Gossypol gave a *dianilide*, m. p. 302—303°, and a *dioxime*, m. p. 315°; on acetylation it gave a *hexa-acetate*, m. p. 276—277° (decomp.); four of the acetyl groups were hydrolysed readily, two with greater difficulty; gossypol therefore contains two carbonyl groups and six hydroxyl groups, of which two are much more acidic in character than the remainder.

C. R. HARINGTON.

Isolation of the physiologically active principles contained in the leaves of the ombú (*Phytolacca dioica*). F. REICHERT (Anal. Asoc. Quím. Argentina, 1927, 15, 221—224).—Physiologically active solutions were obtained by extraction of dried leaves of the ombu with water and alcohol. By precipitation of the aqueous extract with lead acetate and afterwards with basic lead acetate, decomposition of the lead compounds by hydrogen sulphide, and precipitation with alcohol, four fractions were obtained which gave the characteristic reactions of saponins. Three of these were toxic, causing hæmolysis.

R. K. CALLOW.

Utilisation by *Aspergillus niger* of gein, the eugenol-yielding glucoside of the roots of *Geum urbanum*. H. HÉRISSEY (Bull. Soc. Chim. biol., 1927, 9, 943—946, and J. Pharm. Chim., 1928, [viii], 7, 5—8; cf. A., 1925, i, 487, 1383).—The growth of *A. niger* on a culture medium, the sucrose of which has been replaced by gein, is inhibited considerably when the medium is acid, and almost entirely when it is non-acid.

W. O. KERMACK.

Nitrogen nutrition of moulds. Assimilation of urea-nitrogen. D. BACH (Compt. rend., 1927, 185, 1309—1310).—Of 24 species of *Mucorinæ* grown in liquid media containing urea as the only source of nitrogen, only 6 developed normally.

B. W. ANDERSON.

Plant growth-promoting substances, hydrogen-ion concentration, and the reproduction of *Lemna*. N. A. CLARK (Plant Physiol., 1926, 1, 273—279).—The rate of reproduction of *Lemna major* is increased when the hydrogen-ion concentration is kept uniform and the amount of bacterial growth diminished. The optimum p_H probably varies with the composition of the culture solution.

CHEMICAL ABSTRACTS.

Ultrafiltration of small amounts of liquid by means of the centrifuge. A. TÓTH (Biochem. Z., 1927, 191, 355—362).—A method is described for carrying out ultrafiltration experiments using the centrifuge, with amounts of liquid up to 5—6 c.c. Collodion solutions in acetic acid are better than in ether-alcohol for ultrafiltration purposes, since the latter dry too readily, and a thicker membrane is required for the same filtration with the centrifuge than with the water-pump. The preparations of a viscose solution and of a viscose membrane are described and the permeability of the membrane is tested against a series of colloids.

P. W. CLUTTERBUCK.

Use of Stolte's ashing method in micro-analysis. C. EGG and K. KLINKE (Biochem. Z., 1927, 191, 439—441).—Stolte's method (A., 1911, ii, 946) of ashing, which avoids loss of alkali chlorides, is shown to be trustworthy.

P. W. CLUTTERBUCK.

Reagents for the chemical fractionation of biologically active raw material. C. FUNK (Biochem. Z., 1927, 191, 181—185).—A general method is described for attempting the fractionation of trypsin, pepsin, pituitrin, vitamins-*B* and -*C*, and insulin by the use of various reagents, such as the sodium, barium, lead, silver, and mercury salts of picric acid and to a less extent of picrolonic and flavianic acids, the salts being more specific than the free acids and scarcely affecting the activity of the material.

P. W. CLUTTERBUCK.

Precipitation of magnesium ions by tropæolin-*OO* and the use of this reaction for its colorimetric determination. J. ZAHRADNÍCEK.—See this vol., 145.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1928.

General, Physical, and Inorganic Chemistry.

One-metre vacuum spectrograph. R. A. Sawyer (J. Opt. Soc. Amer., 1927, **15**, 305—308).—A convenient type of vacuum spectrograph designed to use the standard N.P.L. one-metre grating and to operate from 3000 to 1700 Å. is described.

R. W. Lunt.

Fine-structure constant as a numerical constant. S. Ray (Naturwiss., 1927, **15**, 408; Chem. Zentr., 1927, ii, 15).—According to Jeans ("Report on radiation and the quantum theory") $hc/2^{-4}=(4^{-e})^2$; hence the fine-structure constant $\alpha=2^{-e^2}/hc-16$.

A. A. Eldridge.

Extension of the irregular doublet law. M. N. Saha and P. K. Kichlu (Nature, 1928, **121**, 244—245).—"On comparison of the spectra of a group of successive elements which are reduced by electric discharge to the same electronic constitution, frequencies of corresponding lines arising out of a transition in which the total quantum number remains unchanged will form an arithmetical progression." Hence, if the spectra of two elements, preferably successive, in any group be known, the spectra of the remaining elements can be predicted.

A. A. Eldridge.

Width of the lines of the Balmer series. (Mlle.) M. Hanot (Ann. Physique, 1927, [x], **8**, 555—625).—The width of a line is defined as the wave-length interval over which the average intensity of illumination is equal to one half of the intensity maximum, although this does not necessarily completely characterise the distribution of energy over the line as supposed by some. The width of the primary lines in the Balmer series has been studied for a spark spectrum in hydrogen, the conditions being closely defined by measurements of capacity, potential, and frequency of the circuit. The width of the lines was measured by a microphotometric method, using a Rowland grating.

For a given initial temperature and pressure, the width l of the lines is determined by the intensity of the current traversing the spark, according to the law $l=f(I_0)$, where I_0 is given by $I_0=V\sqrt{C/L}$ and so represents the maximum intensity of current in an undamped circuit. The width increases very rapidly with rising I_0 for small intensities and then tends to a maximum; its variation with pressure p is given approximately by $l=l_1\times p^m$, where l_1 is a constant and m is very close to unity for small intensities but decreases with increasing I_0 down to 2/3.

The chief causes of the enlargement of lines are (*a*) the absorption by the source of some of its own radiation and (*b*) the intermolecular field due to ions and quadruplets. The magnitude of the former was studied experimentally by passing radiation from one spark through a second; for $I=300$ amp. the width of the lines due to a very small region of the source is thus found to be 85—90% of the total width. The main cause of enlargement, however, is the intermolecular field due to the ions, which has a mean value of 10^5 volts/cm. and is proportional to the 2/3 power of the ionic density. The effect of the quadruplets is secondary, being greater for large currents than for small, whilst the absorption effect is greater in the small-current region, as expected by theory. The sum of these two effects is approximately constant at 10—15% of the width of the line. Like l, the current density in the spark follows a law of the form $i=\varphi(I_0)$, so that the theory explains the independence of the width of the lines and the damping of the circuit.

S. J. Gregg.

Continuous spectrum of hydrogen. J. Kaplan (Proc. Nat. Acad. Sci., 1927, **13**, 760—763).—A mechanism is suggested to account for the continuous spectrum emitted by the blue glow which occurs when hydrogen at pressures less than 1 mm. is excited by electrons of less than 15 volts.

R. W. Lunt.

Reversal of helium lines. T. Takamine and T. Suga (Phil. Mag., 1928, [vii], **5**, 141—149).—An examination of the reversal of helium lines has been made first with a long capillary tube viewed end-on and, secondly, with a long tube of wider bore placed between the capillary tube and the spectrograph. The lines of the principal and of the diffuse series show reversal, but there are great differences in the manner of their reversals. The lines of the principal series connected with the metastable states $2s$ and $2S$ are strongly absorbed in passing through the wider tube. This effect of the less luminous vapour is marked for the lines 5016 and 3889 Å. The lines of the diffuse series, such as 6678 and 5876 Å., are seen reversed with the capillary tube alone excited, the wider tube having little effect. The polarity of the capillary has a marked effect on the clearness of the reversals, indicating the effect of a heterogeneous distribution of the excited atoms along its length.

A. E. Mitchell.

Excitation of the auroral green line in discharge tubes. D. A. Keys (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 257—261).—In an apparatus which is described, spectrograms have been taken of the light emitted from the electrical discharge

through mixtures of (1) helium and oxygen and (2) argon and oxygen. With a large pressure of helium, *e.g.*, 15 mm. of helium to 1·5 mm. of oxygen, the auroral green line, 5577 Å., was obtained with a suitable current density. Under other conditions bands, which appeared to be the second group of Swan bands, were obtained instead, probably due to hydrocarbons present as impurities. With argon at a pressure of about 40 mm. and oxygen from 8 to 10 mm., the auroral green line was brought out with great intensity (cf. A., 1927, 179), but it was difficult to suppress the bands. The results support McLennan's view (Proc. Roy. Soc., 1927, **A**, **114**, 1) that the auroral green line is due to oxygen excited with enhanced intensity by the presence of helium or argon at comparatively high pressures. The diameter of the tube had a marked effect, a wide tube favouring the appearance of the line. M. S. Burr.

Spark spectrum of oxygen (O II). H. N. Russell (Physical Rev., 1928, [ii], **31**, 27—33).—Ninety-nine lines, including all the strong lines not previously classified, are accounted for, and the electron configurations corresponding with the new terms have been identified. Bowen's conclusions concerning the origin of the nebular lines near 3727 Å. are confirmed. A. A. Eldridge.

Distribution of ionised oxygen in the gaseous nebulæ. J. H. Reynolds (Nature, 1928, **121**, 206—207).—There is no recorded evidence of the existence of neutral oxygen in the gaseous nebulæ; the distribution of O III and O II in Orion's nebula is discussed. A. A. Eldridge.

Nebulium spectrum in new stars. S. R. Pike (Nature, 1928, **121**, 136—137).—Elvey's reasoning (this vol., 98) is criticised. Alternatively, it may be supposed that the oxygen and hydrogen shells originate in different layers of the star.
A. A. Eldridge.

Metallic spectra excited by active nitrogen. J. Okubo and H. Hamada (Phil. Mag., 1928, [vii], **5**, 372—380).—An examination of the after-glow spectrum of active nitrogen has confirmed the results of Strutt and of Johnson and Jenkins (A., 1926, 991). No evidence for the second group of positive bands reported by Ruark and others (A., 1927, 395) was obtained. The emission spectra of the vapours of mercury, cadmium, zinc, magnesium, sodium, potassium, thallium, and calcium under the bombardment of active nitrogen have been examined. Owing to the immediate formation of solid nitrides, only negative results were obtained with calcium. In the other cases the arc lines but none of the spark lines were excited. The highest energy level developed was the $4d$ level of mercury corresponding with an excitation potential of 9·51 volts. Although the ionisation potentials of the other metals are less than 9·51 volts (so that ionisation of their vapours should be possible), no energy levels higher than those corresponding with 9·51 volts were developed. No traces of band spectra due to the formation or decomposition of metallic nitride were obtained. The results are in support of the hypothesis of Sponer (A., 1926, 8) that active nitrogen is neutral atomic nitrogen produced as the result of triple collisions the dissociation energy of which should be between 11·4 and 13 volts, so that the spectral lines of other gases excited in the after-glow should have energies less than 11·4 volts. A. E. Mitchell.

Reversal of neon lines. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1927, **3**, 586—589).—By means of a combination of a Lummer–Gehrcke plate with a concave grating, the interval of reversal has been determined for a number of neon lines of the type $1s-2p$, beginning with 5852 Å. ($1s_2-2p_1$) and extending to 6507 Å. ($1s_4-2p_8$).
R. A. Morton.

Spectrum of ionised sodium. F. H. Newman (Phil. Mag., 1928, [vii], **5**, 150—159).—Accurate measurements of the Na II spectrum excited by an electrodeless discharge have been made and 137 lines between 2386·41 and 4830·9 Å. measured. The lines at 2138·4 and 3318·0 Å., previously observed by Schillinger (A., 1909, ii, 369) and Foote, Meggers, and Mohler (A., 1922, ii, 598), respectively, were not obtained. The series includes a number of lines not reported by these observers and does not include other lines attributed by them to the Na II spectrum. A preliminary analysis of the results shows no sequences or lines obeying the Ritz formula, but there are many pairs of lines with constant frequency separations.
A. E. Mitchell.

Series spectra of chlorine, Cl II, Cl III, Cl IV, Cl V, and of Si II, P III, and S IV. I. S. Bowen (Physical Rev., 1928, [ii], **31**, 34—38).—Twenty-six lines in Cl II, 88 in Cl III, 26 in Cl IV, and 17 in Cl V are classified. Five additional lines in Si II, 15 in P III, and 13 in S IV are identified. A. A. Eldridge.

Spectrum of the corona. I. M. Freeman (Nature, 1928, **121**, 169—170).—About two thirds of the coronal lines given by Campbell and Moore can be connected with the argon lines and terms given by Meissner. A. A. Eldridge.

Inverse Stark effect in principal potassium series. W. Grotrian and G. Ramsauer (Physikal. Z., 1927, **28**, 846—856).—The inverse Stark effect in the second term of the potassium lines 4047·201 and 4044·140 Å. and in the third term of the lines 3447·701 and 3446·722 Å. has been determined as a function of the electric force up to 10^5 and 8×10^4 volts cm.$^{-1}$, respectively. The total displacement towards the red varies as the square of the electric force. The shorter wave-length component of each doublet is resolved into two further components. The results are in good agreement with the theories of Becker and Thomas. R. W. Lunt.

Intensities of forbidden multiplets. J. Taylor (Phil. Mag., 1928, [vii], **5**, 166—172).—Measurements have been made of the intensities of the $1^2S-3^2D_{5/2}$ and $1^2S-3^2D_{3/2}$ lines of potassium. The results show that for dilute concentrations the ratio of the intensities is given by the Sum rule and in conjunction with the results of Ornstein and Burger (Naturwiss., 1927, **15**, 32) it is concluded that the ratio is normal for forbidden multiplets. The relative change of the ratio of the maximum intensity of these lines to the non-forbidden $1^2S-3^2P_{3/2}$ and $1^2S-3^2P_{1/2}$ lines shows that the relative intensity of the forbidden to the

permissible lines increases with both current and vapour density. It is suggested that the forbidden lines are brought up by the action of ionic electric fields and that their intensities increase with the field strength, a view which is in accordance with the results of Takamine and Werner. A. E. MITCHELL.

New lines in the arc spectrum of manganese and rectification of these between 2500 and 2300 Å. S. PINA DE RUBIES (Anal. Fis. Quím., 1927, **25**, 494—502).—Since a previous investigation of the arc spectrum of manganese (A., 1927, 802) yielded a spectrum different from that of Fuchs (A., 1915, ii, 497) in the region 2500—2300 Å., this portion of the spectrum has been re-examined. It is shown that the difference is due to the presence of 22 new lines of manganese and to the absence of 20 lines due to iron and nickel considered by Fuchs as lines of manganese. Various other lines in Fuchs' spectrum which are apparently due to impurity are recorded and attention is drawn to errata in Kayser's "Tabelle der Hauptlinien der Linienspektra aller Elemente (1926)." J. S. CARTER.

Arc spectrum of antimony. S. L. MALURKAR (Proc. Camb. Phil. Soc., 1928, **24**, 85—88).—Provisional term values are given for the arc spectrum of antimony. Certain levels have been fitted into the Hund–Heisenberg scheme. R. A. MORTON.

Under-water spark spectra of various metals. (MISS) E. J. ALLIN (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 231—235).—A continuation of previous work (Clark and Cohen, A., 1926, 766). The under-water spark spectrum of tungsten shows about 90 reversals between 4000 and 2300 Å. Tellurium and thorium also show some reversed lines in the region 2100—2600 Å. and 2400—3000 Å., respectively. No reversed lines have been observed in the under-water spark spectrum of uranium. The spectrum is perfectly continuous and intense, with neither absorption nor emission lines in it, and extending well below 2000 Å. The under-water spark between uranium terminals should, therefore, be useful as a source of continuous radiation in the ultra-violet. The intensity remains practically constant to about 2050 Å., after which it falls off rapidly. M. S. BURR.

Iodine resonance spectra excited by the yellow mercury lines. C. N. WARFIELD (Physical Rev., 1928, [ii], **31**, 39—51).—The spectrum of iodine vapour excited by the yellow mercury line 5771·2 Å. consists of a series of doublets the main lines of which conform closely to Mecke's formula. That excited by the yellow line 5792·3 Å. consists of three series of doublets, one of which embraces two anti-Stokes members, and another one such member. A. A. ELDRIDGE.

Emission spectra of various elements in the lower quartz region. (MISS) M. C. M. MCDONALD (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 223—230).—A continuation of previous work (A., 1927, 390). In the lower quartz region, spark spectra only of the following elements have been determined: thulium, lutecium, praseodymium, europium, and hafnium, and both arc and spark spectra of samarium, gadolinium, erbium, ytterbium, dysprosium, and niobium. A few new lines are recorded for thulium, dysprosium, ytterbium, lutecium, praseodymium, and europium; niobium has more; hafnium resembles zirconium in having many lines in this region. M. S. BURR.

Double excitation of upper levels in the mercury atoms by collisions of the second kind. H. BENTLER and B. JOSEPHY (Phil. Mag., 1928, [vii], **5**, 222).—An explanation of the observations of Wood (*ibid.*, 1927, [vii], **4**, 466) of the abnormal excitations of the mercury lines at 2856 and 4916 Å. is offered from the author's results (Naturwiss., 1927, **15**, 540). There it was shown that the upper levels of an atom are excited in high selectivity by collisions of the second kind if the energy of the colliding atom can be accepted very completely by the atom struck. It is suggested that at the collision of two metastable mercury atoms this effect of resonance can have the result that one absorbs the whole energy, $2\times4{\cdot}68$ volts, whilst the other returns to the normal state. It is significant that mercury has a resonance level at 9·25 volts, leaving only 0·11 volt to be transformed into translational energy. The level giving rise to the above-mentioned lines would then be that under the resonance point $3S$. A. E. MITCHELL.

Fine structure of mercury lines. W. H. MCCURDY (Phil. Mag., 1928, [vii], **5**, 386—392).—See this vol., 100.

Laws of X-ray absorption. J. A. GRAY (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 179—184).—Certain empirical formulæ connecting the wave-length of X-rays with the atomic absorbing coefficient and atomic number of the absorbing body have been tested by application to the available experimental data for the K, L, and M absorptions, respectively, and have been found to be in much closer agreement with the experimental observations than those hitherto proposed. Values for the ratio of the fluorescent mass absorption coefficients $(\tau/\rho)_K/(\tau/\rho)_L$, $\lambda-\lambda_K$ have been calculated. M. S. BURR.

Intensity relationships in L X-ray series. A. JONSSON (Z. Physik, 1928, **46**, 383—391).—The intensities of the stronger lines in the L-spectra of molybdenum, rhodium, palladium, and silver have been obtained by the use of the Geiger chamber, and the results corrected for anticathode absorption. The doublets $L\alpha_1$, α_2, β_1, as well as l, η, obey the intensity rules valid in the optical region, but the β_2, doublet fits these rules only for metals in which the N IV and N V levels have the full complement of electrons. For the doublets, $\alpha_1:\alpha_2:\beta_1$ the calculated intensities are 9 : 1 : 5; for $l:\eta$, 2 : 1; for $\beta_2:\gamma_1$, 2 : 1; for silver and palladium the observed intensity ratios are in good agreement, but for rhodium and molybdenum the results do not agree, *e.g.*, $\beta_2:\gamma_1$ for molybdenum is 2 : 1·7. R. A. MORTON.

***K*-Series spectrum of tungsten.** K. C. MAZUMDER (Z. Physik, 1928, **46**, 449—450).—The line (0·218 Å.) in the X-ray spectrum of tungsten has been observed in the first order. R. A. MORTON.

Discontinuities of absorption in the intermediate region (*K*-bands of carbon, nitrogen, and oxygen). J. THIBAUD (Compt. rend., 1928,

186, 308—309).—By means of the author's spectrograph (A., 1927, 803) using a current of 100 milliamp. on an anticathode of high at. wt., a continuous radiation has been observed for carbon, nitrogen, and oxygen similar to that produced by ordinary *X*-rays, but with abrupt discontinuities. The discontinuities which show a fine structure and are bounded on the high-frequency side by a white ray decrease in intensity in the order carbon, nitrogen, oxygen, and their wave-lengths are 43·5, 31·1, and 23·5 Å., respectively. Since the absorption bands are produced with much smaller quantities of absorbing material than in the case of ordinary *X*-rays, a very sensitive method of analysis is indicated. J. GRANT.

Scattering of *X*-rays by gases. J. A. GRAY and H. M. CAVE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 157—161).—A continuous-flow method for measuring the distribution of *X*-rays scattered by gases is described, and the results of preliminary experiments on carbon dioxide, nitrogen, and oxygen are given. The intensity I_θ of the radiation scattered per unit solid angle in the direction θ, by the extra-nuclear electrons of an atom, ion, or a molecule, equals $I(e^4/2m^2c^4)F^2(1+\cos^2\theta)$, where I is the intensity of the primary radiation per sq. cm., e the charge and m the mass of an electron, and c the velocity of light. F, the scattering function for a single molecule, depends on the wave-length, and θ on the distribution and natural frequencies of the electrons, and, in the case of a molecule, on the orientation. The wave-lengths used were 1·50 and 0·9 Å. For small angles of scattering, F is proportional to the number n of electrons in the molecule, and, for zero angle, is probably equal to n, whilst I_θ varies as n^2. $I_0/I_{\pi/2}$ is of the order $2n$ and $F_0/F_{\pi/2}$ of the order $n^{\frac{1}{2}}$. These values are considerably smaller than those obtained for atoms by measurement of the intensities of *X*-rays reflected from crystal planes, probably because, in the latter, the unmodified radiation alone contributes to the final result. Curves are also given showing the distribution of the scattered radiation from thin plates of paraffin wax and graphite. M. S. BURR.

Experimental study of the absorption formula of the *X*-rays. I. M. ISHINO and S. KAWATA (Mem. Coll. Sci. Kyoto, 1927, **10**, 311—316).—The variation of the absorption coefficient of *X*-rays with the atomic number of the absorbers has been studied for the absorption of the $K\alpha$ line of molybdenum. The absorbers were chiefly used in the form of salts dissolved in water. The results are in substantial agreement with those of Wingårdh (A., 1922, ii, 249). W. E. DOWNEY.

Measurement of *X*-radiation in *R*-units. H KÜSTNER (Physikal. Z., 1927, **28**, 797—803).—The technique appropriate to the measurement of *X*-radiation in terms of a new unit of dosage called the Röntgen- or *R*-unit is described. R. W. LUNT.

Excitation of spectra by high-frequency oscillations. M. PONTE (Nature, 1928, **121**, 243—244).—Clarke's results (A., 1927, 1119) are attributed to the kind of discharge employed, and not to the wave-length. An oscillator of wave-length 1·90 m., and power only 20 watts, produces a brilliant electrodeless mercury discharge. This mode of excitation is extremely sensitive to the presence of organic impurities. Experiments with the electrodeless or one-electrode discharge, using wave-lengths of 1·90 or 5—10 m., have not demonstrated any modification of the emitted wave-lengths, alterations in the relative intensities of the lines being due to changes in pressure or strength of excitation. A. A. ELDRIDGE.

Duration of Stark effect in hydrogen and nitrogen. H. KERSCHBAUM (Ann. Physik, 1927, [iv], **84**, 930—938).—The duration of the Stark effect in H_β and H_γ has been determined from observations on canal rays and is found to be constant; the duration of the negative nitrogen band 4278 Å. is $2{\cdot}54\times10^{-8}$ sec., *i.e.*, approximately twice that of the spark-excited band. R. W. LUNT.

Measurement of the life-period of excited atomic states. K. W. MEISSNER and W. GRAFFUNDER (Ann. Physik, 1927, [iv], **84**, 1009—1046).—Experimental methods are reviewed and a new arrangement is described. The maximum half-life period for the s_5 state of neon is about 7×10^{-4} sec., and for argon 3×10^{-3} sec. The investigation of the relation between life-period and pressure discloses a maximum for neon at 1·5—2 mm. The half-value period for the absorption capacity varies with different lines with the same end term. The interpretation of this result is discussed. Intense irradiation decreases the persistence of metastable states. R. A. MORTON.

Ionisation potential and atomic number. G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **6**, 305—311).—It is shown that a family of parabolic curves is obtained if the difference between the primary ionisation potential of an element and that of the element possessing but one electron in the outermost orbit of the first element be plotted as a function of the atomic number. R. W. LUNT.

Relations between the first- and second-order ionisation potentials of homologous elements. G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **6**, 428—431).—Using the relationships found previously (cf. preceding abstract), the following ionisation potentials have been calculated: germanium 7·52, arsenic 9·04, antimony 8·46, bismuth 8·48, selenium 9·02, tellurium 8·43, polonium 8·46, chlorine 12·26, bromine 10·47, iodine 9·76, element 85 9·65, xenon 12·33, radon 11·96. It is shown that the first- and second-order ionisation potentials (V_{I} and V_{II}) of a group of homologous elements are related by the expression $V_{\mathrm{II}}:V_{\mathrm{I}}=r$, where r is constant in any but the alkali metal group, with a value of 1·9—2·2. Use is made of this relationship to calculate the first-order ionisation potentials of radium and of the missing element 87 from the known value of 10·23 of the second-order ionisation potential of radium. The values are 5·35 and 4·24 volts, respectively. O. J. WALKER.

Actino-electric effects in argentite. W. A. SCHNEIDER (Physical Rev., 1928, [ii], **31**, 82—89).—The seat of conversion of light into electronic energy is at both contacts as well as at certain points on the crystal; if the crystal structure is destroyed, no effect is observed. The current $i=Ae^{-at}$, where t is the total time of exposure and values of a depend on the time of recovery. A. A. ELDRIDGE.

Photo-electric effect. P. W. BRIDGMAN (Physical Rev., 1928, [ii], **31**, 90—100).—The equality of the stopping potentials follows from very general considerations, not involving any assumptions as to mechanistic details, or even the third law of thermodynamics. The differences between (*a*) the photo-electric and thermionic work functions, (*b*) the specific heat and surface charge, (*c*) the entropy and surface charge at 0° Abs. are universal constants for all metals, and probably each zero.

A. A. ELDRIDGE.

Spatial distribution of photo-electrons produced by *X*-rays. E. J. WILLIAMS (Nature, 1928, **121**, 134—135).—Results of an investigation of the longitudinal distribution of photo-electrons indicate an average forward component of momentum of the photo-electrons which is appreciably greater than the momentum, $h\nu/c$, of an incident quantum. The results of other observers, except those of Auger, exhibit an "excess asymmetry." Experimental results on dispersion seem to prohibit all theories except Auger and Perrin's "$\cos^2 \theta$" law.

A. A. ELDRIDGE.

Work of evaporation of thermions. A. SMEKAL (Z. Physik, 1928, **46**, 451—452).—Michel (A., 1927, 919) claims that the work of evaporation $\Delta\varphi$ of thermions from alkaline-earth oxides is better expressed by the relation $\Delta\varphi \,.\, b^2$—constant than by $\Delta\varphi \,.\, b$=constant, b being the shortest distance between two atoms at the surface of the emitting oxide. On the basis of measurements by Espe (A., 1927, 604), it is contended that the claim rests on inadequate evidence.

R. A. MORTON.

[Work of evaporation of thermions.] G. MICHEL (Z. Physik, 1928, **46**, 453—454).—A reply to Smekal (preceding abstract). The data of Espe do not invalidate the argument. Sommerfeld (Naturwiss., 1927, **15**, 825) uses a formula for the work of evaporation of thermions, which corresponds with the use of b^2 rather than b.

R. A. MORTON.

Behaviour of slow electrons in mercury vapour. H. BEUTHE (Ann. Physik, 1927, [iv], **84**, 949—975).—Ramsauer's method for determining the effective cross-sectional area of a gas has been adapted to mercury vapour by using thermions instead of photo-electrons. The effective cross-sectional area has been plotted against electron velocities expressed in volts$^{1/2}$; the curve exhibits two maxima, one at 3 volts being well marked, and another at 4·9 volts being less definite. At low pressures (0·002—0·006 mm.) the maximum at 3 volts is higher and more clearly defined than at higher pressures. The effective cross-sectional area is very small for small electron velocities, so that mercury vapour resembles the noble gases in respect of its behaviour towards very slow electrons. The mercury atom seems capable of accumulating and retaining for a fairly long period those electrons which strike it at velocities too small to effect excitation.

R. A. MORTON.

Energy distribution among secondary electrons from nickel, aluminium, and copper. D. A. WELLS (Phil. Mag., 1928, [vii], **5**, 367—371).—An examination of the distribution of secondary electrons from nickel, aluminium, and copper has shown that in all cases there are a few secondary electrons with energies of the same order as those of the primary beams. The number having high energy values is relatively small. Within a certain range the number of electrons having a given energy or greater up to the maximum energy of any being emitted is a probability function of the secondary current and secondary voltage.

A. E. MITCHELL.

Tracks and radiation of electrons emitted by hydrogen. T. ENGST (Ann. Physik, 1927, [iv], **84**, 880—890).—Mathematical.

R. W. LUNT.

New evidence of the existence of charges smaller than the electron. (*a*) The micro-magnet. (*b*) Law of resistance. (*c*) Computation of errors of the method. F. EHRENHAFT and E. WASSER (Phil. Mag., 1928, [vii], **5**, 225—241).—A new method for the measurement of heterogeneous strong magnetic fields of small dimensions is described. By this means the mass susceptibilities of colloidal particles of silver and selenium have been shown to be in perfect agreement with the accepted values for the materials in bulk. The results of measurements of 140 particles of various densities show that single particles produced in different ways have their normal densities and structures. The smallest charge associated with a particular particle has been shown to be less than the electron. For gold particles the value 1×10^{-10} *E.S.U.* was often found. Depending on whether the law of resistance is linear or exponential, these values may vary by 10—15%, but in any case they do not approach the charge on the electron.

A. E. MITCHELL.

Production of the atomic and molecular rays of sodium and of iodine. W. JONO (Sexagint [Osaka celebration], Kyoto, 1927, 273—278).—Sodium to be used for the production of atomic rays may be obtained by the thermal decomposition of sodium azide. Apparatus for the production of the atomic rays of sodium and of iodine is described.

H. F. GILLBE.

Production and measurement of molecular beams. T. H. JOHNSON (Physical Rev., 1928, [ii], **31**, 103—114).—The beam is detected and its intensity measured by the increase in pressure produced in an ionisation gauge when the gauge is moved to allow the beam to enter it through a narrow slit. The method is applicable to beams of non-condensible and chemically inactive gases, as well as to condensible or chemically active molecules. A change of pressure of 3×10^{-8} mm. (3 mm. galvanometer deflexion) corresponds with a beam intensity of about 5×10^{13} mol./cm.^{2}/sec. The probability of adsorption of a mercury molecule on glass is found to be 10^{-4} per collision.

A. A. ELDRIDGE.

Cathode rays in the electrodeless ring discharge. G. HERZBERG (Phil. Mag., 1928, [vii], **5**, 446—448).—An investigation of the electrodeless ring discharge in hydrogen in a quartz tube has shown a phosphorescence of the tube walls, continuing after the discharge has ceased, similar to that reported by J. J. Thomson (A., 1926, 988) on glass walls. Contrary to Thomson's experience, it is shown that the radiation causing the phosphorescence is affected

by adjacent magnetic fields, thus indicating that it is composed of cathode rays coming from the middle of the tube where the discharge took place under ordinary conditions. The velocity of these rays is heterogeneous. A mechanism for their production is suggested. A. E. MITCHELL.

Continuous emission spectra produced by electrodeless discharge. G. BALASSE (Compt. rend., 1928, **186**, 310—311).—The theory previously proposed (A., 1927, 490) and the fact that elements in five different columns of Mendeléev's table show continuous emission spectra produced by electrodeless discharge indicate that this phenomenon is characteristic of all elements. The spectra, which appear to increase in intensity with the atomic number of the element used, may be correlated with the continuous spectra observed in the *X*-ray region. J. GRANT.

Influence of very small quantities of substances on the running-voltage in noble gas [discharges]. F. M. PENNING (Z. Physik, 1928, **46**, 335—348).—Quantitative experiments have been made on the discharge voltages of mixtures of mercury, argon, etc., in very small amount, in otherwise practically pure neon. The results indicate that the foreign atoms become ionised by the metastable neon atoms. This process is conditional upon the relation $V_i' < V_{met.}$, V_i' being the ionisation potential of the foreign gas and $V_{met.}$ the energy of the metastable states of neon, *i.e.*, 16·5 and 16·6 volts. The validity of this explanation has been tested for mercury, argon containing 0·01—0·05% of krypton, hydrogen, and nitrogen. Similarly, experiments with argon as the principal gas ($V_{met.}$ 11·5 and 11·7 volts) and mercury, iodine, krypton, xenon, carbon monoxide, carbon dioxide, and nitric oxide as added substances indicated that the only departure from the above explanation was with nitric oxide. The term-scheme of nitric oxide does not render this result very surprising. Preliminary experiments with helium as the main gas also fall into line with the theory. R. A. MORTON.

Measurement of mobilities of ions in gases. M. LAPORTE (Ann. Physique, 1927, [x], **8**, 710—745).—The experimental results so far obtained in this field support the view that ionic mobilities are distributed according to a continuous curve (cf. this vol., 102). Zeleny (Phil. Trans., 1901, **A**, **195**, 193) supposed that his extrapolated figure for the ionic mobility from the gas-stream method indicated the presence of only one mobility, but actually it may be only an average figure. The results of Erikson (Physical Rev., 1922, [ii], **20**, 117) also demand the existence of ions of different velocities and cannot be explained by ions of different ages. Nolan (Proc. Roy. Irish Acad., 1920, **35**, 38) on plotting the current passing through the ionised gas against voltage obtained breaks, and concluded thence that the ions were divided into groups each with a specific mobility; most of the breaks, however, are probably due to irregularities in his gas stream, and the remainder can be explained by changes of curvature in the mobility distribution curve. Franck and Pohl's method (Verh. Physikal. Ges., 1907, **9**, 69) gives very different results from those of other workers, since the metallic gauze employed does not completely divide the auxiliary field which separates the positive and negative ions from the field of observation. Tyndall and Grindley (A., 1926, 219) have studied the effect of humidity on the mobility of ions in air, and their results, which agree with those of the authors, give continuous curves with no maxima, showing that ionic mobilities do not fall into a number of sharply separated groups. S. J. GREGG.

Ionisation by collision. J. TAYLOR (Phil. Mag., 1928, [vii], **5**, 445—446).—A reply to a discussion by Huxley (A., 1927, 709) of the author's previous contribution to the controversy. A. E. MITCHELL.

Unsold's theory of the chromosphere. W. ANDERSON (Z. Physik, 1928, **46**, 445—448).—The theory of the chromosphere developed by Unsold (A., 1927, 1006) is open to serious objections. The partial pressure of singly-ionised calcium atoms in the upper layers of the chromosphere is calculated to be not greater than 10^{-13} atm., whilst the partial pressure of electrons is of the order 10^{-11} atm., whereas Unsold's theory assumes that the partial pressure of calcium is of the order 10^{-8} atm. Milne's theory is also criticised. R. A. MORTON.

Diamagnetic susceptibility of hydrogen and of helium. S. C. WANG (Proc. Nat. Acad. Sci., 1927, **13**, 798—800).—Mathematical. R. W. LUNT.

Report of the German Commission on atomic weights. VIII. M. BODENSTEIN, O. HAHN, O. HONIGSCHMID, and R. J. MEYER (Ber., 1927, **61**, [*B*], 1—31).—The report is divided into three sections treating respectively determinations of at. wts. by physico-chemical and chemico-gravimetric processes and the progress in the question of isotopes among ordinary, non-radioactive elements. The values A=39·94 instead of 39·88, Ti=47·90 instead of 48·1, and Y=$88{\cdot}9_3$ instead of 88·90 are adopted. For certain elements the at. wts. of which depend more or less directly on that of silver (107·880), regarded as affected with a possible uncertainty of 1 in 10,000, the second decimal is given as sub-index since new investigations of the at. wt. of silver tend greatly to confirm the value adopted previously. H. WREN.

Exact determination of radon. J. VON WESZELSZKY (Physikal. Z., 1927, **28**, 757—761).—Modifications introduced into the author's earlier technique (A., 1911, ii, 453; Physikal. Z., 1912, **13**, 240) are described. The procedure for the exact determination of radon by the intensity of its radiations is given. Probable errors and methods of calibration are discussed. R. W. LUNT.

Number of α-particles emitted by thorium-*C*+*C'*. S. W. WATSON and M. C. HENDERSON (Proc. Camb. Phil. Soc., 1928, **24**, 133—138).—By an ionisation method, the α-particle emission of thorium-*C*+*C'* has been determined as $4{\cdot}26 \pm 0{\cdot}08 \times 10^{10}$ particles per sec. per curie-equivalent of γ-ray activity when in equilibrium with radiothorium, and when measured by the γ-rays of thorium-*C''* through 18 mm. of lead. Data on the Bragg curve over the first 3 cm. of the range are in agreement with the work of I. Curie and Behounek, but not with that of Henderson (A., 1921, ii, 617). R. A. MORTON.

Ionisation curve of an average α-particle. N. FEATHER and R. R. NIMMO (Proc. Camb. Phil. Soc., 1928, **24**, 139—149).—Photographs have been taken under controlled illumination of the tracks of α-particles in a cloud expansion chamber, and the plates used have been calibrated. Photometry of the track images makes possible the calculation of the variation of the light-scattering power of an α-particle track over the last 2 cm. in dry air at 15° and 760 mm.; this quantity varies with the ionisation along the track. In air, helium, and hydrogen, the maximum ionising efficiency of the α-particle occurs at velocities respectively appropriate to the distances 3·0, 2·55, and 2·25 mm. from the end of its path in dry air at 15° and 760 mm. R. A. MORTON.

Passage of α-rays and β-rays through matter. E. J. WILLIAMS (Mem. Manchester Phil. Soc., 1926—1927, **71**, 23—39).—The primary ionisation due to β-rays of approximate velocity 5×10^9 cm./sec. has been determined by Wilson's cloud method (Proc. Roy. Soc., 1923, **A**, **104**, 192) in hydrogen, nitrogen, and oxygen. The theoretical values calculated on the basis of J. J. Thomson's theory account for only about half of the observed ionisation. If, however, the motion of the atomic electrons is taken into account, there is good agreement between observed and calculated values, especially for hydrogen, for which the data on which the calculation is based are most certain. The atomic stopping powers for α- and β-rays and the relation between them are discussed. Bohr's theory (Phil. Mag., 1913, [vi], **25**, 10; 1915, [vi], **30**, 581) does not give values for the stopping powers of oxygen, nitrogen, hydrogen, and argon in agreement with the experimental results of Williams and Nuttall (A., 1926, 1191). Fowler's values (Proc. Camb. Phil. Soc., 1923, **21**, 521) calculated from Henderson's theory (Phil. Mag., 1922, [vi], **44**, 680) also differ considerably from the experimental results, but the discrepancy is markedly reduced by allowing for the motion of the atomic electrons. The residual discrepancy is probably real, and there are indications that it may be greater for α- than for β-rays. M. S. BURR.

Relative ranges of β-rays. J. A. GRAY and B. W. SARGENT (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 173—178).—The relative ranges of the β-rays of radium-*E* and uranium-X_2 in carbon, aluminium, copper, tin, and lead have been determined by an ionisation method which is described. The range is the product of the total length of path traversed and the density of the substance. The average range of the β-rays of uranium-X_2 in lead is 2·2 times that of the β-rays of radium-*E*. The range increases with the atomic number of the substance penetrated, and the stopping power of an atom for the β-rays of uranium-X_2 is approximately proportional to the atomic number. M. S. BURR.

Absorption and scattering of γ-rays of radium. J. A. GRAY and H. M. CAVE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 163—171).—The formulæ generally employed for the variation of the mass scattering coefficient σ/ρ and the fluorescence mass absorption coefficient τ/ρ with λ give a value for the wave-length of hard γ-rays of 0·018 Å. This is too large to account for the observed properties of recoil electrons (cf. A., 1925, ii, 84), and, according to Compton's formulæ for the intensity of radiation scattered per unit mass and unit solid angle (Physical Rev., 1923, [ii], **21**, 483), it should be either less than 0·008 Å. or consist of a mixture of rays of wave-length 0·024 and 0·008 Å. in equal proportions. Absorption experiments have been made which indicate that there is only a small difference in wave-length between γ-rays filtered through 2 and 5 cm. of lead, respectively, and hence that hard γ-rays can have only a small proportion of rays of wave-length 0·024 Å. The formulæ generally accepted for the variation of σ/ρ and τ/ρ with λ give a value of 0·015 Å. for the most penetrating radiation obtained by filtration, and hence cannot be relied on. Experiments on the distribution of scattered radiation have been made, and there is no evidence of the presence in hard γ-rays of rays of wave-length of the order of 0·024 Å. The wave-length is probably nearer to 0·007 than to 0·008 Å. τ/ρ varies approximately as λ^2, and values of τ/ρ and σ/ρ for different values of λ are tabulated. M. S. BURR.

Spectrography of γ-rays by crystalline diffraction. FRILLEY (Compt. rend., 1928, **186**, 137—139).—A rotating-crystal method is described for spectrographical experiments with γ-rays, in which the crystal consists of a plate of mineral salt. Spectra attributed to radium-*B* and radium-*C* (35—284 X) were obtained from a tube of radon, the shortest wave-length measured (35 X) corresponding with 353 kilovolts and an angle of reflexion of 21·5′. J. GRANT.

Action of heat on pleochroic haloes. J. H. J. POOLE (Phil. Mag., 1928, [vii], 5, 132—141).—Examination of some biotites has shown that the pleochroic haloes disappear when the minerals are heated at 500—700°. The haloes disappear owing to a progressive darkening of the body of the mineral and not to a change in the portion forming the haloes. The darkening of the mica is accompanied by dehydration. It is suggested that the formation of the haloes by α-rays is due to the decomposition of the weakly held water of the biotite leading to local areas of dehydration. Application of the results of Duane and Scheurer for the α-ray decomposition of water do not render the theory untenable. A. E. MITCHELL.

Formation of pleochroic haloes in biotite. J. H. J. POOLE (Phil. Mag., 1928, [vii], **5**, 444).—As an alternative to the theory advanced previously (preceding abstract) it is suggested that the water liberated from biotite under the action of α-rays causes direct oxidation of ferrous to ferric iron with the consequent change in colour and formation of haloes. A. E. MITCHELL.

Pleochroic haloes and the age of the earth. J. JOLY (Nature, 1928, **121**, 207—208).—Lotze's theory (this vol., 150) would involve a large reduction of density, of which there is no optical indication. Poole's theory is preferred. A. A. ELDRIDGE.

Inversion phenomenon of biotite exposed to the action of α-rays. H. JEDRZEJOVSKI (Compt. rend., 1928, **186**, 135—137).—The determination by means of a potassium photo-electric cell of the

blackening produced in a leaflet of biotite during exposure to α-rays has yielded a curve which shows that the amount of light traversing the leaflet falls off rapidly to a minimum (the inversion point) and then slowly increases. It is concluded that a phenomenon of inversion, analogous to that of an over-exposed photographic plate, actually occurs, but that the determinations of the ages of minerals from the haloes produced may lead to incorrect results.

J. GRANT.

Influence of high-velocity electrons on lead and copper. A. KOENIG (Physikal. Z., 1927, **28**, 838—841).—The conductivity of the space surrounding a copper anticathode alone, and when covered with lead foil, has been examined by a sensitive method immediately after the anticathode had been bombarded by electrons of from 4 to 60 kilovolts. The results show that if a new element is formed from lead under such conditions it cannot have a β-particle emission of half-life from 33 seconds to 1300 years or an α-particle emission of half-life from 5×10^6 years to 2 seconds.

R. W. LUNT.

Evolution of elements. B. CABRERA (Compt. rend., 1928, **186**, 228—230).—The formation of atoms by means of the association of protons and electrons is discussed in the light of Aston's conception of "packing fractions," with special reference to the building-up and disruption of atoms by cosmic processes and to the explanation of the stability of an atom in terms of its radioactive properties.

J. GRANT.

Wave-mechanics of an atom with a non-Coulomb central field. I. Theory and methods. II. Results and discussion. D. R. HARTREE (Proc. Camb. Phil. Soc., 1928, **24**, 89—110, 111—132).—I. Methods are given for the determination of the characteristic values and functions of the wave equation of Schrödinger for a non-Coulomb central field, for which the potential is given as a function of the distance from the nucleus.

II. For a given atom it is possible by a method of successive approximations to find a field such that the solutions of the wave equation for the core electrons in this field (corrected in certain ways) give a distribution of charge which reproduces this "self-consistent" field. The field has been calculated for He, Rb^+, Na^+, and Cl^-; satisfactory agreement is shown between observed and calculated *X*-ray and optical terms, and for helium between observed and calculated ionisation potentials.

R. A. MORTON.

Simple derivation of the hydrogen energy levels in wave mechanics. A. E. RUARK (J. Opt. Soc. Amer., 1928, **16**, 40—43).—Mathematical. The values of the energy levels corresponding with the circular orbits in Bohr's theory of the hydrogen atom have been derived by wave mechanics.

W. E. DOWNEY.

Waves associated with moving electrons. (SIR) J. J. THOMSON (Phil. Mag., 1928, [vii], 5, 191—198).—The existence of the waves accompanying a moving electron, postulated by de Broglie in his theory of wave mechanics, is shown to be a consequence of classical dynamics if that be combined with the view that an electric charge is not a point without structure but is an assemblage of lines of force starting from the charge and stretching into space. The core of the uniformly moving electron is considered.

A. E. MITCHELL.

Quantum theory of aperiodic effects. J. R. OPPENHEIMER (Physical Rev., 1928, [ii], **31**, 66—81).—Mathematical. (*a*) The normalisation of the characteristic functions corresponding with a continuous spectrum satisfies the requirements of the δ-normalisation of the Dirac–Jordan theory. (*b*) The validity of classical mechanics is considered in relation to Rutherford's formula for the scattering of α-particles. (*c*) A method for computing the transition probabilities between states of the same energy and represented by almost orthogonal eigen-functions is applied to the ionisation of hydrogen atoms in a constant electric field.

A. A. ELDRIDGE.

Interaction between radiation and electrons. A. H. COMPTON (Physical Rev., 1928, [ii], **31**, 59—65).

Thermodynamic equilibrium and reciprocal effects in the new gas theory. W. BOTHE (Z. Physik, 1928, **46**, 327—334).—Reciprocal effects of atoms, molecules, electrons, and light quanta are discussed theoretically in terms of the methods of Bose and Einstein, Fermi, Pauli, Dirac, and others.

R. A. MORTON.

Theory of molecular spectra. F. HUND (Physikal. Z., 1927, **28**, 779—784).—A short and non-mathematical review of recent theories of molecular spectra.

R. W. LUNT.

Hydrogen molecule. R. T. BIRGE (Nature, 1928, **121**, 134).—Data and constants for the hydrogen molecule and molecule ion, in terms of the older mechanics, are reviewed. The ionisation potential of the neutral molecule is $15{\cdot}34\pm0{\cdot}01$ volts, and the normal heat of dissociation 4·42 volts. The moment of inertia of H_2 in the normal state is $1{\cdot}99\times10^{-40}$. Richardson's method of calculating I_0 gives values 8—9% in error for the non-polar molecules tested. The heat of dissociation of H_2^+ is 2·62 volts.

A. A. ELDRIDGE.

Triatomic hydrogen as an emitter of the secondary spectrum. C. J. BRASEFIELD (Physical Rev., 1928, [ii], **31**, 52—58).—To obtain a correlation between the intensities of various parts of the secondary spectrum and the concentrations of H_2^+ and H_3^+, simultaneous positive-ray and spectroscopic observations were made on a discharge in hydrogen under various conditions. The concentration of H_3^+ in the positive column of a glow discharge decreases rapidly with pressure and becomes negligible at 0·01 mm. The relative concentration of H_3^+ has no effect on the intensity of the lines of the secondary spectrum, with the possible exception of some weak lines such as those of the Allen and Sandeman bands.

A. A. ELDRIDGE.

"Non-combination" part systems in band spectra. E. HULTHEN (Z. Physik, 1928, **46**, 349—353).—Band spectra of diatomic molecules are always divisible into two partial systems, between which only very weak intercombinations occur. The "non-combination" systems are designated as symmetrical and anti-symmetrical, since they are connected with

the distribution of symmetrical and anti-symmetrical rotation states through the different electron terms.

R. A. MORTON.

Infra-red absorption spectra of several gases. C. F. MEYER, D. W. BRONK, and A. A. LEVIN (J. Opt. Soc. Amer., 1927, **15**, 257—265).—The infra-red absorption of the following gases has been examined in the range 3—4 μ using a grating with 1134 lines per cm.: acetylene, ethylene, *n*-butane, *n*-hexane, *n*-octane, benzene, toluene, cumene, ethyl alcohol, ethyl ether, and sulphur dioxide. The wave-number differences between the observed absorption maxima are discussed with reference to the structure of the bands.

R. W. LUNT.

Nature of the glow on heating finely-divided oxides and metals. M. RABINOVITSCH (Kolloid-Z., 1928, **44**, 84—85).—The glow which is observed on heating finely-divided metals is not due, as Böhm has supposed (A., 1927, 823), to the liberation of the latent heat of crystallisation caused by the production of crystalline metal from the amorphous state, but is due to the sudden liberation of energy through the reduction of the total surface of the particles. The explanation given by Bohm is not probable for metals such as rhodium, ruthenium, platinum, gold, and silver, and the phenomenon is shown equally by many finely-divided oxides.

E. S. HEDGES.

Radiation from glowing oxides. F. SKAUPY (Physikal. Z., 1927, **28**, 842—846).—The intensity of the radiation from the following oxides has been determined at temperatures from 1500° to 2000° in the range 0·5—10 μ: aluminium oxide, sapphire, aluminium oxide + 2% of chromium oxide, ruby, chromium oxide, titanium dioxide, anatase, silicic acid, fused silica, thorium dioxide, and magnesium oxide. The maxima of intensity lie at about 2 μ, whilst the computed value for the oxygen in these substances is about 3·9 μ.

R. W. LUNT.

Displacement of spectra during the formation of compounds (observations with compounds of praseodymium). F. EPHRAIM and R. BLOCH (Ber., 1928, **61**, [*B*], 65—72; cf. A., 1927, 121).—The work is based on the hypothesis that the electrostatic attraction of the cation for the electrons of the remaining sheaths becomes more pronounced when the anion involves the valency electrons of the cation with greater intensity; consequently these sheaths are drawn towards the nucleus and contraction ensues. The paths of the vibrating electrons therefore become shorter, thus causing emission of light of shorter wave-length and displacement of the spectrum towards the violet. This displacement is very marked in the series anhydrous iodide, bromide, chloride, and fluoride of praseodymium. Since the anhydrous compounds can unite with water, ammonia, etc. by means of residual affinities, the atom does not exert its full chemical affinity in them. This is, however, unfolded in solution in which the atom is freed from the circle of restricting atoms. The contraction thereby caused explains the observed displacement of the spectrum towards the violet in solution, and the lessened importance of the anion by reason of electrolytic dissociation renders account of the disappearance of the differences in position of the lines observed in solid salts. As expected, the definite hydrates occupy a well-marked, intermediate position. The specific action of the halogen is of less importance, since its contracting action is less marked owing to penetration of the water between it and the metallic atom. On the other hand, the water itself exercises compressive action on the metallic atom, which is more noticeable as the number of its molecules increases and the contracting action of the halogen is less. The production of ammonates results similarly in compression of the praseodymium atom, which is less marked than in the case of hydrates. It follows, therefore, that the valency demand of the praseodymium atom can be deduced from the position of the lines of its spectrum, being greater as they are displaced towards the violet. Explanation is thus afforded of the ability of the iodide to form a higher hydrate than the chloride. The insolubility of the fluoride is accounted for by the observation that its spectral lines are further towards the region of shorter wave-length than those of praseodymium solutions; solvate formation could therefore be brought about only by addition of energy which does not occur spontaneously. It is therefore remarkable that praseodymium fluoride is precipitated in the hydrated state and loses water only with relative difficulty. The spectra of the anhydrous and hydrated forms do not, however, differ appreciably from one another. The water has therefore little to do with the metallic atom and is regarded as "packing water" retained by capillarity as in a gel.

Anhydrous *praseodymium bromide* is prepared by heating a mixture of hydrated bromide and ammonium bromide (but not the hydrated bromide alone) in a current of hydrogen bromide. A similar process fails to yield anhydrous praseodymium iodide (corresponding *nonahydrate* and *hexahydrate*) completely free from basic salt. Evaporation of a solution of praseodymium iodide and 2 mols. of mercuric iodide followed by desiccation of the residue at 120° yields the double *salt*, (?) $PrOI,2HgI_2,9H_2O$, which, when moderately heated in hydrogen, is converted into the basic *salt*, $PrOI,2H_2O$.

H. WREN.

Spectrum of praseodymium salts of oxygenated acids. F. EPHRAIM and R. BLOCH (Ber., 1928, **61**, [*B*], 72—80; cf. preceding abstract).—Great differences, similar to those observed in the spectra of praseodymium halides, are not encountered with praseodymium salts of oxygenated acids, since in the latter the element is directly united in every case with many oxygen atoms. The contraction of the atom thereby produced is so great that the spectrum of the sulphate is greatly displaced towards the violet when compared with that of the chloride or iodide, slightly towards the red in comparison with that of the fluoride. The spectrum of the hydroxide is of slightly longer wave-length than those of the oxygenated salts. The presence of water of crystallisation has little influence. In the nitrate, in which the metallic atom is influenced by nine oxygen atoms, the contraction is greater than in the fluoride. In the double nitrate, $(NH_4)_2[Pr(NO_3)_5],4H_2O$, contraction attains its maximum observed value and the spectrum of the dissolved salt is displaced towards

the red in comparison with that of the solid. The alkali double sulphates are interesting, since the praseodymium atom is a component of a complex anion. It is united with many oxygen atoms and the spectra indicate considerable contraction and little influence of the portion of the molecule other than the SO_4-residues; replacement of sulphur by selenium somewhat diminishes the contraction. Many of the spectra exhibit a duplication of the lines, particularly in the third group, which is most marked in cases in which the opportunity of complex formation exists and the praseodymium atoms function differently from one another, *e.g.*, in the nitrate, $Pr[Pr(NO_3)_6]$. A complete duplication of the spectrum is not observed, possibly because the effect causes merely a broadening of the bands, showing actual duplication only of the narrowest.

The following compounds are incidentally described: cæsium praseodymium sulphate, $CsPr(SO_4)_2,4H_2O$ (a salt richer in cæsium does not appear to exist); *potassium praseodymium sulphate, dihydrate*, and *monohydrate* (in place of hemihydrate described previously); *praseodymium chromate* and its *hexahydrate*; *potassium praseodymium chromate*, $KPr(CrO_4)_2,H_2O$; *praseodymium oxalate nonahydrate*; praseodymium nitrate hexahydrate and *dihydrate*. H. Wren.

Reflexion spectrum of praseodymium in covalent compounds. F. Ephraim (Ber., 1928, **61**, [*B*], 80—83; cf. preceding abstracts).—In homopolar praseodymium oxide the metallic atom is surrounded by more electrons than in the chloride; its volume must consequently be greater since the electrostatic attraction of the nucleus is distributed over a great number of electronegative points and this expansion may be expected to find its expression in a displacement of the spectrum towards the red, which is actually observed. It is doubtful, however, if the individual lines of the chloride spectrum are exactly represented in that of the oxide, and the entirely different electronic configuration renders this scarcely probable. Praseodymium oxide of form B_1 is prepared by reducing the oxide, Pr_6O_{11}, with hydrogen at 900°; at 550°, a second *modification*, possibly B_2 or C, is produced, differing in density and spectrum from the variety B_1. Indications of the existence of further modifications of the oxide are found in the observation that specimens which have been preserved for some time in the apparatus in which they were prepared become brown and absorb oxygen when exposed to air, whereas this behaviour is not shown by freshly-prepared specimens. The spectrum of the compound PrOS differs completely from that of the oxide, having particularly well-defined lines beyond 600 mμ. H. Wren.

Resolution of an absorption band common to praseodymium and neodymium. L. Fernandes (Atti R. Accad. Lincei, 1927, [vi], **6**, 413—417).—Solutions of salts of the above elements give a common absorption band in the region 4690 Å. It is shown that in the sharper spectra obtained with the crystalline sulphates (especially at a temperature near that of liquid air) this band is broken up into a series of finer bands which are different for the two elements. O. J. Walker.

Organic media as spectral filters in the ultraviolet. T. M. Dahm (J. Opt. Soc. Amer., 1927, **15**, 266—284).—The extinction point for a constant source of ultra-violet radiation in aqueous solutions of concentration varying by the factor 0·5 has been determined for the following substances: mercuric chloride, methyl, ethyl, and allyl alcohols; oxalic, acetic, citric, tartaric, citraconic, mesaconic, fumaric, maleic, crotonic, aconitic, benzoic, salicylic, phthalic, *p*-hydroxybenzoic, gallic, tannic, phenylacetic, and picric acids; aniline arsenate, arsanilic acid, *p*-dichlorobenzene, acetanilide, benzamide, triphenyl phosphate, heliotropin, diphenyl, phenanthrene, quinine sulphate, thiocarbamide, phenol, quinol, phloroglucinol, strychnine sulphate; quinine, berberine, and cryptopine hydrochlorides; thiophen, 2:5-dimethylpyrazine; aconitine, atropine, cinchonidine, cinchonine, cocaine, morphine, narcotine, and their hydrochlorides. Curves are given in which the logarithm of the concentration at which extinction occurs is plotted as a function of the frequency. After a discussion of the procedure appropriate to the choice of a solution for use as a filter with a given transmitting power, the theory of the method employed is described and suggestions are made for improving the extinction-point method. R. W. Lunt.

Absorption of light in the ultra-violet by simple amino-acids. H. Ley and B. Arends (Ber., 1928, **61**, [*B*], 212—222; cf. A., 1926, 1080).—Contrary to the observations of Abderhalden and Haas (A., 1926, 959), a difference in optical behaviour of alanine and glycine is not detected when the substances are crystallised from water or precipitated from aqueous solution by alcohol. Further, the optical behaviour of alanine does not appear appreciably influenced by the presence of glycine as shown by direct observation and also by comparison of the effect of solutions of the mixed compounds with those of the components placed singly in series in the path of the rays. For each acid, the absorption is independent of the concentration (contrast Abderhalden and Haas, A., 1927, 451). Determinations of the f. p. of solutions of alanine and glycine fail to disclose any mutual influence of the components. Measurements are recorded of the absorption of glycine, alanine, α-amino-*n*-butyric acid, α-amino*iso*butyric acid, their hydrochlorides and sodium salts. Passage from the amino-acid to the salt or from the $\cdot NH_3\cdot R\cdot CO_2'$ ion to $NH_2\cdot R\cdot CO_2'$ causes in all cases marked displacement towards the red as observed previously (*loc. cit.*) with piperidinoacetic acid. The absorption curves of glycine hydrochloride and sodium aminoacetate appear to intersect at −0·2 (log ε); with increasing number of carbon atoms in the alkyl group R of the ions $NH_2\cdot R\cdot CO_2'$ and $\cdot NH_3\cdot R'\cdot CO_2H$, the point of intersection is displaced towards the region of greater values of ε. H. Wren.

Spectroscopical study of amino-acid anhydrides. II. Light absorptions of some amino-acids, their esters, peptides, and anhydrides. Y. Shibata and T. Asahina (Bull. Chem. Soc. Japan, 1927, **2**, 324—334).—Continuing previous work (A., 1926, 659) solutions of glycine, alanine, leucine, phenylalanine, tyrosine, glycine and

tyrosine esters, glycyl-leucine, glycyl-*l*-phenylalanine, glycyl-*dl*-phenylalanine, and the anhydrides of glycyl-*l*-tyrosine, tyrosine, glycyl-*l*-leucine, leucine, glycyl-*l*-phenylalanine, and phenylalanine were examined spectroscopically. Of the above, only those compounds containing phenyl or hydroxyphenyl groups show selective absorption. Derivatives of tyrosine and phenylalanine absorb identically with the parent substances. The absorption of phenylalanine anhydride is, however, anomalous, end absorption only being observed. The anomalous absorption is possibly due to the mutual effect of the two symmetrically-situated phenyl groups. It is concluded that the substances examined exist only in the keto-form in solution. J. S. CARTER.

Absorption spectra of some triphenylmethane derivatives. L. C. ANDERSON (J. Amer. Chem. Soc., 1928, **50**, 208—212; cf. this vol., 285).—The absorption spectra of triphenylmethane and triphenylcarbinol in ethereal solution show only the four prominent bands of the ten reported for these compounds in alcohol by Orndorff, Gibbs, McNulty, and Shapiro (A., 1927, 764). The absorption spectra of ethereal and alcoholic solutions of triphenylmethyl ethyl ether differ only in intensity. The absorption spectrum of triphenylmethyl chloride in neutral ethyl alcohol is identical with that of triphenylmethyl ethyl ether, indicating that quantitative etherification takes place in the cold. F. G. WILLSON.

Effect of rhodamine on a line spectrum. F. R. TERROUX (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 255—256).—The radiation from a quartz mercury lamp, after passage through a quartz absorption cell containing solutions of rhodamine *B* of different concentrations, has been examined spectrographically. Contrary to the observations of Rây (A., 1926, 1192), there was no shift in position of any of the lines, and no tendency for the line spectrum to become continuous. A few spectra taken with the sodium flame showed a widening of the lines on long exposure, but this was more pronounced when the absorbing solution was absent, and was probably due to creeping of the image on the plate. Rhodamine *B* has important qualities as a spectral filter. A 1% solution 1 cm. thick transmits a narrow band from 6500 to 6100 Å. A 0·05% solution transmits freely over a broad band from 7000 to 5300 Å., and less freely between 4500 and 3700 Å. Outside these limits the solutions appear to absorb completely. M. S. BURR.

Sterol group. I. Absorption spectra of cholesterol derivatives. I. M. HEILBRON, R. A. MORTON, and W. A. SEXTON (J.C.S., 1928, 47—51).—The absorption spectra of a number of cholesterol derivatives have been examined, with the view of determining the class of compound to which vitamin-*D* may be assigned. Selective absorption occurs only when at least two double linkings are present in the molecule. It is shown that the absorption spectrum of cholesterilene resembles that of ergosterol, and it seems probable that two of the three double linkings in the latter compound occupy the same positions as in cholesterilene. Cholestenone and vitamin-*D* also appear to be correlated (A., 1927, 948).
W. A. RICHARDSON.

Absorption spectrum of antirachitic cholesterol. R. POHL (Nachr. Ges. Wiss. Gottingen, 1926, 142—145; Chem. Zentr., 1927, i, 2921).—The absorption coefficient at 280 mμ of cholesterol is reduced by half on irradiation, whereas analysis shows that at least 99·5% of the original cholesterol remains. Hence, the bands which disappear should be due to an impurity which in small concentrations absorbs in the ultra-violet to an extent corresponding with that of ordinary dyes in the visible part of the spectrum. A. A. ELDRIDGE.

Absorption spectrum of antirachitic provitamin and vitamin. R. POHL (Nachr. Ges. Wiss. Gottingen, 1926, 185—191; Chem. Zentr., 1927, i, 2921).—The ultra-violet absorption spectrum of ergosterol is essentially coincident with that of the provitamin, which is present in cholesterol to the extent of about 0·017%. The earlier designation "colouring matter" of the ergosterol is justified.
A. A. ELDRIDGE.

Emission of phosphors. II. Transformation of constituent bands in the samarium–sulphide spectrum. R. TOMASCHEK and (FRAU) H. TOMASCHEK (Ann. Physik, 1927, [iv], **84**, 1047—1073; cf. A., 1927, 1125).—The spectra of calcium sulphide–samarium and strontium sulphide–samarium phosphors being already known, the mixed phosphors, prepared in various ways, have been further investigated. The method of comparing corresponding emission lines or bands has again been used. Two distinct mixed types are disclosed. A series of mixed phosphors has been examined at low temperatures. The CaS-*h* emission consists of 4 sharp lines (6058, 6007, 5697·7, and 5656·6 Å., designated 1, 2, 3, and 4, respectively). A mixed phosphor in which 6·5% of the calcium sulphide has been replaced by strontium sulphide shows 1 greatly broadened and exhibiting a satellite at 6061 Å., 2 unchanged in wave-length but with a satellite on each side, 3 slightly broadened, and 4 showing broadening and two satellites; the 18·8% phosphor is very similar. From 27·5 to 80·7%, the bands are all greatly broadened, and a gradual, uniform shift in the direction of shorter wave-lengths is apparent. The 87·5 and 94·5% phosphors are markedly different. A very definite resolution into lines is observed, and the wave-lengths approximate to those shown by the strontium sulphide phosphor. It is clear that the broad bands are due to the coexistence of two types of emission centres.

The lines in the strontium sulphide–samarium emission corresponding with 1, 2, 3, and 4, are identified as 6034·6, 5993·2 (or 5999·4), 5679·0, and 5642·8 Å., respectively.

The phosphorescence centres are regarded as adsorption compounds of heavy metal salts at the surface of complex aggregates. The constancy of the principal wave-lengths for small strontium sulphide percentages indicates that no change in the binding forces occurs, but that strong fields are set up, causing the resolution into components either by a Zeeman or Stark effect. The adsorption mechanism agrees with the results of *X*-ray investigations on the structure of phosphors and accounts

for the observations throughout the range of calcium–strontium sulphide mixed phosphors.

R. A. MORTON.

Determination of dielectric constants in intense electric fields. J. MALSCH (Ann. Physik, 1927, [iv], **84**, 841—879).—Modifications in the technique of Wien (Physikal. Z., 1922, **23**, 399) are described which permit of the ready determination of dielectric constants of conducting liquids such as water as well as those of good insulators in intense electric fields. A very full discussion is given of the theory of the method and of the probable accuracy. Measurements on water, glycerol, and ethyl ether, using heavily damped oscillation at frequencies of the order of 10^3 kilocycles, indicate that, within the order of experimental error, no change can be observed in the dielectric constant with field strength; the maximum estimated field strength used was 10^5 volt $cm.^{-1}$ The effect of intense fields is discussed at length with reference to Debye's theory, on which, it is shown, an increase of the dielectric constant of from 10 to 20% is to be anticipated in the fields employed.

R. W. LUNT.

Scattering of light by gaseous and liquid chlorine. A. F. W. COLE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 267—268).—Data for the ratio of the intensities of light scattered by chlorine and ether, respectively, are given (cf. A., 1926, 559). The hypothesis that carefully dried chlorine re-radiates absorbed energy has been tested and is found to have no foundation, unless the re-emitted radiation is of frequencies entirely beyond the range of visual observation. The chlorine used contained 2% of carbon dioxide and traces of some other gas, probably carbon monoxide.

M. S. BURR.

Refraction and dispersion of air, oxygen, and gaseous chloroform. Gaseous refractivities of acetone, methyl ether, and ethyl ether. H. LOWERY (Proc. Physical Soc., 1927, **40**, 23—28).—The refractivities of air, oxygen, and gaseous chloroform have been measured for the green mercury line 5461, and the dispersion determined over the range 4800—6700 Å. For air at *N.T.P.* $(\mu-1)=4{\cdot}8286\times10^{-7}/(16774\times10^{27}-\nu^2)$, and for oxygen $(\mu-1)=3{\cdot}4343\times10^{27}/(12970\times10^{27}-\nu^2)$, for chloroform $(\mu-1)_d=14{\cdot}622\times10^{-7}/(10659\times10^{27}-\nu^2)$, where ν is the frequency of the light, and $(\mu-1)_d$ refers to the same number of molecules as 1 c.c. of hydrogen contains at *N.T.P.* The values of $(\mu-1)_d$ for acetone, dimethyl ether, and diethyl ether were 1096×10^{-6}, 8876×10^{-7}, and 1509×10^{-6}, respectively.

C. J. SMITHELLS.

Optical properties of arsenic. E. GRISCHKIEVITSCH-TROCHIMOVSKI and S. F. SIKORSKI (Bull. Soc. chim., 1927, [iv], **41**, 1570—1585; cf. A., 1927, 614).—Replacement of a chlorine atom or an alkyl group by an aryl group in an arsine in which the hydrogen atoms have been replaced by chlorine atoms and alkyl groups causes an increase in the atomic refraction of the arsenic, whereas substitution by a cyanide or an oxalate radical has the opposite effect, and replacement of chlorine by alkyl radicals scarcely changes the refraction at all. If a chlorine atom in each of two molecules is replaced by a single oxygen atom, the refraction is not altered, but if two chlorine atoms in the same molecule are replaced, it is reduced.

R. CUTHILL.

Optical refraction of alkaline-earth compounds with oxygen, sulphur, selenium, and tellurium. K. SPANGENBERG [with M. HAASE and W. H. LEHMANN] (Naturwiss., 1927, **15**, 266; Chem. Zentr., 1927, i, 2710—2711).—The tabulated refractivities of the compounds of magnesium, calcium, strontium, and barium with oxygen, sulphur, selenium, and tellurium exhibit the same regularities as those of the alkali halides. The dispersion increased in the order oxide, sulphide, selenide, telluride; with oxides it increases with increasing mol. wt. Barium telluride has the rock salt structure, *d* 7·593, $2d_{100}$ 6·82±0·02 Å.

A. A. ELDRIDGE.

Refractive index of quartz. W. R. C. COODE-ADAMS (Proc. Roy. Soc., 1927, **A**, **117**, 209—213; cf. Lowry and Coode-Adams, A., 1927, 813).—Theoretical. A new formula for the refractive index of quartz is obtained by making use of the ultra-violet frequencies calculated from the optical rotations (*loc. cit.*). Starting from the Kettcler–Helmholtz formula, $n^2=n_\infty^2+\Sigma M_m/(\lambda$, 18 values of n in the visible and ultra-violet regions are calculated from the equation: $n^2=3{\cdot}53445+0{\cdot}008067/(\lambda^2-0{\cdot}0127493)+0{\cdot}002682/(\lambda^2-0{\cdot}000974)+127{\cdot}2/(\lambda^2-108)$. The values are in excellent agreement with the experimental values of Gifford for the ordinary ray in dextro-quartz (Proc. Roy. Soc., 1902, **70**, 329), the average error being only ±0·00001. The new formula also provides an adequate representation of the most reliable data for the infra-red. The constant term 3·53445 should be equal to the specific inductive capacity of quartz.

L. L. BIRCUMSHAW.

Refractive and natural rotatory dispersion. M. L. PAGLIARULO (Atti R. Accad. Lincei, 1927, [vi], **6**, 157—159).—The rotatory dispersion of mono*iso*amyl aspartate is anomalous and of the same type as that of monoethyl aspartate (A., 1927, 610). In this case, also, the existence of a relationship between the rotatory and refractive dispersions is not apparent from the corresponding curves, but is rendered so by means of the curves connecting the differences of the refractive indices with successive changes in wave-length of 100 Å.

T. H. POPE.

Refractivity of normal saturated monobasic aliphatic acids. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1928, **47**, 45—51).—The conclusions of Waterman and Bertram (A., 1927, 1167) with regard to oscillation in the product of the mol. wt. and refractive index, Mn_D, in the normal fatty acid series are not justified by their results, and when the same calculations are applied to their values for the *C*-, *E*-, and *G*-lines (*loc. cit.*), no similar regularities are obtained. The observed fluctuations of $\Delta(Mn)$ for all four wave-lengths lie, for the most part, within the limits of experimental error.

M. S. BURR.

Refractivity and dispersivity of normal saturated monobasic aliphatic acids. H. I. WATERMAN and S. H. BERTRAM (Rec. trav. chim., 1928, **47**, 52—54).—A reply to Verkade and Coops (cf. preceding abstract).

M. S. BURR.

Simultaneous effects of rod- and specific-double refraction. IV. H. AMBRONN (Kolloid-Z., 1928, 44, 1—5).—A posthumous theoretical paper, of date January, 1919, in which equations are derived to represent the changes in the rod- and specific-double refraction of cellulose and celloidin strips on drying. E. S. HEDGES.

Optical activity and polarity of substituent groups. VII. *sec.*-β-Octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids. H. G. RULE, W. HAY, (MISS) A. H. NUMBERS, and T. R. PATERSON (J.C.S., 1928, 178—186).—A number of optically active *sec.*-β-octyl esters of substituted benzoic acids have been prepared and examined (A., 1926, 1038). Two effects are distinguished: (i) the general effect, irrespective of the position of the substituent group, in which the series $NO_2 > CO_2H >$ halogens $> OMe > H > Me$ can be observed for a number of properties, such as molecular rotatory power of the *l-sec.*-β-octyl esters of the substituted benzoic acids, and the dissociation constants of the benzoic acids and substituted acetic acids; (ii) a group effect represented by the series $NO_2 > CO_2H > Ac > H > Me > I > Br > Cl > OMe$, which indicates the relative influence of the substituents on the nitration of a mono-substituted benzene and on the optical activity of the menthyl and *sec*-β-octyl esters of the *o*-substituted benzoic acids. Groups which direct to the *m*-position increase the rotatory power of these esters and *p*-directing groups lower it. Iodine is a partial exception to this rule. On the electron-shift theory of the general effect the direction of the change in rotatory power following *p*-substitution can be predicted from a knowledge of the corresponding acetic esters. The rotatory power of *d*-octyl hydrogen phthalate in solutions at different concentrations at 20° and in the homogeneous state at 90·5° has been measured.

The following compounds are described: d-β-*octyl hydrogen terephthalate*, m. p. 95—96°, $[\alpha]_D^{19}$ +45·17° in acetone; d-β-*octyl* o-*chlorobenzoate*, b. p. 180°/14 mm., d_4^{20} 1·0473; d-β-*octyl* m-*chlorobenzoate*, b. p. 175°/12 mm., d_4^{20} 1·0425; d-β-*octyl* p-*chlorobenzoate*, b. p. 177—178°/12 mm., d_4^{20} 1·0403; d-β-*octyl* o-*bromobenzoate*, b. p. 175°/9 mm., $d_4^{18.9}$ 1·1987; d-β-*octyl* o-*iodobenzoate*, b. p. 202°/12 mm., $d_4^{18.9}$ 1·3522; d-β-*octyl* o-*toluate*, b. p. 154—155°/9 mm., $d_4^{17.6}$ 0·9522; d-β-*octyl* m-*toluate*, b. p. 181·5—182°/17 mm., d_4^{20} 0·9492; d-β-*octyl* p-*toluate*, b. p. 184°/19 mm., d_4^{20} 0·9492. W. A. RICHARDSON.

Crystal form and optical activity. E. HERLINGER (Naturwiss., 1927, 15, 289; Chem. Zentr., 1927, i, 3177).—With regard to van 't Hoff and Le Bel's view of the connexion between optical activity and crystallographic enantiomorphism it must be remembered that the rotation of the plane of polarisation of the light is effected by the rotation of a spatial distribution of polarisation electrons. Hence there follows the possibility of the existence of four optically active isomerides instead of two for a single centre of asymmetry, as is recognised with tartaric acid. On account of the unsymmetrical distribution of radicals about the stereochemical asymmetric centre, dipole-molecules, suitably approaching the dissolved optically active molecule, are able to effect an optical inversion. A. A. ELDRIDGE.

Stereochemical inversions and cross-saturation processes. A. LAPWORTH and E. N. MOTTRAM (Mem. Manchester Phil. Soc., 1926—1927, 71, 63—73).—The evidence relating to cross-substitution, or simple stereochemical inversion, and cross-saturation processes is discussed. The former appears to be general when a linking between saturated carbon and halogen or oxygen is involved in a substitution process in aqueous or alcoholic solution. This is seen, for example, in Holmberg's experiments on halogenated succinic acid (A., 1926, 384, 937), or in the changes in optical rotatory effect observed when compounds of the acetochloroglucose type are used as "intermediates" in syntheses in the sugar group, or, finally, in the contrast between the reactions of esters of different types, *e.g.*, sulphonates as compared with carboxylates (Ferns and Lapworth, J.C.S., 1912, **101**, 273). When halogens, halogen hydrides, or hypohalogen acids are added to a pair of doubly-linked carbon atoms, cross-saturation usually takes place and does not necessarily mean that stereochemical inversion must have occurred at some stage in the reaction. Conversely, on elimination of the same elements, cross-desaturation results. It is suggested that in the series of reactions, *cyclo*hexene⟶*cyclo*hexene chloro- or bromo-hydrin⟶*cyclo*hexene oxide⟶*cyclo*hexanediol, each one is a cross-reaction, resulting finally in a *trans*-compound. Oxidation of *cyclo*hexene by permanganate, however, results in the formation of the *cis*-isomeride of *cyclo*hexanediol. It is possible that the latter case may be best explained by the intermediate formation of a ring compound with the manganese. M. S. BURR.

Electromagnetic rotation of the plane of polarisation by solutes. O. SCHONROCK (Z. Physik, 1928, 46, 314—326).—In recent work (Pfleiderer, A., 1927, 8) the magnetic rotation of a solute has been calculated from the expression $\omega(q_1+q_2)=\omega_1 q_1\ \ _2q_2$, ω, ω_1, and ω_2 being Verdet constants for solution, solvent, and solute respectively and q_1, q_2 the weights of solvent and solute per c.c. of solution. The expression $\omega=\Sigma_m\omega_m q_m/s_m$ (ω_m, q_m, and s_m being Verdet constants, volume contents per c.c., and densities, respectively, for the constituents of a solution) rests on a sound theoretical basis, and is supported by the degree of constancy obtained for ω_2, provided $\Sigma m q_m/s_m=1$ for the solution, within fairly narrow limits. Verdet's contention that determinations of magnetic rotation with only one type of solution suffice, for example, to decide whether a salt exists in the solution as a hydrate or in the anhydrous state, is shown to be erroneous. Krethlow's observations (A., 1925, ii, 1029) on camphor show that, correctly calculated, the Verdet constant for camphor dissolved in benzene is really constant, the values for three solutions being in agreement at four wave-lengths. Similarly for β-methylamyl bornylenecarboxylate, the new equation represents an accurate mixture law, judged by the constancy of ω_2. R. A. MORTON.

Molecular symmetry in solutions. K. WEISSENBERG (Physikal. Z., 1927, 28, 829—834). A

review of the data referring to molecular symmetry with special reference to the electric moments of molecules and to the structure of the recently discovered compounds $C(CH_2 \cdot OH)_4$ and $C(CH_2 \cdot OAc)_4$.

R. W. LUNT.

Dipole moment and anisotropy in fluids. L. EBERT and H. VON HARTEL (Physikal. Z., 1927, **28**, 786—790).—The validity of Born's theory has been investigated by comparing the value of the orientation polarisation of *p*-azoxyanisole, *p*-azoxyphenetole, and *p*-azoxyethyl benzoate calculated from Born's theory, by substituting for the critical temperature the temperature at which the molten substance becomes clear, with the value obtained by taking the difference between the molecular polarisation and the polarisation calculated from the molecular refraction. The values so obtained are of the same order of magnitude and are thought to sustain the view that molecular forces can be calculated to a first approximation from the forces due to dipoles. R. W. LUNT.

Periodic table of the structure of atoms and its relation to ion formation and valency. A. A. NOYES and A. O. BECKMANN (Proc. Nat. Acad. Sci., 1927, **13**, 737—743).—A preliminary account of an attempt to correlate the spectroscopic data relating to ion formation with valency from the point of view of the periodic law. R. W. LUNT.

Classification of metallic substances. W. HUME-ROTHERY (Phil. Mag., 1928, [vii], **5**, 173—178).—A classification of solid metallic phases is suggested as follows: metallic elements, which may be isotopically either simple or complex; primary metallic solid solutions, which form the end phases of the ordinary equilibrium diagrams and in which the crystal structure of the parent metal is retained; secondary solid solutions, in which the crystal structure is different from that of the parent metal, but in which there is no indication of the formation of compound molecules or electron exchange or transference; intermetallic compounds of fixed or variable composition, in which there is evidence either of electron transference and exchange or that a compound molecule is being formed. A. E. MITCHELL.

Structure and dimensions of the benzene ring. J. K. MORSE (Proc. Nat. Acad. Sci., 1927, **13**, 789—793).—A model of a benzene molecule is described which is thought to explain both the chemical properties and the *X*-ray spectrogram of benzene.

R. W. LUNT.

Influence of shape and polarity of molecules on the *X*-ray spectrum of liquids. II. Occurrence of two amorphous rings in substances, the molecules of which contain several equal groups or parts. J. R. KATZ and J. SELMAN (Z. Physik, 1928, **46**, 393—405).—A large number of liquids exhibit one "amorphous ring" only, in their *X*-ray spectra (*ibid.*, **45**, 97). Provided the molecule can be considered as roughly spherical, the mean distance of separation between the centres of molecules may be calculated from the diameter of the ring. Many liquids, however, show two "amorphous" rings in the *X*-ray diagram, the appearance and diameter of the second ring being determined by the structure of the molecules of liquid. Possibly, the liquids showing two rings are made up of small aggregates of a few molecules, in which a certain regular orientation of groupings occurs.

Tertiary amines were studied because it was possible to obtain molecules in which three equal side-chains were grouped around a central atom. As an example, tripropylamine shows two rings of diameters $a_1=7{\cdot}9_5$, $a_2=5{\cdot}2$, whilst propyl alcohol shows one ring $a=5{\cdot}3$, and the distance separating the centres of molecules is calculated in the same units as $b=7{\cdot}6$ from the molecular volume. Similar results were obtained with compounds NR_3 in which R is Bu, Bu^β, and *iso*amyl. Ortho-esters of the following types gave similar results: $CH(OR)_3$ (R=Et, Bu^β, or *iso*amyl); $C(OEt)_4$; $Si(OR)_4$ (R=Et or Me); $B(OR)_3$ (R=Me, Et, and Bu^β, and $PO(OR)_3$ (R=Et or tolyl). The last case is interesting because three amorphous rings, $a_1=9{\cdot}6$, $a_2=6{\cdot}2$, $a_3=4{\cdot}5$, were shown, whilst b is $9{\cdot}1$ and the a values for toluene and methyl alcohol were 6·0 and 4·5, respectively. In general, it is found that the heavier the central atom, the greater is the relative intensity of the inner ring, and the heavier or the more numerous the side-chains the greater is the relative intensity of the outer ring. This result confirms the view that the inner ring indicates the mean distance between the centres of molecules, and the outer ring that between the side-chains.

Trisubstituted benzene and pyridine derivatives and ring hydrocarbons of the type methyl*cyclo*pentadecane also show two rings. The effect of polymerisation is exemplified by: liquid styrene $a=5{\cdot}9$, metastyrene, $a_1=12{\cdot}5$, $a_2=5{\cdot}8$, indene, coumarone, acetaldehyde, propaldehyde, etc.

For short side-chains good agreement obtains between a_1 and b, but for longer chains a_1 is often greater than b. This result appears to be due to departures from the approximately spherical shape of the molecules. Triglycerides and dialkylamines do not behave quite normally. R. A. MORTON.

***X*-Ray spectra of aliphatic hydrocarbons, alcohols, and carboxylic acids.** G. W. STEWARD (Proc. Nat. Acad. Sci., 1927, **13**, 787—789).—A preliminary account is given of data shortly to be published on the *X*-ray spectra of aliphatic hydrocarbons, alcohols, and carboxylic acids which are thought to support an hypothesis of the structure of these substances on the basis of a molecular space array. R. W. LUNT.

Synthesis of molecules. H. LUDLOFF (Naturwiss., 1927, **15**, 409; Chem. Zentr., 1927, ii, 9—10).—Electron impulses in a molecule neutralise one another in pairs; all molecules with an even number of electrons are therefore diamagnetic. This explains the author's principle that even molecules exhibit absorption in the red and odd molecules in the violet.

A. A. ELDRIDGE.

Effective cross-sectional area of gas molecules towards low-velocity ions of the alkali metals. C. RAMSAUER (Physikal. Z., 1927, **28**, 858—864).—The effective target area of helium, neon, and argon to ions of lithium, sodium, potassium, and cæsium has been determined in the energy range 1—50 volts. The target area is a maximum for cæsium and diminishes along the series. In all cases it is large compared

with the value deduced from kinetic theory at 1 volt and diminishes asymptotically to a value approximating to the "kinetic" value in the neighbourhood of 20 volts. R. W. LUNT.

Effective cross-sectional area of gas molecules. E. BRÜCHE (Naturwiss., 1927, **15**, 408—409; Chem. Zentr., 1927, ii, 12).—The effective cross-sectional area of molecules of methane, carbon monoxide, carbon dioxide, and nitrous oxide was determined by measuring the diminution of intensity of a stream of electrons of known velocity which was passed through the gas. The character of the curves is determined chiefly by the number of "valency" electrons of the constituent atoms. A. A. ELDRIDGE.

***X*-Ray spectrum of element 75.** O. BERG (Physikal. Z., 1927, **28**, 865—866).—*X*-Ray spectrograms of mixtures of principally tantalum and tungsten which exhibit the $L\alpha$ and $L\beta$ lines of element 75 are described and discussed. R. W. LUNT.

Calculation of crystal structure by means of Fourier's theorem. J. M. BIJVOET (Chem. Weekblad, 1928, 25, 2—11).—A discussion of the methods by which structure may be calculated from the *X*-ray spectrum and measurements of the intensities of the diffracted rays. From each intensity a Fourier coefficient may be derived, the constant term being given by the total number of electrons in the cell. The history of this method of analysis is outlined, and the difficulties of the application are considered. S. I. LEVY.

Static methods and their application to the study of crystal habits. A. SHUBNIKOV and O. SHUBNIKOV (Bull. Acad. Sci. Petrograd, 1926, No. 6, 363—384).—The "normal" form of wiluite was ascertained by measurement of 335 crystals. CHEMICAL ABSTRACTS.

New kinds of mixed crystals. VII. D. BALAREV (Z. anorg. Chem., 1928, **168**, 292—296; cf. this vol., 110).—The inclusion of ferric chloride in ammonium chloride crystals is probably not a case of true mixed crystal formation, but is analogous rather to the inclusion of permanganates and other salts in the internal surface of barium sulphate crystals; *e.g.*, in both instances the amount of foreign salt in crystals separating from mother-liquor of a given composition is variable, and the crystals also contain free water. Ritzel's observation (A., 1916, ii, 568) that potassium sulphate or sodium nitrate present in the solution of ferric and ammonium chlorides does not appear in the crystals does not conflict with this view, since similar effects have been observed with barium sulphate. When barium chloride is precipitated with ammonium or lithium sulphate in presence of the corresponding chloride, the precipitate contains no chloride unless it has been formed so rapidly that the crystals contain cavities. If barium chloride and potassium sulphate diffuse into a solution of potassium and ammonium chlorides, the resulting precipitate contains potassium sulphate, but no ammonium sulphate is taken up unless the ammonium chloride concentration exceeds a certain limit. Finally, as with $NH_4Cl,FeCl_3,7H_2O$ crystals, some doubly refracting crystals have been found in the systems barium sulphate–alkali sulphate–water, and on warming these crystals become isotropic. R. CUTHILL.

Crystal structure of alkali metals. F. SIMON and E. VOHSEN [with C. VON SIMSON] (Naturwiss., 1927, **15**, 398; Chem. Zentr., 1927, ii, 10).—Sodium, potassium, rubidium, and cæsium are body-centred cubic; the lattice constants (90° Abs.) are 4·24, 5·25, 5·62, 6·05 Å., and *d* 0·996, 0·892, 1·59, 1·98, respectively. Values of *d* and atomic volume at 0° Abs. are calculated. A. A. ELDRIDGE.

Crystal structure of the isomorphous sulphates of potassium, ammonium, rubidium, and cæsium. A. OGG (Phil. Mag., 1928, [vii], **5**, 354—367).—The *X*-ray measurements of Ogg and Hopwood (A., 1916, ii, 594) with the $K\alpha$ radiation of palladium together with some further measurements on potassium and ammonium sulphates with the $K\alpha$ radiation of molybdenum have been systematically analysed. It is shown that the structures are all based on a simple orthorhombic lattice having 4 molecules to the unit cell. The space-group is V_h^{16}. The positions of the atoms have been determined and an explanation of the characteristic twinning of the crystals is given. A. E. MITCHELL.

Crystal structure of potassium, rubidium, and cæsium sulphates. F. P. GOEDER (Proc. Nat. Acad. Sci., 1927, **13**, 793—797).—An analysis of the *X*-ray spectra of the above sulphates indicates that in order to satisfy the internal symmetry of the molecule the only possible space-group is given by $2Di$—13 (V_h^{14}). R. W. LUNT.

Constitution of silver subfluoride. E. BRODY and T. MILLNER (Z. anorg. Chem., 1928, **168**, 349—355).—Assuming that silver subfluoride is formed, as Hettich has suggested (A., 1927, 1155), by introduction of neutral silver atoms into a distended silver fluoride lattice, and calculating the energy of lattice distension by Biltz and Grimm's method (A., 1925, ii, 842), the value —24·5 kg.-cal. is derived for the heat of formation from gaseous fluorine and solid silver, whereas if the fluoride is formed by the introduction of negative fluoride ions into a distended silver lattice the value would be +27·1 kg.-cal. The stability of the fluoride would agree with the latter structure, which is also in harmony with its considerable electrical conductivity, and the probable readiness with which it evolves fluorine. R. CUTHILL.

Crystal structure of silver chlorate. A. FERRARI and C. G. FONTANA (Atti R. Accad. Lincei, 1927, [vi], **6**, 312—314).—From *X*-ray measurements it is shown that the unit cell of silver chlorate is tetragonal and contains 8 molecules; the grating constants *a* and *c* are, respectively, 8·48 and 7·91 Å. R. W. LUNT.

***X*-Ray analysis and crystal structure of cadmium–silver alloys. I.** G. NATTA and M. FRERI (Atti R. Accad. Lincei, 1927, [vi], **6**, 422—428).—A first investigation has been made by *X*-ray methods of the series of solid solutions and compounds in the system Ag–Cd (cf. Petrenko and Fedorov, A., 1911, ii, 281). The results show that the alloys containing from 0 to 44 at.-% Cd (α-phase) consist of solid

solutions of cadmium in the silver lattice in which the length of the unit cell varies linearly with the composition from 4·07 for pure silver to 4·14 Å. for 31 at.-% Cd. The alloys containing 47—51 at.-% Cd (β-phase) consist of the compound AgCd and solid solutions of cadmium in it, the structure being a cube-centred lattice of the cæsium chloride type. It is shown that the transformation which the β-phase undergoes at 460° is not a decomposition into the α- and γ-phases, but a polymorphous change of the compound AgCd to a hexagonal lattice having the structure Ag (0, 0, 0), Cd ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$). O. J. WALKER.

Structure of smoke particles from a cadmium arc. H. P. WALMSLEY (Proc. Physical Soc., 1927, **40**, 7—13).—Using the powder method of X-ray analysis, the particles dispersed in air from a cadmium arc were found to be isometric crystals of cadmium oxide. The primary particles in the smoke had d 8·16, which is normal for cadmium oxide. Photometric measurements gave dimensions for the primary crystals of about 5×10^{-6} cm. The particles grow by aggregation along binary axes of symmetry, uniting on their (110) faces. Models were constructed to show how the aggregates may be formed.
C. J. SMITHELLS.

Crystal structure of the double chloride of cadmium and cæsium, $CsCdCl_3$. A. FERRARI and A. BARONI (Atti R. Accad. Lincei, 1927, [vi], **6**, 418—422).—X-Ray measurements of the above compound indicate that it has a cubic lattice of constant 5·20 Å. with the structure Cs (0, 0, 0), Cd ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), Cl (0, $\frac{1}{2}$, $\frac{1}{2}$) ($\frac{1}{2}$, 0, $\frac{1}{2}$) ($\frac{1}{2}$, $\frac{1}{2}$, 0); 4·14, $d_{obs.}$ 3·75. The interatomic distance Cl—Cd is less than the sum of the radii of the chlorine and cæsium ions as given by Goldschmidt. The above structure, which is identical with that of cæsium mercuric chloride (A., 1927, 1128), is another example of the crystallographic similarities between cadmium and mercury. O. J. WALKER.

Crystal structure of modification C of sesquioxides of the rare earths, indium, and thallium. W. ZACHARIASEN (Norsk Geolisk Tidsskr., 1927, **9**, No. 3—4; Chem. Zentr., 1927, ii, 11).—A consideration of the results of measurements for scandium, yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, indium, and thallium sesquioxides (cf. Goldschmidt, Barth, and Lunde, Norske Vidensk.-Akad. Oslo, Mat.-Nat. Kl., 1925, No. 7, 5). The space-group is T^5 and the disposition $12c+12c+8b$. The atomic distances for scandium—, yttrium—, and samarium—oxygen are 2·18, 2·36, 2·42 Å., respectively.
A. A. ELDRIDGE.

Crystal form of ψ-yohimbine. T. ITO (Z. Krist., 1927, **65**, 303—305; Chem. Zentr., 1927, ii, 408).—ψ-Yohimbine is rhombic, apparently holohedral, $a:b:c=1·042:1:1·690$; $n_{\alpha D}$ 1·571±0·002, $n_{\beta D}$ 1·642±0·003, $n_{\gamma D}$ 1·655±0·002. A. A. ELDRIDGE.

Tetrahedral carbon atom and crystal structure of pentaerythritol. A. SCHLEEDE and E. SCHNEIDER (Z. anorg. Chem., 1928, **168**, 313—321).—Pentaerythritol crystals with a polar tetragonal axis are imperfectly formed; properly grown crystals do not show such an axis, nor do etching experiments give any indication of its existence. It is therefore considered that the crystal class is S_4, and the space grouping S_4^2. This structure requires a tetrahedral, not a pyramidal, form for the carbon atom.
R. CUTHILL.

Space-group of dicyanodiamide and crystal structure of calcium cyanamide. U. DEHLINGER (Z. Krist., 1927, **65**, 286—290; Chem. Zentr., 1927, ii, 541). — Dicyanodiamide, monoclinic, pseudo-rhombic, has d 1·40; a 13·8, b 4·4, c 6·2 Å., β 90° 35′; the elementary parallelepiped contains four molecules. The space group is C_2^3, C^3, or C_{2h}^3. The four nitrogen and four hydrogen atoms in the molecule are not equivalent. Calcium cyanamide is rhombohedral, d 2·20; a 5·11 Å., α 43° 50′. The corresponding trigonal prism has a 3·91, c 14·10 Å. There is one molecule in the elementary cell. The atomic co-ordinates are: Ca (0, 0, 0), C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), N (u, u, u), ($\bar{u}$, $\bar{u}$, $\bar{u}$), where $u=0·37$, and the atomic distances Ca—Ca 3·91, Ca—C 3·26, C—N 1·59, Ca—N 2·40 Å.
A. A. ELDRIDGE.

Crystal form of methyl tetrathionoxalate. H. HIMMEL (Z. Krist., 1927, **65**, 496—499; Chem. Zentr., 1927, ii, 1340).—The *cis*-form, m. p. 71·5°, is monoclinic holohedral, $a:b:c=0·8356:1:1·1684$, β=124° 32′; the *trans*-form, m. p. 101·5°, is also monoclinic holohedral, $a:b:c=0·7919:1:0·6059$, β=99° 48′. A. A. ELDRIDGE.

Scattering of X-rays and electron distribution in the atoms of crystals. R. J. HAVIGHURST (Physical Rev., 1928, [ii], **31**, 16—26).—A critical examination of the method of obtaining the atomic structure factor and of the Fourier analysis method of determining electron distributions in crystals. If the method, as appears, is valid, any modification caused by the Compton effect in the intensity of regular reflexion of X-rays is negligible.
A. A. ELDRIDGE.

Diffraction of X-rays in liquid normal monobasic fatty acids. R. M. MORROW (Physical Rev., 1928, [ii], **31**, 10—15).—The liquid normal fatty acids from formic to undecoic were investigated by the method previously employed (Stewart and Morrow, A., 1927, 1015). The spacing constants, d_2 and d, and the computed densities for the acids are: formic 3·65, 5·2, 1·42; acetic 4·17, 5·9, 1·25; propionic 4·39, 6·0, 1·36; butyric 4·64, 8·5, 1·03; valeric 4·54, 10·2, 1·03; hexoic 4·64, 12·8, 0·90; heptoic 4·54, 14·5, 0·93; octoic 4·54, 17·0, 0·88; nonoic 4·54, 18·4, 0·89; decoic 4·59, 20·3, 0·86; undecoic 4·54, 22·0, 0·88. The arrangement of molecules in the cybotactic state is not that found in the crystalline state.
A. A. ELDRIDGE.

X-Ray diffraction in liquids. Comparison of certain primary normal alcohols and their isomerides. G. W. STEWART and E. W. SKINNER (Physical Rev., 1928, [ii], **31**, 1—9).—X-Ray diffraction curves were obtained for *iso*-, *sec.*-, and *tert.*-amyl and *tert.*-butyl alcohols, diethyl-, methyl-n-butyl-, *sec.*-butyl-, and triethyl-carbinols. The attachment of a methyl group at the side of a chain increases the mean diameter of the chain molecule by 0·6 Å., and that of a hydroxyl group by 0·4 Å., whereas the attachment of both groups to the same carbon atom

increases the diameter by only 0·65 Å. The attachment of three ethyl chains to the same carbon atom increases the diameter by 1·35 Å. With di-*n*-propylcarbinol the side attachment of a hydroxyl group is shown to increase the diameter in one direction by 0·45 Å. and in the other not at all. Associated polar groups give two molecules in a continuous chain for each longitudinal spacing, but when the hydroxyl group is not attached to the last or penultimate atom in the chain this association disappears.

A. A. ELDRIDGE.

[Magnetic transformation of iron.] F. WEVER (Z. anorg. Chem., 1928, **168**, 327—328; cf. A., 1927, 627).—A reply to Ruer's criticism (*ibid.*, 925).

R. CUTHILL.

Transformation of β-brass and the demagnetisation process of ferromagnetic metals. C. H. JOHANSSON (Ann. Physik, 1927, [iv], **84**, 976—1008). —The transformation of β-brass and the transformations occurring in ferromagnetic metals with loss of magnetic properties resemble each other in showing anomalous behaviour when various tests are applied. The idea is advanced that the transformations occur with lattice structures permitting rotational vibrations of the atoms, a phenomenon which does not obtain in normal lattices of metals and alloys. There is reason to regard the sphere of influence of the zinc atoms in β-brass as ellipsoidal rather than spherical, and as the lattice is probably of the cæsium chloride type (Cu : Zn=1 : 1) the copper may be expected to retain the spherical sphere of influence. On this basis, arguments are advanced in favour of the view that the transformation of β-brass in the solid state arises from heat vibrations about the inertia axes, vertically to the symmetry axes of the zinc atoms. A similar mechanism is put forward for the demagnetisation processes, the heat oscillations occurring about the inertia axes and at right angles to the magnetic axes. Possible objections to the view are considered in detail. The magnetic properties are constitutive to the atom (or molecule) concerned and the magnetic moment is independent of thermal oscillations. Phase transformations or chemical reactions bound up with changes in electron configurations, can, however, effect discontinuous changes in magnetic moments. Mixed crystals of weakly magnetic metals and a smaller amount of a ferromagnetic metal must, on account of Larmor's (precessional motion) theorem, be themselves weakly magnetisable, even if the ferromagnetic atom is able to retain its moment unchanged. Weiss' theory is discussed in relation to this kinetic-lattice theory; there is no necessary opposition between the two.

R. A. MORTON.

Evolution of nickel sulphide and cobalt sulphide in contact with water. (MLLE.) S. VEIL (Compt. rend., 1928, **186**, 80—81; cf. A., 1926, 567). Nickel sulphide prepared by precipitation in the cold is less magnetic than the hydroxide obtained under the same conditions. The use of warm water renders it less oxidisable and reduces its magnetism. The magnetic properties of the oxide derived from the sulphide prepared in the cold are of the same order as that from the hydroxide prepared in the cold, and show variations with temperature analogous to those observed for nickelous hydroxide and the hydrate of nickel sesquioxide (A., 1925, ii, 183). In general, cobalt sulphide yielded the same results, except that cobalt sulphide was more magnetic than the hydrate of cobalt sesquioxide, both prepared in the cold, although their coefficients of magnetisation are of the same order (cf. A., 1927, 614).

J. GRANT.

Deformation structures of aluminium crystals and crystal masses and their reciprocal relations. E. SCHIEBOLD (Fortschr. Min. Kryst. Pet., 1927, **11**, 25—28; Chem. Zentr., 1927, i, 2707—2708).—The deformation structures of aluminium crystals and crystal masses on crushing, drawing, rolling, and torsion were studied.

A. A. ELDRIDGE.

Diffusion in crystals with overgrowths. E. DITTLER (Z. anorg. Chem., 1928, **168**, 309—312).— Examination of various natural specimens of crystals with overgrowths and also of similar crystals prepared artificially about 50 years ago has failed to yield any decisive evidence of the occurrence of diffusion between the crystal layers.

R. CUTHILL.

***X*-Ray study of the heat motion of the atoms in a rock-salt crystal.** R. W. JAMES and E. M. FIRTH (Proc. Roy. Soc., 1927, **A**, **117**, 62—87).—The ratio of the intensity of reflexion of *X*-rays by rock-salt crystals at the temperature of liquid air to that at the ordinary temperature has been measured for a number of spectra. The temperature factor is of the form $\exp.\ \{-bf(T)\sin^2\theta_T/\lambda^2\}$, where $f(T)$ is some function of the temperature Abs., and the constant b will in general differ for atoms of different kinds. The experimental results, combined with data obtained previously at high temperatures (Phil. Mag., 1925, [vi], **49**, 585), are compared with the theoretical formulæ of Debye and Waller for the temperature factor of *X*-ray reflexion. Up to about 500° Abs. fairly good agreement is obtained with Waller's theory, but at high temperatures the experimental curve deviates widely from the theoretical. This is to be expected, because the assumptions on which the theory is based need modification at such temperatures. The fact that, for corresponding angles of reflexion, the temperature factor is considerably larger for spectra of the type Cl+Na than for those of the type Cl—Na, is discussed. It is possible that the temperature factor may be a function of the direction of the rays relative to the crystal axes. The absolute value of the integrated reflexion for the (200) spectrum from a rock-salt crystal has been redetermined and found to be 0·000492 for molybdenum $K\alpha$, and 0·000544 for rhodium. An estimate of the "extinction" for this crystal for molybdenum has been made. The reflexions from a number of faces of the rock-salt crystal have been determined in absolute measure by comparison with the (200) spectrum, and from these, the *F*-factors, or atomic scattering factors, have been deduced at 0, 86, 290, and 900° Abs. An attempt has been made to get some idea of the actual amplitude of the heat-motions of the atoms in the rock-salt lattice, by analysing the curves showing the variation of the atomic scattering power with the angle of scattering, using the method of Fourier analysis so as to obtain the distribution of electrons in the crystal unit at different temperatures.

From the broadening of the peaks in the distribution curves, the mean amplitudes of the atomic vibrations have been estimated. Mean amplitudes of about 0·20 Å. at 290° Abs., and of 0·58 Å. at 900° Abs., explain the observed changes in the distribution curves. This estimate of the amplitudes is checked by means of a rough calculation, which gives results of the same order. L. L. BIRCUMSHAW.

Structure of liquids and vitreous solids. H. JEFFREYS (Proc. Camb. Phil. Soc., 1928, **24**, 19—31). —Whilst the kinetic theory and the ionic lattice theory present a consistent picture of the gaseous and crystalline solid states, no adequate theory is available for the liquid and amorphous states. The description of vitreous solids as supercooled liquids is open to objection. The three states of matter are regarded as gaseous, crystalline, and vitreous. In the typical gas, single molecules move freely at intervals much greater than their own dimensions; the crystal is built according to a regular repeating pattern, and the vitreous solid is held together by the same kind of forces as the crystal, but the structure is less regular. It is probably comparable in stability with the crystal except near the m. p. The liquid is a compromise between the vitreous and gaseous states, the clots of molecules in a liquid resembling small pieces of vitreous solid, whilst themselves playing a part similar to molecules of a gas in producing viscosity. Migration of molecules from one clot to another will occur. This point of view is in harmony with the rigidity, density, strength, cleavage, conductivity, and other properties of vitreous solids. R. A. MORTON.

Electrical conductivity of silicon. H. J. SEEMANN (Physikal. Z., 1927, **28**, 765—766).—The electrical conductivity of a number of single crystals of silicon has been determined in the range −180° to −80°; the mean value of the coefficient α is approximately +0·002. R. W. LUNT.

Electrical conductivity of crystalline zinc oxide. R. BACH (Arch. Sci. phys. nat., 1927, [v], **9**, 426—430).—The specific resistance of crystalline zinc oxide has been investigated over the temperature range −183° to +297°. The specific resistance is minimal (0·1 ohm cm.) at −100° and 0·14 ohm cm. at the ordinary temperature. Over the temperature range investigated the conductivity is entirely metallic, although it is probable that, at temperatures of the order of 1000°, conductivity of the ionic type is superposed. Neither polarity nor variation of resistance with axial direction was observed. J. S. CARTER.

Effect of magnetic, electric, and mechanical forces on "mesophases." H. ZOCHER (Physikal. Z., 1927, **28**, 790—796).—A mathematical analysis of the effect of magnetic, electric, and mechanical forces on "mesophases," of which anisotropic liquids are considered as typical examples. R. W. LUNT.

Susceptibility of ozone. O. R. WULF (Proc. Nat. Acad. Sci., 1927, **13**, 744—748).—The volume susceptibility of ozone and ozone–oxygen mixtures has been determined by a modification of Gouy's method in the range 11,000—16,000 gauss. The results show, in contradistinction to Becquerel's measurements, that ozone is not more paramagnetic than oxygen, and suggest that ozone is diamagnetic. R. W. LUNT.

Diamagnetic susceptibilities of gases at low pressures. V. I. VAIDYANATHAN (Phil. Mag., 1928, [vii], **5**, 380—386).—A susceptibility balance capable of measuring changes in volume susceptibility of 6×10^{-12} in a field of 1400 gauss is described. Examination of nitrogen, argon, and carbon dioxide, at pressures up to 544 mm., showed strict proportionality between pressure and volume susceptibility. The values obtained for the volume susceptibilities of carbon dioxide, argon, and nitrogen were $-9{\cdot}2\times10^{-10}$, $-11{\cdot}3\times10^{-9}$, and $-5{\cdot}8\times10^{-10}$, respectively. The values for nitrogen and carbon dioxide are in fair agreement with those of Hector (Physical Rev., 1926, [ii], **24**, 418) and of Lehrer (A., 1926, 1086), respectively. The value for argon is 40% higher than that of Hector and 28% higher than that of Lehrer. The mean atomic radius of argon calculated from the author's value is in close agreement with that determined from *X*-ray and viscosity measurements, whilst the gram atomic susceptibility of $25{\cdot}3\times10^{-6}$ approximates to the calculated value of Pauling (Proc. Roy. Soc., 1927, **A**, **114**, 181), viz., $21{\cdot}5\times10^{-6}$. The direct linear relationship between pressure and susceptibility is in agreement with the results of Hamar (Proc. Nat. Acad. Sci., 1926, **12**, 594) and Lehrer (*loc. cit.*). A. E. MITCHELL.

Photometric determination of the permeability of olive oil towards ultra-violet light. E. ROUSSEAU (Compt. rend. Soc. Biol., 1927, **96**, 611—612; Chem. Zentr., 1927, i, 2711).

Optical properties of selenium in the conducting form. (MISS) P. M. NICOL (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 60—72).—The extinction coefficient, κ, and refractive index, n, of selenium for wave-lengths of 4400—7100 Å., determined from measurements with selenium mirrors, are independent of the temperature at which the selenium was transformed into the conducting variety, and alter little, if at all, with exposure to light and with increasing age. With increasing wave-length, κ decreases and n increases. R. CUTHILL.

Heterochromic photometry of body colour. K. SCHAUM (Z. physikal. Chem., 1928, **131**, 226—236). —The problem of the analysis of colour from the physical and physiological point of view is discussed, and a method is described for determining quantitatively the degree of contrast between coloured bodies with an error of less than 2%, and for measuring the degree of brightness compared with a standard white substance such as magnesium oxide. H. F. GILLBE.

True temperature scale of carbon. C. H. PRESCOTT, jun., and W. B. HINCKE (Physical Rev., 1928, [ii], **31**, 130—134).—Measurements of the spectral emissive power of Acheson graphite for 0·660 μ at 1250—2700° Abs. are summarised by the relation $\varepsilon=0{\cdot}984-5{\cdot}8\times10^{-5}T$. A. A. ELDRIDGE.

Specific heat of hydrogen at high temperatures. W. H. MCCREA (Proc. Camb. Phil. Soc., 1928, **24**, 80—84).—The specific heat of hydrogen has been

recalculated on the basis of empirical values for the energy levels involved in the production of ultra-violet bands of the hydrogen molecule, as determined by Hori (A., 1927, 1005). It would appear that a simultaneous confirmation of Hori's work and of the expression $C_v=4{\cdot}659+0{\cdot}00070T$, proposed by Partington and Shilling, has been obtained. For other gases, the same statistical methods applied to vibrational frequencies deduced from band spectra lead to erroneous results. R. A. Morton.

Latent heat of fusion and heat of transformation of some metals [manganese, thallium, iron, and steel]. S. Umino (Sci. Rep. Tohoku Imp. Univ., 1927, **16**, 775—798).—The total heat content and specific heat at different temperatures up to the m. p., the heat of transformation, and the latent heat of fusion of manganese, thallium, pig iron, and various plain carbon steels have been determined by a differential calorimetric method and the results are shown in tables and graphs. The heat of transformation in g.-cal./g. of thallium at 232° is 0·6 and of manganese 2·88 at 835° and 4·43 at 1044°. The latent heat of fusion of thallium is 3·67, of manganese 64·8, and of pig iron containing 4·31% C 46·63 g.-cal./g. The heat of the A0-transformation of carbon steel at 215° increases with the carbon content, being 0·86, 1·38, and 1·63 g.-cal./g. with 0·57, 0·94, and 1·16% C, respectively; hence the heat of magnetic transformation of cementite is 9·72 g.-cal./g. The true specific heat of carbon steels rises sharply in a smooth curve to a maximum, which is greater the higher the carbon content, at 215°, then falls abruptly to little more than the value at 20°; at higher temperatures, the rise is relatively small and the curve is almost a straight line. The true specific heat of thallium falls abruptly at the transformation point and that of manganese is erratic between the two transformation points. Redeterminations of the m. p. of thallium and manganese gave 303° and 1221°, respectively. A. R. Powell.

Heats of vaporisation of *iso*propyl alcohol and ethyl alcohol. G. S. Parks and W. K. Nelson (J. Physical Chem., 1928, **32**, 61—66).—The heats of vaporisation of these alcohols have been determined in an apparatus of the type described by Awbery and Griffiths (A., 1924, ii, 541) in which the weight of alcohol vaporised at its b. p. by a measured amount of electrically supplied energy is found. The values are for *iso*propyl alcohol at 82·2°, 161·7 g.-cal./g., and for ethyl alcohol at 78·4°, 208·7 g.-cal./g. After a consideration of the values found by Brown (J.C.S., 1903, **83**, 991) and by Mathews (A., 1926, 462), the best value for *iso*propyl alcohol is suggested to be 161·0±1·5 g.-cal./g. The value now determined for ethyl alcohol lies between those found by these workers. L. S. Theobald.

Thermal magnitudes. W. Herz (Z. anorg. Chem., 1927, **168**, 86—88).—Division of the product of the cryoscopic constant and the latent heat of fusion by that of the ebullioscopic constant and the latent heat of evaporation yields an approximately constant value for all substances. H. F. Gillbe.

M. p. of benzene derivatives. T. Beacall (Rec. trav. chim., 1928, **47**, 37—44).—Examination of the m.-p. data for a large number of halogen-substituted benzene derivatives brings to light the following regularities: (i) The introduction of a pair of chlorine (or bromine) atoms in the *p*-position increases the m. p. in an approximately constant ratio, viz., by about 23% for two chlorine atoms, 26% for one chlorine and one bromine atom, and 30% for two bromine atoms. When two iodine atoms, however, are introduced, the increase in m. p. becomes progressively less as the complexity of the molecule increases. (ii) The introduction of a single asymmetric halogen atom into benzene or a symmetrically-substituted halogenobenzene, lowers the m. p. in an approximately constant ratio, *i.e.*, by about 22%. The bearing of these regularities on the structure of the molecule is discussed. Similar relationships may also be recognised between m. p. and molecular volume, but the available data are scanty. M. S. Burr.

Thermal and electrical conductivity of fused quartz as a function of temperature. H. E. Seemann (Physical Rev., 1928, [ii], **31**, 119—129).—The thermal conductivity of clear fused quartz between 235° and 1225° Abs. is represented by the equation $K=3{\cdot}83\times10^{-6}T+0{\cdot}00163$. There is an abrupt change in the thermal conductivity in the vicinity of 1140° Abs. Interpolated values of the specific resistance (ohms/cm.³) are: 550° Abs., $4{\cdot}46\times10^{9}$; 750° Abs., $2{\cdot}09\times10^{7}$; 950° Abs., $1{\cdot}35\times10^{6}$; 1150° Abs., $2{\cdot}69\times10^{5}$. A. A. Eldridge.

Hydrogen cyanide. H. Sinozaki and R. Hara (Proc. Imp. Acad. Tokyo, 1927, **3**, 590—594).—The vapour pressure of hydrogen cyanide has been determined over the temperature range 0—190°, and the pressure range 100—830 mm. The data agree well with equations of the type $PV/WT=R-bP-CP^2$ and $PV/WT=R-bP$, the former being valid for lower and the latter for higher temperatures. On the basis of an equation of state proposed by Keyes, the molar fraction of double molecules formed by association may be calculated. The fraction varies from 0·00040 to 0·0655.

The density of liquid hydrogen cyanide has been determined by the dilatometric method at approximate intervals of 5° from 0° to 30°. The results agree well with the empirical equation $V_t=V_0(1+0{\cdot}00200201t-10^{-7}\times6{\cdot}175t^2)$, where V_0 is 1·39588 c.c./g. R. A. Morton.

Determination of the vapour pressure of arsenic tri-iodide. S. Horiba and R. Inouye (Sexagint [Osaka celebration], Kyoto, 1927, 279—287).—The vapour pressure of the orange form of arsenic tri-iodide has been determined from 11° to 182°. The T-$T.\log p$ curve shows the m. p. to be about 144°; the molar heat of vaporisation is 19·2 kg.-cal. Experiments are described on the vapour pressure of the yellow modification, which is stable at low temperatures. H. F. Gillbe.

Vapour pressure, dissociation, and transition point of mercuric sulphide. J. Rinse (Rec. trav. chim., 1928, **47**, 28—32).—The vapour pressure of mercuric sulphide has been determined between 333 and 651° using a glass spring indicator. On plotting vapour pressure against temperature two curves are

obtained, intersecting at 386°±2° and 0·8 cm. of mercury. Below this temperature the red sulphide is the stable form and above it the black. This is confirmed by the change in colour and density on heating. The ($T \log p-T$) graph is not straight, indicating a change in the heat of vaporisation. This has been shown to be due to the dissociation of the sulphide, which is complete at least up to 530°. The abnormal behaviour is a result of the changing degree of association of the sulphur vapour. Changes in colour and density below the transition temperature have been observed. These are explained on Smits' theory of allotropy. Under certain conditions a high vapour pressure may be observed at temperatures at which the vapour pressure of mercuric sulphide should be very small. This may indicate the presence of an unstable mercurous sulphide, Hg_2S. M. S. BURR.

Vapour pressure and dissociation of mercuric iodide. J. RINSE (Rec. trav. chim., 1928, **47**, 33—36).—The vapour pressure of mercuric iodide has been determined between 130° and 347° by a statical method using a glass spring indicator. When $T \log p$ is plotted against T the graphs are nearly straight and intersect at the m. p., 255·5°. The heat of sublimation of the solid salt, calculated from the vapour pressure, is 20·0 kg.-cal., and the heat of vaporisation of the liquid is 15·1 kg.-cal. The difference, 4·9 kg.-cal., represents the latent heat of fusion. The degree of dissociation at 500°, 550°, and 600° has also been determined by vapour-pressure measurements. The average values of $K=(P_{Hg}\times P_{I_2})/P_{HgI_2}$ at these temperatures are, respectively, 0·01, 0·05, and 0·14. At 400° the vapour is colourless, but at 500° a slight brown colour, due to free iodine, is visible. M. S. BURR.

Vapour pressures of *iso*propyl and *tert.*-butyl alcohols. G. S. PARKS and B. BARTON (J. Amer. Chem. Soc., 1928, **50**, 24—26).—The vapour pressures of the above alcohols, measured by static methods, are recorded between 0° and 90°. The heats of vaporisation are calculated for three temperatures; the molal entropies of evaporation indicate that these alcohols are associated. S. K. TWEEDY.

Internal pressure of pure and mixed liquids. W. WESTWATER, H. W. FRANTZ, and J. H. HILDEBRAND (Physical Rev., 1928, [ii], **31**, 135—144).—The change in pressure with temperature at constant volume, γ, was determined for heptane, acetone, carbon tetrachloride, benzene, carbon disulphide, ethylene chloride, ethylene bromide, and bromoform, and for 12 50 mol.-% mixtures of these substances. The results are tabulated together with derived values for the compressibilities. γ is a function of the specific or molal volume only. For each pure liquid $v^2T_1\gamma-a$ (where v is the molal volume, and T_1 the temperature at which the pressure is 1 atm.) is constant. The values for the mixtures are less than additive, and less than those calculated from Biron's equation, but generally accord with the expression $a=(a_1a_2)^{1/2}$; still better agreement is obtained by considering that γv is additive. A. A. ELDRIDGE.

New additive property of liquids. I. N. LONGINESCU (Compt. rend., 1927, **185**, 1472—1474).—The formula $a^{1/2}V^{1/6}=KT^{1/2}V^{2/3}$, where K is a constant, a the van der Waals coefficient, T the critical temperature, and V the critical volume, respectively, expresses the additive character of the property more exactly than that of van Laar. From this, generalised forms of the equations of G. G. Longinescu and of Walden are obtained, and also an expression from which the critical temperature of a compound may be calculated from the critical data of its components. J. GRANT.

One-component system SiO_2. I. Dilatometric measurements on tridymite and cristobalite. C. J. VAN NIEUWENBURG and H. I. ZIJLSTRA (Rec. trav. chim., 1928, **47**, 1—12).—An apparatus is described for the measurement of changes in the rate of linear expansion with increase of temperature of small quantities (less than 1 g.) of powdered materials. It has been used for the determination of the following transition points: α- β-cristobalite, 220°±5°; α- → β-tridymite, 100°±7°; β- → γ-tridymite, 141°±7°. The values for tridymite are considerably lower than those found by Fenner (cf. B., 1913, 22). Certain irregularities in the behaviour of tridymite have also been observed in the neighbourhood of 440°. A semi-quantitative estimation of the composition of mixtures of tridymite and cristobalite can be made by observing the amount of expansion at the transition points relative to that of the pure constituents. The alterations in length are due to changes of crystalline form and bear no simple relation to the variations in density. Although it is possible to determine the transition point of cristobalite by the change in density, as indicated by a liquid dilatometer, this method cannot be employed for tridymite, of which the changes in density at the transition point must be less than 0·2%. M. S. BURR.

Entropy of hydrogen chloride. Heat capacity from 16° Abs. to b. p. Heat of vaporisation. Vapour pressures of solid and liquid. W. F. GIAUQUE and R. WIEBE (J. Amer. Chem. Soc., 1928, **50**, 101—122).—The vapour pressures of solid hydrogen chloride, in international cm. of mercury, are given by $\log p=-1114/T-1\cdot285\log T-0\cdot0_49467T+11\cdot005$, in agreement with the single observation of Henning and Stock (Z. Physik, 1921, **4**, 226), but in slight disagreement with the values of Henglein (A., 1923, ii, 124) and Karwat (A., 1924, ii, 822). Karwat's equation for p does not reproduce that observer's own values. The vapour pressures of the liquid acid are well represented by Henning and Stock's equation. The heat capacity of hydrogen chloride between 17·29° and 188·07° Abs. (b. p.) is recorded; a transition occurs at 98·36° Abs. and the m. p. at 158·91° Abs. The observed latent heats of transition, fusion, and evaporation are 284·3, 476, and 3860 g.-cal. per mol., respectively. The entropy of hydrogen chloride gas at the b. p. is 41·2 g.-cal./1° per mol. or 44·5 at 25°, in agreement with the values calculated from spectroscopic data, using the Lewis and the Tetrode equations. The same values, within experimental error, are calculated using the third law of thermodynamics, thus confirming the validity of this law. A pink form of hydrogen chloride, possibly a third crystalline modification, was observed. The

entropy of a gas obeying Berthelot's equation of state is lower than that of an ideal gas by $27RT_c^3p/32T^3p_c$.
S. K. TWEEDY.

Internal friction and number of molecules [per unit volume]. W. HERZ (Z. anorg. Chem., 1927, **168**, 89—92).—The variation with temperature of the internal friction between the molecules of any normal liquid is such that the sixth root of the viscosity η is proportional to the number of molecules N per unit volume. For associated liquids $N\eta^{1/6}$ increases with rise of temperature.
H. F. GILLBE.

Hagenbach correction in the determination of viscosity by the efflux method. W. RIEMAN III (J. Amer. Chem. Soc., 1928, **50**, 46—55).—The Hagenbach correction was calculated from determinations of the viscosity of water and of methyl alcohol in a viscosimeter of the Bingham type having a uniform, nearly circular, bore (cf. Knibbs, J. Proc. Roy. Soc. New South Wales, 1895, **29**, 77). The value $1{\cdot}124\pm0{\cdot}006$ was obtained (neglecting the Couette correction), in agreement with the theoretical value of Bousinesq (Compt. rend., 1891, **113**, 49). The data do not support the view that the correction decreases when the Reynolds' number exceeds 700.
S. K. TWEEDY.

Measurement of diffusion constants in liquids. G. VON BÉKÉSY (Physikal. Z., 1927, **28**, 812—814).—An interferometric method is described for the measurement of diffusion constants of liquids; data are cited relating to aqueous $0{\cdot}25N$-carbamide and water, and of aqueous $0{\cdot}25N$-potassium chloride and water, which show that the accuracy of the method is approximately 0·7%.
R. W. LUNT.

Deviations of gaseous mixtures from Dalton's law of partial pressures due to chemical causes. I. Hydrogen chloride and water. J. SHIDEI (Sexagint [Osaka celebration], Kyoto, 1927, 143—169).—Observed values of the vapour pressure of a mixture of hydrogen chloride and water in the neighbourhood of 100° are smaller than the theoretical values, but with rise of temperature approach the latter; the two values become identical at about 150°. The equilibrium constant K_c ($\times10^6$) for the equilibrium $HCl+H_2O$ H_2O,HCl at constant volume is 1026 at 110°, 1193 at 120°, 1406 at 130°, and 1898 at
H. F. GILLBE.

Dielectric constants of binary mixtures. V. Electric moments of certain organic molecules in carbon disulphide and hexane solution. J. W. WILLIAMS and E. F. OGG (J. Amer. Chem. Soc., 1928, **50**, 94—101; cf. A., 1927, 819).—Dielectric constant and density data for 25° are recorded for carbon disulphide solutions of phenol, cinnamic acid, iodine, anthracene, and hexane, and for both carbon disulphide and hexane solutions of benzoic acid, naphthalene, benzene, nitrobenzene, and chlorobenzene. The polarisation, and therefore the electric moment, of a solute molecule is independent of the non-polar solvent; benzene and the above two solvents are non-polar. The electric moment of naphthalene is in agreement with the known difference between the chemical behaviour of the two benzene rings in the molecule.
S. K. TWEEDY.

Dielectric properties of aqueous-alcoholic mixtures. P. BRUN and J. GRANIER (Compt. rend., 1928, **186**, 77—80).—If the critical miscibility of aqueous-alcoholic mixtures is accompanied by changes in the molecular condition of the liquids, variations in their dielectric capacity should also be evident. A study of mixtures of water and ethyl alcohol with *iso*butyl or *iso*amyl alcohol has shown these variations to exist and to be similar in nature to those observed for the other physical properties of such mixtures. Maxwell's rule connecting refractivity and specific inductive capacity holds for the pure liquids, but for the mixtures the dielectric capacity increases as the refractive index falls (cf. A., 1926, 683).
J. GRANT.

Binary azeotropes. VIII. M. LECAT (Rec. trav. chim., 1927, **47**, 13—18).—In continuation of previous work (A., 1927, 617, 1133), data for 154 binary mixtures are given. A number of these are azeotropes, positive or negative, some of which form two phases, either liquid or solid, at temperatures very near the constant b. p. Ten new negative azeotropes are included, eleven eutectics, and twenty-four non-azeotropic mixtures for some of which the isobars are practically rectilinear.
M. S. BURR.

Chemical affinity in metallic alloys, especially solid solutions. Compressibility. R. F. MEHL and B. J. MAIR (J. Amer. Chem. Soc., 1928, **50**, 55—73).—The compressibility data for alloys are discussed and new measurements on sixteen alloys of copper, iron, and aluminium (including "constantan") are recorded. In all cases the compressibility was less than that calculated by the rule of mixtures, the divergence being greater the greater the chemical dissimilarity of the two metals. The difference between the measured and calculated compressibility is an indication of the intensity of the chemical affinity between the unlike metal atoms. This affinity results in an increase in the lattice rigidity, so that compressibility is a measure of "chemical hardness" as distinct from "physical hardness" (slip resistance). The experimental results are correlated with the mechanical properties of the alloys. The quenching hardness in steels is not caused by increase in the cohesive forces. Attempts to measure the heat of formation of alloys of aluminium with magnesium and zinc by determining the heat of dissolution in hydrochloric acid are recorded.
S. K. TWEEDY.

Solubility of hydrogen in silver. E. W. R. STEACIE and F. M. G. JOHNSON (Proc. Roy. Soc., 1928, **A**, **117**, 662—679; cf. A., 1926, 1089).—The apparatus and experimental procedure have previously been described (*loc. cit.*). A containing vessel of fused silica was used, and corrections were made for the diffusion of hydrogen through silica. This was measured separately at temperatures from 200° to 900° and at pressures from 5 to 80 cm. The ratio P/D, where P is the pressure and D the rate of diffusion, is constant at constant temperature. This is in agreement with the results of previous investigators and indicates that the gas diffuses through silica as molecular hydrogen. The solubility of hydrogen in silver, in the form of foil (0·40 and 0·12 mm. thick),

was measured over the same range of temperature and pressure. Below 400° the solubility is extremely small; it increases rapidly with rising temperature and the values of log absorption/temperature are practically constant. At constant temperature the ratio where Q is the absorption, is constant. It follows from Henry's law that the dissolved gas must be dissociated into atoms, or else it must exist in the form of a dissolved hydride containing one atom of hydrogen to the molecule. The influence of extent of surface was found to be negligible. The absorption of hydrogen is compared with that of oxygen, the chief difference being that the solubility minimum for oxygen at 400° does not occur with hydrogen. The diffusion of gases through metals is discussed on the basis of Langmuir's theory of the mechanism of adsorption, and the connexion between absorption, adsorption, and diffusion is considered.

L. L. Bircumshaw.

Distribution and solubility of gases in fats. S. Schmidt-Nielsen (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 12).—Cod-liver oil, herring oil, linseed oil, olive oil, and mineral (transformer) oil, saturated with air at 20°, evolve the following volumes of gas per 100 g. of oil (measured at N.T.P.) when heated at 100° in a vacuum: 9·6, 5·9, 10·1, 5·0, 8·4 c.c., respectively, containing separately 21·8, 10·8, 19·1, 15·7, and 30·6% of oxygen. The amount of air absorbed at 50° is almost the same, but the oxygen contents are approximately halved in every case except that of the mineral oil, where it is practically unaltered. The lower oxygen values are probably due to the increased rate of oxidation. The four first-named oils absorb in a similar manner 13·5, 13·4, 160, and 117 c.c. of carbon dioxide per 100 g. of oil.

G. A. C. Gough.

Di-, tri-, and tetra-chloroethylene as solvents in ebullioscopy. P. Walden (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 23).—These solvents are suitable for use in the determination of the mol. wt. of many organic compounds; carboxylic acids, however, give results corresponding with double molecules. It is suggested that this is due to the combination of pairs of intramolecularly ionised molecules. The following values for the molecular elevation of b. p. are given by the data for hydrocarbons, amines, ketones, and esters on extrapolation to infinite dilution of the solute: di-, 34·4°; tri-, 44·3°; tetra-chloroethylene, 55·0°.

G. A. C. Gough.

Solubility of cellulose esters. I. II. G. Kita, I. Sakurada, and T. Nakashima (Cellulosechem., 1928, 9, 13—17, 27—29).—See this vol., 124.

Effect of impurities on the consolute temperature of the system water–phenol. G. MacKinney (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 265—266).—The discrepancy between Hill and Malisoff's value, 65·85±0·15°, for the consolute temperature of the system water–phenol (A., 1926, 571) and Rothmund's value, 68·4° (A., 1898, ii, 503), is probably due to the presence of small traces of impurities in the latter case. Experiments have been made with four different samples of phenol giving values ranging from 65·75° to 68·3°. After purification by the method of Rhodes and Markley (A., 1922, i, 135), all the values lay between 65·65° and 65·85°. By the addition of 0·85% of *o*-cresol the temperature was raised to 68·4°. Since benzoquinone, produced by oxidation of phenol, is a likely impurity, 0·17% was added, and the consolute temperature was raised from 65·75° to 66·0°, whilst 0·8% gave 66·5°. To check the shape of the solubility curve near the critical solution temperature, 29% and 35% phenol solutions were examined. They gave miscibility temperatures of 65·65° and 65·75°, respectively, in close agreement with the results of Hill and Malisoff (*loc. cit.*). The consolute temperature is probably a better test of the purity of phenol than the m. p. or b. p.

M. S. Burr.

Separation of binary liquid mixtures by silica gel. I. H. G. Grimm and H. Wolff. **II.** H. G. Grimm, W. Raudenbusch, and H. Wolff (Z. angew. Chem., 1928, **41**, 98—103, 104—107).—I. An investigation of the efficiency of processes involving silica gel in effecting a separation of binary liquid mixtures which cannot be separated by fractional distillation. Three methods have been investigated. The first consists in allowing the liquid mixture to percolate through a column of gel. In the second method the liquids are boiled and the vapours passed into a fractionating column packed with gel. In the third method the fractionating column is surrounded by a vapour jacket, so that both substances are maintained in the vapour phase. Liquid retained by the gel is recovered by heating to about 250° and collecting various fractions. The gel is regenerated by heating at 250—300° in a vacuum. The present measurements have reference to the mixture of ethyl alcohol (15·85%) and carbon tetrachloride (84·15%) of minimum b. p. The composition of the various fractions was determined refractometrically. In all cases the first fractions consist almost entirely of carbon tetrachloride. The degree of separation increases with decreasing grain size, decreasing size of pores, and increasing diameter of the column used. Using a gel of fine grain and having narrow pores, about 60% of pure carbon tetrachloride was obtained by the percolation method. The separations effected under comparable conditions by the three methods are roughly the same. On account of its simplicity the first method is to be preferred.

II. The separations effected when certain binary mixtures of various organic liquids are allowed to percolate through a column of silica gel have been investigated. When the heat changes produced by wetting silica gels with the components of the binary mixtures are compared with the results of the percolation experiments it is found that the component producing the greater heat effect is most strongly adsorbed and that the degree of separation increases with increasing difference between the heats of wetting.

The heat of wetting is influenced by various factors, *e.g.*, grain size, size of pores The following values (g.-cal./g. of gel) refer to a gel of grain size 0·2—0·5 mm. having very narrow pores: *cyclo*hexane, 6·25; hexane, 6·5; carbon tetrachloride, 7·3; chloroform, 10·9; toluene, 11·3; benzene, 11·3; propyl alcohol, 20·8; water, 20·95; methyl alcohol, 22·95; ethyl

alcohol, 23·7. A gel having much wider pores gave values about 50% smaller. Addition of small quantities of ethyl alcohol to carbon tetrachloride produces a remarkable increase in the heat of wetting, addition of 0·125% of alcohol raising the heat of wetting to a value which is approximately the arithmetic mean of the values for the two components.
J. S. CARTER.

Adsorption of substances dissolved in water by inactive and active carbon. K. SKUMBURDIS (Kolloid-Z., 1928, **44**, 127—133).—Measurements of the adsorption of a number of non-colloidal and colloidal substances by five different samples of carbon show that for all the substances investigated the samples of carbon retain the same order of effectiveness. The best adsorbents were "supra-norit 5X," "supra-norit 4X," and "carboraffin." Among the non-colloidal substances the adsorption of *iso*amyl alcohol, *iso*valeric acid, diethylamine, and sodium *iso*valerate was followed stalagmometrically by comparing the drop number with a curve relating this value to the concentration. The adsorption of sucrose was followed polarimetrically, and that of *d*-tartaric acid and quinine hydrochloride by titration. In the latter case, the solution was titrated with 0·1*N*-potassium hydroxide solution, using cresol-red as an indicator. Surface-active substances such as *iso*amyl alcohol can displace sugar from the adsorption surface to an extent depending on the nature of the carbon. The importance of this in the sugar industry is pointed out as a means of preventing loss through adsorption in the decolorisation of sugar by carbon.
E. S. HEDGES.

Sorptive power of lignin. E. WEDEKIND and G. GARRE (Z. angew. Chem., 1928, **41**, 107—112).—Lignin is a gel carrying a negative charge capable of adsorbing alkalis, ammonia, and basic dyes. The sorption is irreversible and hence indicative of subsequent formation of compounds, probably of a molecular type. The quantity of substance taken up depends on various factors (water content of the lignin, duration of the process, etc.). Sulphurous and hydrochloric acids are also fixed, the latter acid by moist lignin only, formation of solid solutions being followed by a chemical combination. Lignin takes up considerable quantities of iodine. Of the amount taken up only a fraction can be removed by thiosulphate. The fact that the solution of iodine acquires no measurable acidity, even on long keeping in contact with lignin, indicates that there is no substitution of hydrogen in the lignin molecule by iodine, but rather the saturation of some unsaturated linking. Neutral salts are not adsorbed, although there is considerable sorption of potassium hydrogen sulphite. Three types of lignin were used, obtained by Willstatter's method from oak, beech, and a wood of Japanese origin, respectively. The sorptive powers were, in general, very similar.
J. S. CARTER.

Configuration of polymethylenedicarboxylic acid. II. Adsorption of the hexahydrophthalic acids. R. KUHN and A. WASSERMANN (Helv. Chim. Acta, 1928, **11**, 70—79).—The proportion of acid adsorbed by animal charcoal under the same conditions, viz., water 5 c.c., acid 4·170 mg., and animal charcoal 5·300 mg., has been determined for all the hexahydrophthalic acids. For the *o*-, *m*-, and *p*-derivatives of the *cis*-acids the percentage amounts adsorbed were 29, 24, and 24, respectively, and for the corresponding *trans*-acids, 24, 27, and 33. The relative adsorptions of *cis*- and *trans*-acids in the *m*- and *p*-series are, qualitatively, in accordance with the solubility relationships. The greater dissociation constant of the *trans*-*p*-acid reinforces the effect of the smaller solubility, hence the large difference in adsorption between the *cis*- and *trans*-acids. In the *m*-acids the two factors oppose one another, however, and the difference in adsorbability is only small. In the case of the *o*-acids, both on account of the smaller solubility and the larger dissociation constant, the *trans*-acid might be expected to be more readily adsorbed than the *cis*-acid. That this is not so is probably due to configurative influence, the directive influence of the water on the carboxyl groups (cf. Langmuir, A., 1917, ii, 525) making it more difficult for the remainder of the molecule of the *trans*-*o*-acid to accommodate itself to the adsorbing surface than will be the case for any of the other acids. The adsorption experiments lead to the same views as to configuration as the dissociation constants (cf. this vol., 240), and since the former refer chiefly to undissociated acid and the latter to ions, it may be concluded that ionisation is not accompanied by any marked change in configuration. The adsorption isotherms for the *cis*- and *trans*-*o*-acids have been determined at 21°; the adsorption exponents of the two are almost identical, *i.e.*, $1/n = 0·42$. The adsorption isotherm of benzoic acid has also been determined at 20°
M. S. BURR.

Adsorption on barium sulphate and ultramicroscopical examination. M. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1928, **44**, 63—68).—Barium sulphate for adsorption experiments was prepared by mixing solutions of barium chloride and potassium sulphate, this method giving smaller particles than the employment of solutions of barium hydroxide and sulphuric acid of equivalent concentration. The size of the particles was determined by observation of the velocity of fall in a liquid of known viscosity. Particles of radius down to $2·5 \times 10^{-3}$ cm. could be followed with the unaided eye, and the ultramicroscope was used for the finer particles. Counting the particles under the ultramicroscope gave values for the size in agreement with those obtained by determining the velocity of fall under gravity. The phenomena of adsorption depend not only on the surface of the adsorbing substance, but also on the nature of the solution. A parallelism was observed between the adsorption and the water content of the barium sulphate particles. The results support Langmuir's view of a unimolecular adsorption layer.
E. S. HEDGES.

Absorption velocity of carbon dioxide by the still surface of sodium hydroxide solution. S. MITSUKURI and Y. SAKAMOTO (J. Chem. Soc. Japan, 1927, **48**, 495—500).—The absorption velocity of carbon dioxide by a still surface of 1—8*N*-sodium hydroxide solution at about 20° has been obtained from the rate of change of the partial pressure of the

dioxide. When the concentration of the solution is 1—3*N*, the absorption velocity is proportional to the partial pressure of the gas, which is expressed as follows: $-\Delta m/\Delta t=kp$, where $-\Delta m$ is the quantity of the dioxide absorbed during time Δt, p the partial pressure of the gas, and k a constant depending only on the concentration of the solution. For 4—8*N*-solutions of sodium hydroxide, the absorption velocity increases rapidly, which is said to be due to the auto-catalytic action of carbon dioxide which exists in the solution. The maximum absorption velocity at about 20° is obtained when the concentration of the solution is 3 or 4*N*. K. KASHIMA.

Capillarity. IX. K. SCHULTZE (Kolloid-Z., 1928, **44**, 120—127; cf. A., 1927, 625).—Theoretical. A series of symbols is proposed for use in dealing with capillary phenomena. E. S. HEDGES.

Structure of surface films. X. Phenols and monoglycerides. N. K. ADAM, W. A. BERRY, and H. A. TURNER (Proc. Roy. Soc., 1928, **A**, **117**, 532—541; cf. A., 1926, 1002).—Two series of compounds have been found in which the areas of the liquid expanded films, at no compression, differ widely from 48 Å.², and the hypothesis of coiled chains, previously advanced (*loc. cit.*), must be abandoned. The areas at no compression of the expanded liquid films of dodecylphenol, nonylphenol, α-monomyristin, and α-monopalmitin, respectively, are 37, 39, 70±3, and 70±3 Å.² The possibilities of tilted molecules are discussed, but from the evidence available it is only possible to say that there is either a definite and uniform angle of tilt at each stage of compression of the expanded films, or a motion of the molecules through various angles of tilt. Langmuir's view that the chains hold the films together against a disruptive force exerted by the heads appears to be incorrect, since the heads seem to make a considerable contribution to the lateral attraction between molecules, both in the condensed and expanded states. The monoglycerides form condensed liquid films of the close-packed head variety, the area at no compression being 26·3±0·5 Å.² Muller's suggestion (A., 1927, 503) that the chains are tilted is not incompatible with the theory of close-packed heads. The condensed film of dodecylphenol shows hysteresis, or "elastic after-working," on compression and decompression. L. L. BIRCUMSHAW.

Films of oil inside a small bubble of gas in water. H. A. MCTAGGART (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 242—254).—By a method previously described (A., 1925, ii, 509) the behaviour of minute traces of different oils on the inner surface of air bubbles in water has been observed. The following liquids with a positive spreading coefficient against pure water, viz., benzene, chloroform, oleic acid, typewriter oil, xylol, aniseed, cedarwood, castor, olive, and lavender oils, form small globules in Brownian movement on the inner surface of the bubbles. When the bubble is absorbed these are dispersed in the water, but still retain their identity. After repeated formation of these bubbles an emulsion of oil in water is ultimately obtained. If a minute trace of thorium nitrate is present there are no globules showing Brownian movement, and no dispersion of oil in water takes place. As previously shown (Phil. Mag., 1924, [vi], **27**, 297), the sign of the electric charge at the surface of the air bubble is annulled or reversed. Three liquids with negative spreading coefficients, carbon disulphide, acetylene bromide, and methylene iodide have been examined. They do not spread over the surface of the bubble, but form a pool round the edges of which globules in Brownian movement collect. This Brownian movement persists, even in the presence of thorium nitrate solution, but it may be reduced to some extent. The globules finally unite without giving an oil dispersion in water. M. S. BURR.

Laws governing molecular collisions at a surface reacting with the gas. A. PREDVODITELEV (Z. Physik, 1928, **46**, 406—419)—Cantor (Ann. Physik, 1897, **62**, 482) investigated the reaction between chlorine and a copper surface, with the view of testing the validity of the Maxwell distribution law for the gaseous pressure in a system involving collisions at a reactive surface. Cantor's results are regarded as erroneous. The question has been investigated theoretically and the equations have been tested by means of the hydration of anhydrous oxalic acid; the experimental work involved the use of a sensitive torsion balance and a microbalance; results in agreement with the theory were obtained. R. A. MORTON.

Diffusion of gaseous mixtures through membranes. D. ALEXEJEV and V. MATALSKI (J. Chim. phys., 1927, **24**, 737—741).—Previous work on the diffusion of air through rubber and cellulose (Bull. Inst. Rech. biol. Univ. Perm, 1923, **2**, 165) indicated that the solubility of the gas in the membrane is a determining factor in the coefficient of diffusion obtained. This has now been definitely demonstrated by using a membrane of water supported by cellulose which, when dry, was impervious to the gas. Atmospheric air was first dissolved by the water and then emitted in the vacuum on the other side of the membrane. In the same apparatus, which is described, the coefficients of diffusion of carbon dioxide, oxygen, acetylene, and nitrogen through a rubber membrane have been determined at different temperatures. The coefficient of diffusion $q=0{\cdot}4343\,.\,1/t\times v/PS\,.\log P/(P-p)$, where P is the external pressure of the gas, S the surface of the membrane, and t is the time during which the pressure on the other side of the membrane passes from 0 to p. The ratios of the diffusion coefficients are $Na : O_2 : C_2H_2 : CO_2 = 1 : 2{\cdot}29 : 9{\cdot}85 : 13{\cdot}7$, whilst Graham found $N_2 : O_2 : CO_2 = 1 : 2{\cdot}56 : 13{\cdot}59$. A study of the rates of diffusion of mixtures of these gases confirms the view that the velocity of diffusion of a gaseous mixture is equal to the sum of the velocities of diffusion of the components, in spite of considerable differences between these velocities and between the relative quantities of the components. M. S. BURR.

Effect of temperature on rate of osmosis. R. N. TRAXLER (J. Physical Chem., 1928, **32**, 127—141).—The influence of temperature on the rate of establishment of equilibrium between pyridine and water separated by a thin rubber membrane and between an aqueous solution of sodium chloride

(0·5M) and water separated by a membrane of collodion has been investigated. For 10° rise of temperature in the first case, the rate increases 100% between 5° and 25°, 50% between 25° and 45°, 33% between 45° and 65°, and from 33 to 25% between 65° and 85°. In the second case, the initial rate of passage of sodium chloride through collodion is greater the higher the temperature, but at the end of 30 min. dialysis, the rate becomes practically uniform for all temperatures between 25° and 65°. The results obtained in the system pyridine–rubber–water are discussed in relation to the theory that water is an equilibrium mixture of hydrol and its polymerides.
L. S. THEOBALD.

Osmosis of ternary liquids. General considerations. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 761—768).—The osmosis occurring with membranes permeable to the solvent and to each of two solutes contained in it has been examined. The theory of the process is discussed, with graphical illustrations. Experimental measurements on the progress of osmosis necessitate the removal of small quantities of liquid for analysis from time to time, and it is shown that with appropriate sampling the theoretical and experimental osmosis paths should be nearly coincident. L. F. GILBERT.

Permeability of artificial colloidal membranes. I. Action of acid-base swelling on the permeability of gelatin and agar membranes. K. J. ANSELMINO (Biochem. Z., 1928, **192**, 390—425).—Increased swelling of gelatin membranes, brought about by change of p_H, results in an increase of permeability to dextrose and surface-inactive non-electrolytes, the minimum permeability being in the neighbourhood of the isoelectric point. The swelling and permeability curves are similar. The absolute increase in permeability is, however, compensated for by increase in thickness. If a series of membranes is used such that all have the same thickness when swelling at the respective p_H values is completed, an apparent maximum permeability is obtained at the isoelectric point. From diffusion experiments it is inferred that the greater part of the water absorbed during swelling by gelatin is bound in such a way that it can no longer serve as a diffusion medium. The diffusion of a number of acid and basic dyes through gelatin and agar membranes at different p_H values has been investigated, the results being summarised in the form of curves. P. W. CLUTTERBUCK.

Cellulose nitrate membranes of graded permeability. H. F. PIERCE (J. Biol. Chem., 1927, **75**, 795—815).—The conditions affecting the permeability of collodion membranes are discussed. The preparation of such membranes of reproducible permeability is described (*a*) by a method involving the drying of the membrane for definite times under constant physical conditions and (*b*) by complete evaporation of solutions of collodion in alcohol and ether to which varying amounts of ethylene glycol have been added.
C. H. HARINGTON.

Solution volume of a solute in liquid mixtures. G. J. BURROWS (J. Proc. Roy. Soc. New South Wales, 1926, **60**. 197—207).—The specific solution volume of acetamide in solution in a mixture of water and acetone is greater than it is in either solvent alone, and the same is true for carbamide dissolved in a mixture of methyl alcohol and water. Since in both cases the formation of the solvent mixture from its components is accompanied by a considerable diminution in volume, it might appear that the apparent solution volume of a solute is determined by the amount of contraction which the solvent can undergo, *i.e.*, its compressibility, the addition of a third substance to a binary solvent mixture which shows the maximum contraction having no effect on the volume. It is not possible, however, to give a complete explanation of the volume changes on this basis. The density of solutions of methyl alcohol and of pyridine in water, acetone, and a mixture of the two has also been measured, the specific contractions for solute in solvent being found to pass through a maximum value, whilst the quotient of the total contraction by the total volume of the three components decreases regularly with the amount of solute added. The specific volume–composition curve of methyl alcohol–acetone mixtures and pyridine–water mixtures shows a minimum, but with methyl alcohol–water mixtures the maximum divergence of the curve from a straight line is not large enough to appear as a minimum on the curve. No satisfactory explanation of these various volume effects can be given, either on the assumption that decreases in volume are a consequence of closer packing resulting from the admixture of molecules of different sizes or on the basis of changes in the molecular complexity of the solvent. R. CUTHILL.

Ebullioscopic determination of the molecular state of resorcinol in aqueous solutions of sodium chloride. F. BOURION and E. ROUYER (Compt. rend., 1928, **186**, 82—84).—The authors' experiments (A., 1927, 515) are extended to solutions of resorcinol in 0·5M- and 1·225M-solutions of sodium chloride. In both cases there is evidence of an equilibrium between simple and double or triple molecules of resorcinol. Association is greater in sodium chloride than in potassium chloride solutions. The results obtained are in disagreement with the authors' view that aqueous solutions of alkali chlorides containing resorcinol should have ebullioscopic properties similar to those of water, but the deviation may be explained by the fixation of water on the salt either in the form of ions or of complete molecules. J. GRANT.

Viscosity and hydration. II. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 465—476).—See A., 1927, 413.

Variation in rotation and conductivity of certain sugars in aqueous solution with and without boric acid. I. R. VERSCHUUR (Rec. trav. chim., 1928, 47, 123—152).—According to Boeseken and Couvert (A., 1921, i, 497), the rise in specific rotation shown by certain sugars in the presence of boric acid is always accompanied by a marked increase in electrical conductivity. It is probable that there is a particular configuration of the terminal hydrogen atoms and hydroxyl groups which favours the formation of compounds with boric acid. Most sugars, on dissolution in water, undergo a transformation which can be followed with the polarimeter, and

is due to the transition from the α- to the β-form, or the reverse, until equilibrium is attained. Such a change may involve an increase or a decrease in the power to combine with boric acid, and hence a corresponding change in conductivity. The behaviour of α- and β-lactose in solution, in the presence and absence respectively of boric acid, has been examined. The effect of boric acid on the rate of change of rotation of both forms is practically negligible. Although, from the structure of lactose, which resembles that of dextrose already examined by Boeseken (*loc. cit.*), an increase in the equilibrium value of the conductivity of the sugar solution, apart from that due to boric acid alone, might be expected, there is, on the contrary, a slight decrease. This suggests that the behaviour of lactose is due to the galactose, and not to the dextrose portion of the molecule. In addition, the equilibrium values for the two forms are not identical. The conductivity of α-lactose alone, after dissolution, first increases and then decreases to the equilibrium point, but in the presence of boric acid there is a continuous decrease. The conductivity of β-lactose alone remains constant at first and then decreases. In the presence of boric acid it increases continuously. In no case is the change unimolecular. The presence of a minute trace of impurity greatly affects the result. Experiments have been made at 12·9°, 15·5°, 20·0°, and 25°. A few experiments have been carried out with melibiose. In this case also there appears to be no increase in conductivity in the presence of boric acid. Methods for the preparation of pure α- and β-lactose are given.

M. S. Burr.

Aqueous solutions of sodium silicates. VIII. General summary and theory of constitution. Sodium silicates as colloidal electrolytes. R. W. Harman (J. Physical Chem., 1928, **32**, 44—60; cf. A., 1927, 519; Cann and Gilmore, this vol., 243).—The results and conclusions of preceding papers are summarised. The data previously presented are correlated and the constitution and behaviour of aqueous solutions of sodium silicate explained. The only definite salts are those represented by Na_2SiO_3 and $NaHSiO_3$, and their hydrolysis and ionisation are in agreement with the various measurements made. Above the ratio $Na_2O:SiO_2=1:2$, colloidal silica is in evidence and its proportion increases with concentration and with the ratio $SiO_2:Na_2O$. In dilute solutions of ratio $Na_2O:SiO_2$ greater than $1:2$, crystalloidal, uncharged silica, probably metasilicic acid, occurs, and these solutions show properties characteristic of colloidal electrolytes with a micelle of complex composition (cf. A., 1927, 415). Silicic acid is an acid stronger than is usually supposed (cf. A., 1927, 519).

L. S. Theobald.

Blue colour of the cuprammonium complex. S. S. Bhatnagar, D. N. Goyle, and M. Prasad (Kolloid-Z., 1928, **44**, 79—82).—The deep blue colour of ammoniacal solutions of cupric salts is believed to be due mainly to the presence of copper hydroxide in colloidal solution. The dissolution by excess of reagent of the greenish precipitate first obtained on adding ammonia to a solution of a cupric salt is analogous to the peptisation of the similar precipitate obtained when sodium hydroxide is added to a copper salt solution in presence of sugar, gum arabic, etc. Further evidence was sought by comparing the physical properties of a cuprammonium sulphate solution with those of a sol of cupric hydroxide prepared by electrolysing a potassium chloride solution with a copper anode in presence of 1·5% of gelatin. The absorption spectra of the two solutions were examined and found to be similar, and a similar behaviour was also observed in cataphoretic experiments, both solutions depositing a greenish precipitate on the anode. On dialysis, no molecularly disperse cuprammonium compound could be found in the outer liquid, but a cuprammonium sulphate solution deposited a greenish precipitate.

E. S. Hedges.

Preparation of readily reproducible red gold sols by means of aqueous extracts of flowers. N. von Weimarn (Kolloid-Z., 1928, **44**, 41—42).—Extracts of a number of flowers (bean, pink, azalea, peony, rose, chrysanthemum) were prepared by boiling the washed petals with water and passing the infusion through a hard filter. Red gold sols of high dispersity were obtained in a few seconds when these extracts were boiled with a dilute solution of chloroauric acid. The colours of the sols produced are characteristic for each extract and are quite reproducible if the same manipulation is followed.

E. S. Hedges.

Preparation of red gold sols by reduction with extracts of fresh leaves and plants. E. Iwase (Kolloid-Z., 1928, **44**, 42—43).—Easily reproducible gold sols of a ruby colour have been prepared by adding the aqueous extracts of leaves to a boiling dilute solution of chloroauric acid. The extracts were prepared by cutting up the leaves (cherry, pine, maple, bamboo, and camellia), boiling in water, and passing through a hard filter. The most stable sols were those prepared from the camellia extract.

E. S. Hedges.

Preparation of colloidal gold solutions. Detection and determination of small amounts of gold. D. Nider (Kolloid-Z., 1928, **44**, 139—140).—Sols of colloidal gold may be prepared rapidly by reduction of an alkaline gold salt by means of a solution of mercuric iodide in excess of potassium iodide. The colour of the sol produced depends on the concentration of the solutions, but red sols are formed if the gold solution contains less than 0·0002 g. of gold per 10 c.c. The method can be applied to the gravimetric determination of small quantities of gold by precipitating the gold by addition of hydrochloric acid and warming at 80°, filtering, and weighing. The results are compared with those of other methods. A colorimetric method of determining gold in small quantities is also devised, depending on the colour of the sol produced. Examination of the gold precipitates showed that, as long as an excess of potassium iodide is used, the precipitate contains no mercury.

E. S. Hedges.

"Solid-phase" rule in the production of coarsely disperse systems. Wo. Ostwald, W. Steinbach, and R. Kohler (Kolloid-Z., 1927, **43**, 227—232).—The rule that in the direct dispersion of

a substance to form a colloidal system the amount of substance peptised at first increases, passes through a maximum, and subsequently decreases with the amount of the solid phase present also holds for the production of coarsely disperse suspensions and emulsions. Results in accordance with the rule were obtained in the emulsification of olive oil and water (with or without the addition of an emulsifier) and in the stabilisation of suspensions of charcoal by picric acid, aniline, and pyridine. It is shown that picric acid not only has a stabilising effect on a suspension of charcoal, but also causes partial dispersion.

E. S. HEDGES.

"Solid-phase" rule. WO. OSTWALD (Kolloid-Z., 1927, **43**, 249—267).—An attempt is made to classify the various types of peptisation under the following headings: adsorption-peptisation (*e.g.*, carbon in picric acid), dissolution-peptisation (metal hydroxides in acids), peptisation of swelling substances (gelatin), spontaneous colloidal dissolution (colloidal dyes), peptisation with chemical reaction (formation of basic bismuth nitrate sol by hydrolysis of the neutral salt). The "solid-phase" rule, according to which the amount of peptised colloid is not independent of the amount of solid phase present, can be explained by the principles of adsorption. If the amount of solid phase is small, adsorption is great and the substance tends to be precipitated; on the other hand, with a large excess of solid phase adsorption is so small that little colloid-chemical effect is produced. Consequently, peptisation is greatest for medium amounts of the solid phase. This view explains why the solid-phase rule applies also to the production of coarse suspensions and emulsions.

E. S. HEDGES.

Ultramicroscopical method for determining the charge on colloid particles. P. TUORILA (Kolloid-Z., 1928, **44**, 11—22).—A direct method of determining quantitatively the velocity of migration of colloid particles under an electric potential gradient is described. The measurements were carried out with the help of a slit ultramicroscope, which is more serviceable for this purpose than the cardioid and paraboloid ultramicroscopes which have been employed formerly. A special type of cuvette for the work is described. The variations in the observed velocities of migration can be expressed by Gauss' error distribution curve. The use of relatively thick cells (3—4 mm.) is recommended, and it is shown experimentally that the formula of von Smoluchowski for the electro-endosmotic velocity of the liquid stream in parallelepipedal cells is valid for the cuvette used. An open type of cell is described, which can be refilled repeatedly during the observations, thus obviating the disturbing effects of degradation products due to the electrolysis. This permits a sufficient number of observations to be made to represent the true cataphoretic velocity of the colloid particles.

E. S. HEDGES.

Nephelometric investigation of starch sols. Nephelometric law of dilution. F. H. RITTER (Biochem. Z., 1928, **192**, 337—350).—A method is described for the preparation of starch sols of high dispersion for nephelometric purposes. With these solutions, deviations from the Kleinmann rule follow a law analogous to the so-called nephelometric law of dilution, suggesting that deviations are due to changes in the particles during dilution.

P. W. CLUTTERBUCK.

Thermodynamics of dispersed systems. A. MARCH (Ann. Physik, 1927, [iv], **84**, 605—623).—From a thermodynamic analysis of dispersed systems it is shown that for particles of radius less than 10^{-7} cm. the degree of dispersion decreases with increasing concentration and increases with rise of temperature, and that the conditions governing the stability of such systems are not to be sought in the thermal agitation nor in the electrical charge of the particles.

R. W. LUNT.

Hydrodynamics of systems of variable viscosity. II. Streaming in the capillary. M. REINER and R. RIVLIN (Kolloid-Z., 1928, **44**, 9—10; cf. A., 1927, 1138).—The following equation for the resistance value of the capillary viscosimeter is derived from the specialised Einstein–Hatschek formula for the viscosity of a sol: $w=(\eta_0-$, where η_0 and η_∞ are respectively the coefficients of viscosity of the sol at rest and under extreme shearing, R is the inner radius of the capillary, l its length, p the driving pressure, and c_1 is a constant for the sol. E. S. HEDGES.

Complete solutions of Fourier's partial differential equation for given surface conditions, and application to colloid-chemical problems. E. L. LEDERER (Kolloid-Z., 1928, **44**, 108—120).—Mathematical. The equation is applied to the conductivity of heat, diffusion, swelling, and drying.

E. S. HEDGES.

Flocculation produced by mixing two colloidal solutions having particles with opposite signs. A. BOUTARIC and (MLLE.) M. DUPIN (Bull. Soc. chim., 1928, [iv], **43**, 44—48).—Experiments in which ferric hydroxide sols of varying concentration were added to an arsenious sulphide sol of fixed concentration and *vice versa* show that precipitation occurs only when the concentration of the added sol lies between certain limits. These limits are dependent on a number of factors, *e.g.*, concentration of the sol concerned, duration of previous dialysis, particle size, presence of foreign substances. The stability of each sol is, however, diminished on addition of the other in quantity insufficient to cause actual precipitation. Comparison of the velocity of cataphoresis v_0 of an arsenious sulphide sol with the velocity v of the same sol containing ferric hydroxide shows that the value of v/v_0 decreases with increasing concentration of ferric hydroxide. In the converse case the variation of v/v_0 is not so pronounced. J. S. CARTER.

Relations between hydration and stability of a sol and the anomalous coagulating influence of fluorine ions on some hydrosols. S. GHOSH and N. R. DHAR (Kolloid-Z., 1928, **44**, 149—156).—Hydrosols of cerium hydroxide, thorium hydroxide, ferric hydroxide, and stannic hydroxide prepared at the ordinary temperature were found to be more strongly hydrated than those prepared at the b. p. The coagulating power of chlorine, bromine, and iodine ions was identical for both sets of sols in the

case of cerium hydroxide and thorium hydroxide. The coagulating effect of these univalent ions was, however, greater for a ferric hydroxide sol prepared in the hot way than for such a sol prepared in the cold. For stannic hydroxide sol, the coagulating power of lithium, sodium, potassium, rubidium, and cæsium ions was the same for the sols prepared at the different temperatures. The fluorine ion is 100 times as powerful as the other halogen ions, being very close to the sulphate ion in this respect, and it is suggested that it acts as a bivalent ion F_2''. The cerium hydroxide sol prepared in the cold is of a lyophilic nature, but shows no ion-antagonism, and objections are therefore raised against the explanation of ion-antagonism given by Freundlich and Scholz (A., 1922, ii, 828). The difference between the coagulating powers of ions with the same valency cannot be related to the degree of hydration of the colloid particles or of the coagulating ions, but a high coagulating power may be due to combination of the coagulating ion with an ion already present, which is necessary for the stability of the sol, to form a non-ionised compound. E. S. HEDGES.

Flocculation of agar sols by salt mixtures. E. H. BÜCHNER and D. KLEIJN (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 740—742).—The flocculating power of binary solutions of sodium sulphate and other salts has been determined. The resultant effect follows the simple mixture rule in the case of mixtures of disodium hydrogen phosphate, sodium ferrocyanide, citrate, tartrate, thiosulphate, tungstate, molybdate, formate, acetate, and bromate, which all have positive flocculating power. For mixed solutions of sodium sulphate with sodium chlorate, bromide, iodide, dichromate, nitrate, and nitrite which appear to have negative flocculating power at most concentrations, the mixture rule is also applicable, except in the case of very small concentrations of sodium dichromate, bromide, and iodide, which act positively. Sodium chloride has little influence. These results are correlated with the opposing effects of salts on the swelling, gelatinisation, and viscosity of colloids (cf. A., 1927, 825).

L. F. GILBERT.

Dependence of the velocity of coagulation of sols of ferric hydroxide and sulphur on the concentration of the sol and of the coagulator. A. FODOR and R. RIVLIN (Kolloid-Z., 1928, **44**, 69—76).—The course of the coagulation of sols of ferric hydroxide and sulphur on addition of potassium chloride was followed continuously in an " extinctiometer," which records automatically and continuously the degree of turbidity of the sol. In the precipitation of ferric hydroxide sols by means of potassium chloride, the turbidity increases with time, at first linearly and then more rapidly, then reaches a constant value, and later falls as precipitation commences. The angle which the first, linear portion of the curve makes with the time axis was taken as a measure of the velocity of coagulation. It was found that, with sols of ferric hydroxide and of sulphur, the velocity of coagulation increases greatly with the concentration of the coagulator, the effect being greater for increasing concentrations of the sol. It is considered that with progressive dilution of a strongly solvated sol, the effect of the increase in dispersity of the solid phase becomes evident, but not the change in the number of impacts per unit time, for the particles are *a priori* protected by the sheath of molecules of solvate. E. S. HEDGES.

Coagulation of hæmoglobin in presence of alcohols. III. B. JIRGENSONS (Kolloid-Z., 1928, **44**, 76—79).—In the coagulation of hæmoglobin by potassium chloride or magnesium chloride, the presence of ethylene glycol has a sensitising influence, whilst glycerol has a stabilising effect. Measurements were made of the viscosity of water–alcohol mixtures in presence of potassium chloride and of magnesium chloride, and the viscosity of mixtures of coagulating hæmoglobin and alcohol was also measured. Hæmoglobin is more readily brought into solution by high concentrations of propyl alcohol and magnesium chloride than by low concentrations of these reagents. It is concluded that the general sensitising effect of alcohols in small concentrations is due to dehydration, but the stabilising effect observed at higher concentrations is due to the peptising influence of the salt present. This takes effect in the presence of alcohols which can increase the viscosity of the dispersion medium and lower the dielectric constant.

E. S. HEDGES.

" Acclimatisation phenomenon " in the coagulation of arsenious sulphide sols by barium chloride. W. KRESTINSKAJA and W. JAKOVLEVA (Kolloid-Z., 1928, **44**, 141—148).—When sols of arsenious sulphide are coagulated by addition of barium chloride solution, the amount of barium chloride required depends on the rate at which it is added, more being required if the electrolyte is added in small quantities at long intervals. This " acclimatisation phenomenon " has been studied and the experimental results suggest the following explanation. When barium chloride solution is added gradually, the barium ions react with the hydrolysis products of arsenious sulphide, so quickening the hydrolysis. The barium sulphide produced is adsorbed by the colloid, and consequently the barium-ion concentration of the solution is diminished, so raising the critical amount of barium chloride required for coagulation. The explanation given is supported by the fact that hydrochloric acid, which cannot promote the hydrolysis of arsenious sulphide, does not show the acclimatisation phenomenon.

E. S. HEDGES.

Dispersing action of concentrated aqueous solutions of lithium thiocyanate and lithium iodide. P. P. VON WEIMARN (Kolloid-Z., 1928, **44**, 39).—In regard to the dispersion of natural silk in concentrated solutions of very soluble salts, the author's original observations (A., 1926, 576) led to the conclusion that lithium thiocyanate has a stronger dispersing effect than lithium iodide. This was later corrected to the reverse order. Re-investigation has shown that the order of influence depends on the conditions of preparation of the lithium thiocyanate solution. The dispersing power of lithium thiocyanate is less than that of lithium iodide if the solution has been heated at a temperature of 150° or higher, and

is greater if the thiocyanate solution has been concentrated under reduced pressure at 110° or under. At high temperatures a solution of lithium thiocyanate may lose the property of dispersing silk in the cold. This effect may be due to the formation of an oxidation product. E. S. HEDGES.

Time effect of the dispersion medium in spontaneous colloidal dissolution. P. P. VON WEIMARN (Kolloid-Z., 1928, **44**, 39—40).—Natural silk dissolves completely at the ordinary temperature in saturated solutions of manganese thiocyanate or calcium thiocyanate to give a 2% solution if sufficient time (about 5 weeks) is allowed. This time effect makes it difficult to estimate the tendency of a substance towards spontaneous dispersion. The case is analogous to the extremely slow dissolution of magnesium sulphate monohydrate and of anhydrous chromic chloride in cold water. It is considered that hydration precedes dissolution. E. S. HEDGES.

Kinetics of peptisation. A. VON BUZÁGH (Kolloid-Z., 1928, **44**, 156—162).—The velocity of peptisation of ferric hydroxide gel by hydrochloric acid, of humic acid by sodium hydroxide, and of Prussian blue by potassium oxalate has been measured. The time curves obtained are autocatalytic in nature and can be expressed by the relation $dx/dt=k(1+cx)(1-x)$, where x is the amount peptised in the time t, c and k are constants, and the total amount of peptisation is made equal to 1. With increasing concentration of the peptising agent, the value of k increases and that of c decreases rapidly, so that at higher concentrations of the peptiser the course of the peptisation can be represented by the simple form $dx/dt-k(1-x)$. A study was made also of the change in the viscosity of the system during peptisation. The viscosity first rises to a maximum, then falls suddenly, and approaches a limiting value asymptotically. The maximum is reached earlier the more concentrated the solution of the peptising agent. E. S. HEDGES.

Proteins and the lyotropic series. R. A. GORTNER, W. F. HOFFMAN, and W. B. SINCLAIR (Kolloid-Z., 1928, **44**, 97—108).—A study has been made of the peptising influence of 21 inorganic salt solutions on wheat flour, the salt solutions being used at concentrations of $0 \cdot 5N$ to $2 \cdot 0N$. The results show that the effect of the anion increases according to the following series: $F<SO_4<Cl<$tartrate$<Br<I$, and that the peptising effect of the cation increases thus: $Na<K<Li<Ba<Sr<Mg<Ca$. Differences in hydrogen-ion concentration are not responsible for these results. With increasing concentration of the salt solution, the peptising power of the alkali halides decreases, but with the alkaline-earth halides the peptising effect increases with concentration, especially in the case of magnesium chloride and bromide, strontium chloride, and calcium bromide solutions. The peptisation is not due to hydrolysis, for the peptised material is no richer in amino- or carboxyl groups. The definition of "globulin" as a protein which is soluble in dilute solutions of salts of strong acids and bases is questioned, since equivalent solutions of different salts dissolve very different amounts of protein from wheat flour. E. S. HEDGES.

Influence of volume of solution on degree of swelling of disperse systems. P. N. PAVLOV (Kolloid-Z., 1928, **44**, 134—139).—Experiments were made on the swelling of hide in hydrochloric acid, sodium hydroxide, and some tanning agents, ferric hydroxide in sodium hydroxide, and animal charcoal in acetic acid. In all cases, stronger swelling took place when a large volume of solution was used than in presence of a small volume. The behaviour of ferric hydroxide varied according to its method of preparation, some forms not showing this effect. It is considered that the swelling is brought about by the attraction of the dipolar water molecules by the ions in the surface layer of the solid phase, and an explanation of the observed phenomena is advanced on these lines. E. S. HEDGES.

Relations of the solid phase in the swelling and dissolution of gelatin. WO. OSTWALD and R. KOHLER (Kolloid-Z., 1927, **43**, 233—240).—The swelling of gelatin is influenced by the ratio of the solid phase to the volume of liquid, the relative swelling falling as this ratio increases. The numerical values obtained by Küntzel (A., 1927, 19) for the swelling of gelatin in hydrochloric acid are plotted and lead to a quantitative statement of this relation. This takes the form $q/m=kv^n$, where q is the degree of swelling, m the amount of gelatin, v the relative amount of liquid, and k and n are constants. It is shown that these results are not due to the liquid being impoverished of hydrogen ions through the presence of large amounts of the solid phase. Also, similar effects were observed with three different types of gelatin in pure water. The spontaneous dissolution of gelatin in pure water increases with increasing amount of the solid phase. It is possible to obtain in this way at 20° a weakly viscous, non-gelatinising solution containing 2·5%. The influence of the amount of the solid phase on both the relative swelling and the spontaneous dissolution of gelatin is markedly less at lower temperatures. The curves are similar to those obtained by von Neuenstein (cf. B., 1927, 327) for the spontaneous dissolution of cellulose derivatives, and it is therefore considered that gelatin is a mixture of "state-isomerides" having different spontaneous dissolution tendencies. E. S. HEDGES.

Adsorption and swelling of cellulose in sodium hydroxide solutions. P. N. PAVLOV (Kolloid-Z., 1928, **44**, 44—63).—In order to examine the nature of the equilibrium between cellulose and sodium hydroxide, the adsorption and swelling of ash-free filter paper were measured in solutions of sodium hydroxide, particularly as regards the influence of the volume of solution and amount of cellulose on the adsorption isotherm. It was found that the coefficient of adsorption of sodium hydroxide by cellulose is independent of the volume of the solution or the amount of cellulose. The isotherm of true adsorption has to be differentiated from that of apparent adsorption. The swelling isotherms exhibit a maximum and a minimum. Simultaneous measurements of swelling and adsorption isotherms were undertaken. At the swelling maximum, the true adsorption isotherm shows the taking up of 1 molecule of sodium hydroxide for each molecule of cellulose.

The apparent adsorption isotherm cannot be used for ascertaining the chemical relations between cellulose and sodium hydroxide. It is further shown from the true adsorption isotherm that the compounds $C_6H_9O_5Na$, $C_6H_8O_5Na_2$, $C_6H_7O_5Na_3$, and $C_6H_6O_5Na_4$ exist in a state of electrolytic dissociation in sodium hydroxide solutions of various concentrations. The relations between cellulose and sodium hydroxide do not follow the laws of heterogeneous chemical equilibria. The reaction takes place on the surface of ultramicro-crystals of the solid phase, and the active mass of the molecules on the surface of the insoluble phase is a variable value. A thermodynamic theory is developed for surface chemical equilibria in reactions of combination, hydrolysis, and double decomposition in systems where the solid phase has a variable active mass. A theory of swelling in relation to the electrical double layer on the surface of the micelles is put forward which explains the effect of the volume of the swelling medium on the degree of swelling. E. S. HEDGES.

Electrical phenomena in colloidal solutions. G. GÉNIN (Rev. gen. Colloid., 1927, 5, 691—696, 723—729).

Diffusion of methylene-blue in gelatin gels. S. G. MOKRUSCHIN (Kolloid-Z., 1928, **44**, 32—38).—When a solution of methylene-blue is allowed to diffuse into a gelatin gel for a long period of time, the following phenomena occur. Normal diffusion takes place during the first 24 hrs. During the following 24 hrs. a marked increase in concentration of the dye occurs at the boundary of the gel and the solution. After 5 days, the boundary becomes quite colourless, whilst the colour of the liquid layer above has become lighter. The extent of the colourless zone increases with time, and the colour of the upper liquid diminishes in intensity until, after 50 days, the whole is colourless. Simultaneously, the gelatin gel shrinks. It is considered that the blank space at the boundary of the gel is analogous to the spaces between the bands of precipitate in the Liesegang phenomenon, and an explanation is advanced which is based on Ostwald's "diffusion wave" theory of Liesegang rings. Two independent processes have to be considered: adsorption of methylene-blue by the gelatin, and the decomposition of the dye. In this case, the phenomenon is due to the interference of two waves of diffusion set up by the methylene-blue and the more highly dispersed of the gelatin particles, respectively. This latter process is believed to account for the phenomenon of syneresis.

E. S. HEDGES.

Thixotropy of gelatin solution. H. FREUNDLICH and H. A. ABRAMSON (Z. physikal. Chem., 1928, **131**, 278—284).—Although gelatin gels exhibit thixotropy, the phenomenon cannot be observed easily owing to the great velocity of the reverse transformation, but is rendered more apparent by the considerable decrease of elasticity which is found after a highly elastic gel has passed through a capillary tube. The motion of coarse particles of, *e.g.*, quartz, in a gel undergoing cataphoresis indicates that the cataphoretic movement is also capable of producing thixotropic softening of the gel. H. F. GILLBE.

Viscosity and hydration. Fluids separated by syneresis and the theory of syneresis. S. LIEPATOV (Biochem. Z., 1928, **192**, 91—104).—The solutions formed from dried gelatin, agar, or geranin vary with the conditions of temperature, medium, and content of electrolytes. When a solution of geranin at 50° is cooled to 18°, a sol or gel is obtained according to the concentration. Such a system consists of a saturated solution in the molecular or ionic form and hydrated colloidal particles. Phase separation does not coincide with gelatinisation, but is present already in sol and gel. Such separation increases gradually and leads to syneresis. The concentrated colloidal phase may contain a larger amount of water than the dilute phase and the latter may not exist at all, the whole of the water being necessary for hydration. During gelatinisation, the particles which separate from the saturated solution gradually coalesce and precipitate as hydrated complexes, the velocity of the process depending on the distance between the particles, being greater the greater the gel concentration. A 0·4% gel shows syneresis after 30 days and a 0·8% gel after 2 days.

P. W. CLUTTERBUCK.

Measurement of cataphoresis in suspensoids. H. R. KRUYT and P. C. VAN DER WILLIGEN (Kolloid-Z., 1928, **44**, 22—32).—Macroscopical methods for the determination of the cataphoretic velocity of colloid particles are discussed and the various sources of error are pointed out, both for sols of high electrolyte content and for sols poor in electrolytes. It is essential to have a layer of the intermicellar liquid covering the sol. In the ordinary method of determination with the Burton apparatus, electrolytes collect at the electrodes and the potential gradient is therefore not even throughout the tube. Further, the electrolytes generally fall to the boundary of the sol, where they may undergo chemical reaction or cause other disturbances. An improved form of Burton's apparatus is described in which these and other difficulties are overcome. Some microscopical methods are discussed, and a new type of cuvette, suitable for this work, is described. E. S. HEDGES.

Thermotropism and constants of colpoids. A. L. HERRERA (Atti R. Accad. Lincei, 1927, [vi], **6**, 131—137).—The amœboid forms, termed colpoids, obtained on addition of sodium hydroxide solution to a petroleum solution of olive oil (A., 1926, 244, 435) exhibit distinct positive thermotropism, owing to increased osmosis and to the enhanced intensity of the currents prevailing at the membrane and of the chemical reactions at the hotter side. The influence of lactose, gum arabic, and egg-albumin on the magnitudes and movements of the colpoids is described.

T. H. POPE.

Weigert effect as a more general characteristic of certain colloidal systems. I. S. HORIBA and T. KONDO (Sexagint [Osaka celebration], Kyoto, 1927, 61—71).—The Weigert effect produced by the action of plane polarised light on a silver–gelatin gel has been studied, and the nature of the effect is discussed. H. F. GILLBE.

Weigert effect as a more general characteristic of certain colloidal systems. S. HORIBA and T.

KONDO (Sexagint [Osaka celebration], Kyoto, 1927, 271—272; cf. preceding abstract). By washing gelatin with conductivity water until, after addition of silver nitrate solution to the sol, no Tyndall effect due to silver chloride could be observed, it was found that the formation of colloidal silver proceeds extremely slowly even when the gelatin–silver nitrate sol is exposed to sunlight; addition of a trace of tap-water accelerates the reduction enormously. This catalytic influence of the chloride ion furnishes one of the most sensitive reactions for its detection. Bromide and iodide ions act in a similar manner, but their influence is much smaller. H. F. GILLBE.

Constant of mass action. R. D. KLEEMAN (Phil. Mag., 1928, [vii], 5, 263—271).—Molecules are divided into two classes, those which do not dissociate on isolation termed "sepro-stable" molecules and those which dissociate on isolation termed "sepro-unstable" molecules. Sepro-stable molecules obey the classical gas law, whilst sepro-unstable molecules obey a gas law of the form $v=RT/p+\Sigma A_n/p_n$, where A_n is a function of T. On this hypothesis it is shown that the constant of mass action is not a constant but is a function of the volume of the reacting mixture, its temperature, and the masses of the elementary constituents. The thermodynamic deduction is supported by kinetic considerations. A. E. MITCHELL.

Osmotic pressures of concentrated solutions. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1928, **32**, 1—43; cf. this vol., 14).—The following, equivalent expressions have been derived for the relation between vapour pressure and osmotic pressure: (a) $PV_m=RT\log_e p_0/p_1$ and (b) $PV_1=(RTN/n).\log_e p_0/p_1$, where V_m is the volume in the solution of 1 g.-mol. of the solvent in the state of vapour, and V_1 is the volume in the solution of the solvent containing 1 g.-mol. of the solute. Osmotic pressures cannot be accurately represented by the equation $PV=RT$, but if V be defined as V_1, the data of Morse and Frazer show that the equation $PV_1=RT$ is more applicable than $PV=RT$, where V is the volume of the solution. The heat of dilution represents a work term (not yet evaluated), which invalidates any equation of this form, but for ideal solutions, $PV_1=RT$ holds with an error not greater than 5% when the solute is 10 mol.-% of the solution. From (b), and in so far as $PV_1=RT$ is valid, $n/N=\log p_0/p_1$ is a general equation for the calculation of mol. wt. Raoult's law and Henry's law are said to be essentially different. The objections to van 't Hoff's relation raised by other authors have rested on incorrect definitions of the contained terms, especially of V in the expression $PV=RT$. Further, it is shown that compressibility of the solvent is not a factor in measurements of osmotic pressure. Previous methods of finding the volumes of the components of a solution are discussed and it is shown that the specific volume of the solvent can be calculated from (a) rewritten as $V_g=RT(\log p_0/p_1)/PM$, where V_g is the volume of 1 g. in the solution and M is the mol. wt. of the solvent in the condition of vapour. The value of V_g for either component can be determined from density relationships, subject to a correction, probably insignificant for solutions of moderate concentration, for possible hydrates of varying composition, thus making possible a calculation of osmotic pressures from a knowledge of densities and partial pressures. The osmotic pressures of ideal solutions of benzene and toluene are calculated from (a) and (b) and these values are satisfactorily expressed by an equation of the van der Waals type. L. S. THEOBALD.

Formation of complexes between substances dissolved in non-associated solvents. B. VON SZYSZKOWSKI (Z. physikal. Chem., 1928, **131**, 175—188).—On account of hydration the solubility of compounds containing hydroxyl and carboxyl groups in a non-associated solvent is much greater when the latter is saturated with water. The partition coefficients of salicylic, benzoic, and *o*- and *m*-nitrobenzoic acids between water and benzene at 25° are 0·3575, 0·530, 1·71, and 0·590, respectively. The following solubilities in dry benzene and in benzene saturated with water have been measured: benzoic acid $8\cdot946\times10^{-1}$ and $9\cdot222\times10^{-1}$, salicylic acid $5\cdot616\times10^{-2}$ and $7\cdot370\times10^{-2}$, *o*-nitrobenzoic acid $1\cdot656\times10^{-2}$ and $2\cdot650\times10^{-2}$, *m*-nitrobenzoic acid $1\cdot073\times10^{-1}$ and $1\cdot359\times10^{-1}$, 3 : 5-dinitrobenzoic acid $4\cdot880\times10^{-3}$ and $8\cdot676\times10^{-3}$. The association and hydration coefficients of the five acids in benzene have been calculated. The simultaneous solubility in dry benzene of various pairs of these acids is about 50% greater than the sum of the separate solubilities, and the dissociation constants of the suggested complex acids have been calculated. Measurements of the simultaneous solubility of two, three, and four different acids in dry benzene and in benzene saturated with water indicate the existence of complexes containing up to five molecules. From partition and solubility data conclusions may be reached regarding hydration in the non-associated, but not in the associated, phase. H. F. GILLBE.

Polarity of substituents in the benzene nucleus. R. KUHN and A. WASSERMANN (Helv. Chim. Acta, 1928, **11**, 3—30).—The dissociation constants in water or 50% methyl alcohol of benzoic acid, phenol, and aniline, and also of the *o*-, *m*-, and *p*-forms of dihydroxybenzene, hydroxybenzoic acid, aminophenol, chlorophenol, and chloroaniline, have been determined. Measurements were made by the hydrogen electrode or the quinhydrone electrode. In some cases the vacuum hydrogen electrode had to be employed (Kuhn and Zumstein, A., 1926, 513). It was not possible to use the hydrogen electrode for aniline and the chloroanilines, and the quinhydrone electrode could be employed only in very dilute solutions. Neither the quinhydrone electrode nor the hydrogen electrode in any form gave satisfactory results with nitroanilines. Conductivity measurements were made on these at comparable concentrations. According to Flürscheim (Chem. and Ind., 1925, **44**, 246), the general polarity effect of a substituting group may be deduced from the dissociation constants of the *p*- and *m*-substitution products by the formula $p=(K_m+K_p)/2K_u$, where K_m, K_p, and K_u are the dissociation constants of the *m*-, *p*-, and unsubstituted compounds, respectively. From the

data obtained experimentally, and the data of Farmer and Warth for nitroanilines (J.C.S., 1904, 85, 1726) the effect of different substituents on the polarity of benzoic acid, phenol, and aniline has been calculated. In the polarity series for substituents in benzoic acid (cf. Flürscheim, *loc. cit.*), the electronegative action of the different groups diminishes in the order NO_2, CO_2H, Cl, OH, Me, and NH_2. The phenol and aniline series are almost identical. It is evident, however, that the polarity of an atom or atomic group is not, as has been stated (cf. Flürscheim, *loc. cit.*), a characteristic and constant quantity, but that it depends, to a very large extent, on the nature of the compound into which the group is introduced. The effect of the *o*-substituent is a steric one, and its value, s, may be deduced from the formula $s=(K_o+K_m)/(K_m+K_p)$, where K_o is the dissociation constant of the *o*-substituted compound. In no case is s less than 1, *i.e.*, in all the compounds studied, the effect of *o*-substitution has been to raise the acidity of the compound, whether in acids, phenols, or amines. It is further evident that the *o*-effect of any given group depends to a remarkable extent on the nature of the ionising compound, and the relative effects of the different groups are not the same in the three series. The results cannot be reconciled with the supposition that the influence exercised by *o*-substituents on the dissociation constant depends in any simple manner on their atomic or ionic radii. M. S. Burr.

Dissociation constants of *o*-halogenobenzoic acids. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, 11, 31—44).—To determine the influence of the nature and position of the halogen on the affinity constants of aromatic compounds, the dissociation constants of *o*-, *m*-, and *p*-fluorobenzoic acids in water have been obtained and compared with the data of other investigators for the corresponding chlorobenzoic acids and the *o*- and *p*-bromo- and iodo-derivatives. The dissociation constants of all the monohalogen-substituted derivatives of benzoic acid have been determined in 50% methyl alcohol. The quinhydrone electrode was used and the solutions contained 0·12 g.-mol. of potassium chloride per litre, which prevented changes in the activity of the hydrogen ion through variations in the concentration of the acid and its salt. Within the limits of experimental error, the dissociation constant is practically unaffected by the nature of the halogen substituent. It depends, however, on position, *o*-, *m*-, and *p*-representing the order of diminishing dissociation constants. M. S. Burr.

Dissociation constants of phthalic acids. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, 11, 44—50).—The second dissociation constant of terephthalic acid in water has been determined, using the quinhydrone electrode, and from this, and the data of earlier investigators, it is shown that the ratios of K_1 to K_2 for phthalic, *iso*phthalic, and terephthalic acids are, respectively, 320, 12, and 20. Determinations of the two dissociation constants of all three acids have been made in 50% methyl alcohol, and the ratios are 1000, 31, and 50, respectively. That is, in both solutions, the influence of the two groups on one another is greater in the *p*- than in the *m*-position. This is comparable with the behaviour of the phenylenediamines (Kuhn and Zumstein, A., 1926, 513) and is, perhaps, related to the position of the *p*-substituent at the end of a system of conjugated double linkings. In addition, the first dissociation constant of *iso*phthalic acid is greater than that of terephthalic acid. M. S. Burr.

Configuration of polymethylenedicarboxylic acids. I. Dissociation constants of *cyclo*hexanedicarboxylic acid. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, 11, 50—70).—The two dissociation constants, K_1 and K_2, of the *cis*- and *trans*-forms of the *o*-, *m*-, and *p*-hexahydrophthalic acids have been determined in water and in 50% methyl alcohol. The extent of the influence of the two carboxyl groups on one another may be measured by the ratio K_1/K_2. The values for this ratio in water for the *o*-, *m*-, and *p*-*cis*-acids are 267, 23, and 22, and for the *trans*-acids 56, 26, and 17, respectively. In 50% methyl alcohol the values are 885, 38, and 36 for the *cis*-acids, and 85, 83, and 30 for the *trans*-acids, respectively. The regular decrease from the *o*- to the *p*-hexahydrophthalic acids appears to confirm the view that the smaller value obtained for the ratio K_1/K_2 for the *m*-compound in the phthalic acid series and the phenylenediamines is due to the conjugated double linkings of the benzene nucleus (cf. this vol., 231). The difference between the ratio for the *cis*-*m*- and the *cis*-*p*-acid is very small, being practically within the range of the experimental error. This is because, in the *cis*-compounds, owing to a screening effect of the rest of the molecule, the carboxyl groups are more independent of one another than corresponds with their relative positions in space. The *cis*-hexahydroterephthalic acid has a smaller value for K_2 than the *trans*-compound, corresponding with the difference between maleic and fumaric acids. The hydrogenated *iso*phthalic acids are the first example of *cis*-carboxyl groups which have a smaller influence on one another than the *trans*-carboxyl groups, and this difference is especially great in 50% methyl alcohol. This difference between the influence of the two solvents is greater than appears to correspond with the difference in dielectric constant and is observed also in the case of the other hexahydrophthalic acids, as well as *o*-phthalic acid. The data obtained are discussed with reference to the space models of Sachse. The same configuration cannot be given to *trans*-*o*-hexahydrophthalic acid as that deduced by Baeyer from anhydride formation unless the molecule of the *trans*-acid is not rigid. It is therefore not possible to reach conclusions as to configuration from the ability to form a ring. Similar considerations apply also to the configuration of the hydrogenated *iso*phthalic acids. The configuration of the hexahydrophthalic acids may, therefore, be best explained by the flexibility of the *cyclo*hexane residue, and by the tendency of the carboxyl groups to lie as far from one another as possible. M. S. Burr.

Conjugation relationships in naphthalene. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, 11, 79—87).—The dissociation constants of the naphthylenediamines, except the second dissociation constants of the 1 : 4-, 1 : 8-, and 2 : 3-derivatives,

which were too small to measure potentiometrically, have been determined (cf. this vol., 240). The greatest reciprocal action of the two amino-groups is observed for the 1 : 4-position. The 1 : 8-compound is about 50 times more basic than the 2 : 3-compound. Within the limits of experimental error, the ratio of the dissociation constants of the 1 : 5- and 2 : 7-compounds agree, whilst the reciprocal action between the 2- and 6-positions is double the former. The types of formulæ for benzene and naphthalene are discussed on the basis of these results. M. S. BURR.

Mol. wt. and association of chlorophyll in solution. N. MARINESCO (Compt. rend., 1928, **186**, 315—318).—By means of the expression which is obtained by combining the diffusion and Einstein viscosity equations (A., 1927, 17) the mol. wt. of chlorophyll in solutions of acetone has been found to be 816. Its coefficient of association exceeds 5·6 for 0·1—0·3% solutions, and it is deposited from 3% solutions by centrifuging. In photochemical reactions involving the use of chlorophyll, dilute solutions should be used or the associated molecules de-activate one another by molecular induction, and the reactivity is not proportional to the amount of the activating light. The extraction of chlorophyll from leaves by acetone, followed by light petroleum and methyl alcohol, and adsorption on talc is described, and yields a mixture of α- and β-chlorophylls. J. GRANT.

Behaviour of sodium and barium amalgam electrodes in solutions of amphoteric substances. P. L. KIRK and C. L. A. SCHMIDT (J. Biol. Chem., 1928, **76**, 115—136).—Measurements with sodium and barium amalgam electrodes indicate that the sodium and barium salts of glycine, aspartic acid, and glutamic acid behave as typical strong electrolytes. The curve obtained by plotting the square root of the ionic strength against the activity coefficient plus a constant is practically identical with that obtained with sodium chloride. Similarly, sodium caseinogenate behaves as a strong electrolyte, the caseinogen ion being univalent over the range of reaction investigated. Barium caseinogenate, however, behaves abnormally, owing to formation of complex ions. C. R. HARINGTON.

Theory of binary mixtures and its application to calculating the association degrees of liquids. AWA (Sexagint [Osaka celebration], Kyoto, 1927, 103—141).—The volume change which occurs when two indifferent liquids are mixed isothermally at constant pressure has been investigated mathematically and a formula derived whereby. if the degree of association of one component be known, that of the ot..er be calculated. Consistent results are obtained when the method is applied to data in the literature. H F GILLBE.

[absolute zero] state. W. JAZYNA (Physikal. Z., 1927, **28**, 908—911).—Theoretical. The thermodynamical implications of a distinction between the "quasi-permanent" equilibrium state, corresponding with the expression $Q_{T_2}/Q_{T_1}=T_2/T_1$, and permanent equilibrium state corresponding with Q_T-ST are discussed. R. A. MORTON.

Entropy of a perfect gas at 0° Abs. N. VON KOLOSOVSKI (J. Chim. phys., 1927, **24**, 621—622).—Theoretical. Planck's demonstration that the entropy of an ideal, not degenerated gas approaches infinity at 0° Abs., is disputed. Experimentally it is known that the vapour-pressure curve of a liquid touches the axis of temperature near 0° Abs., and it follows, using the Clapeyron equation, that λ, λ/T, and λ/T^2 have the limiting value 0 at T—0 (λ is the latent heat of vaporisation). Using Nernst's heat theorem and the relation $S_g-S_l-\lambda/T$, where S_g and S_l are the entropies of the gas and liquid, respectively, the result is obtained that the entropy of the gas vanishes at 0° Abs. It follows also that the specific heat of the saturated vapour and the specific heat at constant pressure become identical at this temperature. G. A. ELLIOTT.

Pseudo-constant of integration of Kirchhoff's formula. N. VON KOLOSOVSKI (J. Chim. phys., 1927, **24**, 723—726).—Theoretical. An apparent discrepancy between the limiting values for λ at absolute zero, as deduced from the Clapeyron–Clausius equation (A., 1927, 936) and Kirchhoff's formula, respectively (cf. Bennewitz, A., 1925, ii, 97), is explained. M. S. BURR.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1928, **46**, 427—443).—A general mathematical treatment is given for various equilibrium states in two-component systems. The equations deduced are applied to gold–copper alloys. Mixtures containing three constituents are also discussed. R. A. MORTON.

Theory of the Ludwig–Soret effect. M. BALLAY (Compt. rend., 1928, **186**, 232—234; cf. A., 1926, 1199).—A thermodynamical expression for the available energy of an unequally-heated solution in terms of the molecular heat of dilution and vapour pressure of the dissolved substance is obtained on the assumption that the phenomena involved are reversible, and this is shown to correspond with a series of curves of anisothermal equilibria. The expression provides an explanation of the Ludwig–Soret effect more in accordance with experimental facts than that which is based on the theory of osmosis. J. GRANT.

Activity and free energy of dilution of some salts of cadmium. F. H. GETMAN (J. Physical Chem., 1928, **32**, 91—102; cf. Horsch, A., 1920, ii, 8).—The activity coefficients of the chloride, bromide, and sulphate of cadmium at concentrations ranging from 0·001M to saturation have been calculated from the $E.M.F.$ of the cells $Cd|CdCl_2(M)|Hg_2Cl_2|Hg$, $Cd|CdBr_2(M)|Hg_2Br_2|Hg$, $Cd|CdSO_4(M)|Hg_2SO_4|Hg$, measured at 25°, and compared with the corresponding values calculated from conductivity and f.-p. data. The free energy of dilution for each salt has also been calculated. The heats of formation of cadmium chloride and bromide derived from the cell data by means of the Gibbs–Helmholtz relation are 93,710 and 74,759 g.-cal., respectively, the latter agreeing well with the value obtained by Oblata (A., 1922, ii, 343). L. S. THEOBALD.

Relation between activity of metallic ions and that of hydrogen ions in the hydrolysis of heavy metal salts. M. QUINTIN (J. Chim. phys., 1927, **24**, 712—721).—See A., 1927, 729.

Ebullioscopic paradox. A. Berthoud, E. Briner, and A. Schidlof (J. Chim. phys., 1927, **24**, 587—592).—See A., 1927, 1029.

Dissociation pressure of sodium sulphate decahydrate. II. M. Matsui, S. Fukushima, and S. Nakada (J. Soc. Chem. Ind. Japan, 1927, **30**, 330—341).—The vapour pressure of sodium sulphate decahydrate and of the products of its transition have been measured with an improved form of static isoteniscope. The results agree fairly well with those obtained statically by Wuite (A., 1914, ii, 203), but are lower than those furnished by dynamic methods. From the data, the following vapour-pressure equations are derived: $\log p = -2837{\cdot}83/T + 10{\cdot}7866$ (below 32·4°) and $-2360{\cdot}58/T + 9{\cdot}2254$ (above 32·4°). The transition point thus indicated is 32·6°.

S. Oka.

Equilibrium diagram of the zinc–antimony system. T. Takei (Sci. Rep. Tohoku, 1927, **16**, 1031—1056).—The system zinc–antimony has been re-investigated by thermal, micrographic, dilatometric, and röntgenographic analysis and by the electrical resistance method, and the accepted diagram is very considerably modified. The existence of the compounds Zn_3Sb_2 and ZnSb is confirmed; in addition the compound Zn_4Sb_3 has been found in alloys containing 35—45% Zn. All the compounds form very limited solid solutions α, β, and ε, which undergo transformation between 400° and 500°. The solid solution of Zn_3Sb_2 contains 45—46% Zn and solidifies as the phase, which is transformed into ξ at 437—455° according to the composition, and into ε at 405°. The γ solid solution of Zn_4Sb_3 in Zn_3Sb_2 is stable only above 493°, and undergoes a change at 527—530°, the nature of which is not apparent. The α solid solution exists together with free antimony in the form of a eutectic in all alloys containing up to 42% Sb and undergoes an allotropic change at 300°. The compound Zn_3Sb_2 forms a eutectic with zinc melting at 411° and containing 97% Zn. The polymorphic change at 405° occurs in all alloys containing more than 45% Zn and that at 455° in alloys containing 45—90% Zn. The antimony–ZnSb eutectic melts at 505° and contains 21% Zn. The unstable phase observed by previous investigators in alloys containing 35—42% Zn is really the γ phase supercooled below the peritectic line at 546°.

A. R. Powell.

Determination of the heterogeneous field in the system iron–nickel. K. Honda and S. Miura (Sci. Rep. Tohoku, 1927, **16**, 745—753).—Dilatometric analysis of the system iron–nickel shows that the Ac3 transformation takes place between 860° and 905° in pure iron and between 440° and 557° in the 28% Ni alloy, the temperatures of the beginning and ending of the change falling regularly on smooth curves convex to the temperature axis between these points; these curves therefore define the $\alpha+\gamma$ field in iron–nickel alloys during heating. The boundaries of this field are entirely different when the metal changes from the γ condition. On cooling the change to α starts at 889° and is completed at 850° in pure iron; it starts at 215° and is completed at 0° in the 19% Ni alloy, whilst for the 29% and 33% Ni alloys the starting temperatures are 0° and −78°, respectively. For iron containing only small quantities of nickel the lowering of the A3 transformation follows the law of depression of the f. p. in dilute solutions.

A. R. Powell.

Relationship between liquidus curves and breaks due to liquid mixtures (Fe–FeS; Fe–Cu). Rational expressions for heterogeneous equilibria. C. Benedicks (Z. physikal. Chem., 1928, **131**, 285—296).—Breaks in a binary liquidus curve may be produced by the presence of a third component which is more soluble in one of the pure components than in the mixed mass. Such a break is produced in the liquidus curve of the Fe–FeS system, of which the components are normally totally miscible, by the presence of silicon, which although soluble in molten iron is only very sparingly soluble in molten ferrous sulphide. The small quantity of silicon necessary to produce this effect may easily be introduced into the mass from the glaze of a porcelain vessel. Discrepancies between the liquidus curves of the system Fe–Cu which have been found by a number of observers are attributable to the type of disturbance described, and a diagram is described which is in agreement with the phase rule.

A number of new terms are proposed, such as "eutectol" for a fused mixture of eutectic composition.

H. F. Gillbe.

Thermal dissociation of manganese dioxide. C. Drucker and R. Hüttner (Z. physikal. Chem., 1928, **131**, 237—266).—The thermal decomposition of manganese dioxide into the sesquioxide and oxygen has been studied by a number of methods. Both oxygen pressure curves and X-ray diagrams fail to indicate the presence of either intermediate oxides or manganous oxide during the reaction. The pressure–temperature curves are greatly influenced by the physical condition of the specimen; *e.g.*, a compact form of the oxide has an oxygen pressure of 125 mm. at 530°, whereas a finely-divided form attains the same pressure at 450°. By the static method higher pressures are recorded than by the dynamic, since in the former case the film of manganese sesquioxide produced on the surface of the particles hinders the diffusion of oxygen from the interior. The reaction is practically irreversible. Manganese dioxide and sesquioxide form solid solutions, but since neither the isotherms nor the pressure curves indicate any simple relationship between the pressure and the degree of dissociation, the formation of solid solutions must take place very slowly and in a thin layer inside the particles. As usually observed, the system is therefore in false equilibrium. The heat of decomposition is about −26 kg.-cal.

H. F. Gillbe.

Cooling curves in the binary systems *p*-toluidine–salicylic acid, and *p*-toluidine–benzoic acid. (Miss) E. M. Bartholomew and I. W. Wark (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 388—391).—Cooling curves of fused binary mixtures of *p*-toluidine with salicylic or benzoic acid resemble the curve obtained by Philip for the mixture of the amine with α-naphthol (J.C.S., 1903, **83**, 814), and indicate in each case the existence of a compound

containing the two components in equimolecular proportions. R. CUTHILL.

Distillation of water-soluble organic compounds in a current of steam. A. I. VIRTANEN and L. PULKKI [Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 25].—A large number of experiments have been made to test the validity of Wiegner's equation $(\log y_1 - \log y_2)/(\log \quad - \log x_2) = k$. Consistent results are obtained for typical volatile acids, amines, phenols, aldehydes, and alcohols under constant conditions. Increase in the rate of distillation in general raises the value of k. From the values obtained it is possible to calculate the ratio of two mutually neutral substances in a distillate from their aqueous solution to within 1% of that actually obtained by experiment. The result of adding salt to the aqueous solutions is to raise the value of k. This effect is explained by the absorption of a part of the water by the salt; it is apparently not due to the elevation of the b. p. produced, since the addition of glycerol or other similar substances which raise the b. p. has no influence on the value of k.

G. A. C. GOUGH.

System: water and the sulphates of sodium and magnesium. W. C. BLASDALE and H. L. ROBSON (J. Amer. Chem. Soc., 1928, **50**, 35—46).—New data are given for the temperature range 67—210°. A complete temperature-composition diagram is given for the interval —5° to 210°. The invariant point lowite–hexahydrate–astrakhanite–solution is 59·5° and that represented by lowite–kieserite–van'thoffite–solution is between 180° and 210°, probably 190°. An apparatus is described which enables equilibrium measurements to be carried out in systems composed of two salts and water at temperatures above the b. p. of the solution.

S. K. TWEEDY.

Salting-out effect. Influence of electrolytes on solubility of *m*-cresol in water. J. S. CARTER and R. K. HARDY (J.C.S., 1928, 127—129).—Measurements were made of the solubility of *m*-cresol in electrolyte solutions, and it is shown that for solutions of sodium and magnesium chloride and sulphate the relation between the solubility s of the *m*-cresol and the concentration c of the salt is given by $s = s_0 l^{-kc}$ where s_0 has a value approximately that of the solubility in pure water and k is a constant, characteristic of each salt, which measures the salting-out effect of the salt. k is greater for the sulphates than for the chlorides. The solubility is depressed to a smaller extent in solutions of the corresponding acids, and the logarithmic relation does not hold. Measurements with phosphoric acid solutions show that the salting-out power of phosphoric acid increases in a regular manner when the dissociable hydrogen atoms are replaced by sodium, so long as the solution remains acid or neutral. W. A. RICHARDSON.

Chemical equilibrium between iron, carbon, and oxygen. Theoretical considerations of the reduction of iron ores. K. IWASE and T. WATASE (Sexagint [Osaka celebration], Kyoto, 1927, 185—201).

Equilibria in the system Fe–C–O are derived theoretically from earlier experimental data, and the mechanism of the reduction of iron ores by carbon is explained. H. F. GILLBE.

Causticisation of sodium carbonate by ferric oxide. VIII. Thermal decomposition of sodium carbonate in presence of ferric oxide and some empirical equations for the decomposition pressure. M. MATSUI (J. Soc. Chem. Ind. Japan, 1927, **30**, 180—189).—The decomposition pressure of sodium carbonate in the presence of ferric oxide at various temperatures may be represented by log $A/T + B \log T + CT + D$, and numerical values have been obtained for the various constants in this equation. The molecular heat of sodium ferrite calculated from the author's data is 44·28—44·66 g.-cal., which is greater than that indicated by the law of Neumann and Kopp. The decomposition pressure reaches 760 mm. at 1121·4° Abs.; the heat of reaction is 30,038 g.-cal. and the entropy change 26·8 g.-cal. per degree at that temperature. The entropy change per degree at the ordinary temperature is 33·2 g.-cal.

S. OKA.

Causticisation of sodium carbonate by ferric oxide. X. Thermal change of a mixture of sodium carbonate and ferric oxide in an atmosphere of carbon dioxide and the use of Nernst's micro-torsion balance. M. MATSUI and K. HAYASHI (J. Soc. Chem. Ind. Japan, 1927, **30**, 633—641).—About 2 mg. of a mixture of 1 part of sodium carbonate and 1·8 parts of ferric oxide was heated for 10 min. in a small platinum vessel in an atmosphere of carbon dioxide, and the loss of weight measured by means of a Nernst balance after cooling. The temperature of heating was raised in regular steps, and the temperature at which the loss of weight suddenly increased was taken as an indication that the decomposition pressure had reached 1 atm. The temperature 787·3° was obtained as the mean of 17 values in the range of 774·5—820·2°. This value is lower than that obtained by the authors in previous measurements. S. OKA.

"Saccharate" process and the phase rule. II. System, sucrose–barium oxide–water, at 75°. Y. HACHIHAMA (J. Soc. Chem. Ind. Japan, 1927, **30**, 435—438).—The composition of solutions and solid phases in equilibrium at 75° has been determined. Comparison with the data for 25° and 45° shows that the solubility of "barium saccharate" in the sugar or baryta solution decreases as the temperature rises. The solid phases at 75° are $C_{12}H_{22}O_{11},BaO$ and $C_{12}H_{22}O_{11},3BaO$. The latter compound is new. Y. NAGAI.

System sodium oxide–silica–water. II. Relationship between composition and b. p. of aqueous solutions of sodium silicate. (MISS) J. Y. CANN and K. E. GILMORE (J. Physical Chem., 1928, **32**, 72—90; Cann and Cheek, B., 1925, 498; Harman, this vol., 234).—The b.-p. elevations of sodium silicate solutions of ratios $Na_2O : SiO_2$ 1 : 1·995, 1 : 2·874, 1 : 3·154, and 1 : 3·753 at various concentrations have been measured by the Cottrell–Washburn method, and the activity coefficients calculated. The degree of dissociation of the solute is considered to decrease with the concentration, since the percentage elevation of the b. p. diminishes as the

concentration increases. Dilute solutions of the last ratio show elevations which are abnormally high, whilst those of concentrated solutions are abnormally low, indicating micelle formation in this ratio.

L. S. THEOBALD.

Heat of mixing of molten metals. M. KAWAKAMI (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 915—935).—See this vol., 21.

Heats of combustion and formation of calcium cyanamide. N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1927, **30**, 317—323).—Calcium cyanamide was prepared by the repeated calcination of calcium oxide with dicyanodiamide in a current of nitrogen (B., 1920, 818A). The cyanamide used contained $CaCN_2$ 98·25%, $CaCO_3$ 0·81%, CaO 0·94%. The heat of combustion was measured by a bomb calorimeter, benzoic acid being used to assist ignition. Special experiments were made to ascertain the amount of benzoic acid which sufficed for this purpose. The mean of eight determinations gave $CaCN_2+1{\cdot}5O_2=CaO+CO_2+N_2+161{,}170\pm240$ g.-cal. From this are derived: $Ca+C(diamond)+N_2=CaCN_2+86{,}010$ g.-cal., $CaC_2+N_2=CaCN_2+C(graphite)+72{,}700$ g.-cal.

S. OKA.

Conductivities of some dilute amalgams at various temperatures. A. L. JOHNS and E. J. EVANS (Phil. Mag., 1928, [vii], **5**, 271—289).—The electrical conductivities of dilute germanium, gallium, and copper amalgams of different concentrations have been measured at about 300°. The conductivities at infinite dilution were, respectively, $4{\cdot}7\times10^{-2}$, $5{\cdot}5\times10^{-2}$, and $6{\cdot}5\times10^{-2}$. The corresponding conductivities of silver amalgams have been measured between 15° and 300°. With an amalgam of concentration 0·186% the temperature coefficient of resistivity was found to increase with increasing temperature. The values are always less than those for pure mercury. Between 15° and 100° the temperature coefficient of resistivity of silver amalgams decreases with increasing concentration. For all the amalgams examined, except those of silver at 300°, the increase of conductivity relative to that of mercury at the same temperature is approximately proportional to the concentration, and the ratio of this relative conductivity to the concentration is nearly constant so long as the concentration is small.

A. E. MITCHELL.

Equivalent conductivity of strong electrolytes at infinite dilution. II. Methyl-alcoholic solutions. Effect of temperature on the constants in the equation $\Lambda_0=\Lambda+BC^n$. I. VOGEL (Phil. Mag., 1928, [vii], **5**, 199—204).—Data for solutions of a number of uni-univalent salts in methyl alcohol have been used to show that the equation $\Lambda_0=\Lambda+BC^n$ is more directly applicable than that given by the complete-ionisation theory of Debye and Hückel. For solutions of potassium iodide in nitromethane both the constants B and n increase steadily with temperature up to 55° and then pass through a maximum between 55° and 70°.

A. E. MITCHELL.

Electrical conductivity of beryllium chloride and bromide in some anhydrous organic solvents. J. M. SCHMIDT (Bull. Soc. chim., 1928, [iv], **43**, 49—62).—The solubilities of beryllium chloride at the ordinary temperature in methyl, ethyl, and amyl alcohols and pyridine are 257, 151, 154, and 133 g./litre, respectively. Measurements of the electrical conductivities of solutions of beryllium chloride in the above solvents show that the conductivities vary with concentration in a very complex manner. The molecular conductivity–dilution curves show maxima and minima in two instances and in no case can the value of be calculated from the customary Kohlrausch relation $-\mu_r=K\sqrt{C}$. The measurements are interpreted as indicating the existence of two molecular complexes, one of which exists only in dilute solutions. The solubility of beryllium bromide in ethyl bromide at the ordinary temperature is of the order of 1 g./litre. The degree of ionisation is probably small.

J. S. CARTER.

Electrolytic transference of water in aqueous hydrogen bromide solutions. G. BABOROVSKY and A. WAGNER (Z. physikal. Chem., 1928, **131**, 129—133).—Application of Baborovsky's method for the determination of electrolytic transference of water to solutions of hydrogen bromide yields for the true transport number of the cation 0·878, and for the total water transference 0·50. During the electrolysis transference of water takes place towards the cathode. On the assumption that electro-osmotic effects are negligible and that the hydrogen ion is associated with one molecule of water, each bromine ion is attached to three water molecules.

H. F. GILLBE.

Variation of electrical conductivity of solutions with field strength. M. WIEN (Physikal. Z., 1927, **28**, 834—836).—Data are given for the following solutions: potassium ferrocyanide, cerium trichloride, potassium ferricyanide, magnesium sulphate, copper sulphate, aluminium sulphate, calcium ferrocyanide, barium ferrocyanide, calcium nitrate, sodium chloride, cobalt chloride, and cadmium iodide. For aqueous and acetone solutions it has been found that the increase in conductivity with the strength of the field can be resolved into two components: a thermal effect proportional to the square of the force and a potential effect proportional to the force.

R. W. LUNT.

Behaviour of Debye electrolytes in intense fields. G. JOOS and M. BLUMENTRITT (Physikal. Z., 1927, **28**, 836—838).—It follows from Debye's theory that the conductivity of an electrolyte should increase as a function of the square of the field strength. For solutions of specific conductance 0·0002 in a field of 4×10^4 volt cm.$^{-1}$ the calculated values agree well with Wien's experimental data (cf. preceding abstract) in the case of sodium and barium chlorides and potassium sulphate; qualitative agreement is obtained for copper sulphate, aluminium chloride, and potassium ferrocyanide. It is further shown that, in accordance with theory, the observed increase in conductivity varies inversely as the square root of the dielectric constant of the solvent.

R. W. LUNT.

Free space-charges in electrolytes. A. COEHN and R. SCHNURMANN (Z. Physik, 1928, **46**, 354—373).—Free space-charges occur when a current is passed through a gas, *i.e.*, accumulations of charged carriers occur around the electrodes. A similar

phenomenon in solutions of electrolytes would involve the breakdown of the Hittorf mechanism of ionic migration. In order to obtain such an effect, highly dilute solutions of electrolytes are necessary in order to preserve the analogy with rarified gases. It has been found possible by the use of point electrodes and the investigation of electrostatic charges of gas bubbles in the liquids to demonstrate free space-charges. A recoil stream of gas bubbles is observed and is most marked when the electrode potential is small, the ionic concentration small, and the difference between the mobilities of the two ions great.

R. A. MORTON.

Electrochemical behaviour of glass. M. J. MULLIGAN and J. B. FERGUSON (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 263—264).—The coloration or deposit obtained when soda-lime glass is electrolysed, with mercury first as anode and then as cathode (Ferguson and Ellis, A., 1926, 31), is formed at places at which the high apparent resistance of the anode glass layer has been markedly reduced by current reversal. When glasses are electrolysed at 300—400°, with an anode such as mercury or carbon, soluble with difficulty, the current decreases with time, apparently due to the setting up of a large counter-*E.M.F.* nearly equal to the applied voltages. This counter-*E.M.F.* is a function of the applied voltage, but nearly constant at the higher voltages. This has made it possible to determine the true ohmic resistance of the anode layer. The resistance varies with temperature, in agreement with the rule of Rasch and Hinrichsen. The small temperature coefficient of the apparent resistance of the whole glass sample, for temperatures below 100°, may be traced to the counter-*E.M.F.*, and not to the true ohmic resistance of the anode layers. M. S. BURR.

Alternating-current electrolysis. Relation of frequency. J. W. SHIPLEY and C. F. GOODEVE (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 393—409).—The relation to current density of the rate of generation of electrolytic gases by an alternating current of frequency varying from 5 to 300 cycles has been determined for platinum, copper, and silver electrodes. As previously shown (B., 1927, 633), there is a critical current density above which alternating-current electrolysis follows the laws of direct current electrolysis, and may be made coincident with it by subtracting the critical current density from that actually used. Alternating-current electrolysis is dependent on the "electrolytic capacity of the electrode, *i.e.*, on the average storage capacity (in coulombs) for electrolytic gases of 1 sq. cm. of electrode surface. The electrolytic capacity, at constant frequency but varying current density, is constant for copper but varies with the quarter-wave area for platinum and silver electrodes. The quarter-wave area refers to the quantity of electricity that has passed before reversal of the current. The relation of the electrolytic capacity to the quarter-wave area at all frequencies is represented by the equation $Q_0—Aq_1^n$, where A and n are electrolytic absorption constants, Q_0 is the electrolytic capacity, and is the quarter-wave area. For copper n is zero, so that the electrolytic capacity equals the quarter-wave area. For platinum, n is constant at 0·62 for all frequencies when q_1 is less than 10 millicoulombs, whilst A varies from 1·53 at 20 cycles to 1·34 at 120, above which it remains constant. For silver n is constant at 0·53 up to 150 cycles, but increases to 0·66 at 200 and 0·77 at 250. A is constant at 1·92 below 150 cycles, but decreases to 1·55 at 200 cycles and 1·29 at 250 cycles. Electrolytic capacity decreases to a minimum with increase of frequency, and then remains constant for copper and platinum, but in the case of silver there is a definite rise again. The mechanism of alternating-current electrolysis is discussed. In the case of platinum the electrolytic capacity is probably due to absorption of the gases at the surface. The electrolytic capacities of copper and silver, however, are more likely to be due to the formation of oxides and possibly hydrides. An amount of hydrogen is liberated which is in excess of that required to reduce the oxide previously formed, and conversely for the oxygen. The volume R_1 of electrolytic gas liberated from one electrode per min. per sq. cm. is $4·71[I_1—A(4·44f/1000)^{1-n}I_1^n]$, where I_1 is the current density and f the frequency. The critical current density I_c, when $R_1=0$, is $A^{1/(1-n)}$ (4·44f/1000). These equations agree closely with the experimental results for platinum, copper, and silver. M. S BURR.

Electrocapillary properties of mercury in contact with air. G. COLANGE (Compt. rend., 1928, 186, 74—75).—When a gradually increasing negative potential is applied to pure mercury in a clean vertical tube (more than 0·1 mm. in diameter), the air-mercury meniscus rises to a maximum (at 15,000—20,000 volts) and then falls below its original level. When the apparatus is slowly discharged, the meniscus rises to the maximum level again and then returns to its original position. J. GRANT.

Diffusion potential of hydrochloric acid. A. BÜHL (Physikal. Z., 1927, 28, 767—770).—From measurements of the diffusion potential of hydrochloric acid at various dilutions and from a comparison of these results with the author's earlier data in sodium, potassium, and lithium chlorides it appears that the initial fall in the conductivity of a solution of hydrochloric acid which is observed when the concentration is gradually increased is due to a decrease in the velocity of agitation of the ions and not to a diminution of the degree of ionic dissociation.

R. W. LUNT.

***P.D.* at the boundary between two liquid phases.** L. W. J. HOLLEMAN and J. P. WERRE (Rec. trav. chim., 1928, 47, 105—110).—If two immiscible solvents containing the same electrolyte in solution are in equilibrium with one another, there is a definite difference of potential at their surface of separation. This has been determined for solutions of potassium chloride, hydrogen chloride, and sodium salicylate in amyl alcohol and water by means of the following cell, in which all diffusion potentials are practically eliminated: normal calomel electrode|saturated potassium chloride|2N-ammonium nitrate in methyl alcohol|MA in amyl alcohol|MA in water|saturated potassium chloride|normal calomel electrode. The values obtained are in good agree-

ment with those of Baur (A., 1925, ii, 1164; 1927, 23). They also show that, contrary to the conclusions of Abel (Z. physikal. Chem., 1924, **110**, 587), the value of the *P.D.* is influenced by concentration; *e g.*, for a concentration of 0·1 -hydrogen chloride in the aqueous phase the *E.M.F.* is 54 millivolts, whilst for a 0·04*M*-solution it is 62 millivolts. The theory of the phenomenon is discussed and earlier investigations are critically considered. M. S. BURR.

Boundary potential of textile fibres in water. P. KARRER and P. SCHUBERT (Helv. Chim. Acta, 1928, **11**, 221—229).—An apparatus is described for the determination of the *P.D.* between water and a material in the form of fibres, such as wool, silk, cotton, viscose, acetate silk, and so on. Under the influence of an applied difference of potential, E, water was allowed to pass through a tube packed with the fibres. The boundary potential, ζ, was calculated from two different formulæ. In the first the volume of water V, in mm.³ per min., passing through the tube, is equal to $q\zeta ED/4\pi\eta a$, where D is the dielectric constant of water $=81$, η is the viscosity coefficient, a the distance apart of the electrodes, and q the total cross-section of the capillaries of the fibres calculated by dividing the volume of the dry fibres by the length of the cylinder containing them. According to Smoluchowski's formula, $V=I\sigma\zeta D/4\pi\eta$, where I is the current strength and σ the specific resistance of the liquid. The second formula gives somewhat larger numerical values than the first, but of the same order. The difference may be partly ascribed to the uncertainty in the value of q in the first formula. Natural silk acquires only a very slight negative charge, —0·0005 or —0·0008 volt. Mercerised cotton becomes less acid than cotton wool, but more so than the artificial silks, except acetate silk, which is strongly negative, —0·021 or —0·036 volt. Wool is also strongly negative, —0·028 or 0·048 volt. The results are reproducible. The values obtained for the artificial silks depend on the extent to which they have been purified from adhering grease. Cotton treated with pyridine acquires a positive charge of the same order as that observed for zinc oxide, +0·01 to 0·02 volt. Under the same conditions, viscose also takes up a positive charge of smaller value. M. S. BURR.

Influence of current on solution potential of hydrogen. E. DENNINO and G. FERRARO (Gazzetta, 1927, **58**, 881—899).—The solution potential of hydrogen in sulphuric acid of d 1·22 is a function of the current density passing through the acid between electrodes of nickel and of copper, and of the time of passage of the current. The initial solution potential increases rapidly in the neighbourhood of 0·05 amp. cm.$^{-2}$ and becomes linear at about 0·5 amp. cm.$^{-2}$; when the time of passage of the current is increased to 1000 hrs. this relation persists, but the value of the solution potential, at any given current density, diminishes. R. W. LUNT.

Cuprous chloride electrodes. R. F. NIELSEN and D. J. BROWN (J. Amer. Chem. Soc., 1928, **50**, 9—19).—The *E.M.F.* at 25° of the following cells are recorded: Cu (2-phase amalgam), $CuCl(s)|xM\text{-}HCl|H_2$; H_2(700 mm.)$|HCl,0{\cdot}0478M\text{-soln.}|Cl_2(p)$; and $CuCl(s)|CuCl_2,yM|\text{soln.}|Cl_2(p)$, where x ranges from 0·02029 to 0·03564, y from 0·01 to 5·82, and p has some low value. In each case the cuprous chloride was prepared *in situ* in complete absence of oxygen. The standard potential of the copper amalgam–cuprous chloride electrode is —0·1298 volt, and $\Delta F^0_{298}=2995$ g.-cal. The values for the cuprous chloride–cupric chloride electrode are —0·5758 volt and 13,285 g.-cal., respectively. The standard free energy of solid cuprous chloride is —28,370 g.-cal. and of cupric chloride dihydrate, —44,100 g.-cal. The activity coefficients of cupric chloride over a limited range are recorded. S. K. TWEEDY.

Structure of the platinicyanides. Potential of the platino-platinicyanide electrode. H. TERREY (J.C.S., 1928, 202—206).—Measurements were made of the potential of the platino-platinicyanide electrode. Putting the value $n=2$ in the equation $E=E_0+RT/nF\log i/o$ (where i and o are respectively the concentrations of platinic and platinous ion), leads to a constant value of E_0 for a range of values of i/o, and it is concluded that in the conversion of the platinocyanide into the platinicyanide there is a valency change from 2 to 4, and that the formula for the so-called platinicyanides is more correctly represented by $K_2Pt^{IV}(CN)_4{\cdot}Pt^{II}(CN)_4$ than by the formula $KPt^{III}(CN)_4$. W. A. RICHARDSON.

Potential of solutions containing ferrous, ferric, and iodide ions and free iodine. N. SASAKI and K. NAKAMURA (Sexagint [Osaka celebration], Kyoto, 1927, 241—248).—A new method is described of measuring the potential of solutions which undergo change with time. The potential of solutions containing iron salts and iodide is influenced solely by the concentration of iodide and free iodine. H. F. GILLBE.

Thermodynamic studies of cuprous and mercuric oxides. F. ISHIKAWA and G. KIMURA (Sexagint [Osaka celebration], Kyoto, 1927, 255—269).—The *E.M.F.* of the cells $H_2|N\text{-}NaOH,HgO|Hg$ and $Cu|Cu_2O,N\text{-}NaOH,HgO|Hg$ have been determined, and the influence of various forms of mercuric oxide in the former case has been studied. Only the red form gives a constant *E.M.F.*, which is independent of the method of preparation of the oxide. The free energy changes for the reactions involved have been calculated. H. F. GILLBE.

Cells with unchanged electrodes [*K* cells] and Carnot's principle. V. KARPEN (Compt. rend., 1928, **186**, 230—232; cf. this vol., 23).—A cell formed from a platinum–platinum-black cathode and an Acheson graphite anode immersed in a saturated solution of sodium hydroxide was maintained at 95—100° for 16 hrs. The *E.M.F.* on open circuit was 0·5 volt, and after the passage of a quantity of electricity which would correspond with the dissolution of 5·5 mg. of quadrivalent platinum, the actual loss in weight of the platinum electrode was only 0·1 mg., part of which was due to mechanical losses during the washing and drying processes. The experiment, which cannot be explained by a reaction at the anode and is reproducible with slightly varied conditions, is said to be incompatible with the second law of thermodynamics. J. GRANT.

Becquerel effect. I. C. WINTHER (Z. physikal. Chem., 1928, **131**, 205—213).—The term Becquerel effect should be restricted to photogalvanic effects at the electrodes. Substances which are effective as Becquerel electrodes have a large surface, considerable power of adsorption, and are rendered better conductors by irradiation. The Becquerel effect is ascribed to a primary ionisation followed by a change in the adsorption equilibria, whilst the chemical processes which often occur are secondary side reactions. H. F. GILLBE.

Theory of passivity. I. Theory of polarisation by anodic deposition and passivation of metals. W. J. MÜLLER and K. KONOPICKY (Monatsh., 1927, **48**, 711—725; cf. A., 1924, ii, 743; 1927, 735, 942, 1145).—Electrometric investigations of the passivity of certain metals in acid media have led to the conclusion that the observed effects are most readily explained by assuming the existence of a sparingly conducting film on the metal anode. The formation of such a film, which probably consists of metal salt or basic salt, causes a progressive diminution of the effective surface of the electrode and a consequent increase in current density. Postulating the existence of such a film, an equation is derived which represents the variation of current strength with time. The equation in its abbreviated form is $1/(i_0-i)+2{\cdot}3/i_0\,.\log\{(i_0-i)/(i-i_r)\}]$, where t represents the time elapsed, i the current strength after time t, i_0 the original and i_r the residual current strengths. The quantities C and A are functions of various physical and electrochemical quantities, but may be considered as constants characteristic of the metal concerned. The equation represents in a very satisfactory manner the behaviour of copper, nickel, and iron in solutions of sulphuric acid. The behaviour of chromium is, however, anomalous, the values of A increasing with time. Calculations of the conductivity of the liquid in the pores of the anode sheath show that with iron and copper, but not with nickel, the constituent salts are probably the stable hydrated sulphates. During the deposition the potential of the metal does not change, the observed variation in potential being due to the change in resistance consequent on the growth of the deposit. The similarity between the current-time curves for copper, where no passivation occurs, and iron, which becomes actually passive, shows that passivation is due to a change in the metal and that this change occurs only at the high current densities resulting from the deposition. The present data are not sufficiently comprehensive to permit the precise evaluation of the current density necessary for passivation. Previous values of the order 10 amp./cm.^{2} are now held to be too low, the true values being probably 5—7 times as great. J. S. CARTER.

Electrochemistry of solutions of aluminium bromide in nitrobenzene. V. A. PLOTNIKOV and M. A. BENDETZKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 493—507).—See A., 1927, 832.

Kinetics of simultaneous reactions. A. SKRABAL (Ann. Physik, 1927, [iv], **84**, 624—638).—A mathematical discussion of the kinetics of simultaneous reactions in reply to the criticisms of the author's theory (A., 1927, 188) by Bodenstein (*ibid.*, 492). R. W. LUNT.

Reaction velocities. II. W. F. BRANDSMA (Rec. trav. chim., 1928, **47**, 94—104; cf. A., 1926, 913).—Theoretical. Scheffer's formula for reaction velocities deduced thermodynamically is log $(\eta_{I_{c=1}}-\eta_t)/R+C$, where k is the velocity coefficient, C a constant independent of the nature of the reacting substances, ε_I is the sum of the molecular energies, $\eta_{I_{c=1}}$ the sum of the concentration-free molecular entropies, and ε_t and η_t are an energy and entropy respectively of the "intermediate state." The latter refers to the condition of those molecules which will react in the next unit of time. A further investigation has been made of the physical significance of ε_t and η_t. With this object two examples of unimolecular reaction mechanism are discussed, one based on the classical theory and the other on the quantum theory. By calculating the energy and entropy terms for these examples, and substituting the calculated values in Scheffer's formula, the same value for the reaction constant is obtained as can be calculated directly by the method of statistical mechanics. It has been shown that η_t has a physical meaning, just like the entropy under normal conditions, and the value depends on the unit of time. The constant C, which must be a universal constant, is apparently zero for the examples considered. M. S. BURR.

Velocity of the explosion wave. P. LAFFITTE and P. DUMANOIS (Compt. rend., 1928, **186**, 146—147).—The author's method (A., 1925, ii, 135) has been used for the determination of the rates of propagation of explosion waves in various mixtures of oxygen with hydrogen, with nitrogen and hydrogen, and with methane, under initial pressures of 1—7 atm. The results have an accuracy of 2%, and show that the velocities are unaltered by the presence of lead tetraethyl (1 in 1000). J. GRANT.

Combustion of carbon monoxide. I. J. P. BAXTER (Phil. Mag., 1928, [vii], **5**, 82—96).—An account is given of preliminary experiments to compare the action of hydrogen, in combination with different elements, on the combustion of carbon monoxide. The methods are similar to those described by Harrison and Baxter (A., 1927, 211). Effects of water vapour on the combustion of carbon monoxide with air at 1 atm. original pressure have been examined. There is no apparent relationship between flame velocity and moisture content, the relationship varying with the composition of the mixture. The addition of moisture to the gas mixture caused a steady reduction in the time taken to reach the maximum temperature. Violent temperature fluctuations observed in some cases have been shown to be accompanied by corresponding pressure fluctuations. The addition of moisture reduces the time taken for the attainment of the maximum pressure and as this time decreases the rate of the subsequent cooling tends to increase. As the moisture content is increased the amounts of oxides of nitrogen produced decrease considerably. A. E. MITCHELL.

Gaseous combustion at high pressures. IX. Influence of pressure on the "explosion limits" of inflammable gas–air etc. mixtures. W. A. Bone, D. M. Newitt, and C. M. Smith (Proc. Roy. Soc., 1928, A, **117**, 553—576).—Observations have been made on the "explosion-ranges" at the ordinary temperature of hydrogen–air, methane–air, and carbon monoxide–air mixtures at varying pressures between 1 and 250 atm. In the first two cases, whilst the composition of the lower-limit mixture giving 100% combustion remains practically unchanged, the range of explosibility is progressively widened by successive increases in the initial pressure, particularly in the case of methane–air mixtures. The results on the whole confirm those of Berl and Werner (cf. B. 1927, 546). The narrowing of the limits at 10—30 atm. found by these investigators may be ascribed to the fact that they used spark ignition, instead of the electrical fusion of a platinum wire. In the case of carbon monoxide–air mixtures, the explosion range narrows considerably as the initial pressure rises. The same phenomenon is observed when the nitrogen of the air is replaced by argon or, to a much slighter extent, by helium. It is predicted that at some very high initial pressure carbon monoxide–"air" mixtures will become non-explosive at ordinary temperatures.

L. L. Bircumshaw.

Pressures produced on inflammation of mixtures of carbon monoxide and air and of hydrogen and air in a closed vessel. G. B. Maxwell and R. V. Wheeler (J.C.S., 1928, 15—21; cf. A., 1927, 317, 1036).—The authors, having had indications that the values for the dissociation of carbon dioxide found by Nernst and Bjerrum were over-estimated, applied the "maximum pressure mixture" method used by Fenning and Tizard (cf. A., 1927, 826). A mixture containing 35·5% of moist carbon monoxide gave the maximum pressure of 6·72 atm. Using Fenning and Tizard's method of calculation, the values of K_p at 2543° Abs. obtained were: Maxwell and Wheeler $1{\cdot}35\times10^{-2}$, Fenning and Tizard $1{\cdot}66\times10^{-3}$, Bjerrum $6{\cdot}4\times10^{-3}$. Expressed as % at 1 atm. the results are, respectively, 30·1%, 14·9%, and 23·4%.

In view of this result the authors criticise the method of determining the dissociation, the more particularly as it is based on the assumption that the gases are in chemical equilibrium at the moment of attainment of maximum pressure. Ellis and Wheeler have observed the phenomenon of "after burning" on exploding mixtures of carbon monoxide and air.

Similar discrepancies in the values of K_p for steam deduced by this method were observed. By repressing the dissociation with an excess of hydrogen, mean values for C_v for steam from 15° to 2120° were obtained. Details of the method of calculation are given. The value 10·8 g.-cal./g.-mol. does not alter appreciably over the range 1400—2120°. The results obtained agree well with those of Womersley (B., 1922, 163A).

H. Ingleson.

Propagation of combustion in hydrocarbon mixtures. R. Duchene (Compt. rend., 1928, **186**, 220—223).—The rates of propagation of the explosion-wave fronts in mixtures of C_6-hydrocarbons with air, which were exploded by means of an electric spark following an adiabatic compression (volumetric coefficient 4·2), rise rapidly to maxima and then fall slowly to constant values. The highest initial and maximum speeds attained correspond with an air–gas mixture richer than that required for complete combustion (cf. Pignot, B., 1926, 260), and having an air/hydrocarbon ratio of 6 (approx.). The intensity of the light emitted increases during the propagation of the flame progressively (*e.g.*, with benzene), or discontinuously (*e.g.*, with *cyclo*hexane). The second type is more usual, and since the luminosity often occurs in both the burnt and unburnt portions of the gas mixture, the combustion of the gas in two phases is indicated. The addition of lead tetraethyl (1—2%) inhibits the appearance of the second phase and this confirms the opinion of Aubert, Pignot, and Villey (cf. B., 1928, 5) that this substance reacts during a preliminary phase of the combustion.

J. Grant.

Theory of anti-detonants. P. Dumanois (Compt. rend., 1928, **186**, 292—293; cf. B., 1926, 619).—The experiments of Moureu, Dufraisse, and others (this vol., 180) and of the author have shown that the theory in which anti-detonants act as accelerators of the rate of combustion is not correct. The theory of the former authors, however, that the formation of unstable peroxide in the liquid phase during the compression period is inhibited by anti-detonators, explains the behaviour of hydrocarbons giving rise to detonation in high-compression motors, and also the phenomena associated with self-ignition. The temperature of ignition of the normal hydrocarbon mixture is of more importance than the actual proportion of anti-detonant present. J. Grant.

Thermal decomposition of nitrogen pentoxide. F. O. Rice and (Miss) D. Getz (J. Physical Chem., 1927, **31**, 1572—1580).—The decomposition of nitrogen pentoxide is not a dust reaction, since removal of phosphorus pentoxide dust by an asbestos or by an electrical filter left the velocity unchanged. Phosphorus pentoxide is apparently not a catalyst for the reaction since the velocity coefficients are unchanged when material obtained from different sources is used or when its use in the preparation of the pentoxide is eliminated. Attempts to demonstrate catalytic activity of nitric acid also failed. Nitrogen pentoxide is apparently more stable in 100% nitric acid than it is in the gaseous state or when dissolved in organic solvents. The results of Lueck (A., 1922, ii, 433) for the decomposition of the pentoxide in solutions of carbon tetrachloride have been confirmed by an independent method. L. S. Theobald.

Velocity of ionic reactions. I. R. N. J. Saal (Rec. trav. chim., 1928, **47**, 73—93).—Hartridge and Roughton's method for the determination of large velocity coefficients (A., 1923, ii, 744; 1925, ii, 47) by allowing the reacting liquids to flow together at constant velocity through a tube, and measuring various physical constants at different points, has been applied to the determination of the velocity of a number of ionic reactions. For this purpose,

variations of electrical conductivity and potential with time have been measured. The possibility of using hydrogen, quinhydrone, copper, silver, and silver iodide electrodes, and oxidation and reduction potentials, has been investigated. The reaction between hydrogen and hydroxyl ions appears to be "instantaneous," *i.e.*, it takes place in less than 0·004 sec. This is in general the case for reactions between acids, bases, and salts, provided no secondary reactions occur, such as the hydration of anhydrides, *e.g.*, carbon dioxide, in which the ion or molecule undergoes a fundamental change. These secondary reactions may proceed in measurable time, or they also may be practically instantaneous. For the most part the formation of complexes is immeasurably rapid, but the complex iron and nickel cyanides are an exception. A number of oxidation and reduction reactions are of measurable velocity, but if the difference between the normal potentials of the respective pairs of reactants is large, then the velocity of reaction is generally large also. M. S. Burr.

Rate of hydrolysis and hydrogen-ion concentration. H. Colin and (Mlle.) A. Chaudun (Compt. rend., 1928, **186**, 142—143).—If the power of hydrolysis of an acid in solution is due solely to the hydrogen-ion concentration it produces, then $(p_H - p'_H) = \log k'/k$, where $k'a'/ka$ is the ratio of the rates of initial hydrolysis of two solutions containing the quantities a' and a of sugar $(a' > a)$, and the same amounts of acid. It has been shown for $0{\cdot}1N$-solutions of hydrochloric, sulphuric, oxalic, formic, or acetic acids, containing 5% or 40% of sucrose, that this is not the case, and that in the presence of added sugar or of salts (potassium bromide, chloride, or nitrate) the variations of the hydrolysis coefficient are independent of those of the p_H value. The rate of inversion is always increased by the addition of a salt which does not contain an ion in common with the acid. The p_H value is also modified but no simple quantitative relation exists between these changes. J. Grant.

Velocity coefficient for bimolecular reactions in solution. R. G. W. Norrish and F. F. P. Smith (J.C.S., 1928, 129—138).—Lewis (A., 1918, ii, 263) has given an expression for the velocity coefficient of a bimolecular gaseous reaction, $k_T = m \times 114 \times 10^{21}[(\sigma_1+\sigma_2)/2]^2\sqrt{u_1^2+u_2^2}(e^{-E/RT})$ (1) where σ_1, σ_2 are the molecular diameters, u_1, u_2 are the velocities of the reacting molecules, m is the number of resultant molecules formed at each collision, and E is the energy of activation obtained from the temperature coefficient of the reaction. The authors have examined this equation in relation to non-ionic reactions in solution. The interactions of trimethylamine with *m*- and with *p*-nitrobenzyl chloride in benzene solution were studied at 25°, 30°, and 35°. E_1 and E_2 can be calculated for the reactions from the temperature coefficients. $E_1 - E_2$ was also calculated by using equation (1), making the assumption that no great differences exist in solvation or molecular velocity in the two cases. Thus by division the relation $\log_e k_2/k_1 = (E_1 - E_2)/RT$ is obtained. The first method gave $E_1 - E_2 = 110$ g.-cal., the second, 200 g.-cal.

An expression is deduced in which corrections for dissolution are introduced. On using this to calculate the velocity coefficient for the reaction between *p*-nitrobenzyl chloride and trimethylamine at 30° a result $1{\cdot}2 \times 10^5$ is obtained, whereas the experimental value is 0·00219. The various causes which might account for this difference are discussed.

H. Ingleson.

Comparative studies in oxidation. II. W. H. Hatcher and C. R. West (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 269—276; cf. *ibid.*, 1926, [iii], **20**, III, 327).—In the oxidation of organic substances by potassium permanganate in acid solution, formic acid is frequently an ultimate product. The rate of oxidation of $0{\cdot}02M$-formic acid by $0{\cdot}08N$-permanganate has therefore been studied in solutions of sulphuric acid of different concentrations, and also in phosphoric, acetic, and perchloric acids. The rate of oxidation is inversely proportional to the hydrogen-ion concentration. With no acid other than formic, oxidation was complete in 5 min. The results obtained have been used in the quantitative identification of formic acid as an intermediate oxidation product of the following substances: maleic, malic, oxalacetic, fumaric, malonic, tartaric, lactic, and glycollic acids, and glycol. The curves obtained by plotting time against the amount oxidised indicate two main types of reaction: the first where the oxidation begins with great rapidity and then slows down in accordance with the requirements of the formic acid, and the second where the curve rises more slowly and regularly, following the formic acid curve only after a considerable time. In the latter case there is sometimes a point of inflexion between the first and second parts of the curve. Malic, tartaric, and perhaps lactic acids are members of the first group. The oxidation of lactic acid is not so complete as that of the other acids, and gives rise to acetic acid which is not further attacked. From the form of the curves the number of molecules of formic acid produced can be determined. The following facts relating to the oxidation of these acids are deduced: oxalacetic acid is not an oxidation product of malic acid, nor tartaric of fumaric and maleic acids, pyruvic of lactic acid, oxalic of glycollic acid, nor, finally, oxalic and glyoxylic acids of glycol; malonic acid does not produce mesoxalic acid, but probably passes through tartronic to formic and glyoxylic acids, and thence gives rise to another molecule of formic acid. This method of studying the oxidation of a complex organic compound is claimed to be better than any method depending on the isolation of intermediate compounds.

M. S. Burr.

Effect of constitution of a chloroamine on its hydrolysis constant. F. G. Soper and G. F. Smith (J.C.S., 1928, 138—143).—A continuation of previous work (A., 1924, i, 1176; 1925, i, 381). A 20% acetic acid solution was employed as solvent with the object of increasing the range of concentrations within which determinations could be made. The authors conclude as a result of variation of the aryl and acyl radicals R′ and R, respectively, in the chloroamines NR′RCl that when R′ is kept constant whilst R is varied the hydrolysis constants of the

series decrease when a similar change in R in a series of fatty acids would lead to an increase in the ionisation constants of the acids. Substitution in the aryl nucleus (with R constant) causes an increase in the hydrolysis constant when a similar substitution in the phenol R'·OH would cause an increase in the ionisation constant of the phenol. It is thought that these facts may be explained by assuming that chloroamines can exist in tautomeric forms.

H. Ingleson.

Esterification in mixed solvents. B. V. Bhide and H. E. Watson (J. Indian Inst. Sci., 1927, **10A**, 71—77).—See A., 1927, 1036.

Thermal and photochemical decomposition of caryophyllene nitrosite. P. Valenzuela and F. Daniels (Philippine J. Sci., 1927, **34**, 187—197).—The thermochemical decomposition of caryophyllene nitrosite has been examined quantitatively in nitrobenzene, paraffin, and limonene solutions at 76°, 100°, and 110°. The reaction appears to be complex. The velocity coefficients differ widely in the different solvents; for nitrobenzene solutions they are abnormal, but in the other two solvents at 100—110° they are normal.

E. Holmes.

Reduction of methylene-blue in hexose–phosphate mixtures. G. Blix (Skand. Arch. Physiol., 1927, **50**, 8; Chem. Zentr., 1927, ii, 1352).—With $0 \cdot 5M$-phosphate and p_H 7·5 at 37·5° the decolorisation time falls with increasing hexose concentration; lævulose is oxidised 6—11 times as rapidly as mannose and galactose 15—20 times as rapidly as dextrose. The reaction velocity increases uniformly with increasing phosphate concentration and diminishing hydrogen-ion concentration; it is reduced or unchanged by neutral salts. Apparently, in phosphate solution the hexoses form a readily oxidisable compound (hexose-X) which attains equilibrium at 37° in 2—3 hrs. The velocity of decolorisation is increased by small (max. $10^{-4}M$) and decreased by larger concentrations of ferric or cupric salts. The favourable influence of metallic salts, but not the total oxidation, can be arrested by hydrogen cyanide. The oxidation is not affected by insulin, but is arrested by $5 \times 10^{-5}M$-adrenaline (in alkaline solution) or by $10^{-4}M$-pyrocatechol. The significance of the results is discussed in connexion with the oxidation–reduction system of the cell.

A. A. Eldridge.

Reactions depending on vapour at interface of two immiscible liquids. G. Harker and R. K. Newman (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 45—54).—The rate of the hydrolysis over a given area of an *iso*amyl acetate–dilute hydrochloric acid interface at 100° is practically equal to that of the hydrolysis which occurs over an equal area of a solution of hydrochloric acid of the same concentration when the mixed saturated vapour of water and the ester is passed over it. As in the previous experiments with benzyl chloride (A., 1924, ii, 307), it is therefore clear that at the liquid–liquid interface the saturated vapours of both liquids are present. The rate of reaction at this interface is scarcely altered by increase in pressure.

R. Cuthill.

Heterogeneous reactions with a continuously changing solid phase. I. S. Liepatov [with H. Salgaller] (Ber., 1928, **61**, [*B*], 45—55).—A study of the reaction between barium and copper acetates and nitroalizarin, used in two forms obtained respectively by decomposing the sodium salt by hydrochloric acid and washing the product with water until free from sodium and chlorine and by washing the free acid with alcohol and water. The products are colloidal but differ in degree of dispersivity as shown by their rate of reaction with copper acetate. The chemical nature of the reaction between nitroalizarin and barium acetate is established by observations on the effect of the successive treatment of the acid with barium acetate and barium hydroxide. The change cannot, however, be expressed on the basis of the usual assumption of a constant active mass of the solid phase. It is therefore assumed that the latter is appreciably, although slightly, soluble in water and that the reaction occurs mainly within it; the whole mass of the solid phase therefore participates in the change and its concentration is consequently a variable quantity. Possibly a slow reaction takes place in the liquid phase. The kinetics of the change are expressed by the equation $dx/dt = K(A-yx)$, in which y is a constant dependent on the velocity of the secondary process (cf. Liepatov, A., 1926, 674, 789). Since this equation is also applicable not only to adsorption but also to swelling and diffusion it is regarded as having its origin in Fick's law of diffusion. It is probable that the rate of chemical change is great in comparison with that of diffusion which is experimentally determined.

The influence of electrolytes (acids and salts) on the course of the change has been examined.

H. Wren.

Rate of decomposition of commercial calcium cyanide. M. S. Benjamin (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 38—44).—Treatment of a commercial calcium cyanide with sulphuric acid (1 : 4) under the ordinary pressure gave less than the theoretical amount of hydrogen cyanide, but the yield was much improved by reducing the pressure, and cooling the reactants in a freezing mixture, a fact which is probably a consequence of the readiness with which hydrogen cyanide forms secondary and polymerisation products. The rate of evolution of hydrogen cyanide at 20° in air saturated with water vapour was very low, but was somewhat greater when a growing plant was present, and very much greater in an atmosphere of carbon dioxide saturated with water vapour. Field experiments showed that, weight for weight, calcium cyanide is a more efficient fumigant than the potassium salt and sulphuric acid, presumably because calcium cyanide evolves hydrogen cyanide actually in contact with the living parts of the plant, a higher local concentration thus being attained than is possible when the potassium salt is used.

R. Cuthill.

Metallic corrosion in the light of quantitative measurements. G. D. Bengough, J. M. Stuart, and A. R. Lee (Proc. Roy. Soc., 1927, **A**, **116**, 425—467).—The present position of the theory of corrosion as chemical or electrochemical oxidation of a metal

is reviewed and discussed. The factors, independent of the corroded metal, which influence the process are the temperature, the pressure of the oxygen gas, the hydrogen-ion concentration, the amount and distribution of the oxygen supply, the nature and distribution of the corrosion products, the conductivity of the liquid, and the metal-ion concentration. The factors relating to the metal include the electrical properties of the metal, the state of aggregation, the presence of internal stresses, the overvoltage, and, for impure metals, the nature and concentration of impurities in solid solution. Previous quantitative methods of investigation are criticised and a new oxygen absorption method of measuring corrosion is described. Most of the external factors mentioned above are known and controllable. The oxygen absorption–time curves of zinc undergoing corrosion under various conditions have been obtained with the new apparatus and their interpretation is discussed.

W. E. DOWNEY.

Velocity of dissolution of aluminium. W. KUCZYŃSKI (Rocz. Chem., 1927, 7, 397—401).—The velocity of dissolution of aluminium plates in $1·5N$-hydrochloric acid diminishes if nitrates or chlorates be added to the acid. Aluminium anodes passivated in potassium chromate dissolve unevenly in the acid, giving a pitted surface. R. TRUSZKOWSKI.

Chemical properties [corrosion] of pure aluminium. C. MATIGNON and J. CALVET (Compt. rend., 1927, **185**, 909—912; cf. A., 1927, 657).—The rate of corrosion of pure aluminium (99·3%) prepared by the method of Hoopes (B., 1926, 63) has been measured in terms of the hydrogen liberated. With a $1·67N$-solution of sodium hydroxide at 23° the initial rate for pure aluminium is less than for ordinary aluminium, but the final rates are nearly the same. Pure, clean aluminium is only slightly attacked by pure hydrochloric acid ($2·65N$) at 24°. The rate of attack is greater for an uncleaned sample, and is increased by the addition of impurities such as salts of copper (1·9 mg. copper per litre) or mercury, but not by salts of iron, zinc, or tin. J. GRANT.

Intensive drying. A. SMITS (Chem. Weekblad, 1928, **25**, 82—90).—The methods, apparatus, and conclusions of the author and his co-workers are summarised. The effect of drying is to shift the equilibria which result in fluids from the existence of a very small proportion of the total molecules in an active state; this proportion is of the order of 10^{-10}, which is of the magnitude of the proportion of water molecules necessary for the activation of an inactive, completely dried system. S. I. LEVY.

Mechanism of the oxidative action of hydrogen peroxide in the presence of ferrous iron. Oxidation of glycollic acid. S. GOLDSCHMIDT, P. ASKENASY, and S. PIERROS (Ber., 1928, **61**, [B], 223 233). Hydrogen peroxide, when mixed with ferrous sulphate and glycollic or glyoxylic acid, causes oxidation within a few seconds. The extent of the reaction depends on the molecular ratio of ferrous sulphate to substrate. The change can only be caused by the ferrous salt and comes to an end when ferrous is completely converted into ferric iron. A similar change is not induced by ferric iron or by a previously-prepared mixture of ferrous salt and hydrogen peroxide. The presence of ferric iron causes a very slow consumption of hydrogen peroxide which invariably occurs when the quantity of the latter, in presence of ferrous iron and substrate, is greater than that required in the primary reaction. The greatest proportion of hydrogen peroxide per mol. of glycollic acid which can be used for exclusive production of glyoxylic acid depends on the concentration of ferrous iron and substrate and becomes more nearly equal to that used in the primary reaction as the concentration of iron diminishes. Glyoxylic acid is further oxidised to oxalic acid when its proportion has become considerable. Glycollic acid is not appreciably attacked by hydrogen peroxide alone, whereas in presence of ferric iron it is very slowly oxidised through glyoxylic to formic and carbonic acids.

Since the consumption of peroxide depends on the quantity of ferrous iron, it is highly improbable that the change is truly catalytic. It appears rather to be an induced reaction. It is unlikely, however, that *ferrous glycollate* is an intermediate product (cf. Wieland and Franke, A., 1927, 944) since the maximum consumption of hydrogen peroxide is observed with conditions (p_H 3·6) under which this salt is almost completely converted into glycollic acid. More probably the primary product is a ferrous peroxide (cf. Manchot, A., 1903, ii, 151), formed without change of valency of the metal and in part reacting with glycollic acid to give glyoxylic acid and re-form the ferrous iron, whereas a second part is converted by ferrous into ferric ions. H. WREN.

Catalysis of ethyl formate [hydrolysis] by monochloroacetic acid and of ethyl acetate [hydrolysis] by dichloroacetic acid in neutral salt solutions. H. S. HARNED and J. E. HAWKINS (J. Amer. Chem. Soc., 1928, **50**, 85—93).—On addition of halides of sodium or potassium or of sodium nitrate the velocity of hydrolysis increases rapidly and passes through a maximum; no initial increase occurs in presence of potassium nitrate and with barium chloride salt saturation occurs before the maximum is reached. Addition of sulphates produces a rapid decrease in velocity which passes through a minimum; this is due to the removal of hydrogen ions to form hydrogen sulphate ions. Methods of calculating the activity coefficients of the acids are worked out.

S. K. TWEEDY.

Acceleration of the reduction of indigo by pyridine. A. BINZ and G. PRANGE.—See B., 1928, 83.

Theory of autoxidation and anti-oxygenic action. C. MOUREU and C. DUFRAISSE (Compt. rend., 1927, **185**, 1545—1548).—A comment on the criticism by Perrin (A., 1927, 609) of the authors' theory. J. GRANT.

Autoxidation and antioxygenic action. Theory of the mechanism of the catalysis of autoxidation. C. MOUREU and C. DUFRAISSE (Compt. rend., 1928, **186**, 196—199; cf. this vol., 180).—The authors' discussion of Perrin's theory of the mechanism of oxygenic action, and of his criticism of their own theory, is continued and summarised.

The behaviour of certain catalysts both as antioxygens and as antiluminants is probably the result of independent influences, and a theory which attributes the two effects to the same cause cannot be reconciled with phenomena such as the inversion of catalysis during an auto-oxidation reaction, or the relationship of inverse catalysts. The work of Gaffron (A., 1927, 1225) is explainable by the authors' theory in which the formation of a primary peroxide, containing active oxygen only, is followed by its catalytic destruction with the liberation of all the oxygen. J. GRANT.

Reichinstein's displacement principle. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1928, **14**, 56—64).—An attempt has been made to deduce a new displacement principle for the velocity of a bimolecular reaction at a catalyst surface. Reichinstein ("Die Eigenschaften des Adsorptionsvolumens," 1916) assumed that the total number of molecules of all substances adsorbed by a given surface is constant, and independent of their concentrations in the space around the surface layer. The new work takes into account the lack of heterogeneity of the surface, and the Langmuir–Frankel theory of inelastic collisions of gaseous molecules with a solid surface.
R. A. MORTON.

Catalytic decomposition of nitric oxide. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1927, **30**, 171—180).—The author has previously found that the lowering of the yield of the product of the catalytic oxidation of ammonia by too long contact of the gas mixture on the catalyst was largely due to the catalytic decomposition of nitric oxide into nitrogen and oxygen, and concluded that the reaction is of the first order at 600°, the velocity coefficient being 1/170 of that of oxidation of ammonia for the same catalyst. This conclusion is now confirmed experimentally. The catalytic decomposition of pure nitric oxide was effected by a transpiration method by using platinum gauze and ferric oxide (with or without bismuth oxide) as catalyst at various temperatures in the range of 600—1000°. A part of the effluent gas was passed through 90% sulphuric acid, and the amount of nitric oxide decomposed was calculated from the quantity of the higher nitrogen oxide absorbed in the acid. The reaction is of the first order when the temperature is comparatively low (600—700°). At higher temperatures, however, the velocity coefficient as calculated under the assumption of the first-order reaction varies, and, indeed, it decreases gradually with the time of contact. This may be due to the oxygen set free during the reaction (cf. Green and Hinshelwood, A., 1926, 915). The velocity coefficient (as first-order reaction) at 600° is 0·39 for platinum gauze and 0·013 for ferric oxide. These two values are only 1/80 of those obtained by calculation, but the ratio of platinum and ferric oxide values is fairly concordant with the previous calculated value, *i.e.*, 28 : 1. From the temperature–velocity coefficient diagram, the temperature at which nitric oxide begins to dissociate at a platinum surface was found to be 500°, which was in good agreement with the results of various authors. S. OKA.

Reduction of potassium nitrate by water-gas. J. MILBAUER and V. JUDENIČ (Chem. Obzor, 1926, **1**, 16—22; Chem. Zentr., 1927, ii, 1338).—The action of hydrogen on a mixture of potassium nitrate and potassium or sodium hydroxide at 440—480° affords, in the presence of cupric oxide as catalyst, 96% of the calculated yield of nitrite. The action of carbon dioxide at 200—400° gave 65—70%, and of water-gas 70—75% of the calculated yield. The addition of calcium chloride effects no improvement.
A. A. ELDRIDGE.

Decomposition of calcium cyanamide. II. Action of Japanese acid earth on calcium cyanamide solution. E. TOMITA (J. Soc. Chem. Ind. Japan, 1927, **30**, 194—198).—The freshly-prepared calcium cyanamide was extracted with water, the solution was added with various amounts of Japanese acid earth, and the whole kept stirred for 1 hr. at various temperatures between 0° and 90°, the amounts of cyanamide in the filtered solution being compared. Addition of the acid earth diminished the alkalinity of the extracted solution and lessened the decomposition in the solution. The effect is more marked if the acid earth is previously dried at 105°. The higher the temperature, the greater was the amount of decomposition, the difference being more marked in the case of the undried earth. N. KAMEYAMA.

Catalytic activity of metallised silica gels. III. Synthesis of water. L. E. SWEARINGEN and L. H. REYERSON (J. Physical Chem., 1928, **32**, 113—120; cf. A., 1927, 839, 1038).—The catalytic activity of the gels previously used (A., 1927, 198) in synthesising water from mixtures of oxygen (6—9%), hydrogen (50%), and nitrogen has been determined over the temperature range −17° to 290° at various rates of flow. The silverised gel initiates the reaction below 100° and its efficiency increases with rise of temperature, the most rapid increase occurring between 140° and 180°. Above 200°, the whole of the oxygen present is removed. The copperised gel shows a measurable reaction at 80°, and the efficiency increases steadily to 165°, when a rapid rise occurs, and at 200° complete conversion of the oxygen into water takes place. The platinum and palladium gels are 100% efficient at all temperatures studied provided the rate of flow of the gas mixture is sufficiently slow, and the platinum gel is the more efficient of the two with the faster rates of flow. The copper catalyst compares favourably with that prepared by Pease and Taylor (A., 1922, ii, 701). L. S. THEOBALD.

Catalysis and the dissolution of aluminium. M. CENTNERSZWER (Z. physikal. Chem., 1928, **131**, 214—225).—Metals which reduce the overvoltage of hydrogen greatly accelerate the dissolution of aluminium in acids when the two metals are placed in contact, on account of the activation of the surface due to removal of the passive layer. In sulphuric acid aluminium is so strongly passive that even platinum is incapable of producing activation, which is, however, gradually brought about by addition of chlorine ions to the solution. Amalgamated aluminium dissolves in *N*-hydrogen chloride solutions 25 times as rapidly as does the pure metal, there

being an induction period of 2 hrs. The maximum velocity of evolution of hydrogen from water by the amalgamated metal is 0·12 cm.^{3}/min./cm.^{2}; the surface of the metal rapidly becomes covered with a grey film of aluminium hydroxide, and the dissolution velocity diminishes. H. F. GILLBE.

Copper sulphate as the Deacon chlorine catalyst ? R. A. BEEBE and D. B. SUMMERS (J. Amer. Chem. Soc., 1928, **50**, 20—24; cf. Taylor, A., 1926, 365).—Hydrogen chloride converts anhydrous copper sulphate quantitatively into copper chloride (or oxychloride) at 450° within 6 hrs. The latter compound, therefore, is the true catalyst when copper sulphate is used in the Deacon process.

S. K. TWEEDY.

[Catalytic] conversion of alcohols into petroleum spirit. A. MAILHE and RENAUDIE.—See B., 1928, 117.

Catalytic preparation of formaldehyde. B. NEUMANN and P. BILJCEVIC.—See B., 1928, 82.

Catalytic decomposition of formic acid vapour. C. H. D. CLARK and B. TOPLEY (J. Physical Chem., 1928, **32**, 121—126).—The catalytic decomposition of formic acid vapour has been studied by the methods previously used (Hinshelwood and Topley, J.C.S., 1923, **123**, 1014) at 210° for osmium, nickel, tungsten, molybdenum, and tantalum. The values of the unimolecular velocity coefficient, k_{CO_2}, calculated for 200° and a surface of catalyst 1 cm.^{2} in a reaction bulb of 20 c.c. are for osmium $9{\cdot}2\times10^{-2}$, and for nickel 1×10^{-4}. The values of k_{CO}, calculated on the same basis, for silica, pyrex and soda glasses, and tungsten are 1×10^{-6}, $1{\cdot}5\times10^{-6}$, 4×10^{-6}, and $2{\cdot}5\times10^{-5}$, respectively. With molybdenum and tantalum, the decomposition does not follow the usual course, a marked excess of hydrogen being produced, and with nickel, under the conditions employed, no methane was formed (cf. Wescott and Engelder, A., 1926, 693). L. S. THEOBALD.

Improved activated magnesium for the preparation of the Grignard reagent and a comparative study of various catalysts. H. GILMAN, J. M. PETERSON, and F. SCHULZE (Rec. trav. chim., 1928, **47**, 19—27).—By heating with iodine in a vacuum an alloy of magnesium containing 12·75% of copper, a product is obtained which is much more active in Grignard reactions than Baeyer's activated magnesium. It is only necessary to use this compound to start the reaction, which may be continued with the ordinary magnesium catalyst. The copper-magnesium compound loses its activity by exposure to the air for a short time but becomes still more highly active when re-heated. Comparative tests have also been made with a number of catalysts other than activated magnesium. M. S. BURR.

Negative catalysts for the hydrogenation of fatty oils. IV. Influence of impurities in the catalyst-carriers. S. UENO and T. SAIDA (J. Soc. Chem. Ind. Japan, 1927, **30**, 374—377).—A sample of the kieselguhr was recovered from a spent nickel catalyst by treatment with dilute sulphuric acid and alkali. Nickel catalysts were prepared by using the original and the recovered kieselguhr, and the results were compared. The recovered kieselguhr was as effective as the original material, in spite of the fact that the former contained much impurity, especially calcium sulphate, which would have had a retarding influence on the catalytic reaction. It is concluded that the inhibiting influence of these impurities depends on their existence in the system in a peculiar form. Y. TOMODA.

Electrolytic formation of magnesium amalgam and its decomposition by the air. N. W. KONDYREV (Ber., 1928, **61**, [*B*], 208—212).—Magnesium amalgam is obtained by electrolysis of an ethereal solution of magnesium ethyl bromide using a mercury cathode and a magnesium anode. The product usually contains less than 1% of magnesium but richer alloys are prepared by squeezing the warmed amalgam and collecting the crystalline portion. The amalgam reacts readily with moist air at temperatures below 40—50° with production of magnesium hydroxide and hydrogen. Above this temperature interval reaction does not occur to any great extent in ordinary air although decomposition takes place in air saturated with aqueous vapour at all temperatures between 15° and 100°. Examination of the electrical resistance, cooling curve, and change in *E.M.F.* with varying temperature does not disclose any discontinuity. The increasing apathy of magnesium amalgam towards air with rise of temperature is attributed therefore to the increasing "humidity deficit." H. WREN.

Electrochemical oxidation of β-phenylpropionic acid. F. FICHTER and R. SENTI (Festschr. A. Tschirch. 1926, 410—414; Chem. Zentr., 1927, ii, 54—55).—Electrolytic oxidation of β-phenylpropionic acid partly dissolved, partly suspended, in 2*N*-sulphuric acid, with a current density of 0·004 amp./cm.^{2} (the anode being a lead vessel coated with lead dioxide and the cathode a lead stirrer) yields *p*-hydrocoumaric acid (phlorotic acid), together with quinone, quinol, propionic acid, succinic acid, and phenolic condensation products. β-Phenylpropionyl peroxide, m. p. 37°, explodes at 130°, was obtained from β-phenylpropionyl chloride, b. p. 117—119°/13 mm., acetone, and sodium peroxide solution at 0°; when exploded by heating it yielded αδ-diphenylbutane, m. p. 52°. A. A. ELDRIDGE.

Photochemistry of chlorine. F. WEIGERT and M. NICOLIA (Z. physikal. Chem., 1928, **131**, 267—277).—The occurrence of isochromatic fluorescence in pure dry chlorine has been investigated by means of the Bunsen–Roscoe actinometer employed in conjunction with a mercury-vapour lamp. Contrary to expectation, decrease of the distance between the vessel containing chlorine and the actinometer causes the quantity of hydrogen chloride produced to diminish by about 60%. Lambert's law is held to be invalid for chlorine, and the occurrence of fluorescence could not be substantiated. H. F. GILLBE.

Photochemical union of chlorine and hydrogen. I. S. HORIBA and T. ICHIKAWA (Sexagint [Osaka celebration], Kyoto, 1927, 73—94).—The primary changes during the photochemical reaction between chlorine and hydrogen have been studied by recording

the minute pressure changes of the reacting system on a photographic film with the aid of an optical lever and oscillograph. The photochemical induction period, in the sense of a period immediately after exposure to light during which the reaction does not proceed, does not exist. For an initial period of 1·5—2 sec., however, the velocity of the reaction changes with time, finally attaining a steady value, and it is this phase of the reaction which is more correctly termed the induction period. The existence of a chain mechanism is confirmed by the results.

H. F. GILLBE.

Photochemical formation of carbonyl chloride. III. M. BODENSTEIN and T. ONODA (Z. physikal. Chem., 1928, **131**, 153—174).—The principal reaction between chlorine, carbon monoxide, and oxygen at the ordinary temperature results in the formation of carbon dioxide, whilst as the temperature is raised the quantity of carbonyl chloride produced increases, until at 300° formation of carbon dioxide ceases. The course of the reaction at high temperatures is governed by the equation $d[COCl_2]/dt = kI[Cl_2]/[CO]$, where I is the intensity of light absorbed. The reaction is unaffected by oxygen. From 270° to 300° the velocity coefficient of the carbonyl chloride formation is considerably influenced by hydrolysis of the reaction product by water vapour; at the higher temperatures all the water present is removed in the early stages of the reaction. At 400° simultaneous chemical and photochemical formation of carbonyl chloride may be observed by employing low pressures and intense irradiation. The equilibrium of the reaction in the dark is unaltered by illumination. H. F. GILLBE.

Photochemical synthesis of carbonyl chloride. J. CATHALA (J. Chim. phys., 1927, **24**, 663—711).—An apparatus is described for measuring the rate of combination of carbon monoxide and chlorine under the influence of rays from a gas-filled quartz mercury lamp. The gaseous mixture was prepared by decomposing purified carbonyl chloride at a temperature above 800°. A method for the purification of carbonyl chloride by distillation in a vacuum is described. The progress of the reaction was examined by determining the proportion of combined and uncombined chlorine in the gaseous mixture after definite periods of illumination. The rate of the reaction is best expressed by the equation $d[COCl_2]/dt = k[CO] \times [Cl_2]^{\frac{1}{2}}$, which is the same as that found by Bodenstein (Rec. trav. chim., 1922, **41**, 585) for the thermal synthesis of carbonyl chloride. Oxygen and carbon dioxide have a strong inhibiting effect on the photochemical reaction, but not on the thermal reaction. The retarding effect of carbon dioxide is due to the oxygen produced by the decomposition of the carbon dioxide by ultra-violet light. If the active rays are screened off, carbon dioxide has no longer any influence on the photochemical reaction. If the photochemical synthesis is carried out at 357° the carbon dioxide is again without effect, probably because the retarding effect of the oxygen is destroyed at this temperature. The course suggested for the photochemical synthesis is the same as that adopted by Bodenstein (*loc. cit.*) for the thermal synthesis.

M. S. BURR.

Photolysis of sodium hypochlorite solutions. A. J. ALLMAND and W. W. WEBB (Z. physikal. Chem., 1928, **131**, 189—204).—The quantity of sodium chlorate produced by the photochemical decomposition of sodium hypochlorite solutions is independent of the chloride, sulphate, and free alkali concentrations, the intensity of illumination, and the hypochlorite concentration from $0{\cdot}08M$ to $0{\cdot}01M$; at higher dilutions the chlorate yield diminishes. Increase of the average frequency of the absorbed light results in increased yield. Measurements of the quantum efficiency of the reaction show that at constant frequency decrease of hypochlorite concentration causes the ratio λ (molecules decomposed/quanta absorbed) to decrease markedly, whilst increase of frequency causes a great increase of λ as the 254 $\mu\mu$ group of mercury arc lines is approached. Extinction coefficient measurements show the Lambert–Beer law to be valid for sodium hypochlorite solutions, and that the extinction coefficient is independent of the reaction products. The extinction coefficients for the mercury lines of wave-length **436** and 405 $\mu\mu$ are 0·08 and 0·40, respectively. The mechanism of the decomposition at wave-length 254 $\mu\mu$ cannot be identical with that of the photolysis of aqueous solutions of hypochlorous acid and of chlorine, and a modified scheme is suggested for the reaction. H. F. GILLBE.

Photochemical decomposition of nitrous and nitric oxides. J. Y. MACDONALD (J.C.S., 1928, 1—14).—The decomposition of the gases has been studied using light of wave-length 1860—1990 Å. with the object of calculating the quantum efficiency of the processes and of determining the mechanism of the decompositions. These efficiencies were found to be $3{\cdot}9 \pm 0{\cdot}2$ for nitrous oxide and $0{\cdot}73 \pm 0{\cdot}05$ for nitric oxide. The value for nitrous oxide is constant over the range of temperatures employed (0—40°). The absorption coefficient increases $1{\cdot}47 \pm 0{\cdot}05$ times for a rise of 10°. In the experiments, pressures of about 20—650 mm. and exposures varying from 2 to 66·5 min. were employed. With nitrous oxide there is no induction period. It is shown that nitrous oxide absorbs much more strongly than does nitric oxide. Beer's law holds strictly for both gases.

The gases decompose according to the following general equations: $4N_2O = 2NO + O_2 + 3N_2$, $2NO = N_2 + O_2$, and $3NO = N_2O + NO_2$ the former reaction predominating for nitric oxide. Possible mechanisms of these changes are discussed. H. INGLESON.

Photochemical decomposition of azomethane. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1928, **50**, 123—132; cf. A., 1927, 425, 737).—The ultra-violet absorption curve of azomethane is maximal at about 3390 Å. and minimal at 2700 Å. The photochemical decomposition of this substance in the mercury lines at 3660 Å. was followed by pressure measurements; in each of four experiments at different pressures two molecules of gas were decomposed for each light quantum absorbed, which may be due to the activation of an azomethane molecule by transference of energy from a newly-formed ethane molecule. The temperature coefficient does not exceed 1·02 per 10°. The results are discussed in light of the second theory suggested by Rice and the author. S. K. TWEEDY.

Thermal and photochemical decomposition of azo-compounds, and the problem of reaction rates. H. C. RAMSPERGER (Proc. Nat. Acad. Sci., 1927, **13**, 849—853).—A preliminary account is given of experiments which have established that the rate of thermal decomposition of azo*iso*propane is constant in the pressure range 0·025—4·60 cm., and in the temperature range 250—290°. The observed rate corresponds with a heat of activation of $40,900 \pm 500$ g.-cal. The results are discussed with reference to theory of unimolecular reactions and with the photochemical decomposition of azo*iso*propane.

R. W. LUNT.

Reduction of carbon dioxide by light. E. BAUR (Z. physikal. Chem., 1928, **131**, 143—152).—A discussion of the mechanism. H. F. GILLBE.

Photochemical changes of hydrocarbons. S. TOŁŁOCZKO (Przemysl Chem., 1927, **11**, 245—253; Chem. Zentr., 1927, ii, 546).—On exposure of ethane to light from a mercury lamp (λ 2300—4000 Å.), hydrogen and methane were produced; the contraction was determined. The composition of the condensate was not determined; the reactions $(x+1)C_2H_6 = C_{2(x+1)}H_{1(x+1)+2} + xH_2$ and $(x+1)C_2H_6 = C_{(x+2)}H_{2(x+2)+2} + xCH_4$ are postulated. Methane is not affected by the radiation. A. A. ELDRIDGE.

Formation of formaldehyde and of sugars by the action of ultra-violet rays on alkali and alkaline-earth hydrogen carbonates. G. MEZZADROLI and G. GARDANO (Atti R. Accad. Lincei, 1927, [vi], **6**, 160—165).—The hydrogen carbonates investigated were those of barium, calcium, strontium, magnesium, sodium, potassium, lithium, and ammonium. Of these, the calcium salt is decomposed the most, and the sodium salt the least, rapidly by ultra-violet rays. Ammonium hydrogen carbonate gives a greater proportion of aldehyde than the alkali hydrogen carbonates, but the greatest yield of formaldehyde is obtained from calcium hydrogen carbonate. The amount of formaldehyde formed rises to a maximum and then gradually diminishes, owing to oxidation and polymerisation. The presence of sugar in small amounts is observable immediately formaldehyde appears. T. H. POPE.

Photochemical reactions. Influence of polarised rays on the reaction between sodium and potassium amalgams and water. H. L. ANAND and S. S. BHATNAGAR (Z. physikal. Chem., 1928, **131**, 134—142).—The influence of polarised light on the reaction between water and amalgams of the alkali metals is selective as regards the polarisation; the greatest influence is exerted when the plane of the electric vector is parallel to the plane of incidence, and the least when the two are at right angles. The conception that the first stage in a photochemical reaction consists in the emission of electrons has been confirmed. H F GILLBE.

Becquerel effect. N. SASAKI and K. NAKAMURA (Sexagint [Osaka celebration], Kyoto, 1927, 249—254).—The Becquerel effect exhibited by the light-sensitive solutions of an iron salt and iodide is due to the change of concentration of the iodide ion.

H. F. GILLBE.

Non-activity of infra-red radiation in thermal acceleration of reduction of ceric ions by acetaldehyde in acid solution. C. FROMAGEOT (Bull. Soc. chim., 1927, [iv], **41**, 1585—1588).—When ceric ions are reduced by acetaldehyde in acid solution at the ordinary temperature, only activated aldehyde molecules are oxidised, and the rate of reaction is ultimately determined by the rate of activation. Infra-red radiation does not influence the rate of reaction, nor does the frequency of the absorbed radiation calculated from the temperature coefficient of the reaction velocity appear to correspond with any of the absorption bands of the aldehyde. This reaction, therefore, does not agree with Perrin's view that the thermal acceleration of a reaction is brought about by certain infra-red frequencies occurring at the higher temperature, unless it is assumed that the radiation is absorbed by the water before it reaches the aldehyde molecules. R. CUTHILL.

Characteristic surface of photographic films. H. ARENS and J. EGGERT (Z. physikal. Chem., 1928, **131**, 297—309).—A three-dimensional method of representation has been developed for the relationships between the degree of blackening of a photographic emulsion and the logarithms of the intensity of illumination and time of exposure. H. F. GILLBE.

Tentative hypothesis of the latent image. A. P. H. TRIVELLI.—See B., 1928, 107.

Intensification of the latent image. II. Decomposition of hydrogen peroxide and the mechanism of latent image intensification. E. P. WIGHTMAN and R. F. QUIRK.—See B., 1928, 141.

Intramolecular rearrangement by photochemical action. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1928, **186**, 39—41).—The action of ultra-violet light alone is capable of converting *iso*butyl bromide into *tert.*-butyl bromide and propyl bromide into *iso*propyl bromide without any trace of dissociation. This supports the authors' theory that such changes involve the movement of single electron linkings only, with an intermediate stage in which some of the atoms are linked by semi-valency (cf. Perrin, A., 1927, 1009).

B. W. ANDERSON.

Changes in carbohydrate solutions due to sunlight in presence of uranium salts and to ultraviolet rays. ABELOUS, ALOY, and VALDIGUIE (Compt. rend. Soc. Biol., 1927, **96**, 1385—1386; Compt. rend., 1927, ii, 674).—Lævulose and such sugars as are formed by hydrolysis of other carbohydrates readily suffer change in sunlight in presence of uranium salts and in ultra-violet light with formation of aldehydic substances, particularly formaldehyde.

A. A. ELDRIDGE.

Photolytic action on pure sucrose of the total or filtered radiations of the mercury arc. A. ANDANT and E. ROUSSEAU (Compt. rend., 1928, **186**, 365—366).—The formation of dextrose in a fresh 5% solution of sucrose containing magnesium sulphate and 1% of sulphuric acid has been determined by Grimbert's method at hourly intervals during irradiation at 15° by the mercury arc. By the use of suit-

able screens the separate effects of the infra-red, visible, and ultra-violet radiations could be determined, comparison being made with the absorption coefficients determined by a thermopile. The photolytic effect of the infra-red radiation was of the same order as that of the total naked arc, whilst that of the pure radiation λ 3650 Å. (passed by Wood's filter) was much greater. This is an example of the antagonistic effect of rays of different wave-lengths (cf. A., 1927, 738). J. GRANT.

Photobromination of cinnamic acid and stilbene. III. R. M. PURAKAYASTHA and J. C. GHOSH (J. Indian Chem. Soc., 1927, 4, 553—559).—From theoretical considerations the authors deduce that the velocity coefficient for this reaction in yellow light should be given by the equation $k = (1/t)\{[1/(a-x)^{\frac{1}{2}}]-1/a^{\frac{1}{2}}\}+(1/3Bt)\{[1/(a-x)^{\frac{3}{2}}]-1/a^{\frac{3}{2}}\}$, where a is the initial concentration of the bromine, B is a constant, and k, t, and x have their usual meanings. Berthoud had previously given a similar equation but without the second term. Experiments show that the authors' equation is correct and this supports their view of the mechanism of the reaction. An induction period and an after-effect were observed, and Berthoud's rotating-sector method of varying the intensity of the light is criticised. C. D. LANGFORD.

Photo-activation of cod-liver oil. F. HAFFNER and P. PULEWKA (Klin. Wochschr., 1926, 5, 2113—2130; Chem. Zentr., 1927, i, 3204—3205).—Activation of cod-liver oil by light takes place only in presence of oxygen. Boiling inactivates the oil, but it again affects a photographic plate after renewed illumination. Blood or tissue could not be photo-activated by sunlight, but photoactive substances were obtained by the extraction of animal tissue with alcohol and chloroform. A peroxidic substance, to which the photoactivity is due, can be removed from active cod-liver oil by a current of air or carbon dioxide. Experiments suggest that the peroxidic lipin substance may exercise a catalytic effect similar to that of oxidase in biological systems.

A. A. ELDRIDGE.

Reactions in the solid state. W. JANDER (Z. angew. Chem., 1928, 41, 73—79).—A *résumé* and discussion of recent work, from which it is concluded that reactions may occur between solids, depending on the possibility of changes of position of atoms within the crystals; an apparatus for the examination of heterogeneous equilibria at high temperatures and pressures is described. S. I. LEVY.

Structure of hydrogen peroxide, and mechanism of its reactions. P. N. RAIKOV (Z. anorg. Chem., 1928, 168, 297—304).—It is suggested that hydrogen peroxide is an equilibrium mixture of two tautomeric forms, a true peroxide, $H_2O\cdots\cdots O<$, and a pseudo-form, H·O·O·H. In the true form, which is the source of the oxidising properties of hydrogen peroxide, the reactive oxygen atom is held loosely by the secondary valencies of the other oxygen atom, thus causing the hydrogen atoms also to be held less firmly, so that one of them migrates without difficulty to form the symmetrical pseudo-form. It is presumably owing to the readiness with which this change occurs, and to the presence of only a small proportion of the true form in the equilibrium mixture, that the reducing action of hydrogen peroxide, which must be ascribed to the pseudo-form, takes place so rapidly. The change of the pseudo-form into the true form, on the other hand, apparently occurs relatively slowly, which would account for the comparative slowness with which hydrogen peroxide effects oxidation at the ordinary temperature. The spontaneous decomposition of the peroxide may be ascribed to the interaction of the tautomerides, so that foreign substances will promote or hinder the decomposition according as they accelerate or retard the tautomeric change.

R. CUTHILL.

Hydrogen peroxide as an oxidising agent in acid solution. VIII. W. H. HATCHER and G. W. HOLDEN (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 237—243; cf. A., 1925, ii, 684, *et seq.*).—A method of Clover and Houghton (A., 1904, i, 707) has been adapted to the determination of peracid in mixtures containing relatively large quantities of organic acid and hydrogen peroxide. Iodine is liberated from potassium iodide solution and titrated with 0·0143*N*-thiosulphate solution. With acetic, glycollic, lactic, and formic acids, but not with oxalic acid, hydrogen peroxide forms a peracid. Contrary to the statement of Clover and Richmond (A., 1903, i, 396), the reaction is reversible and a catalyst is not essential. The time required for the attainment of equilibrium at 0°, in the different acids, and for different values of the concentration ratio hydrogen peroxide/acid, has been determined, and the values of the equilibrium constants have been calculated. In addition, the equilibria in acetic and glycollic acids have been studied at the ordinary temperature. M. S. BURR.

Union of helium with mercury. J. J. MANLEY (Phil. Mag., 1927, [vii], 4, 699—720).—Preliminary experiments with certain pure common gases at a pressure of a few mm. are described and the results summarised. For each experiment the gas was contained over mercury within an oscillating barometric tube, and in every instance a solid mercury compound was formed. Similar experiments made with helium resulted in a lessened pressure, from which the synthesis of a helide was inferred. Experiments show that the helide is incondensible at the temperature of liquid air. Various synthesisers were next used, the most efficacious being a form of Siemens ozone generator containing platinised asbestos. For an analysis, the compound was decomposed by a heated platinum spiral and the resultant mercury determined with a special micro-balance. The first quantitative experiment led to the formula $HgHe_{10}$. In all subsequent experiments conducted with the utmost care, pressure changes were almost negligible. In one of these experiments, the density of the gaseous mixture was measured with an Aston micro-balance and from this and the weight of the mercury obtained, the formula found was HgHe or $HgHe_2$. Experiments with a quartz spectrograph led to the conclusion that the helide is rapidly resolved into its constituents when traversed by an intense beam of ultra-violet light; difficulty was therefore experienced in photographing an expected absorption line. The line, a very weak one, was obtained on two occasions only; its wave-

length was 2624; the value found by Messrs. Hilger was 2638 Å. Confirmatory evidence for the synthesis and continued existence of mercury helide was obtained with the aid of interferometers. The pressure most favourable for the synthesis appears to be 6 mm. Similar experiments made with argon in the same apparatus led to results entirely negative.

J. J. MANLEY.

Refractive indices of alkali fluoborates. J. H. DE BOER (Physica, 1927, 7, 99—101; Chem. Zentr., 1927, ii, 205).—Directions, for instructional purposes, are given for the preparation of potassium fluoborate and for the study of its optical properties.

A. A. ELDRIDGE.

Complex copper silicates. A. DUBOIN (Compt. rend., 1928, **186**, 234—235).—The compound $K_2O,CuO,4SiO_2$ has been produced in the form of blue crystals (d^0 2·87), readily decomposed by hydrochloric acid, by the addition of silica and copper oxide to a bath of fused potassium fluoride. The mass is allowed to cool and then reheated in the presence of an excess of potassium chloride. Compounds of the type $Al_2O_3,2CuO,3K_2O,6SiO_2$ (small, blue, prismatic needles, d^0 2·8) are produced by the addition of silica and the oxides concerned to molten potassium fluoride.

J. GRANT.

Recent attempts at the transmutation of the elements. F. WOLFERS (J. Chim. phys., 1927, **24**, 727—735).—An attempt has been made to obtain gold from mercury by passing a current of a few milliamp., at 3000—4000 volts, through powdered mercuric chloride for about 100 hrs. Tests with stannous chloride indicated the presence of a trace of gold corresponding with the limits of sensitiveness of the method. By spectroscopic tests, which were less sensitive, the results were negative. The different methods employed in attempts to transmute the elements are critically examined, and the conclusion is reached that, apart from the work of Rutherford and his colleagues, none of these has given results which may be regarded as undoubtedly positive.

M. S. BURR.

Gold purple. II. C. G. FONTANA (Atti R. Accad. Lincei, 1927, [vi], **6**, 231—235; cf. Levi and Fontana, A., 1927, 1128).—Substances analogous to purple of Cassius may be prepared from an alkaline, red gold sol without the use of a reducing agent such as a stannous salt, the hydroxide of aluminium, zirconium, or thorium serving as supporting material. The aluminium gold purple obtained in this way contains 10·80% Au, 66·60% Al_2O_3, and 21·61% H_2O. X-Ray analysis shows its structure to be identical with that of purple of Cassius, the gold being present in the elementary form and the aluminium hydroxide being practically amorphous; the side of the granule (A), supposed cubic, is 32·8 Å., that of purple of Cassius being 36 Å. The zirconium-gold purple contains 10·21% Au, 63·56% ZrO_2, and 25·37% H_2O; Thorium-gold purple contained 11·80% Au, 63·53% ThO_2, and 24·87% H_2O, but its structure was not rendered evident by X-ray analysis.

T. H. POPE.

Formation of crystallised silicates in aqueous media. V. N. IPATIEV and B. MOUROMTSEV (Bull. Soc. chim., 1927, [iv], **41**, 1588—1593).—See A., 1927, 1044.

Relation between resistance of glass to acids and alkalis, and hydrogen-ion concentration. O. K. BOTWINKIN and A. M. TANCHILEVITSCH (Z. anorg. Chem., 1928, **168**, 356—360).—The loss in weight of powdered samples of a window glass and a bottle glass after being subjected to the action of solutions of potassium hydroxide and hydrochloric acid at concentrations of 0·01—10N for 4 hrs. at the ordinary temperature has been determined. With the window glass, the solvent action of the alkali increased with the concentration up to about 0·25N, beyond which no further change occurred, whereas the action of the acid, which was throughout the smaller, did not vary greatly with the concentration. In no case, however, did the p_H of the solutions show a change as a result of contact with the glass. The relatively high solvent power of the alkali compared with the acid is ascribed to the greater readiness with which it attacks the free silica.

R. CUTHILL.

Separation of metals and their oxides from solutions of salts by hydrogen under pressure. V. N. IPATIEV and V. NIKLAEV (Bull. Soc. chim., 1927, [iv], **41**, 1591—1598).—The effect of hydrogen under pressure on solutions of stannic chloride and sulphate, and suspensions of the hydroxide at 300—400°, has been studied. With the hydroxide, stannous hydroxide and tin result. The sulphate gives mixtures, the composition of which depends on the conditions, but they may contain stannous sulphate and sulphide, a polysulphide, α-metastannic acid, and the metal. Sulphuric acid and copper sulphate hinder the reaction, reduction going no further than stannous sulphate and stannic sulphite, respectively. The chloride yields stannous chloride, and stannous hydroxide or stannic oxide, the separation of tin starting at about 280°, but in relatively small amount. In presence of silver chloride, a compound which is probably a basic stannous chloride appears.

R. CUTHILL.

Physico-chemical properties of stannous oxide. C. G. FINK and C. L. MANTELL (J. Physical Chem., 1928, **32**, 103—112).—The effect of heating pure stannous oxide in various atmospheres in an electric furnace has been followed by microscopic examination of the products formed. Above 385°, in an atmosphere of nitrogen, stannous oxide decomposes into tin and the dioxide, and above 240° moist or dry air readily oxidises it. At higher temperatures, it becomes pyrophoric. Sulphur dioxide in acid solution oxidises, and in alkaline solution reduces this oxide. Ditte's method (Ann. Physik, 1882, **27**, 145) for the preparation of stannous oxide readily gives a product of high purity provided that the final value of the p_H of the solution lies between 5 and 6·5. The reduction of stannous oxide by hydrogen takes place in a single stage above 385°, but below this temperature the two stages represented by the equations $SnO_2+H_2=SnO+H_2O$ and $SnO+H_2=Sn+H_2O$ occur.

L. S. THEOBALD.

Lead tree. V. KOHLSCHÜTTER (Festschr. A. Tschirch, 1926, 425—430; Chem. Zentr., 1927, i, 3178).—A discussion of the processes controlling the

formation of a "lead tree" from zinc and lead salt solution. In addition to ionic reaction and to the influence of crystal form, subsidiary reactions between the deposited metal and dissolved salt influence the development of the tree.

A. A. ELDRIDGE.

Nature of active nitrogen. Synthesis of ammonia from the elements. B. LEWIS (J. Amer. Chem. Soc., 1928, **50**, 27—35).—Experiments are described showing that ammonia is formed only when active nitrogen is mixed with atomic hydrogen, indicating that the former contains nitrogen atoms. No ammonia is produced when the nitrogen or hydrogen alone is activated, and hydrazine is never formed. The current interpretations of the spectroscopic data of nitrogen are supported. Glowing active nitrogen is probably a heterogeneous mixture of nitrogen atoms and excited nitrogen molecules.

S. K. TWEEDY.

Compounds of hydrazine with metallic sulphites and nitrites. P. RAY and B. K. GOSWAMI (Z. anorg. Chem., 1928, **168**, 329—338).—Neutralisation of a solution of manganous sulphite in an excess of sulphurous acid with hydrazine hydrate yields a white, crystalline *compound*, $MnSO_3,N_2H_4,H_2SO_3$. A solution of cobalt hydrogen sulphite treated in the same way gives a red *compound*, $5CoSO_3,9N_2H_4,6H_2O$, but if it is added to an excess of a concentrated hydrazine hydrate solution the product is $CoSO_3,2N_2H_4,H_2O$ (buff). By the action of sulphur dioxide on a suspension of the latter salt, the *compounds* $CoSO_3,2N_2H_4,H_2SO_3,2H_2O$ (red) and $CoSO_3,N_2H_4,H_2SO_3,0{\cdot}5H_2O$ (red) are formed, whilst under the same conditions the other salt gives $2CoSO_3,N_2H_4,3H_2O$ (brown). A solution of nickel hydrogen sulphite added to an excess of a concentrated hydrazine hydrate solution yields a red *compound*, $NiSO_3,3N_2H_4,H_2O$, but with an amount of dilute hydrazine solution sufficient only to produce neutrality, there results the blue *salt*, $NiSO_3,2N_2H_4,H_2O$, which yields green *crystals* of $4NiSO_3,3N_2H_4,7H_2O$ when treated with sulphur dioxide. Addition of a solution of zinc hydrogen sulphite to an excess of concentrated hydrazine solution gives rise to the *compound* $ZnSO_3,2N_2H_4,1{\cdot}5H_2O$ (white), which reacts with sulphur dioxide to give $ZnSO_3,N_2H_4,H_2SO_3$ (white). By neutralising a solution of cadmium hydrogen sulphite with dilute hydrazine hydrate solution, a white *solid*, $CdSO_3,N_2H_4$, is obtained, and from this by the action of sulphur dioxide the *salt* $CdSO_3,N_2H_4,H_2SO_3$ (white). *Compounds* of hydrazine with the nitrites of cobalt, nickel, and cadmium, $2Co(NO_2)_2,3N_2H_4$ (red), $Ni(NO_2)_2,2N_2H_4$ (blue), and $Cd(NO_2)_2,2N_2H_4$ (white), respectively, are formed by the addition of a hydrazine hydrate solution to a mixed solution of the corresponding acetate and an excess of sodium nitrite at 0°.

R. CUTHILL.

Radical-like alkali salts of a new acid containing nitrogen and oxygen. E. ZINTL and O. KOHN (Ber., 1928, **61**, [*B*], 189—199).—A solution of sodium nitrite in liquid ammonia is immediately converted by a similar solution of sodium into the intensely yellow *sodium hydronitrite*, Na_2NO_2; with excess of the metal reduction slowly proceeds further. The salt may also be prepared by cathodic reduction of sodium nitrite in liquid ammonia in a divided cell. Sodium nitrite behaves similarly towards lithium or potassium, but reacts only slowly with calcium. When pure, the alkali hydronitrites appear stable even when gently heated in a vacuum or in nitrogen; at 100—130° violent decomposition ensues with evolution of nitrogen and formation of a lemon-yellow residue containing alkali hydroxide, nitrite, and nitrate. The change appears similar to that observed by Divers (J.C.S., 1899, **75**, 102) with sodium hyponitrite, thus suggesting that the primary change is disproportionation to nitrite and hyponitrite. Slow addition of oxygen under conditions which preclude thermal decomposition results in the absorption of 1 atom of oxygen per mol. of hydronitrite with formation of an unstable, brown *peroxide*, (?) $(Na_2NO_2)_2{:}O_2$, decomposed by water into oxygen, sodium nitrite and hydroxide, and hydrogen peroxide. Sodium hydronitrite (1 mol.) absorbs 1 atom of iodine from its ethereal solution giving a black, additive *product*, which rapidly decomposes into sodium nitrite and iodide; with nitric oxide and carbon dioxide it reacts so violently that the products cannot be investigated. Water vapour decolorises sodium hydronitrite with production of nitrous and nitric oxides, sodium hydroxide, nitrite, hyponitrite, and a little nitrate; the course of the change depends somewhat on the conditions, suggesting an initial disproportionation into nitrous acid and dihydroxyammonia. Determinations of the mol. wt. of alkali hydronitrites are precluded by absence of a suitable solvent. It appears probable that addition of sodium to sodium nitrite occurs at the oxygen rather than the nitrogen atom and the hydronitrites $-N(ONa)_2$ are thus analogous to Schlenk's metallic ketyls.

Reduction of alkali nitrates by alkali metals in the presence of liquid ammonia yields alkali oxide and nitrite; the latter is subsequently transformed into hydronitrite.

H. WREN.

Action of nitric oxide on the thiosulphates of the metals of the eighth group. I. L. CAMBI and A. CLERICI (Atti R. Accad. Lincei, 1927, [vi], **6**, 448—453).—The structure of complex salts of the Roussin's salt type is discussed, and the view that these compounds contain univalent iron, cobalt, or nickel, with the nitrosyl group as a neutral added group, is rejected (cf. Manchot, A., 1927, 33). Investigations of the nitrosothiosulphates of cobalt and of nickel confirm the hyponitrite structure for these compounds. The action of nitric oxide on nickel thiosulphate is discussed and the chemical behaviour of the compound $K_3[NO{\cdot}Ni(S_2O_3)_2],2H_2O$ is described. It is considered that this salt contains hyponitrous residues with the probable structure $>Ni<\genfrac{}{}{0pt}{}{NO}{NO}>Ni<$.

O. J. WALKER.

Arsine from fused glass. H. M. ELSEY (Science, 1927, **66**, 300).—A garlic-like odour was observed when fused borosilicate glass was drawn out so as to expose a fresh surface. The odour is ascribed to arsine, and it is suggested that the odour of arsenic vapour is due to the presence of arsine.

A. A. ELDRIDGE.

Reaction between arsenite and permanganate in sulphuric acid solution. J. Hollùta (Z. anorg. Chem., 1928, **168**, 361—368).—The conclusions of Oryng (A., 1927, 742) respecting the mechanism of the above reaction are critically examined in the light of the results previously obtained by the author (A., 1925, ii, 422). R. Cuthill.

Bismuth nitrates. E. Moles and E. Sellés (Anal. Fís. Quím., 1927, **25**, 453—483; cf. Picon, A., 1926, 36; Hepner, *ibid.*, 487, 488).—On dissolution of bismuth in nitric acid and subsequent treatment of the resulting product (keeping in a vacuum or in a current of dry air or carbon dioxide at various temperatures) the compounds $Bi(NO_3)_3,5H_2O,BiONO_3$ (anhydrous, or +2, 1, or $0·5H_2O$) and $BiONO_3,BiO·OH$, respectively. These compounds are regarded as salts of orthonitric acid and are ascribed the formulæ: $[Bi(H_3NO_4)_2(H_2O)_2]NO_4]$, $BiNO_4$, and $BiNO_4,BiO·OH$. The co-ordination number 4 is that obtaining in the complex compounds of bismuth. The advantages of the classification indicated are pointed out.

When bismuth is dissolved in nitric acid, precautions being taken to keep the temperature as low as possible, and the resulting solution kept at 60—70°, nacreous, tabular crystals of the monohydrated orthonitrate are deposited. On further heating, prismatic crystals of the complex salt are obtained. When heated in a current of dry carbon dioxide the complex salt is converted into the anhydrous orthonitrate. When kept over sulphuric acid the complex salt loses water and nitric acid. J. S. Carter.

Preparation of iodobismuthites. (Miss) E. M. Bartholomew and G. J. Burrows (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 208—210).—By interaction between bismuth iodide and an organic base in hydriodic acid solution, crystalline *hexaiodobismuthites* having the following formulæ have been prepared: with aniline, $(NH_3Ph)_3BiI_6$ (yellow); with pyridine, $(C_5H_5NH)_3BiI_6$ (scarlet); with dimethylaniline, $(NPhMe_2H)_3BiI_6$ (red); and with *p*-toluidine, $(C_6H_4Me·NH_3)_3BiI_6$ (yellow). By taking phenyldimethylarsine and bismuth iodide in the proportions required to give the hexaiodo-compound and treating with excess of hydriodic acid, a *tetraiodobismuthite*, $(AsPhMe_2H)BiI_4$ (scarlet), was obtained.

R. Cuthill.

Element 91; its properties and preparation. A. von Grosse (Ber., 1928, **61**, [*B*], 233—245; cf. Hahn and Meitner, A., 1918, ii, 345; Soddy and Cranston, *ibid.*, ii, 211).—The crude material consisted of residues from Joachimsthal pitchblende in which, after initial purification, protoactinium was present in concentration about 7×10^{-6}. It contained other radioactive substances from which it was freed by treatment with hydrofluoric acid (cf. Hahn and , A., 1920, ii, 147), after which it contained: $ZrO_2(HfO_2)$ 10—15%, TiO_2 about 60%, Fe_2O_3 2—3%, Ta_2O Nb_2O_5 about 3·5%, P_2O_5 13%, together with sulphate, water, and silica. Fusion of the material with potassium carbonate and dissolution of the residue in water removed almost all the oxides of tantalum and niobium as tantalate and niobate with the phosphoric acid, whereas more than 99% of the protoactinium remained with the insoluble basic oxides, thus demonstrating the great difference in basicity between the pentoxides of tantalum and protoactinium. The oxides were evaporated with sulphuric acid or fused with sodium hydrogen sulphate and the solution of the residue, after addition of so much hydrochloric acid that the concentration attained 10—25%, was treated with concentrated phosphoric acid (or phosphate) whereby 80—90% of the protoactinium was precipitated as phosphate together with zirconium and hafnium phosphates, whereas the other metals remained in solution (under ordinary analytical conditions the precipitation of protoactinium by phosphoric acid is quantitative). Fusion of the mixed phosphates with potassium carbonate (1 : 4) removed phosphoric acid, whilst protoactinium oxide remained quantitatively with the oxides of zirconium and hafnium. Further concentration of protoactinium oxide was effected by a "spiral" process involving the three operations (1) precipitation with phosphoric acid, (2) fusion with alkali carbonate, and (3) fractional crystallisation of the oxychlorides from concentrated hydrochloric acid. In this manner, 27·40 mg. of zirconium oxide were obtained containing at least 6% of protoactinium oxide. Isolation of the latter was effected (1) by addition of thorium oxide and precipitation of the latter as thorium oxalate accompanied by 70—90% of the protoactinium; thorium was subsequently removed as the fluoride and protoactinium precipitated from the filtrate by ammonia; (2) by dissolving the oxides in warm, dilute hydrochloric acid and precipitation of protoactinium by oxalic acid. In this manner, about 2 mg. of *protoactinium oxide* (probably pentoxide) were obtained, the activity of which could not be increased by repetition of the separation process, the product being a colourless, difficultly fusible powder which scarcely emitted light. Its mg.-activity was 622,000 α units. The half-life period of protoactinium, deduced from the α-activities of the pure oxides of protoactinium and uranium, is about 20,000 years, thus agreeing within the limits of experimental error with the datum of Hahn and Walling (Naturwiss., 1927, **39**, 803). On the basis of this value the quantities of protoactinium in radioactive equilibrium with a definite amount of uranium are greater than previously supposed. H. Wren.

Composition of ozone and the time-energy factor in ozone formation. P. C. Saunders and A. Silverman.—See B., 1928, 89.

Thio-salts. IV. Derivatives of a hypothetical thio-aquic acid. L. Fernandes (Atti R. Accad. Lincei, 1927, [vi], **6**, 165—170; cf. this vol., 34).—Parathiomolybdates, $[H_2(MoS_4)_6]H_5R'_5$, completely analogous to the paramolybdates, are described. The ammonium salt, $[H_2(MoS_4)_6](NH_4)_5H_5$, may be obtained in three ways: (1) by leaving solid ammonium thiomolybdate, $(NH_4)_2MoS_4$, under a bell-jar in presence of an open vessel containing ammonia solution; (2) from an aqueous solution of the same salt, slowly in the cold, more rapidly on heating; if the latter is too violent the *trithiomolybdate*, $[H_2(MoS_4)_6](NH_4)_4H_6,16H_2O$ may be formed; (3) by saturating a cold concentrated solution of the normal salt with hydrogen sulphide. The last method is

general and is the only known way of obtaining the alkali parathiomolybdates.

These compounds are highly stable and are only slightly soluble in water, by which they are decomposed at the b. p. The action on them of dilute acid precipitates molybdenum sulphide and liberates hydrogen sulphide, the liquid becoming blue owing to the formation of molybdenum-blue. The parathiomolybdates contain 3·5 mols. of hydrogen sulphide of constitution, which, unlike water of constitution, may be determined by ordinary methods. They are derived from a hypothetical thioaquo-acid, $[H_2S_6]H_{10}$ (cf. A., 1927, 636), in which the sulphur atoms may be replaced by the groups MoS_4, co-ordinated by two atoms of hydrogen.

Ammonium parathiomolybdate ($+15H_2O$) forms a deep red, crystalline powder, and the *guanidine* salt ($+8H_2O$) deep red, radiating crystals with green reflexion; the *potassium* salt ($+16H_2O$) is more stable than the two preceding compounds. T. H. Pope.

Detection of intermediate products in oxidations with chromic acid. C. Wagner (Z. anorg. Chem., 1928, **168**, 279—291; cf. following abstract).—If a solution of chromic acid is added to a mixed solution of potassium iodide and sodium hydrogen carbonate, no free iodine is formed, but a reacting mixture of oxalic and chromic acids will liberate appreciable amounts of iodine from the iodide. It is therefore to be concluded that some active intermediate product is formed in the reaction between chromic acid and oxalic acid, and the same is true for the reaction between chromic acid and tartaric acid. This substance is so unstable that it can scarcely be hydrogen peroxide, or a compound of the nature of percarbonic acid, and attempts to detect the formation of these substances have, in fact, been futile, nor is there any evidence in favour of the existence of chromic acid–oxalic acid complexes. In the reaction between chromic acid and lactic acid, however, the intermediate product is more stable, probably owing to the formation of a complex compound with the lactic acid, and proves to resemble pyridinium oxytetrachlorochromanate so closely in behaviour that it is presumably a compound of quinquevalent chromium. This would be in accordance with Jabłczynski's suggested explanation of the apparently autocatalytic nature of the initial stages of the reaction between oxalic acid and chromic acid (A., 1908, ii, 935). In the oxidation of thiocyanic acid, the active substance can be extracted with ether, although it is accompanied by thiocyanogen. The retarding action of manganous salts on the oxidation of formic acid or lactic acid by chromic acid (Dhar, J.C.S., 1917, **111**, 707; Dey and Dhar, A., 1927, 116) is probably to be ascribed to their promoting the transformation of quinquevalent chromium into sexa- and ter-valent compounds. R. Cuthill.

Induction of the reaction between chromic acid and iodide by ferrous salts. C. Wagner and W. Preiss (Z. anorg. Chem., 1928, **168**, 265—278).—Luther's theory (A., 1904, ii, 244; 1907, ii, 555) that the induction of the reaction between chromic acid and iodides by ferrous salts is due to the formation of quinquevalent chromium ions by reaction between ferrous ions and sexavalent chromium ions, these then oxidising other ferrous ions and also iodide ions, has been examined experimentally. Since the equilibrium $Cr^{VI}+Fe^{II} \rightleftharpoons Cr^{V}+Fe^{III}$ is apparently established very rapidly, and the rate of oxidation of ferrous salts by chromic acid is proportional to the square of the concentration of ferrous salt (Benson, A., 1904, ii, 316), the reaction between the Cr^{V} and ferrous ions can primarily involve only one of the latter, the mechanism being somewhat as follows: (*a*) $Cr^{V}+Fe^{II} \longrightarrow ?$; (*b*) $?+Fe^{II} \longrightarrow Cr^{III}+2Fe^{III}$. The reaction with the iodide ion also probably occurs in two stages, with hypoiodous acid as an intermediate product, thus: (*c*) $Cr^{V}+I' \longrightarrow Cr^{III}+HIO$; (*d*) $HIO+H^{\cdot}+I' \longrightarrow I_2+H_2O$. The ratio, K, of k_1 to k_2, the velocity coefficients of reactions (*a*) and (*c*) respectively, has been calculated from the amount of iodine liberated when a solution of potassium dichromate is added to a mixed solution of potassium iodide and ferrous chloride acidified with hydrochloric acid, and containing a considerable concentration of potassium chloride, this last being present in order to eliminate disturbances due to variations in the neutral salt effect and degrees of dissociation. Even if the variation of the hydrogen-ion concentration is taken into account, the values of K obtained in this way show systematic deviations, which are not, however, such as would result if the orders of equations (*a*)—(*d*) were incorrect. The cause of this anomaly seems rather to lie in a splitting up by a side reaction of the Cr^{V} ions, perhaps into sexa- and ter-valent compounds, for the constancy of K is much improved if the reaction mixture contains ferric ions at the outset, and these would, according to the above equilibrium equation, reduce the concentration of Cr^{V} ions. Under these conditions, the value of K does not vary greatly with change in the hydrogen-ion concentration, so that k_1 and k_2 must vary in the same way. Experiments on the addition of solutions of pyridinium oxytetrachlorochromanate in glacial acetic acid (Weinland and Fridrich, A., 1906, i, 37) to aqueous iodide solutions shows that in aqueous solution the Cr^{V} ions are very rapidly transformed into sexa- and ter-valent ions, and also that compounds of this type do actually contain quinquevalent chromium. R. Cuthill.

Hydroxylaminomolybdates and complex molybdomolybdates. Action of hydroxylamine on paramolybdates. G. Canneri (Gazzetta, 1927, **57**, 872—880).—Following a discussion of their structure the preparation of the following complex *molybdates* is described: $4MoO_3,4NH_2OH,(NH_4)_2O$; $4MoO_3,4NH_2OH,K_2O$; $4MoO_3,4NH_2OH,Na_2O$; $4MoO_3,4NH_2OH,(CH_6N_3)_2O$; $Mo_2O_5,4MoO_3,2(NH_4)_2O,8H_2O$, $Mo_2O_5,4MoO_3,Na_2O,10H_2O$, and $Mo_2O_5,4MoO_3,2K_2O,5H_2O$. R. W. Lunt.

Reaction of several metallic ions in the presence of tartaric acid. S. Hakomori (Sci. Rep. Tohoku, 1927, **16**, 841—859).—The behaviour of solutions of uranium, lead, titanium, tin, zirconium, antimony, copper, zinc, nickel, cobalt, manganese, and beryllium salts in the presence of tartaric acid

has been examined by electrical conductivity, refractometric, ultramicroscopic, and spectroscopic methods. Sexavalent uranium in neutral solution appears to form a complex salt containing one atom of metal to one molecule of tartaric acid, which on exposure to bright sunlight undergoes photochemical reduction to the quadrivalent state; alkalis precipitate a greenish-brown hydroxide from the reduced solution. Lead forms a 1 : 1 complex with tartaric acid only in alkaline solution. Nickel and cobalt in neutral solution give a 1 : 1 complex salt and quinquevalent antimony in acid solution yield similarly a 1 : 2 salt. No satisfactory evidence of the existence of complex salts of the other metals in solution could be obtained. The cobalt complex is completely converted into an ammine by treatment with ammonia; the nickel complex is partly so converted and the copper complex remains unchanged. A. R. POWELL.

Action of hydrogen peroxide on ferrous salts. W. MANCHOT and G. LEHMANN (Annalen, 1928, **460**, 179—201).—It is concluded, from the results of four different sets of experiments, that the interaction of hydrogen peroxide and ferrous salts at very low concentrations proceeds in accordance with the equations: (1) $2FeSO_4+3H_2O_2=Fe_2O_5+2H_2SO_4+H_2O$ and (2) $Fe_2O_5=Fe_2O_3+2O$. In presence of potassium iodide, the following equations apply: (1) $2FeI_2+3H_2O_2+6KI=2FeI_5+6KOH$, (2) $2FeI_5=2FeI_3+2I_2$, and (3) $2FeI_3+6KOH=2Fe(OH)_3+6KI$. Manchot's previous assumption of the necessary intermediate formation of the peroxide, Fe_2O_5, is fully substantiated. In concentrated solutions, more hydrogen peroxide is decomposed than is required by the above equations, owing to its interaction with the iron peroxide. This second decomposition cannot be catalytic in action.

In very dilute solutions, a little acid decelerates oxidation of ferrous salts by hydrogen peroxide; addition of more acid after a certain concentration is reached causes, however, an increased velocity of oxidation. The total effect of addition of acid is to cause the initial reaction and the reaction following it to proceed at more equal rates than is the case in absence of acid. In concentrated solutions, the presence of acid diminishes the total decomposition of hydrogen peroxide. The course of the action of hydrogen peroxide on ferrous salts in presence of either potassium iodide or formic acid as acceptor is complicated and difficult to interpret. The peroxide, Fe_2O_5, however, is in all cases formed intermediately. E. E. TURNER.

Transformations of iron in nature. II. Importance of micro-organisms in the dissolution and precipitation of iron. R. L. STARKEY and H. O HALVORSON (Soil Sci., 1927, **24**, 381—402; cf. Halvorson and Starkey, A., 1927, 425).—The activities of mixed cultures of soil micro-organisms in causing oxidation, reduction, and precipitation of iron in various media and under different conditions have been studied. Under aerobic conditions, in solutions containing dextrose, iron may be dissolved as a result of production of acid. Under anaerobic conditions, in dextrose or peptone media, iron as ferric hydroxide may be dissolved and reduced as a result of decreased oxygen pressure and formation of acid; on exposure to air of solutions in which this has taken place, the iron may be reprecipitated. The latter change may occur in absence of bacterial activity. Precipitation of iron from organic compounds depends on the action of organisms which decompose the organic radicals and not on direct action on the iron. The authors consider that, although ferric hydroxide is precipitated by the action of various groups of micro-organisms, such precipitation under natural conditions is much less frequently due to "iron" bacteria than is generally assumed, and that it is not proved that precipitation of ferric hydroxide by these organisms can take place under conditions where it could not proceed independently of them. C. T. GIMINGHAM.

[Bivalent ruthenium.] H. REMY and T. WAGNER (Ber., 1928, **61**, [*B*], 151—153).—The discrepancies between the observations of the authors (A., 1927, 328) and of Gall and Lehmann (this vol., 142) are probably due to differences in the nature of the ruthenium compounds used. H. WREN.

Acid-forming properties of osmium tetroxide. D. M. YOST and R. J. WHITE (J. Amer. Chem. Soc., 1928, **50**, 81—84).—The distribution ratio of osmium tetroxide between carbon tetrachloride and water is greatly diminished when the water contains sodium hydroxide and slightly diminished when it contains potassium chlorate. The acid H_2OsO_5 (which it is proposed to call perperosmic acid) is presumably produced; from the results, $[H^{\cdot}][HOsO_5']/[H_2OsO_5]=K_a=8\times10^{-13}$ at 25°. The acid is thus weaker than carbonic acid. S. K. TWEEDY.

Precipitation of iridium from solution by hydrogen under pressure. V. IPATIEV and I. ANDREEVSKI (Bull. Soc. chim., 1927, [iv], **41**, 1466—1467).—See A., 1927, 844.

Platinum group metals. VIII. Liberation of chloroiridic acid. S. NAGAMI (J. Chem. Soc. Japan, 1927, **48**, 501—503).—Chloroiridic acid ($H_2IrCl_6,6H_2O$) was isolated as blackish-red triclinic crystals by dissolving iridium oxide prepared from potassium chloroiridate in concentrated hydrochloric acid and concentrating the solution in a current of chlorine. The compound is very deliquescent in air, and is a strong acid of the order of hydrochloric acid and chloroplatinic acid. Its dissociation is: $H_2IrCl_6 \rightarrow 2H^{+}+IrCl_6^{--}$. K. KASHIMA.

Preparation of oxygen-free nitrogen or hydrogen. A. V. HILL (J. Sci. Instr., 1928, **5**, 23—24).—The purification of a gas from oxygen by passing through a porcelain filter into alkaline sodium hyposulphite (A., 1926, 699) is rendered more effective by using a negatively-charged filter, which produces much smaller bubbles. C. W. GIBBY.

Isolation of florentium (element 61). L. ROLLA and L. FERNANDES (Gazzetta, 1927, **57**, 704—712).—Details are given of the recrystallisation technique adopted in order to obtain a solid solution containing approximately 5% of the double nitrate of thallium and element 61, $Fr(NO_3)_3,2TlNO_3,4H_2O$. R. W. LUNT.

Magnitude of observation errors in chemical analysis. F. Goudriaan (Chem. Weekblad, 1928, 25, 52—57).—The extent to which results may be influenced by inaccuracies in measurement and observation is considered for typical methods of analysis. In ordinary gravimetric work in which atomic weights approximated to the first decimal place are used, only the first three significant figures can be accurate. Similar degrees of accuracy are obtained with direct titrations and in standardisation of solutions. Indirect titrations and determinations are subject to considerably greater possibility of error.
S. I. Levy.

Titrations by optical methods with the aid of Lowe's interferometer for liquids. E. Berl and L. Ranis (Ber., 1928, 61, [B], 92—99).—Lowe's interferometer, with distilled water as comparison liquid, is well adapted to various types of volumetric analysis. For the titration of acid with alkali hydroxide the apparatus is readily adapted for concentrations of solutions from $2N$ to $N/2000$, the error with the latter being only about 1·6%. The process may be used with strong or weak acids and weak or strong bases and gives accurate results for the titration of weak acids with weak bases. In precipitation analyses (*e.g.*, magnesium chloride and silver nitrate) the solution under investigation is treated with varied quantities of the precipitant, the mixtures are centrifuged, and observations are made with the supernatant liquid. When a combined neutralisation and precipitation analysis is concerned both determinations may be effected in a single solution, as established by the titration of nitrating acid by barium hydroxide. The total alkali in mixtures of sodium hydroxide and carbonate is determined by titration with silver nitrate, only one inflexion in the graph being observed, since the solubilities of silver oxide and carbonate are approximately equal; carbonate is determined by titration with barium hydroxide. With mixtures of magnesium chloride and sulphate the total base is determined with sodium hydroxide, the chloride with silver nitrate in very dilute solution to avoid co-precipitation of silver sulphate. The interferometric method is well adapted to the preparation and control of standard solutions provided they are prepared from pure materials. H. Wren.

Amalgam method. M. Kobayashi (Sexagint [Osaka celebration], Kyoto, 1927, 95—102).—A survey of the employment of liquid amalgams for volumetric analysis and other purposes.
H. F. Gillbe.

Theory of end-point in electrometric titration. P. S. Roller (J. Amer. Chem. Soc., 1928, 50, 1—8).—A general expression deduced for the hydrogen-ion concentration at the inflexion point of an electrometric neutralisation curve shows that such a point appears during the titration of a weak acid by a strong base only when $cK_a>27K_w$, where K_a is the ionisation constant of the acid, K_w the ionic product of water, and $1/c=1/a+1/b$, a being the initial concentration of the acid solution and b that of the alkali solution. This is not in agreement with the calculations of Eastman (A., 1925, ii, 594). The p_H values at the end-point, p_e, and the inflexion point, p_i, differ: $p_e-p_i=0{\cdot}65\sqrt{K_w/cK_a}$; the latter point always precedes the former, except when the acid is strong. Decrease in either K_a or c is accompanied by an increase in the error of locating the inflexion point.
S. K. Tweedy.

Use of A.C. galvanometers for conductometric titrations, and the determination of fixed ammonia. M. Matsui and M. Asai (J. Soc. Chem. Ind. Japan, 1927, 30, 550—552).—A recommendation of use of A.C. galvanometers for the conductometric titration. A rapid method for determining fixed ammonia is described in illustration. S. Oka.

Comparison of different methods of electrometric acidimetry and alkalimetry. M. Matsui and M. Asai (J. Soc. Chem. Ind. Japan, 1927, 30, 544—549).—The four methods examined were: (1) titration with an air electrode, a calomel half-electrode, and a potentiometer, (2) differential titration with platinum electrodes and a potentiometer, (3) titration without a potentiometer with a hydrogen electrode and a neutralisation electrode, (4) titration without a a potentiometer with air electrodes. S. Oka.

Determination of the concentration of active hydrogen ions in oligometallic mineral waters. G. Banchi (Giorn. Chim. Ind. Appl., 1927, 9, 518—519).—The values of p_H and of the corresponding hydrogen-ion concentration are given for a number of well waters of the Fiuggi district. Certain of these waters give low values for p_H (5·67 and 5·65); this is partly due to the presence of dissolved carbon dioxide, since agitation of the waters causes increase in these values to about 6, which agrees well with the value found by Kling and Lassieur (A., 1926, 355) for distilled water saturated with carbon dioxide. Moreover, if the water is left exposed, the indicator present indicates a gradual change to alkalinity, this change occurring first in the upper part of the liquid. The alkalinity acquired by the water reaches its maximum value if the water is either shaken and then left in an open vessel or boiled for 5 min. Determination of the p_H of a water appears to be one of the best means of ascertaining the age of the water. T. H. Pope.

Adipic acid as a standard in alkalimetry F. T. van Voorst (Chem. Weekblad, 1928, 25, 22—23).—Adipic acid, which has an equivalent weight (corrected for weighing in air) of 72·99, is readily prepared pure by recrystallisation from distilled water and drying at 130°. The m. p. is 152·0°±0·1°, and the purity is readily determined by the m. p. of the sample. It is a more convenient standard than oxalic acid, the purification of which is extremely troublesome. S. I. Levy.

Oxalic and adipic acids as standards. N. Schoorl (Chem. Weekblad, 1928, 25, 73; cf. preceding abstract).—Oxalic acid is readily obtained as the pure dihydrate by recrystallisation, powdering, drying at 60°, and keeping the dried powder in a moist atmosphere; it has the advantage that normal solutions may be made up, whereas the solubility of adipic acid allows only $0{\cdot}2N$-solutions in water.
S. I. Levy.

Oxalic acid as a standard. W. P. Jorissen (Chem. Weekblad, 1928, 25, 90—91; cf. preceding

abstracts).—Dilute solutions of oxalic acid, which do not remain constant when kept even in the dark, may be kept satisfactorily, if required for titration of permanganate solutions, by addition of sulphuric acid.
S. I. LEVY.

Determination of hydrogen in complex gaseous mixtures by absorption in colloidal palladium solution. A. E. BEET.—See B., 1928, 113.

Modified apparatus for moisture determination. A. VAN DER WERTH (Chem.-Ztg., 1928, **52**, 23—24).—An apparatus is described for the determination by means of tetrachloroethane. Distillation is continuous, the water driven off being automatically separated in a capillary measuring tube integral with the still-head.
S. I. LEVY.

Volumetric determination of perchlorate ion and of potassium in the presence of sulphates and phosphates. E. S. TOMULA (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 21).—Perchlorates are reduced by boiling in a reflux apparatus with titanic sulphate and cadmium sulphate solutions in the presence of zinc and iron powders; the chlorides thus formed are determined volumetrically. Potassium is determined by conversion into the perchlorate, which is freed from absorbed perchloric acid by washing with alcohol and reduced as above. If sulphates are present they are removed as barium sulphate; phosphates do not interfere.
G. A. C. GOUGH.

Determination of iodine in minerals. E. WILKE-DORFURT.—See B., 1928, 95.

Reaction between atmospheric oxygen and strongly acid iodide solutions as a possible source of error in iodometric analyses. H. DITZ (Z. anal. Chem., 1927, **72**, 360—367; cf. Bottger and Bottger, A., 1927, 222, 330).—Polemical. A review of recent work on the subject indicates that the errors caused by oxidation of acid iodide solutions by atmospheric oxygen are relatively small and under certain conditions negligible.
A. R. POWELL.

Reaction between atmospheric oxygen and strongly acid iodide solutions. W. BOTTGER (Z. anal Chem., 1927, **72**, 367—369).—A reply to Ditz (preceding abstract); the author maintains that removal of dissolved oxygen is advisable, although he admits that some of the high results obtained by him may have been due to presence of chlorine in the hydrochloric acid used.
A. R. POWELL.

Deposition of ammonium sulphide precipitates. J. ROLL (Z. anal. Chem., 1927, **72**, 298—301).—Ordinary, prepared ammonium sulphide solution is liable to cause the precipitation of the alkaline-earth metals owing to the presence of thiosulphate, sulphite, and sulphate. If it is freshly prepared it usually contains sufficient free ammonia to precipitate nickel sulphide as a colloidal sol. By passing a current of hydrogen sulphide through the filtrate containing 10% of 5% ammonia solution, these errors are avoided.
F S HAWKINS.

Determination of nitrogen in soils. C. OLSEN.—See B., 1928, 101.

Rapid micro-determination of the phosphoric ion by ceruleo-molybdimetry. G. DENIGÈS (Compt. rend., 1928, **186**, 318—319).—The author's method (A., 1927, 433, 1156) is applied to the colorimetric analysis of blood, saliva, urine, fermented liquors, etc. containing 2—12 mg. P_2O_5 per litre. The diluted liquid (5 c.c.) is boiled for 12 sec. with 6 drops of reagent and the blue colour matched against that of a suitable standard less than a month old. Coloured liquids are compensated with blanks in the usual way, and milk is precipitated with acetic acid and Tanret's reagent, and filtered.
J. GRANT.

Titration of ammonium phosphomolybdate. G. HAMMARSTEN (Compt. rend. Lab. Carlsberg, 1928, **17**, No. 5, 1—8).—Ammonium phosphomolybdate can be titrated directly in ammoniacal solution in the presence of acetone. The ammonium phosphomolybdate precipitate is dissolved from the filter with ammonia, the filter is washed with water, acetone is added to the combined solution and washings, which are then titrated with 0·1*N*-alcoholic potassium hydroxide with thymolphthalein as indicator. The method is compared with Scheffer's formaldehyde titration procedure (A., 1927, 953).
L. M. CLARK.

Use of strips of mercuric chloride paper in the Gutzeit test. A. F. LERRIGO (Analyst, 1928, **53**, 90—91).—The Gutzeit tube is packed with plumbised cotton wool up to such a height that the mercuric chloride paper strip (4×70 mm.), when placed in the tube and just projecting from it, is supported. All the arsenic in normal quantities (up to 0·05 mg. As_2O_3) is found to be retained at the lower end of the paper, forming a stain proportionate in length and intensity to the amount present. Mercuric bromide paper in use over an extended period was not found very superior to mercuric chloride paper.
D. G. HEWER.

Method of applying the Gutzeit test for arsenic. C. H. CRIBB.—See B., 1928, 89.

Production of uniform stains in the Gutzeit test for arsenic. J. R. STUBBS.—See B., 1928, 89.

Spring clip for Gutzeit tube. J. WHITE.—See B., 1928, 89.

Hypophosphite reaction for arsenic. W. P. H. VAN DEN DRIESSEN MAREEUW (Pharm. Weekblad, 1928, **65**, 70—75).—The hypophosphite test for arsenic recommended by the Dutch and German pharmacopœias does not give satisfactory results with the medicinal iron preparations, particularly where ferric iron is present. It is recommended to reduce the solutions with iron powder, filter, and carry out the test for arsenic with the filtrate; if blank tests are carried out at the same time, the alteration in colour due to the presence of arsenic is readily detected. Limits for the sensitiveness under various conditions are given (cf. Wallrabe, B., 1928, 172).
S. I. LEVY.

Titrimetric determination of tervalent arsenic by oxidation. F. G. GERMUTH (Amer. J. Pharm., 1927, **99**, 751—754).—Arsenious acid is oxidised rapidly and quantitatively by means of 0·1*N*-potassium permanganate solution in the presence of a trace of potassium iodide, which acts catalytically. The reaction takes place in the presence of mineral acids and the use of an indicator or sodium hydrogen

carbonate solution is unnecessary. The titration can be carried out at any temperature up to 95°. A slight correction is necessary for the oxidation of the small amount of potassium iodide added. Other iodides are not as effective as the potassium salt.
S. COFFEY.

Determination of permanganic and arsenious acids. N. KANÔ (Sci. Rep. Tôhoku, 1927, **16**, 873—879).—To avoid the irregularities usually observed in the direct titration of arsenious acid with permanganate, an excess of the latter should be added, a measured volume of standard hydrogen peroxide solution run in until the solution is colourless, and the titration finished with permanganate; with this procedure sharp end-points and regular results are obtained. The oxidation of the arsenite solution may be carried out in alkaline solution, the liquid being acidified after adding an excess of permanganate and the above procedure followed. For the determination of permanganic acid with arsenious acid the solution of the former is added to an alkaline solution of the latter, the mixture acidified with hydrochloric acid, potassium iodide added to reduce manganic compounds, the solution neutralised with sodium hydrogen carbonate, and the excess of arsenious acid determined iodometrically. A. R. POWELL.

Determination of boric acid in glass. A. A. MATSCHIGIN and T. KORZUCHINA.—See B., 1928, 91.

Potentiometric titration of boric acid in the presence of certain inorganic salts. M. G. MELLON and F. R. SWIM.—See B., 1928, 86.

Determination of sodium diborate. M. FRANÇOIS and L. SEGUIN.—See B., 1928, 87.

Volumetric determination of small amounts of carbonic acid and free ammonia present in distilled water. N. BJERRUM (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 1).—Carbonic acid and free ammonia (or ammonium carbonate) may be determined in distilled water, containing about $0{\cdot}5\times10^{-5}$ g.-mol. of either substance per litre, by titration with 0·01*N*-sodium hydroxide in an atmosphere of air free from carbon dioxide, using 0·4 c.c. of a special mixed indicator per litre of water. The indicator is composed of 5 g. of phenolphthalein and 1 g. of methyl-red dissolved in a litre of alcohol. The alkali is added until the tint of the solution is similar to that of a sodium phosphate solution, p_H 8·5—9, containing the same amount of indicator; at this stage the carbonic acid is present as hydrogen carbonate. The p_H value is then adjusted to 5·5—5 with 0·01*N*-hydrochloric acid in a similar manner, when the carbonic acid is present as such. From these values the ammonia and carbon dioxide contents are calculated. The following corrections are applied: (*a*) for the acid and alkali values of the indicator, (*b*) for absorption of the reagents by the walls of the flask, (*c*) for the amount of carbonic acid present in a form other than that assumed at each stage, (*d*) for the amount of hydroxyl and hydrogen ions present at each end-point. The method is tested by analysis of very dilute solutions of sodium carbonate and hydrogen carbonate.
G. A. C. GOUGH.

Substitution of sodium for potassium compounds [as reagents]. A. R. SMITH and F. C. VILBRANDT.—See B., 1928, 122.

Tartrate modification of the cobaltinitrite method for the gravimetric determination of potassium. M. WIKUL (Z. anal. Chem., 1927, **72**, 345—359; cf. A., 1926, 491).—The empirical method previously described has been modified to obtain stoicheiometric results. The potassium chloride solution, which should be at least 0·05*N*, is treated with 1·5—2 times its volume of the reagent described below, the mixture is treated with 3 g. of sodium chloride for every 10 c.c., heated to incipient boiling, allowed to cool, and filtered, and the precipitate of $NaCoOC_4H_4O_6,7K_2NaCo(NO_2)_6,H_2O$ is washed with dilute acetic acid, then with alcohol, dried at 110—120° for 20 min., and weighed; it contains 15·98% of potassium. The reagent, which is prepared immediately before use, is made by mixing 2 vols. of sodium nitrite solution (50 g./100 c.c.) with 1 vol. of cobalt nitrate solution (50 g. of crystals/100 c.c.), and 3 g. of tartaric acid in fine powder are stirred in to every 27 c.c. of the mixture; after evolution of nitrous fumes has ceased, the solution is cooled to 10° and filtered, and the filtrate heated to 75°, treated with hydrogen peroxide, heated to 85°, and cooled for use.
A. R. POWELL.

Origin of the error in the precipitation of barium sulphate. D. BALAREV (Z anal. Chem., 1927, **72**, 303—306).—Determinations of the loss of water and change in specific gravity of specimens of barium sulphate which were precipitated at the ordinary temperature, dried at 120°, and then heated to redness show that the precipitate has a porous structure, and contains many fine capillaries and internal surfaces. Microscopical examination of a specimen which was left in contact with potassium permanganate solution for several days confirmed this view. Hence the error is due to the adsorption of ions and molecules from the solution, and not to the formation of complexes of the type $BaClSO_4,BaCl$.
F. S. HAWKINS.

Volumetric determination of barium as chromate. A. MAZZUCCHELLI and B. ROMANI (Gazzetta, 1927, **57**, 900—913).—It has been shown by a number of control experiments that it is impossible to precipitate quantitatively silver and barium chromates successively since they form solid solutions with each other; approximate results are obtained by successive precipitation in 45% alcohol.
R. W. LUNT.

Volumetric determination of magnesium. J. VONDREK.—See B., 1928, 94.

Rapid determination of lead. G. SPACU and J. DICK (Z. anal. Chem., 1927, **72**, 289—293).—When a solution of ammonium thiocyanate (2 g.) and pyridine (1 c.c.) is stirred with not more than 0·3 g. of lead as an aqueous solution (50 c.c.) of a salt, the compound Pb(OH)SCN is quantitatively precipitated; it is collected on a Gooch crucible, washed with dilute pyridine and ammonium thiocyanate solution, 95% alcohol, and ether, dried for 60 min. in a vacuum, and weighed. The result is accurate to 0·1%, but with larger quantities of lead an appreci-

able error is introduced owing to the solubility of the precipitate in the ammonium salts present. An acetate, if present, must be removed by evaporating with nitric acid. F. S. HAWKINS.

Gravimetric determination of copper as cuprous thiocyanate. I. M. KOLTHOFF and G. H. P. v. D. MEENE (Z. anal. Chem., 1927, **72**, 337—345).—The gravimetric determination of copper by the thiocyanate method gives results which are correct to within 0·15% of the copper present if the precipitation is carried out in warm solutions the acidity of which does not exceed 0·5*N*, and if the amount of thiocyanate added does not exceed that necessary to give a 0·05*N*-solution when all the copper has been precipitated. In more concentrated thiocyanate solutions the precipitate redissolves with the formation of a complex salt. The presence of cobalt, nickel, zinc, manganese, arsenic, and large amounts of iron has no effect on the results, but tartaric acid must be added if the solution contains antimony, bismuth, or tin. After precipitation the solution should be set aside for 24 hrs., then filtered through a glass or porcelain crucible with porous bottom, and the precipitate dried at 110—120° for at least 3 hrs. The method is suitable for the determination of copper in pyrites. A. R. POWELL.

Titrations by Fajans' method. II. Determination of mercurous and bromide ions. R. BURSTEIN (Z. anorg. Chem., 1928, **168**, 325—326; cf. A., 1927, 847).—If mercurous nitrate solution is added to a solution of potassium bromide to which sodium alizarinsulphonate has been added as indicator, the point of equivalence is shown by the yellow colour of the solution changing to reddish-violet. Mercury may therefore be determined by adding to the solution an excess of potassium bromide, and titrating the excess with standard mercurous nitrate solution.

R. CUTHILL.

Dissolution of sulphides in mixtures of acid and hydrogen peroxide. A. S. KOMAROVSKY (Z. anal. Chem., 1927, **72**, 293—295).—Mercuric sulphide dissolves in warm 4*N*-hydrochloric acid, to which 6% hydrogen peroxide solution is added drop by drop. Calomel dissolves in 2*N*-hydrochloric acid containing hydrogen peroxide. Nickel and cobalt sulphides are soluble in a mixture of dilute acetic acid and 3% hydrogen peroxide solution. The presence of mercury can be confirmed by adding alkali hydroxide, when mercury is precipitated in the presence of hydrogen peroxide, and yellow mercuric oxide in its absence. Nickel is confirmed by means of dimethylglyoxime, and cobalt by Vogel's method. F. S. HAWKINS.

Gallium. I. Arc spectrographic detection and determination of gallium. II. Extraction of gallium from lepidolite. J. PAPISH and D. A. HOLT (J. Physical Chem., 1928, **32**, 142—147).—These methods are described together with the results of a spectrographic examination of 55 minerals for the presence of gallium. A 0·007% yield of this element was obtained from lepidolite.

L. S. THEOBALD.

Determination of manganese in steel by the Proctor Smith reaction in presence of phosphoric acid. B. C. MUKERJEE.—See B., 1928, 94.

Detection and determination of small quantities of manganese in water. R. SCHMIDT.—See B., 1928, 110.

Colorimetric determination of [traces of] manganese. A. C. JANZIG.—See B., 1928, 142.

Detection of cobalt by Tananaev's spot method. A. KOMAROVSKI and B. OVETSCHKIN (Chimiko-farm. Vestnik, 1926, Nos. 5—6, 9—10; Chem. Zentr., 1927, i, 3021).—Tananaev's method for the detection of cobalt with potassium thiocyanate, stannous chloride, and aniline has no advantage over Vogel's method using potassium thiocyanate alone.

A. A. ELDRIDGE.

Digallic acid as a reagent for earth-acids. W. R. SCHOELLER.—See B., 1928, 87.

Volumetric determination of antimony and arsenic. P. E. WINKLER (Helv. Chim. Acta, 1927, **10**, 837—842).—See A., 1927, 1160.

Determination of antimony as tetroxide with membrane filters and porcelain filtering crucibles. A. SIMON and W. NETH (Z. anal. Chem., 1927, **72**, 307—316).—The antimony is precipitated as sulphide by passing hydrogen sulphide for 1 hr. through a boiling solution containing 10% of concentrated hydrochloric acid. An equal volume of saturated aqueous hydrogen sulphide is added, the mixture cooled (30 min.), the precipitate collected and washed with 0·5*N*-hydrochloric acid saturated with hydrogen sulphide. In this way the formation of a colloidal sol is avoided. If a membrane filter is used, the sulphide is transferred to a weighed crucible, and oxidised gradually with nitric acid of increasing concentration. The sulphuric acid formed is removed by evaporation on a water-bath, followed by gentle heating, and the crucible is gradually heated to 820—900° in an electric oven, and dried at this temperature for 30 min. When a filtering crucible is used, the oxidation is effected by placing the sulphide over bromine and fuming nitric acid in a desiccator. By using these filters no filter-paper contaminates the precipitate and no reduction to the trioxide occurs on heating. Results accurate to 0·1% are obtained by both methods.

F. S. HAWKINS.

Determination of gold and silver in sea-water. M. YASUDA (Bull. Chem. Soc. Japan, 1927, **2**, 321—323).—Mercuric chloride is added to the sea-water and reduction effected by magnesium and hydrochloric acid. The mercury deposit containing the gold and silver originally present in the water is separated and ignited. A bead of metal is then obtained by the usual assay methods. If white, the bead is treated at once with nitric acid. If yellow, it is first dissolved in a drop of mercury. Quantities of gold and silver of the order 3—20 and 20—70 mg./m.^{3}, respectively, were found in Japanese sea-water. J. S. CARTER.

Hand spectroscope with new reagent tube condenser. F. LOWE (Chem. Fabr., 1928, 3—4).—Two tubes for the solution to be examined are mounted in the prism, which is fixed relatively to the lamp and condenser. The spectra corresponding with the two tubes appear in the eye-piece as vertical bands side

by side and having a common boundary; a wave-length scale is projected so as to appear at one side of the double band. S. I. LEVY.

Apparatus for observing fluorescence by ultra-violet illumination. G. KÖGEL (Chem. Fabr., 1928, 55—56).—The light from a "spot-light" tungsten arc lamp is filtered through a water-cooled quartz filter silvered on the outside to remove visible rays, and the remaining ultra-violet rays are reflected on to the illuminating mirror of a microscope if transparent objects are to be examined, or on to the surface of opaque objects by means of a spherical dark-field illuminator. In order to photograph the fluorescence the ultra-violet rays must be absorbed by passing the emergent light from the eye-piece of the microscope through a 5 mm. layer of a solution containing 0·5 g. of triphenylmethane in 70 c.c. of alcohol. The luminescence rays pass unabsorbed through this solution and are photographed on panchromatic ultra-rapid plates. A. R. POWELL.

Immersion fluid. S. H. BERTRAM (Chem. Weekblad, 1928, **25**, 24).—A very cheap fluid, having almost the same refractive index and dispersion as cedar oil, is prepared by dissolving 35 parts of pale colophony and 15 parts of naphthalene in 50 parts of sesame oil by gentle warming, treating with a little fuller's earth, and filtering. S. I. LEVY.

Comparison of attack and utility of modern filtering apparatus. A. SIMON and W. NETH (Chem. Fabr., 1928, 41—49).—The resistance of Jena, Berlin, Haldenwanger, and quartz filtering crucibles to attack by various reagents has been compared by observing losses in weight suffered under comparable conditions. A study has also been made of the rapidity and efficiency with which the various types of filter can deal with the different kinds of precipitate commonly obtained in analysis, *e.g.*, aluminium hydroxide, barium sulphate, silver chloride, etc. There is little difference between the types of crucible examined as regards resistance to attack by reagents other than hot alkali. For hot alkalis quartz and Jena glass are considered best. The authors do not recommend the use of Jena blue frit crucibles.

H. INGLESON.

Rotary filter stand. W. M. SHAW (Ind. Eng. Chem., 1928, **20**, 100—101).—A circular filter stand possesses three shelves fastened by set screws to a tube slipped over the central upright. They accommodate respectively wash-bottles, funnels, and beakers and can be rotated as a unit for easy access, enabling 12 filtrations to be performed simultaneously in very limited space. C. IRWIN.

Hydraulic lift for gas-analysis apparatus. E. J. TAUCH.—See B., 1928, 71.

Improved lighting source for m.-p. apparatus. E. V. FASCE (J. Amer. Chem. Soc., 1928, **50**, 252—253).—The light from an enclosed 100-watt lamp is directed on to the substance in the m.-p. tube by means of a rod of glass or quartz, 4 cm. × 8 mm.

F. G. WILLSON.

B.-p. apparatus for calibrating thermocouples. T. DE VRIES.—See B., 1928, 71.

Electrical heating equipment for chemical work. G. ANGEL.—See B., 1928, 97.

Constant temperature bath. A. V. HILL (J. Sci. Instr., 1928, **5**, 24—25).—The temperature of water in a Dewar vessel, a few degrees above that of the room, may be kept constant within 0·0005° by hand adjustment of a rheostat. Incipient changes in temperature are detected by a resistance thermometer actuating a very sensitive galvanometer.

C. W. GIBBY.

Continuous vacuum distillation apparatus. R. KUMMER (Chem. Fabr., 1927, 7).—The apparatus is entirely of glass, with ground joints, all parts being standardised. Two receivers are provided, so arranged that the distillate may be passed from the first to the second, and thence withdrawn, without interrupting the distillation. By means of a dropping funnel with joint ground in to the distilling flask, continuous addition of fresh liquid to the latter may be made. S. I. LEVY.

Isothermal calorimetry at high temperatures. A. MAGNUS and F. OPPENHEIMER (Z. anorg. Chem., 1928, **168**, 305—308).—An isothermal calorimeter suitable for determining the latent heat of fusion of substances with high m. p. is described. The substance is placed in a crucible with a double jacket between the walls of which is a heating coil; the crucible is contained in a tube surrounded by an evacuated jacket containing a second heating coil. By means of the latter coil, the substance is heated almost to its m. p., and when the temperature has become steady a current of known strength and voltage is passed through the coil round the crucible until a sharp rise in temperature of a thermocouple in the melting mass indicates that fusion is complete. From the total quantity of electricity passing through the coil nearer the crucible and the voltage, the latent heat of fusion may be calculated. R. CUTHILL.

Dispersion electricity. I. H. G. BOS (Chem. Weekblad, 1928, **25**, 66—72).—The name is suggested for the static charges resulting from the dispersion of a substance throughout a medium or milieu. An apparatus consisting of a spray jet and insulated chamber is employed to examine the electrification resulting from the spraying of liquids by compressed air; the potential is measured by means of an electrometer and condensers. Tables are given of the potentials obtained with water, aqueous solutions, petroleum, and alcohol, using pressures up to 4 atm. The maximum potential obtained in any series of readings is termed the "Dispersel." Both brass and iron sprays gave potentials of the same sign with the liquids treated. S. I. LEVY.

Explosion of liquid-air-cooled charcoal tubes. J. TAYLOR (J. Sci. Instr., 1928, **5**, 24).—An explosion may be caused by liquid air coming into contact with highly activated charcoal through cracking of the charcoal tube. It is suggested that the latter should be surrounded by a thin metal tube.

C. W. GIBBY.

Apparatus for preparing [active] aluminium chloride. G. A. DAWSON (J. Amer. Chem. Soc., 1928, **50**, 133—134).—A simple pyrex apparatus

consists of a wide tube, heated in a combustion furnace, bent at one end (the portion near the bend being wound with nichrome wire) and opened out to a funnel which fits on to a vessel having an outlet. Hydrogen chloride is passed over aluminium kept at dull red heat in the horizontal tube, the wound portion near the bend being heated to the necessary temperature before the furnace is lit. S. K. TWEEDY.

Florentium. L. ROLLA and L. FERNANDES (Gazzetta, 1927, **57**, 924, and Z. anorg. Chem., 1927, **169**, 319—320).—Polemical; a claim for priority. R. W. LUNT.

Geochemistry.

Relation between the variations of pressure and density of the air. D. ESPURZ (Anal. Fis. Quím., 1927, **25**, 490—493).—A theoretical paper in which arguments are advanced in support of the Loomis–Morley–Guye hypothesis (cf. Moles, A., 1927, 194). J. S. CARTER.

Dust storms and salt storms. F. BORDAS and A. DESFEMMES (Compt. rend., 1928, **186**, 159—161; cf. A., 1927, 1049).—As the result of a dust storm in November, 1927, a sample of rain-water from Montpellier was found to contain the chlorine equivalent of 3·3 g./m.^{2} of sodium chloride. It is calculated that during the dust and rain storm of November, 1926 (*loc. cit.*), the dust particles were suspended in the atmosphere for 57 days, and 24 g./m.^{2} of sodium chloride were deposited during this period. J. GRANT.

Composition of the thermal waters from Bareges (Hautes-Pyrenees). R. ROBINE and M. DEJUSSIEU (J. Pharm. Chim., 1928, [viii], **7**, 9—13).—Detailed analyses of these waters, originating from 15 springs, are given, together with those of previous investigators. The main constituents appear to be sodium, calcium, aluminium, chlorides, sulphides, sulphates, and silicates, with traces of lithium, iron, and phosphates. One water contains a measurable quantity of manganese, another iodine, and a third magnesium. All contain a fairly large proportion of arsenic. S. COFFEY.

Rare gases from some Bulgarian thermal springs. N. P. PENTCHEV (Compt. rend., 1928, **186**, 249—251; cf. A., 1927, 955).—Further determination of the gases from three Bulgarian thermal springs have shown them to contain nitrogen (96·7—98·7%), with traces of oxygen (0·1%), carbon dioxide (0·2%), argon (1·3—1·7%), and helium (0·014—0·254%). The radium emanations were 1·1—$110{\cdot}0\times10^{-10}$ curie per litre. The results confirm the astrophysical theory of Moureu and Lepape and are an indication of the geological origin of the rocks. J. GRANT.

Mutual relation of carbon dioxide and p_H in sea-water of varying salt content. E. M. KREPS (Int. Rev. ges. Hydiobrol. H., 1926, **15**, 240—257; Chem. Zentr., 1927, i, 3182).—Tables are given. With increasing carbon dioxide concentration the buffer action of sea water is more marked, and by diminution of the alkali reserve it is smaller. A. A. ELDRIDGE.

Salinity of water of Gulf of Carpentaria. G. J. BURROWS (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 211—212).—The chlorine content of water taken in 1911 from various parts of the Gulf of Carpentaria was less than that of a sample of sea water collected off the coast of Sydney, indicating that the water of the Gulf is diluted with water containing little or no salt, and probably discharged from the artesian basin. R. CUTHILL.

Determinative mineralogy. P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (Amer. J. Sci., 1928, [v], **15**, 89—102).—Lists of reagents and apparatus for a "field kit," with general remarks on the selection of material and on micro-chemical tests, are given. L. J. SPENCER.

Atomic number and terrestrial distribution. P. VINASSA (Atti R. Accad. Lincei, 1927, [vi], **5**, 940—945).—The large proportion of iron, nickel, and cobalt, and of elements of atomic number less than 26, in the earth's crust is discussed with reference to atomic stability and the periodic classification. R. W. LUNT.

Silicic acid as a protective colloid in the origin of Mediterranean red soils. A. REIFENBERG (Z. Pflanz. Dung., 1927, **10A**, 159—186).—Silicic acid sol acts as a protective and peptising agent towards ferric and aluminium oxides and hydroxides. In cataphoresis experiments ferric hydroxide hydrosol in the presence of silicic acid sol migrates to the anode or cathode according to whether silica or ferric hydroxide is in excess. When considerable amounts of alkali are present migration is always to the anode irrespective of the relative proportions. The iron sol is protected by silica against the flocculating action of neutral salts. The nature of several typical red soils is described and explained on this basis, as also is the high silica content of ferruginous strata of natural limestones. Ferric hydroxide hydrosol protected with silicic acid acquires the property of remaining deflocculated in the presence of limestone. Further, dialysed silicic acid is shown to be an active peptising agent for naturally occurring iron in veins of limestone. A. G. POLLARD.

Isomorphous replacement of silicon by aluminium. W. WAHL (Annal. Acad. Sci. Fennicæ, 1927, A, **29**, No. 22).—It is suggested that the apparent anomaly of the isomorphous replacement of quadrivalent silicon by tervalent aluminium in substances of the pyroxene and mellilite groups is actually a normal phenomenon in which silicon with a co-ordination number of six is replaced by aluminium of the same co-ordination number. G. A. C. GOUGH.

Manganiferous mineral from Kara-Tschaguir in Fergana. A. SAUKOV (Compt. rend. Acad. Sci. U.R.S.S. [Russia], 1926, 77—79; Chem. Zentr., 1927, ii, 796—797).—The black mineral has *d* 2·985±

0·09, and contains Fe_2O_3 2·7, Al_2O_3 9·8, ZnO 10·4, NiO 11·8, CoO 1·4, CuO 5·41, CaO 0·08, V_2O_5 4·3, MnO_2 23·6, H_2O (−110°) 4·6, H_2O (+110°) 19·9, insoluble 2·95; molybdenum also is present.

A. A. ELDRIDGE.

Natural hydrated magnesia. N. KURNAKOV and V. ČERNYH (Mem. Soc. Russe Min., 1926, [ii], **55**, 74—95; Chem. Zentr., 1927, ii, 797).—Brucite has *d* 2·360—2·396, ω 1·5634, ε 1·5840, $2V=2—8°$; nemalithite has *d* 2·310—2·397, $2V=18—26°$. Dehydrated brucite has ω_{Na} 1·6282, ϵ_{Na} 1·6192. The positive double refraction becomes negative on dehydration of brucite, and again positive when the dehydrated mineral remains in the air. The two minerals cannot be differentiated by chemical or thermal investigation. A. A. ELDRIDGE.

Hydrotalcite and pyroaurite. N. KURNAKOV and V. ČERNYH (Mem. Soc. Russe Min., 1926, [ii], **55**, 118—128; Chem. Zentr., 1927, ii, 797).—The brucite nucleus is present in both minerals; in hydrotalcite it is associated with alumina and in pyroaurite with ferric oxide. Carbon dioxide (0—10·84%) and water (about 8 mols.) are also present.

A. A. ELDRIDGE.

Helium content of uraninite from Karelia. V. CHLOPIN (Compt. rend., Acad. Sci. U.R.S.S. [Russia], 1926, 195—197; Chem. Zentr., 1927, ii, 798).—Six samples contained 4—5 c.c. per g., and two 0·3—0·4 c.c. The helium content is thus not proportional to the lead : uranium ratio.

A. A. ELDRIDGE.

System iron–oxygen–sulphur in the formation of stone meteorites, and the mineralogical nature and genesis of the black veins in such meteorites. P. CHIRVINSKY (Z. Min. Geol. Palaont., 1927, **A**, 199—205; Chem. Zentr., 1927, ii, 800).—The reactions taking place in the formation of the meteorites are: $6Fe+3O+S=6Fe+SO_2+O=2Fe+3FeO+FeS$. Oxidation of iron by oxygen occurs only after complete oxidation of silicon and manganese has taken place, whilst sulphur shows a relatively greater affinity for iron, forming troilite, which on account of its lower f. p. fills the veins and cracks. The black veins in the stone meteorites consist of josite, FeO, and troilite, with scorified silicate material and some iron. The ferrous oxide–ferrous sulphide eutectic, m. p. 1060°, may also be formed. The reaction $3Fe+SO_2=FeS+2FeO$ is exothermic, and proceeds from left to right at fairly low temperatures. A. A. ELDRIDGE.

Formation of radioactive manganiferous deposits from Tanokami, and the source of manganese in the deep-sea nodules. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 249—252).—See this vol., 42.

Green kaolin from Tanokami. S. IIMORI (Sci. Papers Ind. Phys. Chem. Res. Tokyo, 1927, **7**, 253—257).—See this vol., 42.

Microscopic zircons as guide minerals. J. ZERNDT (Bull. Acad. Polonaise, 1927, **A**, 363—377).—Statistics are given of the crystallographic features of microscopic zircons in granites and porphyries from various localities. Similar data are given for the zircons present in the Carpathian sandstones, and conclusions are reached therefrom as to the probable sources of the materials of these sedimentary rocks.

L. J. SPENCER.

Hypersthene-andesite of Blair Duguid, near Allandale, N.S. Wales. W. R. BROWNE and H. P. WHITE (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 372—387).—The hypersthene-andesite of the Blair Duguid hills appears some distance away in an altered form as the pebbles of a conglomerate. This change has apparently been effected by solutions of magmatic origin, and has involved the addition of both sodium and potassium to the rock, and the transformation of the hypersthene into iddingsite in some places and into carbonates in others.

R. CUTHILL.

Mineral constitution of the Broken Hill lode. F. L. STILLWELL (Austral. Inst. Min. Met., 1926, **64**, 97—172).—The argentiferous ore now worked at Broken Hill, New South Wales, consists of a granular mixture of blende and galena, other minerals being quite inconspicuous. Polished sections of the ore were examined under the microscope, and, with the aid of etching and chemical tests, the following minerals were identified: pyrite, pyrrhotine, mispickel, willyamite, enargite, cubanite, chalcopyrite, tetrahedrite, dyscrasite, pyrargyrite, etc. These occur in small amount enclosed in or intimately intergrown with the blende and galena. Gangue minerals present in the granular aggregate are garnet, rhodonite, and calcite. L. J. SPENCER.

Zoning of mineral deposits in British Columbia. G. HANSON (Trans. Roy. Soc. Canada, 1927, [iii], **21**, IV, 119—126).—The known mineral deposits of British Columbia were plotted on a map to show their relation to the intruded masses of igneous rocks. In the mineralised areas the general succession is tungsten, gold, copper, zinc, lead, and silver, as one proceeds away from the igneous rock.

L. J. SPENCER.

Organic Chemistry.

Photochemical changes of hydrocarbons. S. TOŁŁOCZKO.—See this vol., 255.

Formation of hydrocarbons from propyl alcohol. A. MAILHE and RENAUDIE (Compt. rend., 1928, **186**, 238—240).—When propyl alcohol is passed over uranium oxide at 400—420° hydrogen, methane, unsaturated hydrocarbons, and carbon monoxide and dioxide are evolved and a yellow liquid consisting mainly of propaldehyde condenses. The liquid, after removal of the aldehyde with water, can be separated into a hydrocarbon fraction consisting chiefly of hexane and hexene and an aldehyde fraction containing β-methylpentenal and αβ-di-

methyl-$\Delta^{\alpha\beta}$-heptadienal, to the breaking down of which the gases mentioned above owe their origin.

B. W. ANDERSON.

Preparation of higher acetylenes. I. Dehalogenation of αα-dichloroheptane in the vapour phase. A. J. HILL and F. TYSON (J. Amer. Chem. Soc., 1928, **50**, 172—177).—αα-Dichloroheptane is obtained in 70% yield by adding heptaldehyde to a stirred suspension of phosphorus pentachloride (1—1·25 mols.) in benzene at not above 20°. It is dehalogenated when passed over soda–lime at 360—430°, the highest yield, 10%, of Δ^{α}-heptinene being obtained by passing 100 g. of dichloroheptane over 300 g. of soda–lime (50% NaOH) at 420°. Substitution of aluminium silicate for soda–lime results in increased decomposition. The Δ^{α}-heptinene is best determined by adding it to a 5% silver nitrate solution in 95% alcohol, when the double salt, $C_5H_{11}\cdot C\cdot CAg,AgNO_3$, is precipitated. The salt may be weighed after drying at 60°, or, preferably, the liberated nitric acid titrated after filtration and removal of excess of silver by addition of sodium chloride (cf. Behal, A., 1888, 930).

F. G. WILLSON.

Intramolecular rearrangement [of alkyl halides] by photochemical action. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR.—See this vol., 255.

Identification of alkyl and aryl halides. E. L. HILL (J. Amer. Chem. Soc., 1928, **50**, 167—168; cf. A., 1926, 144).—Mercuric alkyl halides may be prepared as previously described from secondary alkyl and aryl halides, for identification of these compounds. The following are described: *mercuric* n-*nonyl*, m. p. 109°; n-*lauryl*, m. p. 108°; iso*propyl*, m. p. 93·5°; β-*phenylethyl*, m. p. 169°; o-*tolyl*, m. p. 168°, and *p*-tolyl bromide, m. p. 231° (cf. Pope and Gibson, J.C.S., 1912, **101**, 736).

F. G. WILLSON.

Alcoholysis and hydrolysis of some alkyl halides in neutral solution. B. H. NICOLET and D. R. STEVENS (J. Amer. Chem. Soc., 1928, **50**, 135—139).—The rates of hydrolysis and alcoholysis of propyl and *iso*propyl bromides and iodides in boiling alcohol containing small known amounts of water have been measured in presence of calcium carbonate to remove free halogen acids. The secondary halides react in each case more rapidly than the corresponding primary halides (cf. Conant and Hussey, A., 1925, i, 493), and all the reactions are strongly catalysed by the corresponding mercuric halides (cf. Burke and Donnan, A., 1909, ii, 987).

F. G. WILLSON.

Reaction between aluminium and bromoform. S. GAMBARJAN (Ber., 1928, **61**, [*B*], 177—179).—Aluminium turnings, suspended in chloroform, are converted by bromine into a black, voluminous material insoluble in all media. The same product is formed when aluminium is treated with a deficiency of bromine and subsequently with chloroform and, consequently, directly from well-cleaned aluminium and bromoform. The change probably occurs through production of acetylene and action of aluminium bromide on the latter. A similar behaviour is exhibited by *s*-tetrabromoethane, ethylene dibromide, and methylene dibromide. After being heated in a vacuum at 200°, the product retains much aluminium. Treatment of it with solvents for aluminium bromide (carbon disulphide, pyridine, acetophenone) leaves residues containing aluminium, whereas an almost ash-free material containing 38% of oxygen is obtained by means of acetone. The ratio C : H appears to be 1 : 1.

H. WREN.

Reaction of *iso*propyl iodide with mercuric chloride. B. H. NICOLET and W. M. POTTS (J. Amer. Chem. Soc., 1928, **50**, 212—216).—Mercuric chloride reacts with *iso*propyl iodide in absolute ether at 25°, with practically quantitative formation of *iso*propyl chloride (cf. Conant, Kirner, and Hussey, A., 1925, i, 494). The reaction velocity is proportional to the product of the concentrations of the two reactants and of the mercuric iodide formed. It is suggested that the reaction between the *iso*propyl iodide and the mercuric chloride is extremely slow, but that the complex $Pr^{\beta}I,HgI_2$ is formed, which then reacts more rapidly with either mercuric chloride or chloride ion.

F. G. WILLSON.

Oxidation of certain aliphatic and aromatic carbon compounds by dichromate. H. ARK (J.C.S., 1928, 46—47).—Oxidation by potassium dichromate and sulphuric acid is used to determine lower alcohols and some other compounds, by titrating the residual dichromate ion (cf. Grey, J.C.S., 1914, **105**, 2204; A., 1924, ii, 208). Formic acid is oxidised at concentrations of sulphuric acid at which propionic acid is stable; as acetic acid is not attacked, it is suggested that mixtures of the acids might be analysed by oxidation. The method is unsuitable in presence of aldehydes, or of halogen or imino-compounds; succinamide, acetamide, carbamide, and α-amino*iso*-butyric acid are unaffected.

E. W. WIGNALL.

Oxidation of polyhydric alcohols with periodic acid. L. MALAPRADE (Compt. rend., 1928, **186**, 382—384).—Oxidation of ethylene glycol, glycerol, erythritol, adonitol, and mannitol with periodic acid proceeds in the cold and reaction is complete after 12 hrs. The number of molecules of periodic acid reduced to iodic acid is one less than that of the hydroxyl groups in the alcohol. The method can be used to determine small quantities of polyhydric alcohols in aqueous solution, and the composition of a mixture of iodic and periodic acids.

When aqueous solutions of pure periodic acid are treated with at least sufficient alcohol to ensure complete reduction, there are formed acids from all compounds except ethylene glycol. Increase in the quantity of the reacting alcohol causes a diminution in the amount of acids produced. When neither of the reacting substances is in excess the change is $[CH_2\cdot OH]_2[CH\cdot OH]_n+(n+1)HIO_4=2H\cdot CHO+nH\cdot CO_2H+(n+1)HIO_3$.

H. BURTON.

Catalytic action. XIX. Catalytic action of reduced copper on methyl alcohol. S. KOMATSU and S. SUZUKI (Mem. Coll. Sci. Kyoto, 1927, **10A**, 339—341).—Primary alcohols can generally be decomposed by heat either into olefine and water or into hydrogen and aldehyde. Methyl alcohol in presence of reduced copper as catalyst gives a mixture of formaldehyde and ethylene. The yield of ethylene is always small, but rises to a maximum of 3% when

the copper is made from copper oxide prepared by igniting the nitrate and the temperature is about 500°. The yield of formaldehyde rises to 34·4% at 600° with the same form of metal. Lower temperatures or copper made by other methods gave lower yields. C. D. LANGFORD.

Reaction between diaryloxy*iso*propyl alcohols and phosphorus oxychloride in presence of pyridine. D. R. BOYD and D. E. LADHAMS (J.C.S., 1928, 215—221).—When di-*p*-tolyloxy*iso*propyl alcohol reacts at 0° with excess of phosphorus oxychloride in presence of pyridine, the product obtained on treating the reaction mixture with ice is mainly *di*-p-*tolyloxy*iso*propyl phosphate*, $(C_7H_7{\cdot}O{\cdot}CH_2)_2CH{\cdot}O{\cdot}PO(OH)_2$, m. p. 158°, but if the reaction mixture is heated at 100° before decomposition with ice, di-*p*-tolyloxy*iso*propyl chloride is formed, together with a comparatively small amount of the corresponding pyridinium salt, isolated as 1-$\alpha\gamma$-*di*-p-*tolyloxy*iso*propylpyridinium nitrate*, $C_5H_5N{\cdot}CH(CH_2{\cdot}O{\cdot}C_7H_7)_2NO_3$, m. p. 165° (decomp.) [*chlorate*, m. p. 153° (violent decomp.); *thiocyanate*]. The pyridinium nitrate is decomposed by cold aqueous alkali, giving *p*-cresol and certain resinous products, one of which condenses with aniline, yielding a deep red *compound*, m. p. 117—119° (decomp.). When a large excess of phosphorus oxychloride is not present and the reaction mixture is heated at 100° before decomposition with ice, an excellent yield of *bis*-$\alpha\gamma$-*di*-p-*tolyloxy*iso*propyl phosphate*, m. p. 160°, is obtained, together with a small quantity of a phosphorus-containing *compound* (tri-ester?), m. p. 205—207°, and of di-*p*-tolyloxy*iso*propyl chloride. The following substances have been prepared by analogous reactions: $\alpha\gamma$-*diphenoxy*iso*propyl phosphate*, m. p. 137—137·5° [*sodium* salt ($+10H_2O$), m. p. 54°]; *bis*-$\alpha\gamma$-*diphenoxy*iso*propyl phosphate*, m. p. 105°; $\alpha\gamma$-*di*-o-*tolyloxy*iso*propyl phosphate* (*sodium* salt, $+10H_2O$); 1-$\alpha\gamma$-*di*-o-*tolyloxy*iso*propylpyridinium nitrate*, m. p. 154°; 1-$\alpha\gamma$-*di*-p-*nitrophenoxy*iso*propylpyridinium nitrate*, m. p. 182°; $\alpha\gamma$-*di*-p-*nitrophenoxy*iso*propyl chloride*, m. p. 186°.

In the absence of pyridine, diaryloxy*iso*propyl alcohols do not yield the corresponding chlorides. Only the mono- and bis-esters are obtained. An explanation of these reactions and of the part played therein by the crystalline additive compound, $(C_5H_5N)_2,POCl_3$, formed from pyridine and phosphorus oxychloride is advanced. M. CLARK.

Preparation of $\alpha\eta$-dihydroxyheptane (heptamethylene glycol) and $\alpha\eta$-dibromo-*n*-propane. A. MÜLLER and E. RÖLZ (Monatsh., 1927, 48, 733—736).—Reduction of ethyl pimelate by the Bouveault and Blanc method affords *n*-heptane-$\alpha\eta$-diol (60% yield), b. p. 148—149°/10 mm. [phenylcarbimide, m. p. 137° (corr.); cf. Dionneau, A., 1915, i, 491]. Treatment of the glycol with hydrobromic acid at 130—140° yields $\alpha\eta$-*dibromoheptane*, b. p. 132°/11 mm., in 74% yield. H. BURTON.

Acetone compounds of pentaerythritol. L. ORTHNER (Ber., 1928, 61, [*B*], 116—118).—*Pentaerythritol* iso*propylidene ether*,

$CMe_2{<}^{O\cdot CH_2}_{O\cdot CH_2}{>}C(CH_2{\cdot}OH)_2$ m. p. 128—129°, is prepared by treating pentaerythritol with aqueous acetone containing hydrogen chloride. The *di*iso*propylidene ether*, m. p. 117—117·5°, is obtained from pentaerythritol or its *iso*propylidene ether by the use of anhydrous acetone and copper sulphate. The compound prepared by Bougault by the action of sulphur chloride on pentaerythritol is identified as the disulphite, m. p. 153—154°; its formation is ascribed to the presence of thionyl chloride in the reagent. H. WREN.

Monoacetals of pentaerythritol. A. SKRABAL and S. KALPASANOV (Ber., 1928, 61, [*B*], 55—57; cf. A., 1927, 27).—The monoacetals are prepared by treatment of 1 mol. of pentaerythritol with 1 mol. of the necessary aldehyde in the presence of concentrated hydrochloric acid. The diacetals simultaneously produced are separated by treatment of the product with cold benzene; the residue is extracted with hot benzene in which the monoacetals dissolve, whereas unchanged pentaerythritol is not appreciably soluble. The following compounds are described: *monoformal*, $CH_2{<}^{O\cdot CH_2}_{O\cdot CH_2}{>}C(CH_2{\cdot}OH)_2$, m. p. 40°; *monoacetal*, m. p. 104°; *monopropal*, m. p. 70°; *mono*iso*butyral*, m. p. 107°. The dipropal has m. p. 25°. H. WREN.

Isomerisation of aromatic trisubstituted ethylene oxides and the re-arrangement phenomena involved. R. LAGRAVE (Ann. Chim., 1927, [x], 8, 363—446).—Treatment of $\alpha\alpha$-diphenyl-Δ^{α}-propene, m. p. 51° (*dimeride*, m. p. 130°), with perbenzoic acid in chloroform solution gives $\alpha\alpha$-*diphenyl*-β-*methylethylene oxide*, b. p. 178—180°/21 mm., m. p. 34°, d_0^4 1·1038, n^{15} 1·5755 (cf. Stoermer, A., 1906, i, 583), which isomerises on slow distillation into $\alpha\alpha$-diphenylpropan-β-one. $\alpha\alpha$-Diphenylpropaldehyde does not isomerise under the same conditions. Dehydration of $\alpha\alpha$-diphenylbutan-α-ol with sulphuric–acetic acids furnishes $\alpha\alpha$-*diphenyl*-Δ^{α}-*butene*, b. p. 160—163°/10 mm. (*dimeride*, m. p. 110—111°), which yields $\alpha\alpha$-*diphenyl*-β-*ethylethylene oxide*, b. p. 175—180°/18 mm., d_0^4 1·1114, n^{15} 1·5790. This oxide isomerises at its b. p. into $\alpha\alpha$-diphenylbutan-β-one (85%) and $\alpha\alpha$-diphenylbutaldehyde (15%). Magnesium *iso*butyl bromide and benzophenone or magnesium phenyl bromide and ethyl *iso*valerate form $\alpha\alpha$-*diphenyl*-γ-*methylbutene*, b. p. 169—170°/20 mm., d_0^4 0·9946, n^{15} 1·5754, which yields $\alpha\alpha$-*diphenyl*-β-iso*propylethylene oxide*, b. p. 182—183°/20 mm., d_0^4 1·0507, n^{15} 1·5550, isomerised to $\alpha\alpha$-diphenyl-γ-methylbutan-β-one (82%) and $\alpha\alpha$-diphenyl-β-methylbutaldehyde (18%). $\alpha\alpha$-*Diphenylpentene*, b. p. 170°/13 mm., d_0^4 1·0139, n^{15} 1·5768, yields $\alpha\alpha$-*diphenyl*-β-n-*propylethylene oxide*, b. p. 175—180°/10 mm., d_0^4 1·052, n^{15} 1·5595, which isomerises into $\alpha\alpha$-diphenylpentan-β-one. $\alpha\alpha$-*Diphenyl*-β-iso*butylethylene oxide*, b. p. 196—197°/17 mm., d_0^4 1·035, n^{15} 1·5555, isomerises into $\alpha\alpha$-diphenyl-δ-methylbutan-β-one (80%) and $\alpha\alpha$-diphenyl-γ-methylvaleraldehyde (20%), and $\alpha\alpha$-*diphenyl*-β-n-*butylethylene oxide*, b. p. 195—197°/17 mm., d_0^4 1·037, n^{15} 1·5485, gives $\alpha\alpha$-diphenylhexan-β-one (80%) together with $\alpha\alpha$-diphenylhexaldehyde (20%). $\alpha\alpha\gamma$-Triphenylpropene, b. p. 228—229°/15 mm. (cf. Paterno and Chieffi, A., 1910, i, 41), furnishes $\alpha\alpha$-*diphenyl*-β-*benzylethylene*

oxide, m. p. 69°, which on distillation at 290°/95 mm. isomerises into ααγ-triphenylpropan-β-one (42%) and ααβ-triphenylpropaldehyde (58%), whilst distillation under ordinary pressure gives diphenylmethane and diphenylacetaldehyde. *Triphenylethylene oxide*, m. p. 77°, furnishes phenyl diphenylmethyl ketone, also produced when triphenylethylene glycol is heated at 180°. If this last reaction is carried out in presence of zinc chloride, a small amount of triphenylacetaldehyde is produced in addition to the ketone. Distillation of triphenylacetaldehyde furnishes triphenylmethane. Triphenylethylene when treated with excess of perbenzoic acid yields in addition to the oxide about 20% of phenyl diphenylmethyl ketone, whilst hot 50% oxalic acid converts the oxide into the corresponding glycol. The examples of isomerisation cited above are explained thus: $CPh_2{\cdot}O{\cdot}CHR \longrightarrow \overset{-O}{CPh_2}{\cdot}CHR \longrightarrow CHPh_2{\cdot}COR$ (I)$+CPh_2R{\cdot}CHO$ (II); where R=Me, Pr^a, and Ph, (I) is the sole product, but if R=Et, Pr$^\beta$, Bu^a, Bu$^\beta$, or CH_2Ph, (I) and (II) are formed at the same time. The saturation capacity of the two phenyl groups is greater than any combination studied.

Magnesium anisyl bromide reacts with diphenylacetaldehyde to form *αα-diphenyl-β-anisylethan-β-ol*, m. p. 160°, which is oxidised by chromic–acetic acids to *anisyl diphenylmethyl ketone*, m. p. 129—130°, and dehydrated by acetyl chloride to *αα-diphenyl-β-anisylethylene*, m. p. 84—85° (*dibromide*, m. p. 132°). Hydrolysis of the above ketone with alcoholic potassium hydroxide gives anisic acid and diphenylmethane. Treatment of the ethylene with perbenzoic acid in ether yields *αα-diphenyl-β-anisylethylene oxide*, m. p. 104°, which isomerises at its b. p. into anisyldeoxybenzoin, m. p. 85—86°. This change is represented $CPh_2{\cdot}O{\cdot}CHR \longrightarrow \underset{O\cdot}{CPh_2}{\cdot}CHR \longrightarrow COPh{\cdot}CHPhR$, thus demonstrating the high saturation capacity of the anisyl group. These results are discussed fully, as are the cases described by Tiffeneau and Lévy (A., 1926, 383, 818). H. BURTON.

Hydrolysis of *n*-butyl nitrate. H. RYAN and V. J. R. COYLE (Proc. Roy. Irish Acad., 1927, **37**, 361—367).—*n*-Butyl nitrate is slowly hydrolysed by 56% aqueous potassium hydroxide at 100°; when refluxed with the reagent some potassium nitrite and tarry substances are formed. Alcoholic potassium hydroxide yields similar products together with traces of an ether. Acetic anhydride and sodium acetate have no action on the ester, whilst the action of alcoholic ammonia is very slow. The addition of an excess of hydrogen sulphide to the latter reagent causes rapid hydrolysis with the deposition of sulphur and the formation of traces of a mercaptan. The ester may also be slowly hydrolysed with iron and acetic acid. G. A. C. GOUGH.

Natural optically active inositoltetraphosphoric ester. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1928, **186**, 261—263).—The picric acid extract of the phosphorus compounds in wheat grain in which the phosphatase had been destroyed was treated with barium acetate and the precipitate thus formed dissolved in just sufficient 10% hydrochloric acid. The crystalline precipitate which then settled corresponded with the formula $(C_6H_{12}O_{21}P_5,2H_2O)_2Ba_5$ (cf. Anderson, A., 1920, i, 801) and consisted of the mixed salts of inositolhexaphosphoric acid and *inositoltetraphosphoric acid*, $\alpha_D^{14.5}$ −3·92° for the free acid, $\alpha_D^{14.5}$ −7·94° after neutralising with sodium hydroxide. The syrupy, uncrystallisable acid last mentioned forms insoluble alkaline-earth and heavy-metal salts and by means of the former it was isolated; it is formed also by the action of phosphatase on sodium inositolhexaphosphate, and this is probably the manner in which it originates in the seed.

B. W. ANDERSON.

Hexaphenylethane alkyl sulphide additive compounds. V. C. ROGERS and G. DOUGHERTY (J. Amer. Chem. Soc., 1928, **50**, 149—156).—Additive *compounds*, $(CPh_3)_2,SR_2$, can be obtained by preparing triphenylmethyl from triphenylmethyl chloride and mercury in methyl, ethyl, or propyl sulphide solution. In bromobenzene solution, the rate of oxidation of triphenylmethyl is increased by the presence of either of the above alkyl sulphides. When heated at 150°, the methyl sulphide additive product decomposes, with formation of complex hydrocarbons and, apparently, methyl triphenylmethyl sulphide, from which it is concluded that the additive compounds have a sulphonium structure.

F. G. WILLSON.

Chlorination products of ββ′-dichlorodiethyl sulphide. S. A. MUMFORD and J. W. C. PHILLIPS (J.C.S., 1928, 155—162).—The compounds described by Mann and Pope (J.C.S., 1922, **121**, 594) as (I) αββ′-trichloro- and (II) αββδ′-tetrachloro-diethyl sulphides, obtained by the chlorination of ββ′-dichlorodiethyl sulphide, are re-investigated. Analytical figures for (I) and (II) agree better with the formulæ $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, respectively, than with the formulæ assigned; it is suggested that the compounds are β-chloroethyl-α′β′(or β′β′)-dichlorovinyl and α′β′β′-trichlorovinyl sulphides respectively. This view is supported by their stability towards hydrolysis, by their red colour with sulphuric acid, and by their physical properties (cf. Lawson and Dawson, this vol., 153). E. W. WIGNALL.

Action of thionyl chloride on organic acids. L. MCMASTER and F. F. AHMANN (J. Amer. Chem. Soc., 1928, **50**, 145—149).—Thionyl chloride converts chloroacetic acid, but not trichloroacetic acid or glycine, into the acid chloride. Oxalic and tartaric acids are unattacked by thionyl chloride, succinic and glutaric acids yield anhydrides, and malonic, suberic, and sebacic acids form dichlorides; maleic acid yields the anhydride, whilst fumaric acid is unattacked. The nitrobenzoic acids all yield acid chlorides with thionyl chloride, but with difficulty in the case of the *p*-derivative. *m*- and *p*-Aminobenzoyl chlorides can be obtained similarly, but anthranilic acid is unaffected. Salicylic acid yields the acid chloride, but *p*-hydroxybenzoic acid is unaffected, whilst *m*-hydroxybenzoic acid and the hydroxytoluic acids yield vitreous solids of indefinite composition. Phthalic acid is converted by thionyl chloride into the anhydride, *iso*phthalic acid yields the dichloride, but terephthalic acid is unaffected. F. G. WILLSON.

Preparation of *iso*butyryl chloride. A. RÉCSEI (Chem.-Ztg., 1928, **52**, 22).—*iso*Butyric acid is treated with phosphorus trichloride and the product distilled at ordinary pressure. S. I. LEVY.

Purification of palmitic and stearic acids. A. L. WILKIE (J.S.C.I., 1927, **46**, 471—472T).—Reasonably pure palmitic and stearic acids may be obtained by fractional distillation under diminished pressure of a mixture of the ethyl esters through a column of the Dufton type, 150 cm. long, maintained at a uniform constant temperature. The appropriate fractions are hydrolysed. W. J. POWELL.

Hydrogenation of methyl oleate, erucate, cetoleate, and clupanodonate. S. UENO and N. KUZEI (J. Soc. Chem. Ind. Japan, 1927, **30**, 268—275).—The ester (0·5 g.) was hydrogenated in solution in glacial acetic acid or ethyl alcohol in the presence of platinum-black. Methyl oleate and erucate were found to require nearly equal lengths of time for complete hydrogenation; methyl erucate and cetoleate required less time than methyl clupanodonate. It is concluded that the length of time required for the complete hydrogenation is nearly equal for all those members of normal unsaturated acids that belong to the same series and have nearly equal mol. wt., but for acids of different degree of unsaturation the time required depends entirely on the degree of unsaturation, being longer as the acid is more unsaturated. N. KAMEYAMA.

Cork. II. F. ZETZSCHE, C. CHOLATNIKOV, and K. SCHERZ (Helv. Chim. Acta, 1928, **11**, 272—276).—When pure cork (A., 1927, 541) is treated with iodine in chloroform solution for 9–13 weeks there is left an inelastic, sandy residue (30—38%), consisting of suberin-free cork cells, and the total cellulose. It does not contain iodine, whereas the portion soluble in chloroform contains about 45% of iodine and gives on hydrolysis traces of fatty acids. Cellulose acetate is not affected by iodine even after 5 months. The results using oxidised and phosphoric acid corks are also given. It is concluded that the cellulose in cork is not in stable combination with the suberin. H. BURTON.

Mechanism of the oxidative action of hydrogen peroxide in presence of ferrous iron. Oxidation of glycollic acid. S. GOLDSCHMIDT and P. ASKENASY.—See this vol., 251.

Biochemical formation of optically active lactic acid. Preparation of zinc *d*(—)-lactate. C. NEUBERG and M. KOBEL (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 8).—In the previous experiments (A., 1927, 592) it is probable that a small amount of lactic acid was formed directly from the yeast. G. A. C. GOUGH.

Determination of lactic acid in sugar solutions decomposed by alkali. T. E. FRIEDEMANN (J. Biol. Chem., 1928, **76**, 75—87).—The author's method (A., 1927, 800) for the determination of lactic acid may be applied to the mixture of substances obtained by the action of alkali on a sugar, the error under these conditions being 5—10%. C. R. HARINGTON.

Determination of mercury salicylate and lactate. A. JONESCO-MATIN and C. V. BORDLEANO.—See this vol., 313.

Complete history of Wohler's first organic synthesis. W. H. WARREN (Ber., 1928, **61**, [*A*], 3—7).—Attention is directed to the fact that Wohler's work on the action of cyanogen on ammonia led him to the isolation and identification of oxalic acid in 1824 and of carbamide, the identification of which was published only in 1828. In one reaction, therefore, Wohler effected the synthesis of organic compounds of vegetable and animal origin, respectively. H. WREN.

Influence of the substitution sequence CH_2, O, S on reactivity of some aliphatic acids and their esters. M. H. PALOMAA and R. LEIMU (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 10).—The velocity coefficients of hydrolysis and esterification, determined in a 50% mixture of water and the respective alcohol at 25° with hydrogen chloride as catalyst, of the following esters are, respectively: 0·146, 0·424 for methyl glutarate; 0·089, 0·109 for ethyl glutarate; 0·217, 0·357 for methyl diglycollate; 0·152, 0·113 for ethyl diglycollate; 0·115, 0·272 for methyl thiodiglycollate; 0·076, 0·081 for ethyl thiodiglycollate; 0·304, 0·532 for methyl glycollate; 0·221, 0·183 for ethyl glycollate; 0·288, 0·762 for methyl propionate; 0·186, 0·219 for ethyl propionate. It is observed that each substituent has almost the same influence on the velocity coefficients of the ethyl esters as it has on those of the corresponding methyl ester. G. A. C. GOUGH.

Determination of tartaric acid in presence of other organic acids. E. BERNHAUER (Oesterr. Chem. Ztg., 1928, **31**, 4—7).—Tartaric acid is precipitated as potassium hydrogen tartrate by boiling with potassium acetate and glacial acetic acid in presence of a large volume of 96% alcohol. The precipitate is washed with 66% alcohol, dissolved in warm water, and titrated with standard alkali. Details of the procedure and of the limits of accuracy in the presence of other organic acids are given. S. I. LEVY.

Bismuth salicylates and citrates. P. GODFRIN.—See this vol., 288.

Hydroxy-acids of the sugar group. I. *d*-Saccharic and *d*-gluconic acids. K. REHORST (Ber., 1928, **61**, [*B*], 163—171).—Crystalline polyhydroxy-acids of the sugar group, free from the corresponding lactones, are prepared by treating solutions of suitable salts with slightly less than the calculated quantity of mineral acid and pouring the products into ethyl alcohol mixed with *iso*butyl or amyl alcohol. Evaporation of the solutions leaves a residual solvent consisting mainly of the higher alcohol, from which the crystalline acid usually separates after further concentration. If ethyl alcohol alone is used, water is the main residual solvent, and from it the acid separates as the lactone. Thus, potassium hydrogen saccharate is converted by use of *iso*butyl alcohol into d-*saccharic acid*, m. p. 125—126°, $[\alpha]_D^{18}$ +6·86° to +20·60°; mutarotation is due to the formation of the lactone and occurs simultaneously with a decrease in the acidity of the solution. From calcium

d-gluconate and oxalic acid, d-*gluconic acid*, $[\alpha]^{20}$ $-6{\cdot}7°$ to $+12°$, is obtained by use of amyl alcohol; *iso*butyl alcohol causes extensive esterification. The acid passes at 78°/12 mm. into a mixture, $[\alpha]_D$ $+61°$ to $+20°$, containing much δ- and little γ-lactone with possibly some unchanged acid. H. WREN.

Allenetetracarboxylic acid. II. J. PIRSCH (Ber., 1928, 61, [*B*], 33—38; cf. A., 1927, 856).—The action of sodium hydrogen carbonate on ethyl γ-bromo-αγ-dicarbethoxyglutaconate proceeds analogously to that of potassium ethoxide (*loc. cit.*), leading very slowly to the formation of ethyl sodio-αγ-dicarbethoxyglutaconate. This compound is also produced when sodium carbonate in boiling absolute alcohol is used, but ethyl allenetetracarboxylate is also formed in minor quantity. The latter compound is the main product of the action of anhydrous normal sodium phosphate (prepared by heating the crystalline material slowly to 240°, powdering the product, and heating it for 8 hrs. at 260° in absence of air) under similar conditions. Ethyl carbonate and minimal quantities of ethyl sodio-αγ-dicarbethoxyglutaconate are also formed. The phosphate apparently behaves merely as acceptor for the liberated hydrogen bromide. Simultaneous oxidation and reduction are observed during the action of potassium acetate on ethyl γ-bromo-αγ-dicarbethoxyglutaconate, the products being ethyl dicarbethoxyglutaconate (identified as ethyl 6-ethoxy-2-pyrone-3 : 5-dicarboxylate, m. p. 94°), ethyl carbonate, and ethyl ethanetetracarboxylate; oxidation thus appears to result in the removal of the central carbon atom of the glutaconic acid skeleton. Pyridine and ethyl γ-bromo-αγ-dicarbethoxyglutaconate afford the *pyridine* salt of ethyl 6-hydroxy-2-pyrone-3 : 5-dicarboxylate, decomp. 181°, converted by boiling concentrated hydrochloric acid into carbon dioxide and glutaconic acid, but unchanged by boiling ethyl alcohol. H. WREN.

Nature of the hydrocarbon group of thymonucleic acid. P. THOMAS and E. MAFTEI (XII Int. Cong. Physiol., 1926, 159; Chem. Zentr., 1927, i, 2435).—The six-carbon sugar of thymonucleic acid is considered to be related to glycuronic acid.

A. A. ELDRIDGE.

Sulphopyrotartaric acids. II. H. J. BACKER and J. BUINING (Rec. trav. chim., 1928, 47, 111—122; cf. this vol., 46).—Methylsuccinic acid is sulphonated by excess of sulphur trioxide, forming mainly *α-sulpho-α-methylsuccinic acid* ($+H_2O$), m. p. 121° (decomp.) [*thallium, barium* ($+2H_2O$), *calcium* ($+$[illegible]H_2O), *potassium* ($+H_2O$), *copper* ($+6H_2O$), *nickel* ($+7H_2O$), and *cobalt* ($+7H_2O$) salts]. This acid is produced by the interaction of ammonium sulphite and ammonium citraconate, mesaconate, or α-bromo-α-methylsuccinate, although in the last case some α-hydroxy-α-methylsuccinic acid is formed at the same time. Treatment of the sulphonic acid with brucine gives the *brucine hydrogen* salt ($+4H_2O$), which on decomposition with ammonia yields *ammonium* d-*α-sulpho-α-methylsuccinate*, $[M]_D$ $+31°$ in water. The d-*acid* has $[M]_D$ $+33°$ in water, whilst the *sodium* salt has $[M]_D$ $+31°$. *Ammonium*-l-*α-sulpho-α-methylsuccinate*, $[M]_D$ $-31°$, is obtained by decomposition of the normal *strychnine* salt ($+2H_2O$). Racemisation of the acids or their salts is not effected by heating at 100°. H. BURTON.

Constitution of the hydrogen sulphite compounds of aldehydes and ketones. F. RASCHIG and W. PRAHL (Ber., 1928, 61, [*B*], 179—189; cf. A., 1926, 598).—Schroeter's observation (A., 1926, 1226) that the production of β-hydroxypropyl-β-sulphonic acid by hydrolysis of phenyl propane-ββ-disulphonate and its non-identity with "acetone bisulphite" has been overlooked by the authors (*loc. cit.*) and has led to a repetition of Schroeter's work in this direction (A., 1919, i, 517). Phenyl methanedisulphonate (methionol) is conveniently prepared by the action of methanedisulphonyl chloride on phenol in the presence of benzene and pyridine at 0° and is converted by $2N$-sodium hydroxide at 80° into the sodium derivative; this, with methyl sulphate in boiling toluene, affords phenyl ethane-αα-disulphonate, converted by the successive action of sodium and methyl sulphate into phenyl propane-ββ-disulphonate, identical with Schroeter's compound. Treatment of the compound with barium hydroxide leads to the formation of barium sulphite (mixed with a little barium carbonate) in amount corresponding closely with the loss of one sulphonic acid residue. The solution contains a mixture of barium salts which are converted for purposes of separation into the corresponding copper salts, one of which (A), characterised by very sparing solubility in hot acetic acid, approximates in composition to copper β-hydroxypropane-β-sulphonate. A second salt, which separates when the solution of the mixture in hot acetic acid is cooled, resembles closely *copper propane-β-sulphonate* (prepared for comparison from *iso*propyl chloride through *iso*propyl mercaptan), but identity cannot be assumed. Attempts to prepare further quantities of the salt A by the same method were unsuccessful and the copper salt which separated in these cases from the acetic acid is not identical with that described above, since it yields a barium salt, $C_6H_{12}O_7S_2Ba$, transformed into a non-homogeneous sulphonamide and oxidised by permanganate to oxalic and sulphuric acids, with, possibly, methanesulphonic acid. The non-identity of salt A with *copper β-hydroxypropane-α-sulphonate, γ-hydroxypropane-α-sulphonate*, and *α-hydroxypropane-β-sulphonate* is established by direct comparison. The first two are prepared by sulphonation of *iso*propyl and propyl alcohols. To obtain the last, glycerol is converted by sodium hydroxide into propylene glycol and thence into the corresponding chlorohydrin, which yields the monoacetate. This substance with thionyl chloride affords *β-chloropropyl acetate*, b. p. 152°, transformed by saturated potassium sulphite solution at 120° into *potassium α-hydroxypropane-β-sulphonate*; the copper salt derived from it differs entirely from salt A.

Further criticisms of the authors' views have been made by Binz (A., 1926, 1123); these are regarded as answered by Bazlen (A., 1927, 842). Further confirmation of the view that the hydrogen sulphite compounds of aldehydes and ketones are hydroxysulphonic acids is found in the Rontgen-spectrographic observations of Stelling ("Zusammenhang

zwischen chemischer Konstitution und *K*-Rontgen-Absorptionsspektra," Lund, 1927, p. 168).

H. WREN.

Formation of formaldehyde and of sugars by the action of ultra-violet rays on alkali and alkaline-earth hydrogen carbonates. G. MEZZADROLI and G. GARDANO.—See this vol., 255.

Nonaldehyde from the tetradecenoic acid from sperm oil. A. WAGNER (Allg. Öl- Fett-Ztg., 1927, 24, 340—341; Chem. Zentr., 1927, ii, 708).—Tetradecenoic acid, d_4^{20} 0·9018, n_D^{20} 1·4549, iodine value 107, was isolated from sperm-whale oil, and converted into the ozonide which on decomposition with water yielded nonaldehyde (semicarbazone, m. p. 80—84°; after purification with hydrogen sulphite, semicarbazone, m. p. 100°; oxime, m. p. 64°).

A. A. ELDRIDGE.

Oxidative synthesis of a dialdehydic carbohydrate, $C_{15}H_{28}O_{15}$, from dextrose. J. A. MANDEL and J. B. NIEDERL (XII Int. Cong. Physiol., 1926, 104—105; Chem. Zentr., 1927, ii, 242).—Oxidation of dextrose with barium hypochlorite solution yields an amorphous *compound* of the composition $C_{15}H_{28}O_{15}$, $[\alpha]_D$ +64°. Reduction affords a *compound*, $C_{15}H_{32}O_{15}$, $[\alpha]_D$ +98° (*acetyl* derivative, m. p. 112—114°). The bisosazone, $C_{39}H_{48}O_{11}N_8$, has m. p. 194°. Oxidation yields monocarboxylic and dicarboxylic *acids*, $C_{14}H_{27}O_{14}\cdot CO_2H$ and $C_{13}H_{26}O_{13}(CO_2H)_2$, respectively.

A. A. ELDRIDGE.

Effect of certain β-substituents in the alcohol on affinity and reactivity in acetal formation. J. N. STREET and H. ADKINS (J. Amer. Chem. Soc., 1928, 50, 162—167; cf. A., 1927, 1172).—Under the conditions previously laid down, the percentage conversions, at equilibrium, of the following β-substituted ethyl alcohols into acetals are in the following decreasing order: β-amino-, β-phenyl-, β-iodo-, β-ethoxy-, β-methoxy- (allyl alcohol), β-bromo-, β-chloro-, β-carbethoxy-, and β-nitro-ethyl alcohol. Generally, the affinity of ethyl alcohol for acetal formation is little affected by β-substitution, as compared with α-substitution. The following acetals are described: *acetal* of *ethylene chlorohydrin*, b. p. 109—110°/30 mm.; *ethylene bromohydrin*, b. p. 129—130°/20 mm.; β-*methoxyethyl alcohol*, b. p. 100°/20—30 mm.; β-*ethoxyethyl alcohol*, b. p. 83—85°/10—15 mm.; β-phenylethyl alcohol, b. p. 201°/15 mm.

F. G. WILLSON.

Rate of synthesis and hydrolysis of certain acetals. H. ADKINS and A. E. BRODERICK (J. Amer. Chem. Soc., 1928, 50, 178—185; cf. preceding abstract).—The rates of reaction of acetaldehyde with methyl, ethyl, *iso*propyl, and *n*-butyl alcohols have been determined with specially purified reagents, in presence of hydrogen chloride (0·000465 g. per mol. of alcohol; cf. Adkins and Adams, A., 1925, i, 785). Only slight differences in the reactivities of the alcohols for acetal formation were observed. Assuming the immediate formation of a semiacetal, with subsequent bimolecular reaction between the latter and the alcohol, the values of the bimolecular reaction constant diminish steadily in the period between 2 and 100 min. from commencement of reaction. Consistent values of the constants are, however, obtained on the assumption that the water eliminated in the acetal formation is largely consumed in hydrolysis of the semiacetal. With the same concentration of catalyst, the rate of hydrolysis of *iso*propyl acetal is much less than that of the synthesis, whilst the hydrolytic reaction constant increases somewhat as the reaction proceeds, both these phenomena being ascribed to the poisoning effect of water.

F. G. WILLSON.

Relation of structure of ketones to their reactivity and affinity in acetal formation. H. E. CARSWELL and H. ADKINS (J. Amer. Chem. Soc., 1928, 50, 235—241; cf. preceding abstract).—Ethyl formate may be determined in presence of alcohol, ethyl orthoformate, a ketone and its acetal by treatment of the mixture with sufficient sodium to react with the alcohol and with sodium ethoxide, and measuring the carbon monoxide evolved (cf. Geuther, Chem. Zentr., 1868, 39, 632). Approximately 2 mols. of carbon monoxide are obtained from 3 mols. of ethyl formate, but the actual amount varies slightly with the amount and kind of ketone present, probably owing to Claisen condensation of the ethyl formate. Applying this method, the extent of acetal formation from ethyl orthoformate and the following ketones has been determined: acetone, methyl ethyl, diethyl, methyl *n*-hexyl, and methyl *tert.*-butyl ketones, acetophenone, propiophenone, and benzophenone. Ethyl orthoformate does not condense with ketones in toluene or xylene solution in presence of hydrogen chloride, this reaction taking place only in presence of hydrogen chloride and a considerable proportion of alcohol. The greatest extent of acetal formation (about 90%) was observed with acetone, and the least (12·5%) with methyl *tert.*-butyl ketone. Substitution of higher *n*-alkyl radicals for the methyl group or groups in acetone reduces slightly the extent of acetal formation, still greater reductions being observed progressively through acetophenone, propiophenone, and benzophenone. The *diethylacetals* of *methyl n-hexyl ketone*, b. p. 101—103°/16 mm., 0·8798, and *propiophenone*, b. p. 118—120°/15 mm., d_{25}^{25} 0·9406, are described.

F. G. WILLSON.

Nitrosyl chloride and ketones. H. RHEINBOLDT and O. SCHMITZ-DUMONT (Ber., 1928, 61, [*B*], 32—33; cf. A., 1925, i, 1131).—Contrary to the observations of Lynn and Lee (A., 1927, 544), "nitrosochlorination" occurs by the action of nitrosyl chloride on ketones in the absence of solvent. Thus pinacolin affords chloro-oximinopinacolin, m. p. 133—134°. The differing results are due to the different relative quantities of nitrosyl chloride and ketone employed. Lynn and Lee's supposed conversion of methyl ethyl ketone into its oximino-derivative could not be confirmed, diacetylmonoxime, m. p. 76°, being obtained by this reaction.

H. WREN.

Changes in carbohydrate solutions due to sunlight in presence of uranium salts and to ultra-violet rays. ABELOUS, ALOY, and VALDIGUIÉ.—See this vol., 255.

Comparative reduction values of carbohydrates by the Hagedorn–Jensen, Benedict–Myers, and Folin–Wu methods. G. W. PUCHER and M. W. FINCH (J. Biol. Chem., 1928, 76, 331—

335).—Comparative results of the determination of known solutions of various sugars by the above-mentioned methods are given. The most consistent results were obtained with the method of Hagedorn and Jensen (A., 1920, ii, 641); in general, the figures agree with those determined by previous workers, except that lævulose is found to have a reducing value 10—20% higher than that of dextrose.

C. R. HARINGTON.

Applications of thallium compounds in organic chemistry. IV. Thallium compounds of poly-hydroxy-compounds. R. C. MENZIES and (MISS) M. E. KIESER (J.C.S., 1928, 186—190).—The purity of the yellow compounds formed on mixing concentrated aqueous solutions of thallous hydroxide with those of the sugars etc. (Menzies and Wilkins, A., 1924, i, 704) may be judged by comparing the total precipitated thallium content with the amount of hydrolysable thallium (replacing non-acidic hydroxyl groups) indicated by titration (Christie and Menzies, A., 1926, 55). Dextrose, galactose, and especially lævulose compounds give indefinite analytical figures, showing decomposition to acid products; thallium methylglucoside (Fear and Menzies, A., 1926, 604) when rapidly prepared gives titration values very little less than the total thallium content.

Trithallium methylarabinoside, m. p. 215—220° (decomp.) after darkening at 160—210°, which is unaffected by daylight, gives titration values in close agreement with the total thallium.

Thallous gluconate, $C_5H_{11}O_5{\cdot}CO_2Tl$, prepared from barium gluconate and thallous sulphate, has m. p. 134—144° (darkening), $[\alpha]_D +3{\cdot}3°$ (c=4·24) in aqueous solution; when prepared from gluconic acid and thallous hydroxide it has m. p. 133—138° (darkening), and $[\alpha]_D +4{\cdot}4°$ (c=3·9); crystal nuclei are, however, obtained only in preparations from mercury gluconate and metallic thallium. When this compound is treated with thallous hydroxide, *hexathallium gluconate*, $C_5H_6(OTl)_5{\cdot}CO_2Tl$, lævorotatory in aqueous solution, is obtained; this when freshly prepared gives theoretical titration values for $(OTl)_5$, which diminish on keeping the substance. *Hexathallium sorbitol*, $C_6H_8(OTl)_6$, gives, when freshly prepared, theoretical titration values, which similarly diminish.

Tetrathallium sucrose has been prepared.

E. W. WIGNALL.

Electron-sharing ability of organic radicals; dextrose and other poly-alcohols. J. B. ALLISON HIXON (J. Amer. Chem. Soc., 1928, 50, 168 172; cf. A., 1927, 814).—The conductance of aqueous solutions of glucosamine has been measured, and Vellinger's value (A., 1926, 778) for the basic dissociation constant confirmed. The dissociation constant of glucosamine, the corresponding constant of dextrose, and the heat of replacement of hydrogen in dextrose by sodium all lie midway between the corresponding constants for methyl- and phenyl-amines and hydroxides, indicating that the electron-sharing ability of the radical of dextrose (and of those of other polyalcohols) is intermediate between that of the methyl and phenyl group.

F. G. WILLSON.

Action of superheated water on sugars. I. . KOMATSU and C. TANAKA (Sexagint [Osaka celebration], Kyoto, 1927, 1—12).—2% Solutions of *l*-xylose, *l*-arabinose, rhamnose, dextrose, *d*-galactose, α-methylglucoside, sucrose, maltose, and lactose were heated at 120° and 150° for 2—20 hrs. and the resulting acidity, reducing power, rotation, colour, and percentage of furfuraldehyde were found. All the monosaccharides examined yield pyrone compounds first and subsequently acidic and humic substances. The authors favour the scheme given by Nef: ·CH(OH)·CH(OH)·CHO ⟶ ·CH(OH)·CH(OH)·CH(OH)₂ ⟶ ·CH(OH)·C(OH):CH·OH, and in support show that mannitol, having no carbonyl group, is not appreciably changed by water at 150° in 6 hrs. With disaccharides hydrolysis to monosaccharides occurs first, the rate being related to the rate of hydrolysis by acids. The rate of the subsequent action is found to be related to the ease of attack of *Penicillium glaucum*, but different from the ease of oxidation in alkaline solution. Humic and acidic substances are formed under the same conditions from furfuraldehyde and the humic substances resemble those in the soil.

C. D. LANGFORD.

Action of superheated water on sugars. II. C. TANAKA (Sexagint [Osaka celebration], Kyoto, 1927, 13—26).—A more detailed study of the action of superheated water on lævulose, dextrose, sucrose, rhamnose, and xylose is given and, in support of the view that the reaction takes place in two steps, it is shown that hydroxymethylfurfuraldehyde, methylfurfuraldehyde, and furfuraldehyde yield products apparently identical with those obtained from the sugars from which they would be expected. It is suggested that coal may have been formed by a related series of changes.

C. D. LANGFORD.

Transformation of β-glucosides and β-acetyl-sugars into their α-varieties. E. PACSU (Ber., 1928, **61**, [*B*], 137—144).—Addition of 3 mols. of anhydrous stannic chloride to a solution of 1 mol. of a β-acetyl-sugar in anhydrous chloroform causes quantitative production of the corresponding α-variety; the change is complete within 6—7 days at the ordinary temperature, in 4—5 hrs. in warm solution. Isomerisation of β-glucosides proceeds more slowly and, under similar conditions, gives an equilibrium mixture containing about 92% of the α-glucoside; if the proportion of stannic chloride is reduced to 1 mol., equilibrium is established in the presence of 75% of α-glucoside. Stannic chloride does not appear to cause isomerisation of α-acetyl-sugars or α-glucosides. If the reaction with β-penta-acetyl-glucose is allowed to proceed further, the acetyl group attached to carbon atom 1 is replaced by chlorine with production of the known dextrorotatory aceto-chloroglucose, identified by conversion into tetra-acetyl-β-methylglucoside. It appears therefore that the acetohalogeno-sugars belong to the α-series and not, as previously supposed, to the β-group. This view is in harmony with their high dextrorotation. Replacement of the chlorine atom is therefore accompanied by a Walden inversion. The method of isomerisation described above appears applicable to all similar derivatives of mono- and di-saccharides. Inversion occurs only with respect to the groups

attached to the 1-carbon atom, the remainder of the molecule being unchanged. The following transformations are recorded: β- into α-penta-acetylglucose, $[\alpha]^{20}$ +102·70° in chloroform; β-penta-acetylglucose into α-acetochloroglucose; β- into α-penta-acetylmannose, $[\alpha]^{20}$ +55·26° in chloroform; tetra-acetyl-β- into tetra-acetyl-α-methylglucoside, hydrolysed to α-methylglucoside, m. p. 166—167°, $[\alpha]_D^{20}$ +156·9° in water. H. WREN.

Properties and preparation of lævulose. H. I. WATERMAN, A. ROOSEBOOM, and E. L. OBERG (Chem. Weekblad, 1928, **25**, 50—52).—Lævulose is decomposed even at low temperatures by lime, whether added as calcium oxide or hydroxide. The lime compound consists of fine white needles, which become yellow and decompose when kept in a vacuum over phosphoric oxide. It may be used for the separation of the pure sugar from invert-sugar and from beet molasses, the precipitated compound being filtered, washed, and immediately decomposed with carbon dioxide. S. I. LEVY.

Synthesis of lactose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1928, **11**, 209—215).—Mainly an account of work already published (A., 1927, 960). The following is new. When β-galactose is heated at 150°/14 mm., there is formed *β-galactosan*, m. p. 154—155°, $[\alpha]_D^{20}$ +30·49° to +80·66° in water after 24 hrs. owing to the regeneration of β-galactose. β-Galactosan differs from the α-isomeride (A., 1922, i, 811) in that it is hydrolysed instantaneously with cold, very dilute sulphuric acid forming galactose, and when treated with phenylhydrazine or acetic anhydride gives galactosazone or penta-acetylgalactose. A formula is suggested. When it is heated with β-glucose and a small amount of zinc chloride at 150°/14 mm., and the product is acetylated and hydrolysed, lactose is formed. H. BURTON.

Formulæ of *Digitalis* glucosides. I. Digitoxin. A. WINDAUS (Nachr. Ges. Wiss. Gottingen, 1926, 170—174; Chem. Zentr., 1927, i, 2912—2913).—The formula $C_{41}H_{64}O_{13}$ is ascribed to digitoxin, whence on hydrolysis: $C_{41}H_{64}O_{13}+3H_2O=C_{23}H_{34}O_4$ (digitoxigenin) $+3C_6H_{12}O_4$; tetrahydroanhydrodigitoxigenin is $C_{23}H_{36}O_3$, tetrahydroanhydrodigitoxigenone, $C_{23}H_{34}O_3$, and the derived lactone $C_{23}H_{36}O_5$. Digitoxigenin is a singly unsaturated dihydroxylactone, yielding an unsaturated trihydroxymonocarboxylic acid, dixgenic acid, and when warmed with hydrochloric acid yields, by elimination of the elements of water, a doubly unsaturated monohydroxylactone, anhydrodigitoxigenin, $C_{23}H_{32}O_3$. A. A. ELDRIDGE.

Digitin of Nativelle. P. BOURCET and G. DUGUE (Compt. rend., 1928, **186**, 395—397).—Treatment of the digitin, m. p. 281°, of Nativelle (Mon. Sci., 1874, [iii], 4, 827) with chloroform affords digitonin and a soluble product, m. p. 273°, α_D −66·5° (acetyl derivative, m. p. 244—245°), identical with digin (Tambach, A., 1912, i, 375) and gitogenin (Windaus and Schneckenburger, A., 1913, i, 1213). The authors suggest that the names digin and digitin be replaced by gitogenin. H. BURTON.

Extraction of the active glucosides of *Adonis vernalis*. G. A. PEVZNER (Trans. Sci. Chem.-Pharm. Inst., 1923, No. 3, 78—84).—The whole of the active principle is extracted in a Soxhlet apparatus with absolute ethyl alcohol, by percolation with methyl or ethyl alcohol, or by extraction (20 times) with water. Alcohol increases, whereas heating at 100° diminishes, the activity of the product. CHEMICAL ABSTRACTS.

Alcoholic potassium hydroxide as microchemical reagent for starch and aleurone. F. NETOLITZKY (Festschr. A. Tschirch, 1926, 362—365; Chem. Zentr., 1927, i, 2933).—Starch grains are affected by warm alcoholic potassium hydroxide at rates differing according to their origin. With aleurone grains the globoid is at first clearly observed; after some time the protein crystalloid is removed. The ash of aleurone grains of *Bertholletia* seeds (13—15%) contains P_2O_5 35—36%, CaO 8·5—9·5%, MgO 17—19%, and K_2O 15%. A. A. ELDRIDGE.

Polysaccharides. XXXVII. Behaviour of various celluloses towards snail cellulase. P. KARRER and P. SCHUBERT (Helv. Chim. Acta, 1928, **11**, 229—230; cf. B., 1926, 44, 945).—Enzymic hydrolysis of seven specimens of cellulose shows that after 7 weeks 22—38·4% is degraded. β-Cellulose is hydrolysed more rapidly than α-cellulose, whilst filter-paper is almost completely decomposed (93%) after about 3 months. H. BURTON.

Polysaccharides. XXXVIII. Behaviour of viscose silks towards snail cellulase. O. FAUST, P. KARRER, and P. SCHUBERT (Helv. Chim. Acta, 1928, **11**, 231—233).—Hydrolysis of 12 specimens of viscose silks, 6 from one cellulose and 6 from another, shows that least decomposition occurs when the viscose silk is precipitated from an acid bath containing 5·4% of an aromatic sulphonic acid. The hydrolysis is much decreased when the viscose silk is precipitated from an acid bath containing relatively large amounts of sodium sulphate. H. BURTON.

Depolymerisation of inulin. H. VOGEL and A. PICTET (Helv. Chim. Acta, 1928, **11**, 215—220).—When inulin is heated with glycerol at 120°/15 mm. for 3 hrs. and the reaction mixture diluted with methyl alcohol and ether there is precipitated *trilævulosan*, m. p. 165°, decomp. 173°, $[\alpha]_D$ −29·66° in water (*nona-acetate*, m. p. 91°, $[\alpha]_D$ −35·52° in benzene), which does not reduce Fehling's solution or give an osazone, and is hydrolysed by 5% sulphuric acid to lævulose. When the mixture is heated at 140°/15 mm. for 6 hrs. there are formed a *dilævulosan*, m. p. 96°, $[\alpha]_D$ −24·8° (*hexa-acetate*, m. p. 92°, $[\alpha]_D$ −29·8° in benzene), which is a reducing agent, together with a syrupy *substance*, $[\alpha]_D$ +12·5° in water, probably a compound of lævulosan and glycerol (cf. Pictet and Reilly, A., 1921, i, 544). Hydrolysis of the above acetates by Zemplen's method gives the original lævulosans. The lævulosan of Pictet and Reilly (*loc. cit.*) when heated at 120°/14 mm. with a small amount of zinc chloride furnishes a *dilævulosan*, m. p. 138—140°, $[\alpha]_D$ +21·5° in water (*hexa-acetate*, m. p. 83—84°, $[\alpha]_D$ +6·98° in benzene), which is also a reducing agent. H. BURTON.

Metallic complexes of cellulose nitrates. A. APARD (Compt. rend., 1928, **186**, 153—154).—When

1% solutions of cellulose nitrate are electrolysed, using lead, mercury, copper, zinc, cadmium, and iron as electrodes, gelatinous metal–cellulose nitrate complexes are formed at the anode, whilst some of the metal dissolves. Gelatinous residues of a more variable composition are formed by agitating the oxides of silver, calcium, bismuth, barium, aluminium, etc. with 1% solutions of cellulose nitrate in acetone.

B. W. ANDERSON.

Constitution of pine lignin. VI. Identity of α-lignosulphonic acid with coniferaldehyde-sulphonic acid. P. KLASON (Ber., 1928, 61, [*B*], 171—176; cf. A., 1920, i, 822; 1922, i, 324; 1923, i, 187; 1925, i, 371, 1246).—Vanillin is converted by methyl-alcoholic sodium hydroxide in the presence of toluene into its sodium derivative, which is transformed by the successive action of chloromethyl ether and acetaldehyde in dilute alkaline solution into 3-methoxy-4-methoxymethoxycinnamaldehyde (cf. Pauly and Wascher, A., 1923, i, 342). Treatment of the latter compound with a saturated aqueous solution of sulphur dioxide eliminates the methoxymethoxy-residue with production of coniferaldehydesulphonic acid, isolated as the β-*naphthylamine* salt. This compound has the same percentage composition and properties as the β-naphthylamine salts of the α-lignosulphonic acids. It appears, therefore, that α-lignin of pine, comprising 75% of the total lignin, is formed by condensation of coniferaldehyde, into which it can be degraded by sulphurous acid; the acid is always firmly united to the ethylenic linking of the aldehyde, so that in the technical boiling process the lignin appears mainly as the sulphonic acid of paraconiferaldehyde. These views on the relationship of lignin to coniferaldehyde are strengthened by the observation of the identity of hadromal and coniferaldehyde (cf. Hoffmeister, A., 1927, 1189).

H. WREN.

Synthesis and purification of hexamethylene-imine. A. MULLER and A. SAUERWALD (Monatsh., 1927, 48, 727—732).—Treatment of αζ-dibromo-*n*-hexane (1 mol.) and *p*-toluenesulphonamide (1 mol.) with aqueous-alcoholic potassium hydroxide solution affords N-p-*toluenesulphonylhexamethyleneimine*, m. p. 72—74°, together with αζ-di-*p*-toluenesulphonamido-*n*-hexane. Treatment of the former compound with concentrated hydrochloric acid at 160° gives hexamethyleneimine hydrochloride, m. p. 236° (corr.) (lit. 222°). Pure hexamethyleneimine has b. p. 138·0—138·2°/749 mm., d_4^{15} 0·8841, d_4^{20} 0·8799, d_4^{25} 0·8770, n_D 1·4654; the following derivatives are described: chloroplatinate, decomp. 196—197° (corr.) (lit. 149° and 191°); *chloroaurate*, decomp. 206° (corr.); picrate, m. p. 146·5° (corr.) (lit. 85°); *phenylthiocarbami[illegible]*, m. p. 143° (corr.); the *benzoyl* derivative, m. p. [illegible] (corr.), when treated with phosphorus pentachloride yields αζ-*diphenoxy*-n-*hexane*, m. p. 83—[illegible] (corr.). *NN*-Dimethylhexamethyleneiminium iodide [*chloroplatinate*, decomp. 233° (corr.)] has m. p. 265° (corr.) with slight decomp. (lit. 214—215°).

H. BURTON.

Alkylamino-ethanols and -propanols. J. S. PIERCE (J. Amer. Chem. Soc., 1928, 50, 241—244).—Condensation of allylamine with β-chloroethyl chloroformate affords β-*chloroethyl allylcarbamate*, b. p. 103·5—104·5°/1·3 mm., d_4^{20} 1·1811, n_D^{27} 1·4668. When boiled with 1·5 mols. of alcoholic potassium hydroxide, the latter is converted into 3-*allyl*-2-*oxazolidone*, b. p. 123—125°/0·7 mm., d_4^{20} 1·113, n_D^{27} 1·4691, whilst with 4 mols. of alkali, β-*allylaminoethyl alcohol*, b. p. 77—80°/1·5 mm., d_4^{20} 0·9398, n_D^{21} 1·4602, is obtained (cf. Pierce and Adams, A., 1923, i, 484). γ-*Chloropropyl allylcarbamate*, b. p. 110—111°/1 mm., d_4^{20} 1·1390, n_D^{23} 1·1390, *methylcarbamate*, b. p. 104·5—106°/1 mm., d_4^{20} 1·1821, n_D^{27} 1·4548, and n-*amylcarbamate*, b. p. 135—137°/2 mm., d_4^{20} 1·0629, n_D^{21} 1·4560, obtained similarly, yield, when boiled with 4 mols. of alcoholic potassium hydroxide, γ-*allylamino*-, b. p. 88—90°/0·8 mm., d_4^{20} 0·9319, n_D^{27} 1·4629, γ-*methylamino*-, b. p. 74—77°/2·5 mm., d_4^{20} 0·9315, n_D^{27} 1·4418, and γ-n-*amylamino-propyl alcohol*, b. p. 103—105°/1·8 mm., d_4^{20} 0·8858, n_D^{21} 1·4493, respectively.

F. G. WILLSON.

Determination of arginine. A. BONOT and T. CAHN (Bull. Soc. Chim. biol., 1927, 9, 1001—1016).—See A., 1927, 269.

Interaction of sulphur monochloride with organic compounds containing the reactive methylene group. Formation and properties of dithioketones and dithioethers. IV. K. G. NAIK and Y. N. BHAT (J. Indian Chem. Soc., 4, 525—530).—*Dithioketones*, $R_2C{<}^{S}_{S}$, are obtained from sulphur monochloride and the following amides: malondiethylamide, m. p. 202° after softening at 186°; malondi-*n*-propylamide, m. p. 180° after softening at 172°; malondi*iso*butylamide, m. p. 202° after softening at 196°; malondiheptylamide, m. p. 125°; malondi-*m*-toluidide, m. p. 180° after softening at 158° [*tetranitro*-derivative, m. p. 166° (decomp.)]. Methylmalondi-*m*-toluidide gives the *dithio-ether*, m. p. 187—188°. *Malondi*-n-*heptylamide*, m. p. 132°, *methylmalondi*-m-*toluidide*, m. p. 157°, and *methylmalondibenzylamide*, m. p. 142°, are incidentally described.

C. D. LANGFORD.

Formation of cyanate in the determination of alkali cyanides with copper sulphate. J. LEBOUCQ (J. Pharm. Chim., 1927, [viii], 6, 20—25).—The percentage of potassium cyanide which combines to form a complex copper cyanide in the volumetric determination of alkali cyanides by means of copper sulphate has been shown never to exceed 85·3% of that present. The remaining 14·7% of the cyanide becomes oxidised during the reaction to cyanate, proved by separating it as hydrazodicarbonamide with semicarbazide. The results are thus in accordance with Treadwell's suggested equations for the reaction: $2CuSO_4+2NH_3+7KCN+H_2O=2K_2Cu(CN)_3+(NH_4)_2SO_4+K_2SO_4+KCNO$, or $2CuSO_4+2NH_3+7KCN+H_2O=K_2(NH_4)Cu_2(CN)_6+2K_2SO_4+NH_4CNO$.

E. A. LUNT.

Coloration of alkali thiocyanates on exposure to light. E. MONTIGNIE (Bull. Soc. chim., 1928, [iv], 43, 106—108; cf. Kahane, this vol., 34).—The pink colour which develops on exposure of solutions of alkali thiocyanates to sunlight is due to the oxidation by dissolved oxygen of the traces of ferrous salts which are usually present. On keeping coloured solutions in the dark for a few hours the colour dis-

appears. Assuming the iron to be present as ferrous sulphate, the observed effects may be represented by the scheme: $2FeSO_4+O+6HCNS \rightarrow H_2O+2H_2SO_4+2Fe(CNS)_3$. The decolorisation effected on boiling is due to hydrolysis of the ferric thiocyanate and subsequent reduction of ferric hydroxide to ferrous hydroxide. Re-oxidation occurs on exposure to the air and the colour returns. Traces of quinol prevent the appearance of the pink colour. Coloration occurs in presence of strong acids and salts which are largely ionised, but not in presence of weak acids. The colour is extracted by ether, amyl alcohol, and ethyl acetate, but not by chloroform or benzene. J. S. Carter.

Residual affinity and co-ordination. XXX. Complex ethylenethiocarbamido-salts of univalent and bivalent metals. G. T. Morgan and F. H. Burstall (J.C.S., 1928, 143—155).—Additive products of unoxidised sulphur compounds to cupric or auric salts readily yield complexes (cf. Morgan and Ledbury, J.C.S., 1922, **121**, 2883) in which the cuprous or aurous state is stabilised. Thiocarbamide has such an action, but forms polynuclear derivatives (cf. Kohlschutter, A., 1903, i, 468; 1906, i, 812; Contardi and Dansi, this vol., 159); thus on mixing aqueous solutions of potassium cyanate and of copper sulphate, saturated with sulphur dioxide, and treating the resultant *substance*, $Cu_2K(CNO)_3$, with thiocarbamide in aqueous solution, *pentathiocarbamidodicuprous cyanate hydrate*, $[Cu_2,5CH_4N_2S](CNO)_2,H_2O$, is obtained as a colourless substance, of which the aqueous solution decomposes on keeping or on heating, or on treatment with sodium hydroxide. This is attributed to the co-ordinating power of the two amino-groups. When the action of the latter is inhibited by forming a cyclic compound, ethylenethiocarbamide (symbolised " etu " in formulæ), this difficulty is largely avoided. Cuprous, aurous, argentous, palladium, cadmium, mercury, and lead salts containing this substance have been prepared.

On mixing aqueous solutions of ethylenethiocarbamide and cupric nitrate, there is a transitory green coloration, followed by separation of sulphur; the solution on evaporation yields colourless *tetrakisethylenethiocarbamidocuprous nitrate*, $[Cu,4\ etu]NO_3$, m. p. 140—141°. *Monoaquopentaethylenethiocarbamidodicuprous nitrate*, $[Cu_2,5\ etu,\ H_2O](NO_3)_2$, is obtained by using a larger proportion of cupric nitrate, and drying over sulphuric acid; this is easily oxidised, as is its *trihydrate* ($+3H_2O$), m. p. 145—146°. When the latter is treated in solution with aqueous sodium hydroxide, followed by heating, *ethylenethiocarbamidocuprous oxide*, darkening at 180°, decomp. 200°, is obtained. *Trisethylenethiocarbamidocuprous sulphate*, $[Cu,3\ etu]_2SO_4$, decomp. 240—251°, and *acetate*, $[Cu,3\ etu]AcOH$, decomp. 250—255°, are obtained from cupric sulphate and acetate, respectively. *Bis ethylenethiocarbamidocuprous chloride*, $[Cu,2\ etu]Cl$, m. p. 166—167°, is obtained from cuprous chloride; the *bromide* has m. p. 162—163°, the *iodide*, m. p. 160—161°.

Tetrakisethylenethiocarbamidoargentous nitrate, $[Ag,4\ etu]NO_3$, m. p. 96—97°, which yields with potassium iodide a white precipitate decomposed on heating, and *trisethylenethiocarbamidodiargentous nitrate*, $[Ag_2,3\ etu](NO_3)_2$, darkening at 200°, exploding at 224°, are similarly obtained. When the former is treated with potassium persulphate solution, *trisethylenethiocarbamidodiargentous persulphate*, darkening at 160°, decomp. 205°; and when with aqueous sodium hydroxide, *ethylenethiocarbamidoargentous oxide*, darkening at 120°, decomp. 170°, or on keeping; and when with potassium iodide, *ethylenethiocarbamidoargentous iodide*, $[Ag,\ etu]I$, m. p. 162°, are obtained. *Trisethylenethiocarbamidoargentous chloride*, $[Ag,3\ etu]Cl$, m. p. 167—168°, is prepared from silver chloride, and is stable and unaffected by light; *bisethylenethiocarbamidoargentous bromide*, m. p. 152°, similarly prepared, resembles the cuprous compound.

Bisethylenethiocarbamidoaurous chloride, $[Au,2\ etu]Cl$, is obtained as a *hydrate* (which becomes anhydrous at 110°, yellow at 210°, and decomp. at 242°), by the interaction of auric chloride solution and ethylenethiocarbamide. When it is treated in solution with dilute nitric acid, the corresponding (anhydrous) *nitrate*, with properties resembling those of tetrakisethylenethiocarbamidocuprous nitrate; and when with potassium iodide, *ethylenethiocarbamidoaurous iodide*, m. p. 225° (decomp.), are obtained. On treating the chloride with sodium hydroxide solution, a precipitate is obtained. If this is treated with hydrobromic acid and ethylenethiocarbamide, *bisethylenethiocarbamidoaurous bromide hydrate*, $[Au,2\ etu]Br,H_2O$, is obtained; this melts in its water of crystallisation at 100°, and resolidifies with m. p. 191°; the *anhydrous* compound is obtained by keeping over sulphuric acid, but reverts in the atmosphere to the hydrate. If, however, the above precipitate is heated by boiling the solution, it forms *ethylenethiocarbamidoaurous oxide*, $[Au,\ etu]_2O$, blackening at 200°. Auric chloride solution and thiocarbamide yield *bisthiocarbamidoaurous nitrate hydrate*, $[Au,2CH_4N_2S]NO_3,H_2O$, decomp. 155°.

Tetrakisethylenethiocarbamidocadmium nitrate, $[Cd,4\ etu](NO_3)_2$, m. p. 178°, and *bisethylenethiocarbamidocadmium chloride*, m. p. 220°, *bromide*, m. p. 208°, and *iodide*, m. p. 165°, $[Cd,2\ etu]X_2$, are similarly prepared, as are *ethylenethiocarbamidoplumbous chloride*, $[Pb,\ etu]Cl_2$, m. p. 183°, *trisethylenethiocarbamidomercuric nitrate*, $[Hg,3\ etu](NO_3)_2$, decomp. 196°, and *tetrakisethylenethiocarbamidopalladous chloride*, $[Pd,4\ etu]Cl_2$, blackening at 210°, m. p. 270°; the latter on treatment with sodium hydroxide gives a precipitate which dissolves in dilute nitric acid and ethylenethiocarbamide to give the corresponding *nitrate*, m. p. 235°, which, like the chloride, is very sparingly soluble in water. The ionic structure of the compounds is discussed and conductivities are tabulated. E. W. Wignall.

Reactions between phosphorus pentachloride or trichloride and acetone cyanohydrin. A. Chrząszczewska and W. Sobieranski (Rocz. Chem., 1927, 7, 470—476).—Acetone cyanohydrin reacts with phosphorus pentachloride to yield *α-chloro*iso*butyronitrile*, b. p. 51·5—52·5°/6 mm.; with phosphorus trichloride *tri-α-cyano*iso*propyl metaphosphate*, b. p. 153—154°/4 mm., is formed.

R. Truszkowski.

Alkylation of hydromolybdenocyanic acid. F. HÖLZL [with G. I. XENAKIS] (Monatsh., 1927, 48, 689—709).—When potassium molybdeno-octacyanide is treated with methyl sulphate there is formed the *compound* $[(CN)_4Mo(CNMe)_2(H_2O)_2],4H_2O$ (I). Methylation of silver molybdenocyanide with methyl iodide affords a complex mixture of compounds from which the *substance* $[(CN)_4Mo(CNMe)_4],2MeOH$ (II) is obtained by extraction with absolute methyl alcohol. When (I) is treated with potassium cyanide solution potassium molybdenocyanide is regenerated, whilst the action of water on (II) is to furnish (I). These reactions suggest that the octa(methylcarbylamine)molybdenum ion, $[Mo(CNMe)_8]^{\cdot\cdot\cdot\cdot}$, is unstable, whereas the corresponding ferrous ion is stable (A., 1927, 864). When (II) is treated with alkali the carbylamine odour is developed, and with silver nitrate a light yellow precipitate is formed which also gives the carbylamine odour with alkali. An aqueous solution of (II) when kept for a long time does not give a precipitate with silver nitrate. Extraction of the residue after removal of (II) with water furnishes the *compound* $[(CNMe)_4(CN)_2Mo(O\cdot)\cdot]_2$ (III), which decomposes in air, gives no precipitate with silver nitrate, but reduces ammoniacal silver nitrate. Treatment of the residue after removal of (II) and (III) with dilute hydrochloric acid and subsequent evaporation of the acid-soluble products in a vacuum gives a residue from which by extraction with warm methyl alcohol and water, *substances* (IV) and (V) were obtained together with an insoluble residue (VI). Compound (IV) titrates as a tribasic acid (*ammonium* salt described), develops a carbylamine odour in aqueous solution, and decomposes on keeping into (V). Its constitution is probably $\{(CN)_4Mo(H_2O)[C(OH)NHMe]_3\} \rightleftharpoons [(CN)_4Mo(H_2O)(CO'NHMe)_3]H_3$. The compound (V) is a weak acid in aqueous solution, and loses 1 mol. of water when dried over phosphoric oxide. It is represented $[(CN)_3(OH)Mo(H_2O)(CO'NHMe)]H \rightleftharpoons [(CN)_3Mo(H_2O)_2CNMe]OH$. The insoluble residue (VI) is formulated as $[(CN)_2(H_2O)CNMe\cdot Mo(O\cdot)\cdot]_2$. Ethylation of silver molybdenocyanide gives a corresponding series of complex compounds.

H. BURTON.

Activated magnesium for the preparation of the Grignard reagent and a comparative study of various catalysts. H. GILMAN, J. M. PETERSON, and F. SCHULZE.—See this vol., 253.

Constitution of Grignard's organo-magnesium compounds. I. L. KIERZIK (Rocz. Chem., 1927, 8, 446—456).—See A., 1927, 1176.

Behaviour of aluminium triethyl with nickel catalyst at high temperatures. A. MÜLLER and A SAUERWALD (Monatsh., 1927, 48, 737—739).— triethyl is not affected by nickel-black I (Zelinski, A., 1925, i, 1052) in presence of hydrogen.

H. BURTON.

***cyclo*Propane derivatives.** P. BRUYLANTS (Bull. Soc. chim. Belg., 1927, 36, 519—532).—See A., 1927, 877.

Propyl*cyclo*butane and *cyclo*butyl ethyl ketone. N. D. ZELINSKI and B. A. KASANSKI (J. Russ. Phys. Chem. Soc., 1927, 59, 659—661).—See A., 1927, 648.

Direct conjugation of benzene rings by means of the diazo reaction. W. BRYDÓWNA (Rocz. Chem., 1927, 7, 436—445).—Ullmann's reaction with bromo-, chloro-, methoxy-, carboxy-, and methyl-substituted anilines does not lead to the production of diphenyl derivatives, only azo compounds or their corresponding chloro-derivatives being formed. Only phenols are produced by the action of anhydrous acetic acid on nitro-, methyl-, and methoxy-substituted diazobenzenes and on diazofluorene. The corresponding hydrocarbons are obtained in about 20% yield by the reduction of *iso*diazo-derivatives of various substituted anilines, of α- and β-naphthylamine, and of diazotised *m*-aminocinnamic acid and *p*-aminoacetophenone. In the case of diazobenzene and of the diazonitrobenzenes diphenyl derivatives were also obtained, whilst the aminobenzoic acids yielded phenols in addition to hydrocarbons; in all other cases azo compounds were formed. It hence appears that the direct conjugation of two aryl nuclei is favoured by the absence of substituents in the nucleus or by the presence of nitro-groups; other substituents inhibit this reaction.

R. TRUSZKOWSKI.

Catalytic action. XX. Catalytic chlorination. I. S. TEI and S. KOMATSU (Mem. Coll. Sci. Kyoto, 1927, 10, *A*, 325—330).—When a mixture of benzene and chlorine is passed over reduced copper (made from the oxide prepared by igniting the nitrate) the products are benzene hexachloride (2 forms), chlorobenzene, 1 : 2 : 4-trichlorobenzene, and a little 1 : 2 : 4 : 5-tetrachlorobenzene. Low temperature favours substitution, higher temperature (200—300°) and previous treatment of the catalyst with chlorine favours the formation of the hexachloride; under these conditions 59% may be formed. Chlorobenzene and copper that had been treated with chlorine gave 1 : 2 : 4 : 5-tetrachlorobenzene, β-monochlorobenzene hexachloride, pentachlorobenzene, *p*-dichlorobenzene, and traces of 1 : 2 : 4-trichlorobenzene. This shows that previous substitution favours substitution and not addition. In the second case the additive product was found in only one form, which corresponded with the variety found in smaller amount in the unsubstituted product.

C. D. LANGFORD.

Synthesis of benzene hydrocarbons by organo-magnesium compounds. L. BERT (Compt. rend., 1928, 186, 373—375).—Benzyl chloride and its homologues are produced from the corresponding benzene compounds, trioxymethylene, hydrogen chloride, and fused zinc chloride. ω-Chloroethyl- and ω-chloropropyl-benzenes are prepared from magnesium aryl or aralkyl bromides and β-chloroethyl *p*-toluenesulphonate, or from the requisite alcohol obtained from magnesium aryl or aralkyl bromides and ethylene chlorohydrin. A list of 21 hydrocarbons prepared in 30—80% yield by decomposition of magnesium aralkyl chlorides by water is given. H. BURTON.

Detection and colorimetric determination of nitrotoluene in nitrobenzene. H. MURAOUR (Bull. Soc. chim., 1928, [iv], 43, 71—73).—*m*-Dinitro-

benzene and 2 : 6-dinitrotoluene give no coloration with alcoholic sodium hydroxide and 2 : 4-dinitrotoluene only a feeble coloration. In presence of *m*-dinitrobenzene, however, 2 : 6-dinitrotoluene affords a red and 2 : 4-dinitrotoluene an intense blue coloration, and the reaction is applied to the determination of nitrotoluenes in nitrobenzene, comparison being made colorimetrically with known mixtures after further nitration. The red coloration given by dinitrothiophen disappears with excess of alcoholic sodium hydroxide. Traces of dinitrotoluene in nitrotoluene may also be determined by the method, but the reaction is less sensitive when applied to the detection of dinitrobenzene in nitrobenzene (2 : 4-dinitrotoluene is used). R. BRIGHTMAN.

Synthetic musks. R. DE CAPELLER (Helv. Chim. Acta, 1928, **11**, 166—170, 170—172).—3-*n*-Butyltoluene, b. p. 84°/19 mm., obtained from *m*-xylyl bromide, *n*-propyl bromide, and sodium, is nitrated by fuming nitric–sulphuric acids yielding 2 : 4 : 6-*trinitro*-3-n-*butyltoluene*, m. p. 78·5°, which is inodorous. When toluene is condensed with excess of *tert*.-butyl chloride in presence of aluminium chloride or ferric chloride, there is formed 3 : 4-*di*-tert.-*butyltoluene*, b. p. 227·5—228°/735 mm., 117—118°/15·5 mm., m. p. 31·5—32°. 2 : 4 : 6-*Trinitro*-3-n-*amyltoluene*, m. p. 65·2—65·6°, obtained from 3-n-*amyltoluene*, b. p. 220·5—222·5° (corr.)/738 mm., is also inodorous. H. BURTON.

Elimination of side-chains during the nitration of aromatic compounds. H. BARBIER (Helv. Chim. Acta, 1928, **11**, 157—161; cf. this vol., 291).—In the nitration of 2-*iso*butyl-*m*-tolyl methyl ether there are formed as by-products a *dinitro*-m-*tolyl methyl ether*, m. p. 101°, and trinitro-*m*-tolyl methyl ether, m. p. 92° (cf. Baur, A., 1894, i, 449; Blanksma, A., 1903, i, 164), thus demonstrating the elimination of the *iso*butyl group. Nitration of 2 : 4-dimethyl-6-*iso*butylacetophenone furnishes, in addition to the 3 : 5-dinitro-derivative, a small amount of 2 : 6-dinitro-5-*iso*butyl-*m*-xylene, m. p. 68° (cf. Baur-Thurgau, A., 1898, i, 523; 1900, i, 639).

If a compound containing several side-chains is nitrated it is usually a group in one of the *m*-positions which is partly eliminated.

A summary of examples of elimination of different groups during the nitration of aromatic compounds is given. H. BURTON.

***d*-Bromo-Δ^{α}-butenylbenzene.** R. QUELET (Compt. rend., 1928, **186**, 236—238).—p-*Bromophenylpropylcarbinol*, b. p. 147°/11 mm., d_4^{11} 1·339, n^{11} 1·558 (*phenylurethane*, m. p. 83°), may be obtained either by condensation of butaldehyde with the magnesium derivative of *p*-dibromobenzene (48% yield), or by condensation of *p*-bromobenzaldehyde with magnesium *n*-propyl bromide (90% yield). The above alcohol, when dehydrated by heating with potassium hydrogen sulphate, forms p-*bromo*-Δ^{α}-*butenylbenzene*, m. p. 30°, b. p. 126—127°/14 mm., d_4^{21} 1·282, n_D^{21} 1·580, the addition of bromine to which gives $\alpha\beta$-*dibromo*-α-(p-*bromophenyl*)*butane*, m. p. 78°. The corresponding *ethylene oxide*, $C_6H_4Br\cdot\underset{\text{CHEt}}{\overset{|}{\text{CH}}}\!>\!O$, has b. p. 138°/12 mm., d_4^{15} 1·362, n_D^{15} 1·557. *p*-Bromo-Δ^{α}-butenyl benzene readily forms with magnesium a Grignard compound which yields Δ^{α}-butenylbenzene when treated with water. B. W. ANDERSON.

Derivatives of *p*-dichlorobenzene containing sulphur. E. GEBAUER-FULNEGG and H. FIGDOR (Monatsh., 1927, **48**, 627—638).—2 : 5-Dichlorobenzenesulphonanilide, m. p. 160°, when suspended in chloroform and treated with sodium hypochlorite, gives the *sulphonphenylchloroamide*, m. p. 101—103°. When the sulphonyl chloride is reduced by zinc and sulphuric acid, 2 : 5-*dichlorothiophenol*, m. p. 27°, b. p. 112—116°/50—52 mm., is obtained (yellow *lead* salt); this can be oxidised to 2 : 5 : 2′ : 5′-tetrachlorodiphenyl sulphide and converted by methyl sulphate into 2 : 5-*dichlorothioanisole*, m. p. 51°, and by chloroacetic acid into 2 : 5-*dichlorophenylthioglycollic acid*, $C_6H_3Cl_2\cdot S\cdot CH_2CO_2H$, m. p. 130° (Kalle and Co., G.P. 241910, 243087), from which 4 : 7 : 4′ : 7′-tetrachlorothioindigotin is obtainable.

The energetic action of chlorosulphonic acid on *p*-dichlorobenzene yields a crude disulphonyl chloride, m. p. 75°, which by slow evaporation of a carbon disulphide solution yields mainly large crystals of p-*dichlorobenzene*-2 : 6-*disulphonyl chloride* (I), m. p. 114° (identified by conversion by phosphorus pentachloride into 1 : 2 : 3 : 5-tetrachlorobenzene), separated by sorting from small crystals of the by-product, p-*dichlorobenzene*-2 : 5-*disulphonyl chloride* (II), m. p. 182° (*disulphonamide*), converted by phosphorus pentachloride into 1 : 2 : 4 : 5-tetrachlorobenzene.

The isomeride (I) is converted into p-*dichlorobenzene*-2 : 6-*disulphonic acid*, into the corresponding *disulphonamide*, and *disulphonanilide*, m. p. 215—217°, and the latter into p-*dichlorobenzene*-2 : 6-*disulphonphenylchloroamide*. (I) is reduced with difficulty to 2 : 5-*dichloro*-1 : 3-*dithiolbenzene*, m. p. 85° (*lead* salt), which easily oxidises; the *dimethyl thioether*, m. p. 179°, and the 2 : 5-*dichloro*-m-*phenylenedithioglycollic acid*, m. p. 189—190°, are prepared, and from the latter a dithioindigoid *dye*.

Whereas the action of sodium chlorosulphonate on *p*-dichlorobenzene at 150—180° yields only the monosulphonyl chloride, that of chlorosulphonic acid and sodium chloride at 210—220° gives a 50% yield of hexachlorobenzene. Attempts to prepare a sulphonyl chloride from 2 : 5-dichloronitrobenzene failed; the action of fuming nitric and sulphuric acids on *p*-dichlorobenzenesulphonyl chloride gave, however, a 2 : 5-*dichloronitrobenzenesulphonyl chloride*, m. p. 65°, characterised by giving an intense orange colour on heating with potassium hydroxide solution.

E. W. WIGNALL.

Indene halogenohydrins. C. COURTOT, FAYET, and PARANT (Compt. rend., 1928, **186**, 371—373).—Hydrolysis of 2 : 3-dichlorohydrindene with water yields 2-chloro-3-hydroxyhydrindene, m. p. 126° (Spilker, A., 1893, i, 518; Heusler and Schieffer, A., 1899, i, 365), together with an *isomeride*, m. p. 110—111°. These compounds when oxidised with chromic–sulphuric acids give the same *chlorohydrindone*, m. p. 38—39° [*mononitro*-derivative, m. p. 115°; *amino*-derivative, m. p. 149°; *dinitrophenylhydrazone*, m. p. 205° (decomp.)], and are probably *cis*- and *trans*-isomerides.

2-Bromo-3-hydroxyhydrindene, m. p. 130° (Kramer and Spilker, A., 1891, i, 205; cf. Read and Hurst, J.C.S., 1922, **121**, 2550), when oxidised yields 2-bromo-1-hydrindone, m. p. 38°, and reacts with *p*-toluidine to form a secondary *base* (2-p-*toluidino*-3-*hydroxyhydrindene*), m. p. 115°, also formed from the chloro-compound, m. p. 126°. The chloro-compound, m. p. 110—111°, and *p*-toluidine yield an isomeric *base*, m. p. 148°.

The iodohydrin, m. p. 120°, of Tiffeneau and Orékhoff (A., 1920, i, 313) is 2-iodo-3-hydroxyhydrindene.

H. Burton.

Conjugated unsaturated hydrocarbons. I. Synthesis of diphenyl derivatives. II. Synthesis of diphenylene derivatives. III. Addition of hydrogen and bromine. IV. Molecular compounds and colour reactions. R. Kuhn and A. Winterstein (Helv. Chim. Acta, 1928, **11**, 87—116, 116—122, 123—144, 144—151).—I. Phenylacetic acid reacts with cinnamaldehyde in presence of boiling acetic anhydride and lead oxide to form αδ-diphenylbutadiene (34% yield, cf. Thiele, A., 1899, i, 612). Reduction of cinnamaldehyde with aluminium amalgam in moist ether affords *s*-distyrylethylene glycol (*dicinnamoyl* derivative, m. p. 159°), which with 99% formic acid at 40° yields *s*-*tetrastyryldiethylene dioxide*, m. p. 133·5—134°. αζ-Diphenylhexatriene, m. p. 200° (dibromide, m. p. 124—125°) (cf. Farmer and others, this vol., 151), is obtained by reduction of the above glycol with phosphorus di-iodide or titanous chloride, by the action of phosphorus tribromide in chloroform, and from the dibromide by reduction with zinc dust and acetone, hydrogen and platinum-black, by the action of silver carbonate, acetate, and nitrate, and quantitatively by treatment with potassium iodide and acetone. αθ-*Diphenyloctatetraene* (16%), m. p. 232°, is best obtained from succinic acid (1 mol.), cinnamaldehyde (2 mols.), acetic anhydride (3 mols.), and lead oxide (1·5 mol.). Other methods of preparation are given (cf. Fittig and Batt, A., 1904, i, 744). Condensation of cinnamaldehyde and dihydromuconic acid affords ακ-*diphenyldecapentaene* (7%), m. p. 253° (partial decomp.). From benzylidenecrotonaldehyde and succinic and hydromuconic acids there are formed αμ-*diphenyldodecahexaene* (10%), m. p. 267° (decomp.), and αο-*diphenyltetradecaheptaene* (4%), m. p. 279° (decomp.). αϛ-*Diphenylhexadecaoctaene* (4%) is obtained from succinic acid and cinnamylidenecrotonaldehyde and has m. p. 285° (decomp.). The solubilities of these hydrocarbons in benzene and chloroform diminish with increase of mol. wt. The action of potassium permanganate in acetone towards some of the compounds has been studied.

Fluorenone condenses with succinic acid in presence of boiling acetic anhydride and lead oxide to n αδ- i(*diphenylene*)*butadiene* (6·5%), sublimes at 360°, and with dihydromuconic acid to give αζ-*di*(*diphenylene*)*hexatriene* (2·1%), m. p. 340° (decomp.). Condensation of fluorene with cinnamaldehyde in presence of sodium ethoxide gives α-phenyl-δ-diphenylenebutadiene (63%), m. p. 155° (cf. Thiele and Henle, A., 1906, i, 571) (picrate, m. p. 179°); with benzylidenecrotonaldehyde there is formed α-*phenyl*-ζ-*diphenylenehexatriene* (11%), m. p. 155·5°, and with cinnamylidenecrotonaldehyde α-*phenyl*-θ-*diphenyleneoctatetraene* (5%), m. p. 166°, is produced. α-*Phenyl*-δ-(2 : 7-*dibromodiphenylene*)*butadiene* and α-o-*nitrophenyl*-δ-*diphenylenebutadiene* have m. p. 210° and 186°, respectively.

III. Reduction of αζ-diphenylhexatriene with aluminium amalgam and moist ether or sodium amalgam and alcoholic benzene affords αο-*dibenzylbutadiene* (50—60%), m. p. 79°, which is hydrogenated in presence of platinum oxide or palladium-black to αζ-*diphenyl*-n-*hexane*, m. p. 137°, and yields on ozonolysis phenylacetic acid. αζ-*Dibenzylhexatriene* (50%), m. p. 68° (ozonolysis product, phenylacetic acid), and αθ-*dibenzyloctatetraene* (50%), m. p. 109—110°, are obtained similarly from αθ-diphenyloctatetraene and ακ-diphenyldecapentaene. In these reductions addition of hydrogen is at the terminal carbon atoms. When α-phenyl-δ-diphenylenebutadiene is reduced with aluminium amalgam there is formed α-benzyl-β-fluorenylethylene (cf. Thiele and Henle, *loc. cit.*) (ozonolysis product, phenylacetic acid), whilst reduction with sodium amalgam and alcoholic benzene affords α-*phenyl*-δ-*diphenylene*-Δ^{γ}-*butene* (60%), m. p. 81° (ozonolysis products, fluorenone and γ-phenylpropionic acid), also obtained from α-benzyl-β-fluorenylethylene by treatment with sodium amalgam and alcoholic benzene. Reduction of α-phenyl-δ-(2 : 7-dibromodiphenylene)butadiene with aluminium amalgam yields a *dihydro*-compound, m. p. 185°.

Hydrogenation of the unsaturated hydrocarbons in presence of platinum oxide or palladium and acetic acid yields αδ-*dicyclohexyl*-n-*butane*, b. p. 294°/725 mm., αζ-*dicyclohexyl*-n-*hexane*, b. p. 212°/14 mm., αθ-*diphenyl*-n-*octane*, αθ-*dicyclohexyl*-n-*octane*, m. p. 26°, and α-*phenyl*-γ-*fluorenylpropane*, m. p. 71°.

Addition of 1 mol. of bromine to αζ-diphenylhexatriene affords a dibromide identical with that obtained from *s*-distyrylethylene glycol, which when treated with lead acetate in acetone yields a αζ-*diphenylhexadienediol* (15% yield), m. p. 158—159°, which differs from the above glycol but regenerates the original bromide. Ozonolysis of the dibromide yields not more than 50% of the theoretical amount of benzoic acid (assuming a γδ-dibromide), together with a small amount of a compound containing bromine, m. p. 270°, thus demonstrating that the addition of bromine is asymmetrical. Diphenylhexatriene *tetrabromide*, m. p. 180—181°, hexabromide, m. p. 279—280° (decomp.) (cf. Smedley, J.C.S., 1908, **93**, 372), *diphenyloctatetraene octabromide*, m. p. 248° (decomp.), *diphenyldecapentaene hexabromide*, m. p. 175° (decomp.), *di*(*diphenylene*)*hexatriene octabromide*, m. p. 218°, and α-*phenyl*-ζ-*diphenylenehexatriene tetrabromide*, m. p. 170° (decomp.), are described. αδ-*Diphenyl*-Δ^{α}-*butene* has m. p. 47° and is obtained from magnesium γ-phenylpropyl bromide and benzaldehyde with subsequent elimination of water.

IV. Molecular compounds of the following hydrocarbons and 2 mols. of picric acid, styphnic acid, or 1 : 3 : 5-trinitrobenzene are described: αδ-diphenyl-Δ^{α}-butene (*picrate*, m. p. 102° with previous sintering; *trinitrobenzene*, m. p. 101°); αζ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (*picrate*, m. p. 112° with previous sintering; *trinitrobenzene*, m. p. 145—145·5°); αζ-diphenylhexatriene

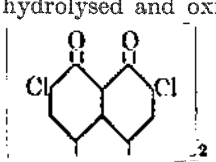
(*picrate*, m. p. 170°; *styphnate*, m. p. 193—194°; *trinitrobenzene*, m. p. 161—162°); αδ-di(diphenylene)-butadiene [*picrate*, m. p. 262° (decomp.); *trinitrobenzene*, m. p. 240° (decomp.)]. The *picrates* of αζ-di(diphenylene)hexatriene and α-phenyl-ζ-diphenyleneh exatriene have m. p. 270° (decomp.) and 179° (decomp.), respectively. The colours of solutions of a large number of the hydrocarbons in concentrated sulphuric acid, chloroform, and concentrated sulphuric acid, and acetic anhydride, chloroform, and concentrated sulphuric acid, and the position of the maximum bands of the absorption spectra are given.

H. BURTON.

Nitration of anthracene to 9 : 9′-dinitro-9 : 9′-dihydroxy-10 : 10′-dihydrodianthracene. J. S. TURSKI and A. BERLANDSTEIN (Rocz. Chem., 1927, 7, 457—466).—Anthracene yields on nitration under certain special conditions 9 : 9′-*dinitro*-9 : 9′-*dihydroxy*-10 : 10′-*dihydrodianthracene*, m. p. 267—268°, soluble in sodium hydroxide and yielding anthraquinone on oxidation.

R. TRUSZKOWSKI.

Perylene and its derivatives. XVI. A. ZINKE, K. FUNKE, and H. IPAVIC (Monatsh., 1927, 48, 741—754; cf. A., 1926, 71; A., 1927, 350).—Chlorination of perylene in ice-cold carbon tetrachloride suspension affords a *compound*, $C_{20}H_{11}Cl_9$, m. p. 235° after previous darkening and sintering. Similar treatment of 3 : 9-dichloro- or 3 : 9-dibromo-perylenes gives the *compounds* $C_{20}H_9Cl_7$ and $C_{20}H_9Cl_5Br_2$, m. p. 260° (decomp.) and m. p. 240° (decomp.), respectively. When perylene is chlorinated in nitrobenzene solution at 130—140° there is formed hexachloroperylene (A., 1925, i, 384), whilst in presence of anhydrous aluminium chloride and nitrobenzene *decachlorotetrahydroperylene*, m. p. above 400°, is produced. This compound is converted by fuming sulphuric acid at 150—160° into *octachloro-octahydroperylene*-3 : 4 : 9 : 10-*diquinone*, m. p. above 400°, which when reduced with alkaline sodium hyposulphite and treated with the appropriate aroyl chloride affords the *tetrabenzoyl*, m. p. 322·5° (decomp.), and *tetra*-p-*bromobenzoyl*, m. p. 375° (decomp.), derivatives of tetrachloroperylene-3 : 4 : 9 : 10-diquinol. The benzoyl derivative is hydrolysed and oxidised at the same time by warm



concentrated sulphuric acid into *tetrachloroperylene*-3 : 4 : 9 : 10-*diquinone* (annexed formula), also produced from the above octachloro-quinone by reduction with amalgamated zinc and hydrochloric–acetic acids.

Reduction of the octachloro-quinone with warm alkaline sodium hyposulphite followed by atmospheric oxidation affords a green substance (probably a quinhydrone) which when treated with cold concentrated sulphuric acid yields a dark brown *substance*, $C_{20}H_5O_4Cl_5$. Treatment of the octachloroquinone with boiling aniline furnishes a *compound*, $C_{38}H_{25}O_4N_3Cl_4$, m. p. 305—307° (decomp.), whilst distillation with zinc dust and zinc chloride gives perylene.

H. BURTON.

Hydrogenation of aniline under pressure in the presence of osmium and iridium. W. S. SADIKOV and A. L. KLEBANSKY (Ber., 1928, 61, [*B*], 131—137).—The osmium catalyst is prepared by reducing osmic acid on asbestos with hydrazine. Hydrogenation is effected at 300° under high pressure; the extent of the reaction depends largely on the purity of the aniline and the mass of the catalyst. An equilibrium appears to be established between catalyst, initial substance, and hydrogenated products. In one instance the final material contained benzene 4%, *cyclo*hexylamine 25%, di*cyclo*hexylamine 20%, *cyclo*hexylaniline 5%, and unchanged aniline 29%. The iridium catalyst is formed by reduction of ammonium chloroiridate and activated by treatment with oxygen at 350—400°. The observed products of hydrogenation of aniline are benzene, *cyclo*hexane, *cyclo*hexylamine, di*cyclo*hexylamine, and unchanged aniline. Hydrogenation occurs more readily in the presence of osmium than of iridium and less decomposition is observed.

H. WREN.

Reduction of nitro-derivatives with iron and soluble chlorides. A. BRETNUTZ and A. PENSA (Notiz. chim.-ind., 1927, 2, 183; Chem. Zentr., 1927, ii, 243—244).—Iron filings, in presence of aqueous ferric chloride (preferably) or sodium chloride solution, stirred at 34 r.p.m. (opt.), was used as a reducing agent for nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene to *m*-nitroaniline, *p*-nitrophenol, and picric acid. Nitrobenzene is readily reduced to aniline (1—1·5 hrs. at 100°) when the chlorine concentration (ferric chloride) is 0·0174—0·0319 g./c.c. *p*-Nitrotoluene (100 g.) gives a theoretical yield with 132 g. of iron and 0·0259 g. of chlorine as ferric chloride in 2 hrs.; *m*-dinitrobenzene gives a theoretical yield of *m*-nitroaniline in 2·5 hrs. using 0·035 g. of chlorine per c.c. *p*-Nitrophenol (25 g.) is completely reduced in 1·25 hrs. on a boiling water-bath with 0·009 g. of chlorine per c.c. of solution. Picric acid is vigorously reduced.

A. A. ELDRIDGE.

Anomalous effect of *o*-*p*-orienting groups on the m. p. of dihalogenated benzene derivatives. G. B. HEISIG (J. Amer. Chem. Soc., 1928, 50, 139—145).—2-*Chloro*-4-*bromo*-6-*iodoaniline*, m. p. 97—97·5°, is obtained by treating 2-chloro-4-bromoaniline in aqueous acetic acid with iodine chloride. 4-*Chloro*-2-*bromo*-6-*iodoaniline*, m. p. 109·5—110°, is obtained similarly from 4-chloro-2-bromoaniline. 2-*Chloro*-6-*bromo*-4-*iodoaniline*, m. p. 115·5—116°, is obtained by brominating 2-chloro-4-iodoaniline in glacial acetic acid, or by chlorinating 2-bromo-4-iodoaniline (*acetyl* derivative, m. p. 140—140·5°). s-*Chlorobromoiodobenzene*, m. p. 85·5—86°, is obtained from either of the above trihalogenated anilines by treatment with sodium nitrite and sulphuric acid in boiling alcohol.

The m. p. of an *o*- or *m*-dihalogenobenzene is always raised by the introduction of a third substituent. The m. p. of a *p*-dihalogenobenzene is raised similarly if the entering substituent is one which causes *m*-substitution, but 2 : 5-dibromo- and 2 : 5-di-iodo-nitrobenzene are exceptional, both having a lower m. p. than the corresponding dihalogeno-derivative. The m. p. of a *p*-dihalogenobenzene is generally lowered by the introduction of a third substituent having *o*-*p*-orienting influence, but 2 : 5-dichlorophenol has a higher m. p. than *p*-dichlorobenzene.

F. G. WILLSON.

Acetylene derivatives. VII. Reaction of trichloroethylene with amines. P. Ruggli and I. Marszak (Helv. Chim. Acta, 1928, **11**, 180—196).—Phenylglycinediphenylamidine (Sabanejev's base, A., 1876, i, 55), $NHPh\cdot CH_2\cdot C(:NPh)\cdot NHPh$ (I), m. p. 190° (*picrate*, decomp. 135—140°), is prepared from trichloroethylene (1 mol.), aniline (3 mols.), and 15% aqueous sodium hydroxide (3 mols.) by heating for 40 hrs.; from phenylglycineanilide, aniline, and phosphorus trichloride at 150°; from phenylglycine, aniline, and phosphorus trichloride at 160°, and from chloroacetic acid, aniline, and phosphorus trichloride at 160°. Benzoylation of the base yields N-*benzoylphenylglycinediphenylamidine*, m. p. 142°, and bromination in presence of chloroform and anhydrous sodium carbonate gives *p*-bromophenylglycine-*p*-bromoanilide. When the base is treated with boiling alcohol for 60 hrs. or with aniline and aniline hydrochloride in boiling alcohol for 24 hrs. there is formed phenylglycineanilide. From trichloroethylene and *p*-toluidine, *p*-anisidine, *p*-phenetidine, and 4-aminodiphenyl there are formed p-*tolylglycinedi*-p-*tolylamidine*, m. p. 157°; p-*anisylglycinedi*-p-*anisylamidine*, m. p. 158—159°; p-*phenetylglycinedi*-p-*phenetylamidine*, m. p. 112—113°, and 4-*diphenylylglycinedi*-4-*diphenylylamidine*, m. p. 189—190°. p-*Anisylglycine*-p-*anisidide* and *phenylglycine*-p-*bromoanilide* have m. p. 132° and 153—154°, respectively. H. Burton.

Odour and constitution among the aromatic mustard oils [thiocarbimides]. I. G. M. Dyson (Perf. Ess. Oil Rec., 1928, **19**, 3—5; cf. B., 1926, 215).—The effect of alkyl substituents on the odour of aromatic thiocarbimides has been examined. In phenylthiocarbimide the introduction of an *o*-methyl group contributes sweetness, the *m*-group pungency, and the *p*-group an anise-like character. In the six xylyl thiocarbimides, duplication of a methyl group in the same orientation strengthens the effect. When both *o*- and *m*-methyl groups are present together the effect of the *m*-group predominates and the 2 : 3- and 2 : 5-xylylthiocarbimides are pungent. The influence of the *p*-groups overwhelms that of the *o*- or *m*-groups. Similar considerations apply in the 2 : 4 : 6-, 2 : 4 : 5-, and 2 : 3 : 5-trimethylphenylthiocarbimides. Pentamethylphenylthiocarbimide has only a very faint floral odour. *p*-Ethyl- and *n*-propylphenylthiocarbimides have a strong anise-like odour, whereas the corresponding 4-iso*propylphenylthiocarbimide*, b. p. 271°, has a harsher odour. 2-*Cymylthiocarbimide*, b. p. 268°, is distinctly pungent. The following compounds are described: o-3-*xylylthiocarbimide*, b. p. 262°, o-3-*xylylthiocarbamide*, m. p. 182°; p-iso*propylphenylthiocarbamide*, m. p. 167°; s-*di*-p-iso*propylphenylthiocarbamide*, m. p. 198°; 2-*cymylthiocarbamide*, m. p. 174°; s-*di*-2-*cymylthiocarbamide*, m. p. 202°. E. H. Sharples.

Orientation effects in the diphenyl series. V. Independence of the two nuclei in diphenyl compounds. R. J. W. Le Fèvre and E. E. Turner (J.C.S., 1928, 245—255; cf. A., 1926, 946, 1029, 1131).—The compound obtained by hydrolysis of the nitration product of phthalylbenzidine is mainly 2-nitrobenzidine (cf. Koller, A., 1904, i, 778). Nitration of 4-acetamidodiphenyl in acetic acid with subsequent hydrolysis of the dinitro-derivative produced affords 3 : 4'-dinitro-4-aminodiphenyl, which is reduced by aqueous-alcoholic ammonium sulphide to 3-*nitrobenzidine*, m. p. 208—210°. Nitration of the *diacetyl* derivative, m. p. 249—250°, of this compound, followed by hydrolysis, yields 3 : 3'-dinitrobenzidine. 4-*Chloro-4'-phthalimidodiphenyl*, m. p. 245°, furnishes after nitration and hydrolysis 4-chloro-2 : 3'dinitro-4'-aminodiphenyl and 4-chloro-3 : 2'-dinitro-4'-aminodiphenyl, which is converted by alcoholic ammonia at 160—180° into 2 : 3'-dinitrobenzidine. Similar results are obtained using 4-*bromo-4'-phthalimidodiphenyl*, m. p. 260°.

By boiling benzidine with an excess of the appropriate ester the following derivatives were prepared: NN'-*di*-o-*carbethoxybenzoyl*-, m. p. above 300°; NN'-*dicinnamoyl*-, NN'-*dicarbethoxy-benzidines*, and 4 : 4'-*diethyloxamidodiphenyl*. Dinitration of these last two compounds with subsequent hydrolysis affords 3 : 3'-dinitrobenzidine (Strakosch's dinitrobenzidine, Ber., 1872, **5**, 236). NN'-*Dicarbethoxy*-derivatives were prepared from the following benzidines and ethyl chloroformate: 2-nitrobenzidine, m. p. 187—188°; 2 : 2'-dinitrobenzidine, m. p. 200—201°; 2 : 3'-dinitrobenzidine, m. p. 158°, and 3 : 3'-dinitrobenzidine m. p. 216—217°.

Chlorination of 4-nitrodiphenyl in presence of a small amount of stannic iodide yields 4-chloro-4'-nitrodiphenyl. The condensation product of benzidine with carbamide is *NN'*-dicarbamylbenzidine (cf. Schiff, A., 1878, 669; Michler and Zimmermann, A., 1882, 182; Snape, A., 1896, i, 241). This compound can be used to detect traces of nitrates in concentrated sulphuric acid, a reddish-purple colour being produced at concentrations of 1 g. in 500,000 c.c.

The orientation experiments show that one nucleus in diphenyl, even if substituted (C_6H_4R–), always exerts an *op*-directing influence. If the 4'-position is occupied by an *op*-directing group the radical C_6H_4R– frequently exerts a small *op*-influence. There appears to be no mobile conjugation (electronic tautomerism) between the two nuclei, and it is concluded that they are independent. Bell and Kenyon's modification (A., 1927, 145) of Turner's *para*-bridge formula for diphenyl (A., 1923, i, 1085) is based on unsatisfactory evidence, and a slight modification (electronic) renders the formula satisfactory as a basis for explaining the laws of substitution in the diphenyl series. H. Burton.

Reduction of azobenzene by Grignard reagents. H. Rheinboldt and R. Kirberg (J. pr. Chem., 1928, [ii], **118**, 1—13; cf. Franzen and Deibel, A., 1905, i, 843; Rheinboldt and Roloff, A., 1925, i, 542; Gilman and Pickens, A., 1925, i, 1336; Gilman and Adams, A., 1926, 947).—Azobenzene reacts with 2 mols. of a Grignard reagent according to the equations: (i) $NPh:NPh+2RMgX=XMg\cdot NPh\cdot NPhMgX+2R\cdot$; (ii) $2R\cdot=(R-H)+(R+H)$; (iii) $2R\cdot=R\cdot R$. If R=Me or Ph, (ii) does not occur, the product being ethane or diphenyl. When R=Et or Pr^a, (iii) is absent, and the products are ethylene and ethane, or propylene and propane. When $R=\cdot CH_2\cdot CHMe_2$, (ii) and (iii) both occur, giving *iso*butylene (dibromide, b. p. 147—149°), *iso*butane, and di*iso*butyl [βε-di-

methylhexane], b. p. 108—110°. The formation of butane from azobenzene and magnesium ethyl bromide (Franzen and Deibel, *loc. cit.*) is not observed.
C. HOLLINS.

Colour and constitution. II. Effect of substituents on the colour of azo dyes. H. H. HODGSON and F. W. HANDLEY (J.C.S., 1928, 162—166).—Reduction of 3-chloro-6-nitrothioanisole with tin and acetic–hydrochloric acids furnishes 4-*chloro*-2-*thioanisidine* (*acetyl*, m. p. 110°, and *benzoyl*, m. p. 106°, derivatives), whilst treatment with sodium disulphide yields 4 : 4′-*dinitro*-5 : 5′-*dimethylthioldiphenyl disulphide*, m. p. 216—217°. Treatment of this compound with hot alkaline sodium sulphide and subsequent addition of methyl sulphate gives 2 : 4-dimethylthiolnitrobenzene, which furnishes 2 : 4-*dimethylthiolaniline* (*hydrochloride*, *acetyl*, m. p. 114°, and *benzoyl*, m. p. 125°, derivatives). 3-Chloro-6-nitroacetanilide and sodium disulphide yield 3 : 3′-*diacetamido*-4 : 4′-*dinitrodiphenyl disulphide*, m. p. 192—193°, which furnishes 6-*nitro*-3-*thioanisidine*, m. p. 116°. 3-*Chloro*-4-*nitrothioanisole* has m. p. 61° and yields 2-*chloro*-4-*thioanisidine* (*hydrochloride*, m. p. 217—218°; *acetyl* derivative, m. p. 129°).

With β-naphthol-6-mono- and -3 : 6-di-sulphonic acids as second components, *azo* dyes have been prepared from the above thioanisidines, and from *o*-, *m*-, and *p*-chloro-, 2 : 4- and 2 : 5-dichloro-, and 2 : 4-dimethoxy-anilines, 5-chloro-2-anisidine, 5-chloro-2-thioanisidine, and aniline. The bathochromic effects of the different groups in different positions are the same as those already described (A., 1926, 515).
H. BURTON.

Preparation of *cyclo*hexanol ethers. Formation of tetrabenzyl*cyclo*hexanones. R. CORNUBERT and H. LE BIHAN (Bull. Soc. chim., 1928, [iv], 43, 74—78).—The sodium compounds of *cyclo*hexanols are readily obtained by the action of sodamide in dilute ethereal solution (cf. A., 1927, 666); with alkyl halides they afford the corresponding ethers. Thus *cyclo*hexanol with sodamide and methyl sulphate gives *cyclo*hexyl methyl ether, b. p. 134·5—135°, $d^{14\cdot5}$ 0·8860, $n^{14\cdot5}$ 1·4390. 4-Methy*cyclo*hexanol similarly yields 4-*methyl*cyclo*hexyl methyl ether*, b. p. 151°, $d^{20\cdot5}$ 0·8612, $n_D^{20\cdot5}$ 1·4321. Commercial "pure" *cyclo*hexanol with allyl chloride or bromide affords cyclo*hexyl allyl ether*, b. p. 83—84°/38 mm., and a small quantity of a substance, $C_{15}H_{22}O$, b. p. 155—158°/18 mm., probably a triallyl*cyclo*hexanone. 2-*Methyl*cyclo*hexyl methyl ether* has b. p. 69—70°/15 mm. With benzyl chloride commercial *cyclo*hexanol gives, in addition to cyclo*hexyl benzyl ether*, b. p. 165·5—166·5°, d^{20} 0·9941, 1·5178, a little *tetrabenzyl*cyclo*hexanone*, m. p. 178°, b. p. above 360°/15 mm. 4-Methyl*cyclo*hexanol similarly affords 4-*methyl*cyclo*hexyl benzyl ether*, b. p. 153·5—154°/17 mm., d^{18} 0·9681, n_D^{18} 1·5090, and a little *tetrabenzyl*-4-*methyl*cyclo*hexanone*, m. p. 184°. R. BRIGHTMAN.

Preparation of 2-bromo-*p*-cresol from *p*-nitrotoluene. H. J. LUCAS and N. F. SCUDDER (J. Amer. Chem. Soc., 1928, 50, 244—249).—2-Bromo-4-nitrotoluene is obtained in 76% yield by adding bromine in slight excess to *p*-nitrotoluene in presence of iron filings, with cooling. After keeping for 24 hrs., the mixture is heated gradually to 150° until evolution of hydrogen bromide ceases (cf. Cohen and Dutt, J.C.S., 1914, 105, 505). Reduction of the bromonitrotoluene with alcoholic ammonium sulphide affords 2-bromo-*p*-toluidine, m. p. 27·3—27·5°, in 84% yield, and from this 2-bromo-*p*-cresol (*benzoate*, m. p. 74·6—75·1°) is obtained in 80·5% yield by adding a solution of the diazotised amine gradually to a solution of sulphuric acid and sodium sulphate at 130—140°, the cresol being distilled off as it is formed by a current of steam at 160—180°.
F. G. WILLSON.

Preparation of iodine-substituted benzonitriles of the phenol ether type. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1928, 83.

Bases obtained from *p*-phenetidine and from *p*-toluidine with formaldehyde in acid solution. R. LEPETIT, G. MAFFEI, and C. MAIMERI (Gazzetta, 1927, 57, 862—871).—In addition to the products already described (A., 1917, i, 452), the action of formaldehyde on *p*-phenetidine hydrochloride at 60° yields: (1) the base, m. p. 132°, obtained by Reverdin (A., 1921, i, 564) by treating methylenedi-*p*-phenetidine with nitric acid; the authors consider the formula of this base to be, not $C_{18}H_{24}O_2N_2$ or $C_{18}H_{22}O_2N_2$, but $C_{19}H_{22}O_2N_2$, which is in good agreement with the results of Reverdin's analyses of the base, its nitrate and nitroso-derivative; (2) a *base*, $C_{19}H_{24}O_3N_2$, m. p. 114°, the salts of which have a bitter taste and anæsthetic properties.

The base, m. p. 140° (*loc. cit.*), gives the following derivatives: *diacetyl*, $C_{21}H_{26}O_4N_2$, m. p. —117°; two *benzoyl* derivatives, $C_{31}H_{30}O_4N_2$ (m. p. 180—181°) and $C_{26}H_{28}O_4N_2$ (m. p. 132—133°); *methyl* derivative, m. p. 114°, identical with the base (2) (see above); *ethyl* derivative, m. p. 82—83°, and the *hydrochloride* of the *allyl* derivative, $C_{21}H_{27}O_3N_2Cl$, m. p. 202°. When oxidised by means of acid permanganate, the base, m. p. 140°, yields a *compound*, m. p. 210°, of indifferent character; when reduced by zinc dust and acetic acid, it gives *p*-phenetidine, methyl-*p*-phenetidine, and a *base*, $C_{20}H_{18}O_4N_2$, m. p. 91°.

The interaction of *p*-toluidine and formaldehyde in acid solution yields: (1) a base, $C_{17}H_{16}ON_2$, m. p. 140°, probably identical with that of, m. p. 146—147° obtained from *p*-phenetidine (*loc. cit.*); (2) a base, $C_{16}H_{16}N_2$, m. p. 158°; (3) methyl-*p*-toluidine; (4) a *base*, $C_{17}H_{20}ON_2$, m. p. 97—98°, which forms an *oxalate*, $C_{17}H_{18}N_2,H_2C_2O_4$, m. p. 255—259° (decomp.); (5) a *base*, $C_{17}H_{18}N_2$, m. p. 137—138°.
T. H. POPE.

Adjacent substitution. I. Reactions of 3-chloro-2-aminoanisole. H. H. HODGSON and A. KERSHAW (J.C.S., 1928, 191—193).—Reduction of 3-chloro-2-nitroanisole with iron powder and 50% acetic acid gives 3-*chloro*-2-*aminoanisole*, b. p. 246° (slight decomp.) (*hydrochloride*, m. p. 211°; *hydrobromide*, sublimes at 250°; *nitrate*, m. p. 137°; *acetyl*, m. p. 123°, *diacetyl*, m. p. 145·5°, and *benzoyl*, m. p. 135°, derivatives). The *sulphate* is very soluble in water. By the usual methods 2 : 3-dichloro-, m. p. 33° (cf. Hollemann, A., 1917, i, 556), 3-*chloro*-2-*bromo*-, m. p. 50°, 3-*chloro*-2-*iodo*-, m. p. 53·5°, and 3-*chloro*-2-*cyano*-*anisoles*, m. p. 114·5°, were prepared.

3-*Chloro-2-thiocyanoanisole* has m. p. 43°. Diazotisation of the aminoanisole yields stable diazonium salts which are unaffected by dilute acids, but the sulphate when treated with bromine gives 3-*chloroanisole-2-diazoperbromide*, m. p. 115—116° (decomp.). This compound when boiled with acetic acid furnishes 3-*chloro-2* : 6-*dibromoanisole*, m. p. 92°, and with ammonia yields 3-*chloroanisole-2-diazoimide*, m. p. 35°. Reduction of 3-*chloroanisole-2-diazonium chloride* affords 3-*chloroanisyl-2-hydrazine hydrochloride*, and the following 3-*chloroanisyl-2-hydrazones* are described: *benzaldehyde*, m. p. 92°; o-*nitrobenzaldehyde*, m. p. 131°; m-*nitrobenzaldehyde*, m. p. 131°, and p-*nitrobenzaldehyde*, m. p. 105°. The *azo dyes* formed from 3-chloro-2-aminoanisole and naphtholsulphonic acids show that the bathochromic effect of the methoxy-group is almost completely inhibited in presence of the *o*-chlorine atom (cf. this vol., 284).

H. BURTON.

Relationship between constitution and taste of some carbamide derivatives. H. F. J. LORANG (Rec. trav. chim., 1928, **47**, 179—190).—The relationship between the constitution and taste of substituted phenylcarbamides described in the literature is reviewed. The following are new: 1-*ethoxy*-2 : 4-*dicarbamidobenzene*, m. p. 215°, obtained from 2 : 4-*diaminophenetole hydrochloride*, decomp. about 180°, and potassium cyanate; 1 : 3-*diethoxy*-4 : 6-*dicarbamidobenzene*, m. p. 233° (decomp.), prepared similarly from 4 : 6-*diamino*-1 : 3-*diethoxybenzene hydrochloride*. 1 : 3-Dicarbamidobenzene and the above carbamides are not sweet.

H. BURTON.

Catalytic action. XVIII. Catalytic reduction of β-naphthol. I. NISHIMATSU and S. KIMURA (Sexagint [Osaka celebration], Kyoto, 1927, 217—228).—The investigation of the hydrogenation of β-naphthol by hot reduced nickel was undertaken to test Mohr's hypothesis of the configuration of hydrogenated naphthalene derivatives. At 135—140° only naphthalene, hydronaphthalenes, and *ar*-hydronaphthols were obtained. The hydrocarbons had presumably been formed from the expected *ac*-compounds by loss of water. Reduction at 120—130° yields a mixture of *ac*- and *ar*-tetrahydro-β-naphthols, hexa-, octa-, and deca-hydro-β-naphthols. Two forms of both *ar*- and *ac*-tetrahydro-β-naphthols were found: *ar*- (1), b. p. 262—264°, m. p. 55—56°, (2) b. p. 272—275°, m. p. 56—58°; *ac*- (1), b. p. 151—154°/21 mm. and 138—143°/15 mm., (2) b. p. 154—157°/23 mm. and 148—149°/18 mm. Of the four possible decahydro-β-naphthols three were isolated, having m. p. 103° and 75°, and a liquid b. p. 122—125°/12 mm. The values of the other physical constants given are in fair agreement with those given by previous workers.

C. D. LANGFORD.

Stability of phenol ethers at an ethylene bridge. H. THOMS and F. A. HEYNEN (Festschr. A. Tschirch, 1926, 211—220).—Eugenol ethylene ether was hydrogenated with palladised barium sulphate, and the product nitrated, yielding *di(nitrohydroeugenol)ethylene ether*, m. p. 167·5°, reduced with stannous chloride and acetic and hydrochloric acids to *di(aminohydroeugenol)ethylene ether*, m. p. 245°; a 2-methoxy-4-propyl-1-phenyl ethylene ether is one of the fission products on hydrogenation of dieugenol ethylene ether.

A. A. ELDRIDGE.

3 : 3′ : 5 : 5′-Tetranitro-2 : 2′-dimethoxydiphenyl. H. RAUDNITZ (Ber., 1928, **61**, [*B*], 246).—Contrary to Borsche and Feske (A., 1927, 661), 3 : 3′ : 5 : 5′-tetranitro-2 : 2′-dimethoxydiphenyl has m. p. 188—189°, whether prepared by the author's process (A., 1927, 453) or by that of Borsche and Scholten (A., 1917, i, 390). The low values recorded are due to the difficulty of purifying the material completely by crystallisation from boiling acetic acid; better results are obtained with alcohol as solvent.

H. WREN.

Oxidation in the benzene series by gaseous oxygen. III. Oxidation of α-phenylcarbinols. H. N. STEPHENS (J. Amer. Chem. Soc., 1928, **50**, 186—190; cf. A., 1927, 48).—The action of gaseous oxygen at about 100° on phenyl-methyl-, ethyl-, -dimethyl-, -*n*-propyl-, and -*iso*propyl-carbinol has been examined. In all cases except that of the last-named compound, small amounts of the direct oxidation products (ketones) were produced. In addition, dehydration takes place under the conditions applied, with formation, on the one hand, of ethers, and, on the other, of unsaturated hydrocarbons. In all cases except that of phenyldimethylcarbinol, from which *iso*propenylbenzene was obtained, the unsaturated hydrocarbons are immediately oxidised with formation of benzoic acid. All these reactions are prevented by the presence of a weight of water equal to that of the carbinol.

F. G. WILLSON.

Tautomerism of hydroxytriarylcarbinols. L. C. ANDERSON and M. GOMBERG (J. Amer. Chem. Soc., 1928, **50**, 203—208; cf. A., 1925, i, 1269).—Examination of the absorption spectra of the two carbinol forms of *p*-hydroxytriphenylcarbinol and of *p*-hydroxy-*m*-tolyldiphenylcarbinol, and those of their respective fuchsones, in ether, supports the conclusion that each carbinol exists in both benzenoid and quinonoid tautomeric modifications.

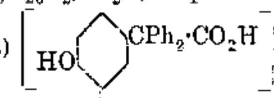
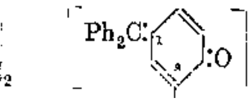
F. G. WILLSON.

Basic triphenylmethane dyes. K. BRAND (I) [with A. MODERSOHN]; (II) [with G. SCHUCK] (J. pr. Chem., 1928, [ii], **118**, 97—137).—Further evidence that the colour changes observed when solutions of crystal-violet or malachite-green are gradually acidified are due to progressive conversion of the dimethylamino-groups into non-auxochromic dimethylammonium ions, is furnished by the study of the corresponding methylated quaternary salts. The methyl ether of *pp′p″*-hexamethyltriaminotriphenylcarbinol yields (*a*) with 1 mol. of methyl sulphate, a *monomethosulphate*, m. p. 234—236°, decomp. from 227°. The corresponding methiodide (Rosenstiehl, A., 1895, i, 377) is hydrolysed by boiling dilute acetic acid to iodine-green, $(NMe_2\cdot C_6H_4)_2C(C_6H_4\cdot NMe_3I)I$; (*b*) with 2 mols. of methyl sulphate, a mixture of products from which was obtained on one occasion an impure *dimethiodide*, which, after hydrolysis and removal of a little iodine-green gave a yellow aqueous, and an orange hydrochloric acid solution; (*c*) with 3 mols. of methyl sulphate a *trimethosulphate*, m. p. 223—224° (decomp.). The corresponding *trimethoperchlorate*, m. p. 303

304° (decomp.), is hydrolysed by dilute acid to the colourless *substance* (I), $C(C_6H_4{\cdot}NMe_3ClO_4)_3OH$, m. p. 291—292° (decomp.), which gives with concentrated mineral acids carbonium salts similar in colour and stability to those of triphenylcarbinol. When the methyl ether (II) of *pp'*-tetramethyldiaminotriphenylcarbinol is successively treated with methyl sulphate (1 mol.) and sodium perchlorate, it affords a *methoperchlorate*, m. p. 167—168°, which is converted by boiling perchloric acid into the orange-red *compound* (III), $CPh(C_6H_4{\cdot}NMe_3ClO_4)_2ClO_4,H_2O$, m. p. 253—254° (decomp.). This is hydrolysed by water to the colourless *methoperchlorate* of *pp'*-tetramethyldiaminotriphenylcarbinol. The *dimethoperchlorate*, m. p. 295—296°, of the ether (II) is hydrolysed by dilute acid to the *dimethoperchlorate* (IV), m. p. 287—288°, of *pp'*-tetramethyldiaminotriphenylcarbinol, which gives halochromic solutions similar to those of triphenylcarbinol.

The *methosulphate*, decomp. 246°, and *methoperchlorate* (V), m. p. 217—218° (decomp.), of *p*-dimethylaminotriphenylcarbinol give yellow solutions in concentrated mineral acids, which are decolorised by addition of water. The carbinol is converted by oxalic acid into a mixture of the colourless oxalate (Baeyer and Villiger, A., 1904, i, 786) with an orange *salt* (VI), and by boiling methyl alcohol into its *methyl ether*, m. p. 90—91°, which forms a *methosulphate*, m. p. 159—164°, and a *methoperchlorate*, m. p. 247°. The ordinary Zeisel method is not applicable to triphenylmethane derivatives containing two or more trimethylammonium groups, since the latter also yield methyl iodide under these conditions. Correct results are, however, obtained by heating the substances with hydriodic acid at 100°. Although iodine-green gives no precipitate with neutral silver nitrate, it is quantitatively converted by sodium perchlorate into the corresponding *diperchlorate*. Conductivity measurements with iodine-green, tetramethyldiaminotriphenylmethane methiodide, crystal-violet, and (I), (III), (IV), and (V) above indicate that in each case all the acid radicals are ionogenic. Accordingly, formulæ (cf. Hantzsch, A., 1922, i, 24) of polyacid salts of triphenylmethane dyes in which acid radicals are included within the co-ordination complex are probably incorrect. The above carbonium salts fall into four groups of decreasing stability, containing (*a*) 3, (*b*) 2, (*c*) 1, and (*d*) 0 dimethylamino-groups. The colours (*a*) violet, (*b*) green, (*c*) orange-red [cf. (III) and (VI)], and (*d*) orange-yellow [cf. (I), (IV), and (V)], are independent of the number of trimethylammonium groups present and are similar to those of the corresponding polyacid salts of crystal-violet. H. E. F. NOTTON.

3 : 3'-Difuchsonyl and related compounds. A. BISTRZYCKI and W. NIEDERBERGER (Helv. Chim. Acta, 1928, **11**, 261—272).—Benzilic acid and 2 : 2'-dihydroxydiphenyl condense in acetic–sulphuric acid solution to form 2 : 2'-*dihydroxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylic acid* (I), $+2H_2O$, m. p. 269—271° (decomp.), which is methylated by methyl sulphate forming *dimethyl* 2 : 2'-*dimethoxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylate*, m. p. 260—261° (decomp.). Treatment of the acid with concentrated sulphuric acid affords *difuchsonyl tetrahydrate*, $C_{38}H_{26}O_2,4H_2O$, m. p. 308° (decomp.) after darkening,

(I.)   (II.)

which when treated with 2*N*-sodium hydroxide solution in ethereal solution affords a *tetrasodium* derivative, $C_{38}H_{26}O_4Na_4$. Successive treatment of a hot alcoholic solution of the tetrahydrate with 10% potassium hydroxide and 1—2% acetic acid furnishes 2 : 2'-*dihydroxy*-5 : 5'-*di*(α-*hydroxybenzhydryl*)*diphenyl*, $+2H_2O$, m. p. 308° (decomp.). 3 : 3'-*Difuchsonyl* (II) has m. p. 331° (decomp.) after previous darkening, and is reduced by zinc and acetic acid to 2 : 2'-*dihydroxy*-5 : 5'-*dibenzhydryldiphenyl*, m. p. 186—187° after softening. 2 : 2'-*Dimethoxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylic acid*, m. p. 291° (decomp.), is obtained from 2 : 2'-dimethoxydiphenyl and benzilic acid, and gives when treated with concentrated sulphuric acid at 75°, 2 : 2'-*dimethoxy*-5 : 5'-*di*(α-*hydroxybenzhydryl*)*diphenyl*, m. p. 163—164° (decomp.). H. BURTON.

Comparative migratory tendencies of acyclic radicals in the semi-pinacolic transpositions of phenyldialkylglycols. Their relation to affinity capacities. M. TIFFENEAU and (MLLE.) J. LÉVY (Compt. rend., 1928, **186**, 84—86).—The dehydration by sulphuric acid of phenyldialkyl glycols involves a semi-pinacolic transposition, with migration of one of the alkyl radicals. In the 13 cases studied, the migratory tendencies of the radicals were found as a rule to be inversely proportional to their affinity capacities. B. W. ANDERSON.

Catalytic action. XVII. New functions of reduced copper. II. S. KOMATSU (Sexagint [Osaka celebration], Kyoto, 1927, 203—216).—Reduced copper as a catalyst for both dehydration and dehydrogenation stands between thoria and nickel. Three forms of reduced copper are described, distinguished by their action on menthol (cf. A., 1925, i, 687, 942).

Nitriles are obtained by passing a primary alcohol and ammonia over reduced copper (cf. A., 1925, i, 893). Copper with chlorine and benzene at 200° gives chiefly the hexachloride. Reduced copper converts unsaturated hydroaromatic compounds into a mixture of aromatic and saturated hydroaromatic compounds. It is also apparently capable of catalysing the keto–enol change, since inversion occurs with *l*-menthone (A., 1925, i, 943). C. D. LANGFORD.

Catalytic action. XXI. Catalytic reduction of nitriles. S. KOMATSU and S. ISHIDA (Mem. Coll. Sci. Kyoto, 1927, 331—337; cf. A., 1925, i, 893).—The reduction of benzonitrile by hydrogen in presence of reduced copper at 150—200° gives a mixture of benzaldimine, benzylamine, and dibenzylamine. The yield of bases is favoured by a low temperature (150°) and by those forms of reduced copper that are most active as oxidising catalysts. A rapid current favours the formation of aldimine. At a higher temperature the nitrile is decomposed to toluene and ammonia. The relative amounts of the products formed under different conditions are in

agreement with the mechanism suggested by Braun, Blessing, and Zobel (A., 1923, i, 1087). The reduction of acetonitrile and *iso*valeronitrile gives no aldimine but only primary and secondary amines.

C. D. LANGFORD.

α-Sulphophenylacetic acid. J. BRUST (Rec. trav. chim., 1928, 47, 153—168).—Ammonium α-chloro- and α-bromo-phenylacetates react with ammonium sulphite in aqueous solution to form mainly mandelic acid, whilst with ethyl α-bromophenylacetate followed by hydrolysis with barium hydroxide solution a good yield of *α-sulphophenylacetic acid* ($+2H_2O$), decomp. 140° after colouring at 130°, is obtained [*barium* ($+H_2O$), *thallium* ($+H_2O$), *cobalt* ($+H_2O$), *nickel* ($+H_2O$), *copper*, *aniline hydrogen*, m. p. 158°; *aniline*, o-*phenylenediamine*, decomp. 216°; *brucine hydrogen* ($+2H_2O$), *brucine* ($+8H_2O$), *strychnine hydrogen* ($+2H_2O$), *strychnine* ($+5H_2O$), and *quinine* ($+2H_2O$) salts described]. Sulphonation of phenylacetic acid with sulphur trioxide or of phenylacetic anhydride with sulphuric acid yields p-*sulphophenylacetic acid* [*barium* ($+2H_2O$), *calcium* ($+3H_2O$), *lead* ($+2H_2O$) salts], oxidised by chromic–sulphuric acids to *p*-sulphobenzoic acid. Fusion of this compound and *p*-sulphophenylacetic acid with potassium hydroxide furnishes *p*-hydroxybenzoic and *p*-hydroxyphenylacetic acids, respectively. l-*α-Sulphophenylacetic acid*, decomp. 225° [*sodium, sodium hydrogen, barium* ($+2H_2O$), *cobalt* ($+4H_2O$), *nickel* ($+2H_2O$), *copper* ($+3H_2O$), *aniline hydrogen*, m. p. 205°, and *aniline* salts], is obtained by decomposition of its brucine salt. Numerous values for the molecular rotations of the acid and its salts for different wave-lengths are given. d-*Sulphophenylacetic acid*, $[M]_D$ +36°, is obtained by the interaction of ammonium *l*-α-bromophenylacetate and ammonium sulphite.

When the normal aniline salt of α-sulphophenylacetic acid is boiled with excess of aniline there is produced the *aniline* salt, m. p. 242° (partial decomp.), of *α-sulphophenylacetanilide*, decomp. 205° [*barium* ($+6H_2O$), *cobalt* ($+8H_2O$), *nickel* ($+6H_2O$), *copper*, *strychnine* ($+3H_2O$), *brucine* ($+3H_2O$), and *quinine* ($+2H_2O$) salts described]. l-*α-Sulphophenylacetanilide*, $[M]_D$ −12° (*ammonium* salt, $[M]_D$ −14°), is obtained from the strychnine or quinine salts and racemises easily when heated. The *o*-phenylenediamine salt of α-sulphophenylacetic acid when heated at 180 yields 2-*benzylbenziminazole-α-sulphonic acid* [*barium* ($+6H_2O$), *cobalt* ($+5H_2O$), *nickel* ($+5H_2O$), and *quinine* ($+2H_2O$) salts]. Decomposition of the purified quinine salt with ammonia furnishes the *ammonium* salt $[M]_D$ −10°, which racemises quickly when heated. *l*-α-Sulphophenylacetic acid and *o*-phenylenediamine react to give the inactive glyoxaline derivative.

H. BURTON.

Resolution of externally compensated *p*-nitrobenzoylalanine. W. M. COLLES and C. S. GIBSON (J.C.S., 1928, 99—108).—*p*-Nitrobenzoylation of alanine in potassium hydroxide solution at 7—10° affords dl-p-*nitrobenzoylalanine*, m. p. 194° [*silver*, *brucine* ($+4H_2O$), and *cinchonidine* ($+3H_2O$) salts, *ethyl* ester, m. p. 117·5—118°]. Since this compound has a great tendency to form partial racemates or series of mixed crystals of the diastereoisomeric salts with various alkaloids, the following method of resolution must be adhered to. Equivalent quantities of the acid and strychnine are mixed in ethyl alcohol at 50° and the crude *lAlB* salt which separates is crystallised from alcohol at 50° until pure. *Strychnine* l-p-*nitrobenzoylalanine* ($+EtOH$), $[\alpha]_{5461}^{20}$ (anhydrous salt) −48·8° in alcohol, when decomposed furnishes l-p-*nitrobenzoylalanine*, m. p. 167·5—168°, $[\alpha]_{5461}^{20}$ (ammonium salt) −51·66° in water, and −15·81° in alcohol. The crystals obtained from the alcoholic mother-liquor after separation of the crude *lAlB* salt are crystallised from much alcohol and finally from water. Decomposition of *strychnine* d-p-*nitrobenzoylalanine* ($+1·5H_2O$), $[\alpha]_{5461}^{20}$ −1·9° in alcohol, so obtained, gave d-p-*nitrobenzoylalanine*, m. p. 168·5—169°, $[\alpha]_{5461}^{20}$ (ammonium salt) +51·4° in water, +15·76° in alcohol (*ethyl* ester, m. p. 121—121·5°, $[\alpha]_{5461}^{20}$ +1·32° in alcohol) identical with a specimen prepared from *d*-alanine and *p*-nitrobenzoyl chloride.

For comparison with the above results *ethyl* dl-*α-naphthalenesulphonylalanine*, m. p. 104°, and *ethyl* d-*α-naphthalenesulphonylalanine*, m. p. 83·5—84°, $[\alpha]_{5461}^{20}$ −47·15° in alcohol, were prepared (cf. A., 1925, i, 137). There is no reversal of sign of the rotatory powers of the *p*-nitrobenzoyl derivatives as is the case with the α-naphthalenesulphonyl derivatives.

The test for amino-acids described by Waser and Brauchli (A., 1924, i, 1068) is more sensitive if the sodium carbonate solution is replaced by pyridine (cf. Ingersoll and Adams, A., 1923, i, 200).

H. BURTON.

Derivatives of phenylanthranilic acid. IV. H. GOLDSTEIN and J. VAYMATCHAR (Helv. Chim. Acta, 1928, **11**, 239—245; cf. A., 1926, 558; 1927, 1186).—2-Chloro-3 : 5-dinitrobenzoic acid reacts with *p*-phenylenediamine in boiling aqueous sodium acetate solution to form 4 : 6-*dinitro-4′-aminodiphenylamine-2-carboxylic acid*, decomp. 274°, which when reduced by stannous chloride and subsequently esterified yields *methyl* 4 : 6 : 4′-*triaminodiphenylamine-2-carboxylate*, m. p. 151°. 4 : 6 : 4′-*Trinitrodiphenylamine-2-carboxylic acid* [*methyl* ester, m. p. 220° (decomp.)] chars at 298° without melting. 4-*Aminodiacetyl*-m-*phenylenediamine*, m. p. 218°, condenses with 2-chloro-3 : 5-dinitrobenzoic acid giving 4 : 6-*dinitro-2′ : 4′-diacetamidodiphenylamine-2-carboxylic acid*, m. p. 255° (decomp.). From *p*-aminophenol and potassium 2-chloro-5-nitrobenzoate, in presence of boiling amyl alcohol, potassium carbonate, and copper powder, there is obtained 4-*nitro-4′-hydroxydiphenylamine-2-carboxylic acid*, m. p. 210°, reduced to 4-*amino-4′-hydroxydiphenylamine-2-carboxylic acid*, m. p. 213° (decomp.) (*methyl* ester, m. p. 164°, obtained from the chlorostannate of the amino-acid, and methyl-alcoholic hydrogen chloride). *Methyl* 4 : 6-*diamino-4′-hydroxydiphenylamine-2-carboxylate* has m. p. 162°.

H. BURTON.

Electrochemical oxidation of β-phenylpropionic acid. F. FICHTER and R. SENTI.—See this vol., 253.

Ring closure of γ-phenyl-α-benzyl-*n*-butyryl chloride. H. LEUCHS [with H. KOHLER and G.

GRUNOW] (Ber., 1928, **61**, [*B*], 144—146; cf. von Braun and others, this vol., 174).—The ring closure leads to the production of a six-membered in preference to a five-membered group; the latter does not appear to be formed. Benzyl-β-phenylethylmalonic acid passes when heated into *γ-phenyl-α-benzyl-n-butyric acid*, m. p. 54°, b. p. 233—234°/12 mm. The acid is converted by 0·8 mol. of phosphorus pentachloride in the presence of chloroform into a mixture of the corresponding chloride (*γ-phenyl-α-benzyl-n-butyramide*, m. p. 133—134°) and *1-keto-2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene*, b. p. 222—223°/12 mm., m. p. 53—54·5° [*semicarbazone*, m. p. 224—226° (slight decomp.) after softening at 218°]. The constitution of the latter compound is established by its preparation by hydrolysis of *ethyl 1-keto-2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate*, m. p. 76—77°. H. WREN.

Co-ordination valency of aluminium in its salicylato-derivatives. G. J. BURROWS and I. W. WARK (J.C.S., 1928, 222—229).—*Aluminosalicylic acid*, $H_2[(C_7H_4O_3)_2Al(OH)OH_2]$, is prepared by the interaction of hot aqueous solutions of potassium aluminium sulphate and sodium or ammonium salicylate, from aluminium chloride and salicylic acid in hot aqueous solution, from aluminium hydroxide and aqueous-alcoholic salicylic acid, and from salicylic acid and aluminium ethoxide in anhydrous alcohol. The acid is dibasic; the *sodium* (+1 and $2H_2O$ and +2MeOH), *barium* (+$2H_2O$), and *strychnine* salts are described. Resolution of the acid was not effected through the agency of several alkaloids. The co-ordination valency of aluminium in this complex is six. *Aluminium methyl* and *ethyl salicylates*, $(C_8H_7O_3)_3Al$ and $(C_9H_9O_3)_3Al$, and aluminium ethyl malonate, $(C_7H_{11}O_4)_3Al$, are obtained by the interaction of aluminium alkoxides and the appropriate ester. H. BURTON.

Bismuth salicylates and citrates. P. GODFRIN (J. Pharm. Chim., 1927, [viii], **6**, 49—62).—The following crystalline bismuth salicylates and citrates have been prepared by slow crystallisation from a mixture of bismuth nitrate and the appropriate sodium salt in an aqueous solution of glycerol: bismuth salicylate, $(C_7H_5O_3)_3Bi,H_2O$; *sodium bismuth salicylate*, $(C_7H_5O_3)_2Bi_2,(C_7H_5O_3)Na,H_2O$; *bismuthyl acid salicylate*, $(C_7H_5O_3)_2Bi\cdot OH,\frac{1}{2}H_2O$; *bismuthyl salicylate*, $C_7H_5O_3BiO$; *bismuth citrate*, $(C_6H_5O_7)Bi,4H_2O$; *bismuthyl acid citrate*, $(C_6H_5O_7)_2Bi(OH)_3,xH_2O$. Certain *basic bismuth salicylates* have also been prepared: $(C_7H_5O_3BiO)_4Bi_2O_3,2H_2O$, as the final dissociation product of neutral bismuth salicylate in ether, and $(C_7H_5O_3BiO)_2Bi_2O_3,2H_2O$ as the final dissociation product of neutral bismuth salicylate in boiling water or alcohol. E. A. LUNT.

Bismuth salicylates and citrates. PICON (J. Pharm. Chim., 1927, [viii], **6**, 307—309).—Experiments are described from which it has been deduced that neutral bismuth salicylate does not dissociate in aqueous solution, and it is therefore thought that the basic bismuth salicylate, $(C_7H_5O_3BiO)_2Bi_2O_3,2H_2O$, (cf. Godfrin, preceding abstract), does not exist. E. A. LUNT.

Carbomethoxy-derivatives of hydroxy-acids. A. MCKENZIE and M. S. LESSLIE (Ber., 1928, **61**, [*B*], 153—163).—In the hope of establishing a general synthesis of benzoins, *r*-carbomethoxymandelyl chloride, m. p. 39—40° (cf. A., 1913, i, 1194), has been subjected to the action of benzene and aluminium chloride in the presence of carbon disulphide, benzene, or pyridine, whereby, however, phenyldeoxybenzoin, m. p. 134—135°, is produced. Analogously, r-*carbethoxymandelic acid*, m. p. 79—82°, prepared from *r*-mandelic acid and ethyl chloroformate in the presence of chloroform and dimethylaniline, is converted through its chloride into phenyldeoxybenzoin. Since benzoin is stable towards hydrogen chloride in hot benzene but is converted into phenyldeoxybenzoin, presumably through desyl chloride, if aluminium chloride is present, the change is represented: $CHPh(O\cdot CO_2Me)\cdot COCl \longrightarrow CHPh(O\cdot CO_2Me)\cdot COPh \longrightarrow CHPh(OH)\cdot COPh \longrightarrow CHPhCl\cdot COPh \longrightarrow CHPh_2\cdot COPh$. *l*-Mandelic acid yields successively l-*carbomethoxymandelic acid*, m. p. 111—112°, $[\alpha]_D^{17}$ −137·6° in acetone (hydrolysed to *l*-mandelic acid without racemisation by sodium hydroxide), l-*carbomethoxymandelyl chloride*, m. p. 42—43°, $[\alpha]_D^{15}$ −138·1° in acetone, and phenyldeoxybenzoin. Carbomethoxymandelyl chloride is converted by an excess of magnesium phenyl bromide into triphenylethylene glycol, m. p. 167—167·5°, which affords phenyldeoxybenzoin when treated with sulphuric acid, thionyl chloride, or hydrochloric acid. *Carbomethoxybenzilic acid*, m. p. 94—95°, prepared by the action of methyl chloroformate on benzilic acid in the presence of chloroform and pyridine, is unexpectedly transformed by thionyl chloride into diphenylchloroacetic acid, m. p. 118—119°. r-*Carbomethoxyatrolactic acid*, m. p. 134—135°, yields the corresponding *chloride*, m. p. 88—89°, converted by aluminium chloride and benzene into αα-diphenylpropionic acid, m. p. 173—174° (*silver* salt). *l*-Atrolactic acid yields the corresponding *carbomethoxy*-derivative, m. p. 77—79°, $[\alpha]_D^{17}$ +33·2° in ethyl alcoholic solution, which is hydrolysed without appreciable racemisation by sodium hydroxide. r-*Carbomethoxy-α-hydroxy-β-phenylpropionic acid*, m. p. 97—98°, is described. H. WREN.

Dibromides of methylcoumaric and methylcoumarinic acids. M. REIMER and M. HOWARD (J. Amer. Chem. Soc., 1928, **50**, 196—203).—Treatment of methylcoumarinic or of methylcoumaric acid with bromine in carbon disulphide affords two isomeric dibromides, m. p. 177° (decomp.) (I), and m. p. 134° with slight decomposition and subsequent resolidification and then decomposition at 170° (II). Separation can be effected by fractional extraction with, and crystallisation from, toluene, in which solvent (II) gradually isomerises to (I) at the b. p. (cf. Biilmann and Lund, A., 1923, i, 218). Treatment of (II) with cold aqueous 50% potassium hydroxide affords α-bromo-*o*-methoxycinnamic acid, m. p. 171° (cf. Perkin, J.C.S., 1881, **39**, 418), whilst (I) affords similarly a small proportion of an isomeric *α-bromo-o-methoxycinnamic acid*, yellow, m. p. 136° (III), together with α-bromo-*o*-methoxystyrene. Formation of (III) is favoured by substitution of alcoholic for

aqueous alkali. Conversion of (III) into the isomeride of m. p. 171° is effected by exposure to sunlight in aqueous solution. Esterification of (III) cannot be effected by methyl-alcoholic hydrogen chloride, but the *methyl* ester, a yellow liquid, was obtained by the action of diazomethane. It is concluded that (III) is probably the *cis*-isomeride. Treatment of (II) with aqueous bromine affords a small proportion of αβ-5-tribromo-2-methoxycinnamic acid, m. p. 201°, which is converted by saturated methyl-alcoholic potassium hydroxide into two isomeric *α-5-dibromo-2-methoxycinnamic acids*, m. p. 163—164° (*methyl* ester, m. p. 94°), and m. p. 221° (*methyl* ester, m. p. 106—107°), respectively. Isomerisation of the former to the latter is effected by exposure to sunlight in benzene. Both isomerides yield 5-bromo-2-methoxyphenylpropiolic acid, decomp. 174°, when treated with boiling aqueous 10% potassium hydroxide. Treatment of both (I) and (II) with water affords the same α-bromo-β-hydroxy-2-methoxyphenylpropionic acid, m. p. 134°, which on treatment with aqueous bromine yields α-5-dibromo-β-hydroxy-2-methoxyphenylpropionic acid, m. p. 137°, with subsequent resolidification (IV) and m. p. 154° (V). Both (IV) and (V) yield the same *methyl* ester, m. p. 93—95°, and it is concluded that the two hydroxy-acids are dimorphic rather than isomeric. Treatment of (I) with cold methyl alcohol yields α-bromo-β-2-dimethoxyphenylpropionic acid, m. p. 118°, whilst (II) yields similarly the isomeride, m. p. 136° (cf. Werner, A., 1906, i, 180°). F. G. WILLSON.

Chlorobenzoylacetic esters. A. WAHL and J. ROLLAND (Compt. rend., 1928, **186**, 37—39).—The action of nitrous vapours on methyl *o*-, *m*-, and *p*-chlorobenzoylacetates in presence of acetic anhydride and ether causes decomposition in each case with formation of the corresponding chlorobenzoic acid. Small amounts, however, of the respective αβ-diketonic esters are also formed, and the following derivatives have been isolated by treatment of the reaction mixture with phenylhydrazine: *methyl benzeneazo*-o-, -m-, and -p-*chlorobenzoylacetates*, m. p. 95—96°, 132°, and 90—91°, respectively, and 1-*phenyl*-3-o-, -m-, and -p-*chlorophenyl*-4 : 5-*diketodihydropyrazole-4-phenylhydrazones*, m. p. 195°, 166—167°, and 204°, respectively. B. W. ANDERSON.

Derivatives of 2 : 3-hydroxynaphthoic arylamides. BRIT. DYESTUFFS CORP., LTD., J. B. PAYMAN, and H. WIGNALL.—See B., 1928, 118.

Direct substitution in the benzene nucleus. J. VAN ALPHEN (Rec. trav. chim., 1928, **47**, 169—173). Treatment of $\Delta^{2:6}$-dihydrophthalic acid with concentrated sulphuric acid at 60°, or in presence of acetic anhydride in the cold, yields phthalic acid or the anhydride. Cold absolute nitric acid or nitrogen peroxide in acetic acid solution gives similar results. When the acid is treated with bromine, Δ^{1}-3 : 6-dibromotetrahydrophthalic acid is produced, which when heated begins to decompose at 100°, phthalic anhydride begins to sublime at 160°, and at 200° decomposition into hydrogen bromide, water, and phthalic anhydride is complete. All the reactions are explained by 1 : 4-addition with subsequent elimination of hydrogen and the reacting constituent. These observations do not support Prins' objections (A., 1919, i, 71) to Holleman's addition theory of aromatic substitution. H. BURTON.

Constitution of ethyl succinylsuccinate and of ethyl *p*-dihydroxyterephthalate. D. MIGLIACCI (Gazzetta, 1927, **57**, 914—923).—If the preparation of diethyl succinylsuccinate from diethyl succinate is not properly carried out, the mother-liquors yield a compound, m. p. 123—124°, which Gibbs and Brill (A., 1915, i, 648) regard as the ketonic form of diethyl succinylsuccinate. This compound is, however, diethyl *p*-dihydroxyterephthalate, since, on condensation with primary arylamines, it gives, not diethyl 2 : 5-diarylamino-$\Delta^{1:4}$-dihydroterephthalates,

$CH_2{<}{\substack{C(NHR){:}C(CO_2Et)\\ C(CO_2Et){:}C(NHR)}}{>}CH_2$, but only diethyl 2 : 5-diarylaminoterephthalates,

$CH{\lessdot}{\substack{C(CO_2Et){:}C(NHR)\\ C(NHR)\cdot C(CO_2Et)}}{\gtrdot}CH$. Thus, the action of *p*-anisidine on diethyl succinylsuccinate in acetic acid, either with or without alcohol, yields *diethyl* 2 : 5-*di*-p-*anisidino*-$\Delta^{1:4}$-*dihydroterephthalate*, pale violet, m. p. 190—191°, whereas *p*-anisidine and Gibbs and Brill's ester, m. p. 123—124°, give *diethyl* 2 : 5-*di*-p-*anisidinoterephthalate*, orange-red, m. p. 171°.

Confirmation of Hantzsch's view that diethyl succinylsuccinate is rigidly enolic and diethyl *p*-dihydroxyterephthalate a quinol-*p*-dicarboxylic ester (A., 1917, i, 685) is obtained, since it is found possible (1) by oxidation by means of iodine (2 atoms), to pass from diethyl 2 : 5-di-*p*-anisidino-$\Delta^{1:4}$-dihydroterephthalate to diethyl 2 : 5-di-*p*-anisidinoterephthalate; (2) to convert the latter into a *dibenzoyl* derivative, m. p. 220°, and (3) by hydrolysis of the ester with potassium hydroxide, to obtain 2 : 5-*di*-p-*anisidinoterephthalic acid*, m. p. 276° (decomp.).

Diethyl 2 : 5-*di*-p-*phenetidino*-$\Delta^{1:4}$-*dihydroterephthalate*, m. p. 197°, *diethyl* 2 : 5-*di*-p-*phenetidinoterephthalate*, m. p. 180° (*dibenzoyl* derivative, m. p. 163°), and 2 : 5-*di*-p-*phenetidinoterephthalic acid*, $C_{24}H_{24}O_6N_2$, m. p. 280° (decomp.), are described. T. H. POPE.

Condensation of *cyclo*hexanealdehyde and malonic acid. S. S. G. SIRCAR (J.C.S., 1928, 54—57).—*cyclo*Hexanealdehyde condensed with malonic acid in presence of pyridine and piperidine (or diethylamine) forms β-cyclo*hexylacrylic acid*, b. p. 153—154°/11 mm., m. p. 57—58° (*silver* salt; *acid chloride*, b. p. 142°/12 mm.; *methyl* ester, b. p. 92—93°/15 mm.; *ethyl* ester, b. p. 119°/11 mm.; *amide*, m. p. 158—159°; *anilide*, m. p. 142°; *dibromide*). If condensation is effected in presence of a small amount of diethylamine, with subsequent heating, there is produced β-cyclo*hexylglutaric acid*, m. p. 153—154° [*silver* salt; *acid chloride*, b. p. 159—160°/12 mm.; *ethyl* ester, b. p. 118—120°/17 mm.; *methyl* ester, b. p. 106—108°/17 mm.; *diamide*, m. p. 190°; *dianilide*, m. p. 237° (decomp.); *anhydride*]. The *monoanilide*, m. p. 151°, of this acid when heated at 200° for a short time passes into the *anil*, m. p. 181°. When condensation takes place in alcoholic diethylamine there is obtained cyclo*hexane*spiro*butyrolactone*, b. p. 152—155°/15 mm. (the *silver* salt of the hydroxy-acid is described). Small amounts of β-*cyclo*hexyl-

acrylic acid are also formed in both these condensations.

Oxidation of the αβ- and βγ-unsaturated ketones from *cyclo*hexanealdehyde and acetone (Kon, A., 1926, 952) with alkaline hypobromite yields β-*cyclo*hexylacrylic acid and a *βγ-acid* (*silver* salt), respectively. This last compound when oxidised with dilute potassium permanganate gives *cyclo*hexanone, whereas the former furnishes *cyclo*hexanealdehyde.

H. Burton.

Hydrolysis by alkalis of ethyl phenylethylmalonate. E. Tassilly, A. Belot, and M. Descombes (Compt. rend., 1928, **186**, 149—151).—Hydrolysis of ethyl phenylethylmalonate with hot aqueous or alcoholic sodium hydroxide yields phenylethylmalonic acid and α-phenyl-α-ethylacetic acid in the proportions 4 : 1 and 1 : 9, respectively, the hydrolysis in alcoholic solution being completed much the more rapidly. Hydrolysis with powdered potassium hydroxide at the ordinary temperature gives the same acids in the ratio 4 : 1. By using a limited quantity of cold aqueous-alcoholic sodium hydroxide, *ethyl hydrogen phenylethylmalonate*, m. p. 94°, is obtained.

B. W. Anderson.

3-Methyl-4′-*iso*propyldiphenyl-2 : 2′-dicarboxylic acid. H. P. Fogelberg (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 4).—*3-Methyl-4′-*iso*propyldiphenyl-2 : 2′-dicarboxylic acid*, m. p. 188—189·5°, formed by the oxidation of retenequinone with hydrogen peroxide in glacial acetic acid, gives the *anhydride*, m. p. 111—112°, on treatment with acetyl chloride and acetic anhydride, yielding the *monoamide*, m. p. 196—197°, on warming with aqueous ammonia. The acid forms soluble alkali, barium, and calcium salts and insoluble silver, copper, and lead salts.

G. A. C. Gough.

5-Bromo-2 : 4-dimethoxybenzoylacrylic acid and its esters. G. P. Rice (J. Amer. Chem. Soc., 1928, **50**, 229—235).—Condensation of succinic anhydride with resorcinol dimethyl ether in carbon disulphide in presence of aluminium chloride (cf. Perkin and Robinson, J.C.S., 1908, **93**, 506) affords, in addition to 2 : 4-dimethoxybenzoylpropionic acid, (I) (*ethyl* ester, m. p. 44°, with subsequent resolidification and m. p. 68·5°), *2-hydroxy-4-methoxybenzoylpropionic acid* (*methyl* ester, m. p. 87°). Bromination of (I) in chloroform affords β-5-*dibromo-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 165° (decomp.) (*methyl* ester, m. p. 103°; *ethyl* ester, m. p. 114·5°), and this, when treated with potassium acetate in glacial acetic acid at 100°, yields *5-bromo-2 : 4-dimethoxybenzoylacrylic acid*, yellow, m. p. 208° (*methyl* ester, m. p. 138° after softening at about 129°, m. p. 129° after resolidification; *ethyl* ester, yellow, m. p. 115·5°). Treatment of the latter acid with aqueous sodium hyposulphite affords *5-bromo-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 187° (*methyl* ester, m. p. 117°). When ethyl 5-bromo-2 : 4-dimethoxybenzoylacrylate is exposed to sunlight, it is converted into two colourless *dimerides*, m. p. 266° and 129—130°, respectively. The former becomes yellow when kept in diffused daylight, and the latter is gradually depolymerised in molten camphor. Treatment of methyl 5-bromo-2 : 4-dimethoxybenzoylacrylate with methyl alcohol and a trace of concentrated aqueous potassium hydroxide at below 0° affords *5-bromo-α : 2 : 4-trimethoxybenzoylpropionic acid*, m. p. 189°, together with its *methyl* ester, m. p. 117°, whilst boiling dilute hydrochloric acid yields *5-bromo-α-hydroxy-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 172°. *5-Bromo-β-hydroxy-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 179° (decomp.) (*methyl* ester, m. p. 134·5°), is obtained by treating β : 5-dibromo-2 : 4-dimethoxybenzoylpropionic acid with cold aqueous sodium carbonate. *5-Bromo-α-ethoxy-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 139—140°, and its *ethyl* ester, m. p. 97°, are obtained analogously to the corresponding α-methoxy-derivatives.

F. G. Willson.

Synthesis of 3 : 4 : 5-trimethoxy-*o*-phthalic acid. K. Feist and G. L. Dschu (Festschr. A. Tschirch, 1926, 23—29; Chem. Zentr., 1927, ii, 58).—(*a*) 3 : 4 : 5-Trimethoxybenzoic acid, m. p. 163—164° (from gallic acid, methyl sulphate, and sodium hydroxide) yields with chloral hydrate 3 : 4 : 5-trimethoxytrichlorophthalide, m. p. 71—72°, which by heating with methyl-alcoholic sodium hydroxide, diluting with water, evaporating off the alcohol, saturating with hydrogen chloride, and methylating the product with methyl sulphate yields 3 : 4 : 5-trimethoxyphthalidecarboxylic acid, m. p. 147—148° (with diazomethane, methyl ester, m. p. 121°). The acid, when heated at 2 mm., yields 3 : 4 : 5-trimethoxyphthalide, m. p. 134—135°, which on oxidation with potassium permanganate in sodium hydroxide solution affords 3 : 4 : 5-trimethoxy-*o*-phthalic acid, m. p. 163° (anhydride, m. p. 143°; methyl ester, m. p. 64—65°).

(*b*) Gallic acid trimethyl ether, when heated in chloroform solution with bromine and iron powder, yields bromogallic acid trimethyl ether, m. p. 148°; the mother-liquor contains a molecular compound of the two ethers. The latter with diazomethane affords the methyl ester, m. p. 33°, which by boiling in ethereal solution in presence of iodine with magnesium turnings yields 1-methyl-3 : 4 : 5-trimethoxy-*o*-phthalate, m. p. 138—141°, which with diazomethane gives the dimethyl ester.

A. A. Eldridge.

Di*cyclo*pentanone derivatives. N. J. Toivonen (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 20; cf. A., 1920, i, 1017; J.C.S., 1901, **79**, 786; 1920, **117**, 1362).—Triethyl 4 : 5 : 5-trimethyl*cyclo*pentan-3-one-1 : 2 : 4-tricarboxylate yields 4 : 5 : 5-trimethyl*cyclo*pentan-3-one-1-carboxylic acid, m. p. 117—118°, on boiling with 20% sulphuric acid. This acid or its *triethyl* ester, b. p. 132·5—134·5°/14 mm., on oxidation with potassium permanganate yields γ-acetyl-γ-methyl-*n*-butane-αδ-dicarboxylic acid, m. p. 123—124° (*semicarbazone*, m. p. 138°; *anhydride*, m. p. 139—140°), which may in turn be oxidised to γ-methylbutane-αβγ-tricarboxylic acid, m. p. 157—158°, by sodium hypochlorite. Oxidation with nitric acid yields the final product directly. Fusion of γ-hydroxy-αββ-trimethylbutane-αβδ-tricarboxylic acid lactone (Perkin, Thorpe, and Walker, J.C.S., 1901, **79**, 729) with potassium hydroxide yields trimethylsuccinic, formic, acetic, and propionic acids.

G. A. C. Gough.

Action of aniline on vanillin. P. Carré and P. Baranger (Bull. Soc. chim., 1928, [iv], 43, 73—74).—When melted with 1 mol. of aniline vanillin affords *vanillin-aniline*, $OH\cdot C_6H_3(OMe)\cdot CH(OH)\cdot NHPh$, m. p. 155—156°, converted at 115° into 4-hydroxy-3-methoxybenzylideneaniline, m. p. 156—157° [*hydrochloride*, m. p. 177° (decomp.)]. *Vanillin-aniline hydrochloride*, m. p. 143° (decomp.), is obtained by warming vanillin with aniline hydrochloride or by dissolving 4-hydroxy-3-methoxybenzylideneaniline in 18% hydrochloric acid. Both hydrochlorides when heated afford a *substance*, m. p. 196—198°. R. Brightman.

Asarylaldehyde [2 : 4 : 5-trimethoxybenzaldehyde]. II. J. van Alphen (Rec. trav. chim., 1928, 47, 174—178; cf. *ibid.*, 1927, 46, 195).—Treatment of asarylaldehyde with absolute nitric acid in acetic anhydride at —10° affords 1-nitro-2 : 4 : 5-trimethoxybenzene, m. p. 130°, by displacement of the aldehydo-group. When this reaction is carried out in presence of a trace of concentrated sulphuric acid the product formed is 5-*methoxy*-p-*benzoquinone-2-aldehyde diacetate*, m. p. 145°. 2 : 4 : 5-*Trimethoxycinnamic acid*, m. p. 169°, obtained by heating asarylaldehyde and malonic acid in pyridine, is nitrated in acetic acid solution to 3 : 6-*dinitro-2 : 4 : 5-trimethoxycinnamic acid*, m. p. 166—167° (decomp.). H. Burton.

Campnospermonol, a ketonic phenol from *Campnospermum brevipetiolatum*. T. G. H. Jones and F. B. Smith (J.C.S., 1928, 65—70).—Extraction of the oily exudate from *C. brevipetiolatum* with dilute sodium hydroxide solution and liberation of the dissolved phenol by carbon dioxide gives *campnospermonol*, $C_{27}H_{40}O_2$ or $C_{28}H_{44}O_2$, b. p. 260°/5 mm. (decomp.), $d^{15\cdot5}$ 0·9454, n_D^{20} 1·4925 [*acetate*, b. p. 255—260°/5 mm., $d^{15\cdot5}$ 0·9550, n_D^{20} 1·489; *oxime*, b. p. 240°/5 mm. (decomp.), $d^{15\cdot5}$ 0·9195, n_D^{20} 1·489]. *Campnospermonyl methyl ether* has b. p. 240°/5 mm., $d^{15\cdot5}$ 0·9342, n_D^{20} 1·496, $[R_L]_D$ 128·8, iodine value 131 (*oxime*, b. p. 215°/4 mm., $d^{15\cdot5}$ 0·901, n_D^{20} 1·478), and when oxidised with potassium permanganate in acetone at 0° furnishes *m*-methoxybenzoic acid, formic, nonoic, and azelaic acids. Treatment of the methyl ether with ozone gives nonoaldehyde, formic and nonoic acids, and unrecognisable products.

Campnospermonyl methyl ether is reduced by sodium and alcohol, forming the corresponding *secondary alcohol*, b. p. 250°/5 mm., $d^{15\cdot5}$ 0·9191, whilst reduction with hydrogen in presence of platinum dioxide and ether gives *tetrahydrocampnospermonyl methyl ether*, m. p. 54° (*oxime*, m. p. 43°). Reduction of the ether with amalgamated zinc and hydrochloric acid furnishes an unsaturated *methoxyhydrocarbon*, $C_{28}H_{46}O$(?), b. p. 226°/5 mm., $d^{15\cdot5}$ 0·9093, n_D^{20} 1·495, which with hydrogen and platinum is reduced to a saturated *methoxyhydrocarbon*, ?), m. p. 45°. Reduction of campnospermonyl acetate by hydrogen in presence of platinum dioxide affords *tetrahydrocampnospermonyl acetate*, m. p. 61°, from which is obtained *tetrahydrocampnospermonol*, m. p. 70°.

Oxidation of hydrocampnospermonyl methyl ether with potassium permanganate in boiling acetone gives *m*-methoxybenzoic, oxalic, and margaric acids, whilst treatment with amyl nitrite and sodium ethoxide yields an impure oximino-compound, from which by the action of phosphorus pentachloride, stearic acid was obtained. Campnospermonol is formulated as either β-*m*-hydroxyphenyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,

$OH\cdot C_6H_4\cdot C(:CH_2)\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot Me$,

or β-*m*-hydroxybenzyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,

$OH\cdot C_6H_4\cdot CH_2\cdot C(:CH_2)\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot Me$.

H. Burton.

6-Acetyl-2-*iso*butyl-*m*-tolyl methyl ether and its nitration products. H. Barbier (Helv. Chim. Acta, 1928, 11, 152—156).—2-*iso*Butyl-*m*-tolyl methyl ether and acetyl chloride react in presence of aluminium chloride and carbon disulphide to form 6-*acetyl-2-*iso*butyl-*m*-tolyl methyl ether*, b. p. 281°/730 mm., 155°/10 mm., m. p. 91°. Nitration of this with 92—95% nitric acid at —10° affords *nitro-6-acetyl-2-*iso*butyl-*m*-tolyl methyl ether*, m. p. 97°, dinitro-2-*iso*butyl-*m*-tolyl methyl ether (I), m. p. 85° (musk ambrette, cf. Baur, A., 1894, i, 449), and *dinitro-6-acetyl-*m*-tolyl methyl ether* (II), m. p. 84°, together with a small amount of a substance, m. p. 96°. During the formation of (I) and (II) elimination of the acetyl and *iso*butyl groups, respectively, has occurred. *m*-Tolyl methyl ether and acetyl chloride yield 6-acetyl-*m*-tolyl methyl ether, b. p. 116°/4 mm., oxidised by 20% nitric acid to 5-methoxy-*o*-toluic acid, and nitrated by fuming nitric acid at 10° forming II. H. Burton.

Hydrogenation of distyryl ketone and di-β-phenylethyl ketone. V. Ipatiev and N. Orlov (J. Russ. Phys. Chem. Soc., 1927, 59, 537—539).—See A., 1927, 880.

Constitution of the internally complex salts of the mono- and di-oximes of α-diketones. P. Pfeiffer and J. Richarz (Ber., 1928, 61, [*B*], 103—107; cf. Hieber and Leutert, this vol., 46).—Whereas the formation of metallic salts of mono- and di-oximes of α-diketones is readily explained if the α-oximes are regarded as *syn*-compounds, difficulties arise when Meisenheimer's view of their configuration is adopted (cf. A., 1922, i, 152). These are avoided by regarding the metal as attached to the nitrogen atom as in $\begin{matrix}CR\cdot NO \\ CR{=}O\end{matrix}\!\!>\!X$. The complex nature of the salts is established by the isolation of the *compound* $[en_2\,Co(C_{14}H_{10}O_2N)]I_2$, by the successive action of hydroxoaquodiethylenediaminecobalt bromide (cf. A., 1927, 362) and potassium iodide on α-benzilmonoxime in aqueous alcohol. β-Benzilmonoxime does not react analogously. H. Wren.

Constitution of keto-enols from β-diketones. C. Weygand [with E. Bauer, H. Günther, and W. Heynemann] (Annalen, 1927, 459, 99—122).—Attempts to prepare pairs of isomeric keto-enols of the types, $CPh(OH):CH\cdot COR$ and $CR(OH):CH\cdot COPh$ [R being (*a*) *p*-tolyl, (*b*) *p*-anisyl, (*c*) *p*-nitrophenyl, (*d*) *p*-bromophenyl], by hydrolysis of the corresponding methyl ethers or dimethylacetals yield only one product in each case. This is apparently homogeneous and is shown by bromine titration to contain 100% of enol, but determinations of its constitution

by different chemical methods yield conflicting results (cf. Scheiber and Herold, A., 1914, i, 926; Claisen, A., 1926, 406). The tautomerism of these substances is thus closely similar to that of 5-phenyl-3-methylpyrazole. *p*-Anisyl αβ-dibromo-β-phenylethyl ketone is converted by boiling sodium methoxide into p-*anisyl α-bromostyryl ketone*, m. p. 126°, and by methyl alcohol and anhydrous sodium acetate into p-*anisyl β-methoxystyryl ketone*, m. p. 83—85°, identified by its ozonisation to methyl benzoate and anisic acid. This is hydrolysed by methyl-alcoholic hydrochloric acid to *p*-methoxydibenzoylmethane (I), m. p. 130—131°, and by acetic acid to a labile *isomeride*, m. p. 125—126°, similar to that of dibenzoylmethane (cf. A., 1926, 1248). Both isomerides are ozonised to phenyl- and anisyl-glyoxal, with benzoic and anisic acids. With hydroxylamine, (I) yields a single phenylanisyl*iso*oxazole, and with diazomethane principally the ether (II). Phenyl α-bromo-β-methoxy-β-anisylethyl ketone and sodium methoxide give *phenyl β* : p-*dimethoxystyryl ketone* (II), b. p. 165—170° [(*e*) in a cathode-ray vacuum], which is hydrolysed by acid to *p*-methoxydibenzoylmethane. *Phenyl α-bromo*-p-*methylstyryl ketone*, m. p. 65—66°, b. p. 225—228°/12 mm., prepared from phenyl αβ-dibromo-β-*p*-tolylethyl ketone and pyridine, is converted by sodium methoxide into *phenyl β-methoxy*-p-*methylstyryl ketone*, b. p. 145—150° (*e*), which is hydrolysed by acid to p-*methyldibenzoylmethane*, m. p. 84—85° (*copper* salt, m. p. 235·5°). Similarly *p*-tolyl αβ-dibromo-β-phenylethyl ketone affords successively p-*tolyl α-bromostyryl ketone*, m. p. 66—67°, b. p. 230—231°/11—12 mm., and p-*tolyl β-methoxystyryl ketone*, b. p. 140—145° (*e*), which is hydrolysed to the above *p*-methyldibenzoylmethane. With ozone the last yields benzoic and toluic acids, with hydroxylamine a mixture of *iso*oxazoles, and with diazomethane a mixture of ethers. Benzaldehyde and *p*-nitroacetophenone afford p-*nitrophenyl styryl ketone*, m. p. 146·5—147°, from which are prepared: a *dibromide*, m. p. 193·5—194°; p-*nitrophenyl α-bromostyryl ketone*, b. p. 153—155° (*e*), and p-*nitrophenyl β-methoxystyryl ketone*, m. p. 77°, b. p. 210° (*e*), which is hydrolysed to *p*-nitrodibenzoylmethane (Wieland, A., 1904, i, 432). *Phenyl α-bromo*-p-*nitrostyryl ketone*, m. p. 106°, b. p. 187° (*e*), obtained from the dibromide of phenyl *p*-nitrostyryl ketone, could not be converted into phenyl *p*-nitro-β-methoxystyryl ketone. The preparation of *phenyl* p-*bromostyryl ketone*, m. p. 123·5° (*dibromide*, m. p. 179·5°); p-*bromophenyl αβ-dibromo-β-phenylethyl ketone*, m. p. 184°; *phenyl α : 4-dibromostyryl ketone*, m. p. 131—131·5°; p-*bromophenyl α-bromostyryl ketone*, b. p. 136—143° (*e*); *phenyl* p-*bromo-β-methoxystyryl ketone* (III), b. p. 170° (*e*), and p-*bromophenyl ββ-dimethoxy-β-phenylethyl ketone* (IV), b. p. 176—180° (*e*), is described. (III) and (IV) are hydrolysed by acids to p-*bromodibenzoylmethane*, m. p. 94° (*copper* salt, m. p. 276°), of which a labile *form*, m. p. 86·5°, was obtained. H. E. F. NOTTON.

Additive character of heterogeneous conjugated systems. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1926, 3, 18—40).—See A., 1925, i, 1153.

Catalytic hydrogenation under pressure in presence of nickel salts. XII. Alkylated anthraquinones. J. VON BRAUN, O. BAYER, and L. F. FIESER (Annalen, 1927, 459, 287—304).—The ease of hydrogenation of the side-nuclei in anthraquinone is considerably increased by α-alkylation, but scarcely affected by β-alkylation, whilst 2 : 3-dialkylation (in 1′ : 2′ : 3′ : 4′-tetrahydro-2 : 3-benzanthraquinone) protects the nucleus. The first product is invariably an alkylanthranol (cf. A., 1926, 172, 729). 1 : 4-Dimethylanthraquinone with 8 atoms of hydrogen in decahydronaphthalene at 180°, gives 1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroanthranol*, m. p. 105—106° (*acetyl* derivative, m. p. 66—67°), and a little 1 : 4-*dimethyl*-(?)1 : 4-*dihydroanthranol*, m. p. 112—114°, which is oxidised by chromic acid to 1 : 4-dimethylanthraquinone. The tetrahydroanthranol is oxidised, first to 1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 75°, then by permanganate to phthalic acid. It is further hydrogenated to 1 : 4-*dimethyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthranol*, m. p. 83—84°, and finally to 1 : 4-*dimethyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 90—92°. Octahydrogenation of 1-methylanthraquinone yields an *oil*, b. p. 215—235°/14 mm. (traces of a bimolecular *product*, m. p. 235°), which is probably mainly 1-methyl-1 : 2 : 3 : 4-tetrahydro-9-anthranol, since 1-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 107—109°, may be isolated from its chromic acid oxidation product. It is further hydrogenated to 1-*methyloctahydroanthranol*, b. p. 202—203°/13 mm., and to 1-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 64—66°, b. p. 170°/13 mm. Tetrahydrogenation of 2-methylanthraquinone affords a 2(3)-methylanthranol, m. p. 70—76°, which, like the product of Liebermann and Mamlock (A., 1905, i, 521), is probably a mixture of isomerides. Octahydrogenation yields 2-methylanthracene (10%), its reduction products, and an inseparable *mixture*, m. p. 5—40°, of 2(3)-methyltetrahydroanthranols (*acetyl* derivative, m. p. −5° to 20°), which is oxidised by chromic acid to a *mixture*, m. p. 45—70°, of 2-methyltetrahydroanthraquinones. The 2(3)-*methyl* 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthranol*, m. p. 70—90°, b. p. 200—202°/14 mm., is also a mixture, but it is oxidised to a single 2-*methyloctahydroanthraquinone*, m. p. 155°. The course of hydrogenation of 2-methylanthraquinone is thus exactly similar to that of anthraquinone itself. 1′ : 2′ : 3′ : 4′-Tetrahydro-2 : 3-benzanthraquinone (I) (Schroeter, A., 1921, i, 861) is readily hydrogenated to 1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-*benzanthranol*, m. p. 142°, and reduced by zinc dust and ammonia to a small amount of an isomeric *tetrahydro*-derivative, m. p. 196°, which is oxidised to 2 : 3-benzanthraquinone, and 1′ : 2′ : 3′ : 4′ : 9 : 10-*hexahydro*-2 : 3-*benzanthranol*, m. p. 120°. This is decomposed by heating into 1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-*benzanthracene* (II), m. p. 233°, which is reduced by sodium and amyl alcohol to 1′ : 2′ : 3′ : 4′ : 9 : 10-*hexahydro*-2 : 3-*benzanthracene*, m. p. 128°. Octahydrogenation of the quinone (I) yields some of the anthracene (II) and 1′ : 2′ : 3′ : 4′ : 5 : 6 : 7 : 8-*octahydro*-2 : 3-*benzanthranol*, m. p. 159°, which is oxidised to the *octahydrobenzanthraquinone*, m. p. 264°. Its constitution has not been confirmed by oxidation, but the nature of further reduction products renders

the above the most probable. The quinone (I) is reduced by 13 atomic proportions of hydrogen to a mixture of the impure 1′:2′:3′:4′:1:2:3:4:5:6:7:8-*dodecahydro*-2 : 3-*benzanthranol*, m. p. 129—130°, with the corresponding *dodecahydrobenzanthracene*, m. p. 82—83°, which is oxidised to pyromellitic acid, and by 11 atomic proportions to 1′ : 2′ : 3′ : 4′ : 5 : 6 : 7 : 8-*octahydro*-2 : 3-*benzanthracene*, m. p. 174°, which is more conveniently prepared by hydrogenating the anthracene (II). H. E. F. NOTTON.

A cyclic semipinacolin. J. W. COOK (J.C.S., 1928, 58—65).—The compound $C_{21}H_{14}O_2$, m. p. 133—134°, formed by the action of moist silver oxide on benzylideneanthrone dibromide (A., 1926, 1131) is shown to be a seven-membered ring compound, $C_6H_4<\begin{smallmatrix}CO\cdot CHPh\\ CO\end{smallmatrix}>C_6H_4 \rightleftharpoons C_6H_4<\begin{smallmatrix}CO\cdot CPh\\ C(OH)\end{smallmatrix}>C_6H_4$, formed by a semipinacolinic transformation (Tiffeneau and Orékhoff, A., 1921, i, 565). The compound furnishes an *oxime*, m. p. 191—193°, and a mono-acetate; is reduced by zinc dust and ammonia into a *dihydro*-compound, m. p. 186—188° after sintering, probably $C_6H_4<\begin{smallmatrix}C(OH)\cdot Ph\\ CH(OH)\end{smallmatrix}>C_6H_4$ (*diacetate*, m. p. 154—156°), and by phosphorus and hydriodic acid to 9-benzyl-9 : 10-dihydroanthracene, showing that the semipinacolinic transformation is reversible. Oxidation of the semipinacolin with chromic–acetic acids yields 2-*benzoylbenzophenone*-2′-*carboxylic acid*, m. p. 228° (*methyl* ester, m. p. 165°). Treatment of this acid with boiling acetic anhydride and pyridine gives o-*benzoylphenylacetoxyphthalide*, m. p. 171—173° (cf. von Pechmann, A., 1882, 184; Graebe, A., 1900, i, 547), whilst reduction by zinc dust and sodium hydroxide solution or acetic acid did not yield satisfactory evidence. Treatment of the above acid with concentrated sulphuric acid at 160° affords the spirocyclic *lactone*, $\begin{smallmatrix}CO\cdot O\\ C_6H_4\end{smallmatrix}>C<\begin{smallmatrix}C_6H_4\\ C_6H_4\end{smallmatrix}>CO$ (I), m. p. 238—239°, of 9-*o*-carboxyphenyl-9-hydroxy-anthrone, which is reduced by tin and hydrochloric–acetic acids forming 9-o-*carboxyphenylanthrone*, m. p. 226—227°, or by zinc dust and ammonia yielding 9-o-*carboxyphenylanthracene*, m. p. 250—251°.

Magnesium *o*-tolyl bromide reacts with ethyl benzoate to form phenyldi-*o*-tolylcarbinol, which is oxidised by alkaline permanganate to triphenyl-carbinol-2 : 2′-dicarboxylic acid, isolated as the *lactone*, m. p. 225—227°. Treatment of this compound with concentrated sulphuric acid at 160° affords (I). H. BURTON.

Sulphonation of anthraquinone. Correction. H. E. FIERZ-DAVID (Helv. Chim. Acta, 1928, **11**, 197—198).—β-Sulphonation of anthraquinone is effected with 30% oleum at 145°, and the yield of pure sodium anthraquinone-β-sulphonate is 64% (cf. A., 1927, 463). The solubility of this salt in water at 15° is 1 in 169. H. BURTON.

Migration of the acyl group in partly acylated phenolic compounds. I. A. G PERKIN and R. C. STOREY (J.C.S., 1928, 229—244; cf. A., 1925, i, 1159).—Methylation of 2 : 7-diacetylanthrapurpurin, m. p. 192—193° (lit. m. p. 175—178°), with excess of diazomethane and subsequent hydrolysis of the reaction product affords *anthrapurpurin* 2-*methyl ether*, m. p. 308—309° (7-*acetyl* derivative, m. p. 207°; 1 : 7-*diacetyl* derivative, m. p. 154—155°), together with *anthrapurpurin*-1-*methyl ether*, m. p. 299—300° (2 : 7-*diacetyl* derivative, m. p. 136—137°). 2 : 7-*Diethylcarbonatoanthrapurpurin*, m. p. 166—167°, gives 2 : 7-*diethylcarbonatoanthrapurpurin* 1-*methyl ether*, m. p. 120—121° (5 parts), and 1 : 7-diethylcarbonatoanthrapurpurin 2-methyl ether (2 parts) isolated as the phenolic ether. Benzoylation of 2 : 7-diacetylanthrapurpurin in presence of pyridine yields 2-*benzoyl*-1 : 7-*diacetylanthrapurpurin*, m. p. 201—203°, the acetyl group having migrated from position 2 to 1. Cautious hydrolysis of this compound gives 2-*benzoylanthrapurpurin*, m. p. 272—273°, which when methylated furnishes 2-*benzoyl-anthrapurpurin* 1 : 7-*dimethyl ether*, m. p. 201—203°, together with 1-*benzoylanthrapurpurin* 2 : 7-*dimethyl ether*, m. p. 209—211°. *Anthrapurpurin* 1 : 7-*dimethyl ether* (*acetyl* derivative, m. p. 175—176°) has m. p. 218—219°. 2-*Acetylpurpurin*, m. p. 179—180°, gives 1-*acetylpurpurin* 2 : 4-*dimethyl ether*, m. p. 189—190°, and 1-*acetylpurpurin* 2-*methyl ether*, m. p. 224—225° (1 : 4-*diacetyl* derivative, m. p. 170—172°). *Purpurin* 2 : 4-*dimethyl ether* has m. p. 186—189°, whilst purpurin 2-methyl ether has m. p. 232—233° and is also obtained from potassium purpurin and methyl iodide (J.C.S., 1899, **75**, 447). 3-*Acetylpurpuroxanthin*, m. p. 144°, affords 3-*acetylpurpuroxanthin* 1-*methyl ether*, m. p. 154—155°, as the sole product, which is hydrolysed to *purpuroxanthin* 1-*methyl ether*, m. p. 311—313°.

Benzoylation of 2-acetylalizarin in presence of pyridine yields 2-*benzoyl*-1-*acetylalizarin*, m. p. 172—174°, which on hydrolysis gives 2-*benzoylalizarin*, m. p. 220—221°, also produced from potassium alizarin and benzoyl chloride. Methylation of this compound furnishes 1-*benzoylalizarin* 2-*methyl ether*, m. p. 266—268° (1 part), and 2-*benzoylalizarin* 1-*methyl-ether*, m. p. 203—205° (6 parts). 2-*Ethylcarbonato-alizarin*, m. p. 138—140° (*diethylcarbonato*-derivative, m. p. 150—151°), affords 1-*ethylcarbonatoalizarin* 2-*methyl ether*, m. p. 213—215° (1 part), and 2-*ethyl-carbonatoalizarin* 1-*methyl ether*, m. p. 145—147° (3 parts), whilst from 2-p-*toluenesulphonylalizarin*, m. p. 218—219°, the corresponding 1-*methyl ether*, m. p. 176—177°, is obtained, no migration having occurred. 2 : 3-*Diethylcarbonatoanthragallol*, m. p. 174—175°, yields 2 : 3(or 1 : 2)-*diethylcarbonatoanthragallol* 1(or 3)-*methyl ether*, m. p. 125—127°, and 1 : 3-*diethyl-carbonatoanthragallol* 2-*methyl ether*, m. p. 196—197°. From *diacetylgallacetophenone*, m. p. 107—108°, there were obtained 2 : 4-*diacetylgallacetophenone* 3-*methyl ether*, m. p. 150—151°, yielding gallacetophenone 3-methyl ether, m. p. 134—135° (cf. J.C.S., 1903, **83**, 131), on hydrolysis, together with a compound (not isolated) yielding *gallacetophenone* 2(or 4)-*methyl ether*, m. p. 175°. *Di*-p-*toluenesulphonylgallaceto-phenone*, m. p. 152—153°, gives *di*-p-*toluenesulphonyl-gallacetophenone* 2(or 4)-*methyl ether*, m. p. 111—113°, exclusively.

The results show that with diazomethane the migration of the acetyl group approximates to 85%, the ethylcarbonato-group to 25%, the benzoyl to 20%; the *p*-toluenesulphonyl group does not migrate.

An explanation of these migrations is suggested involving the formation of a loose additive compound of diazomethane and the carbonyl oxygen.

H. BURTON.

Vat dyes [from benzanthronyl ethers]. I. G. FARBENIND. A.-G.—See B., 1928, 83.

New [acid] dyes of the anthracene series. I. G. FARBENIND. A.-G.—See B., 1928, 83.

Colour reactions of caoutchouc. H. PAULY (J. pr. Chem., 1928, ii, **118**, 48—52).—Caoutchouc of various origins and also guttapercha give practically all the colour reactions of the sterols. Buchard's reaction (bordeaux-red to reddish-violet coloration on addition of acetic anhydride and sulphuric acid to a solution in chloroform) is very sensitive towards quality and purity of the caoutchouc, and the change in the coloration on addition of perbenzoic acid varies with samples of different origin. The Buchard test also distinguishes amyrins from caoutchoucs. "Sodium-caoutchouc" gives a completely abnormal reaction (brownish-yellow). The Tschugaev–Golodetz reaction (A., 1908, ii, 330; violet coloration on dissolution in molten trichloroacetic acid, accelerated by a trace of formaldehyde) depends on the strongly acid character of the trichloroacetic acid and on the presence of the trichloromethyl group (trichloroethyl alcohol and anhydrous chloral dissolve caoutchouc, but give no coloration), and is probably given only by unsaturated caoutchoucs. Acyclic unsaturated hydrocarbons, *e.g.*, cold-polymerised isoprene, and isoprenedicarboxylic esters polymerised by light (Pauly and Will, A., 1918, i, 525), give none of the sterol colour reactions, whereas the diolefinic cyclic hydrocarbons give colorations with acetic acid or anhydride (Wallach's reaction). The sterols, amyrins, and resins which give colorations are all cyclic compounds, and a return to the old cyclic formula for caoutchouc is suggested.

Caoutchouc in chloroform solution yields an insoluble, saffron-yellow additive compound with stannic chloride.

C. HOLLINS.

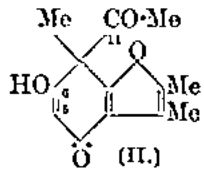
Saponin of *Primula* root. II. L. KOFLER and M. BRAUNER (Festschr. A. Tschirch, 1926, 351—356; Chem. Zentr., 1927, i, 3009).—*Primula elatior* saponin was obtained only in a gelatinous condition; it becomes yellowish-brown at 218° and has m. p. 224—225°. Its hæmolytic index is 50% greater than, and its toxicity half as great as, that of primulic acid. The differences between the saponin and that from *Primula veris* are described.

A. A. ELDRIDGE.

"Balanophorin." A. J. ULTEE (Bull. Jard. bot. Buitenzorg, 1926, **8**, No. 1, 3 pp.; Chem. Zentr., 1927, ii, 95).—Practically pure balanophorin, m. p. 77°, obtained by ethereal extraction, is identical with β-amyrin palmitate. β-Amyrin has m. p. 195°; acetate, m. p. 235°.

A. A. ELDRIDGE.

Constitution of usnic acid. C. SCHOPF and K. HEUCK (Annalen, 1927, **459**, 233—286; cf. Kraus, Diss., Freiburg, 1925).—The observation that usnic acid contains 3 active hydrogen atoms (Zerewitinoff), and, like decarbousnic acid, is not a carboxylic acid but an enol, shows that Widman's formula (A., 1900, i, 235, 347; 1903, i, 96) is incorrect. Usnic acid is decomposed by concentrated alkali into the elements of acetoacetic acid and usnetic acid (Paternò, A., 1882, 1080; Salkowski, A., 1901, i, 152), which by heating is decarboxylated to usnetol, $C_{13}H_{14}O_4$. When this is ozonised in chloroform it affords a *substance* (I), $C_{13}H_{14}O_6$, m. p. 172°, which is readily hydrolysed by alkali to acetic acid (3 mols.) and methylphloroglucinol. Usnetol itself is hydrolysed by 50% potassium hydroxide at 185° to acetic acid (1 mol.) and 4 : 6-*dihydroxy*-2 : 3 : 7-*trimethylcoumarone*, m. p. 178° (decomp.) (*dibenzoate*, m. p. 135—136°), which is ozonised to 2 : 4-*dihydroxy*-6-*acetoxy*-5-*methylacetophenone*, m. p. 161—164°, whilst its *diacetate*, m. p. 148—149°, yields a resinous product which is hydrolysed by alkali to methylphloroglucinol. Further, usnetol yields the following derivatives: *monoacetate*, m. p. 173°; *diacetate*, m. p. 157°; *oxime*, m. p. 221—223°, darkening from 205° (*diacetate*, m. p. 126—127°); *phenylhydrazone*, m. p. 210—213°, and *monomethyl ether*, m. p. 127—128° (*oxime*, m. p. 184—185°; *phenylhydrazone*, m. p. 164—165°), and is reduced by palladium and hydrogen in glacial acetic acid to *dihydrousnetol*, m. p. 162° (*oxime*, m. p. 155—156°, and its *diacetyl* derivative, m. p. 132—134°). The constitution (II) for usnetol explains these and other reactions, acetylation attacking first the 6-hydroxyl, then the enolised acetyl group (11). The oxidation product (I) has therefore the formula,



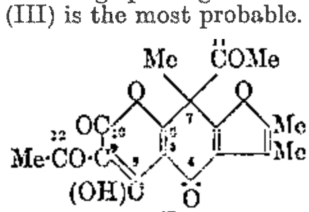
(II.)

CH:C(OH)·CMeAc
CO——CAc:COAc

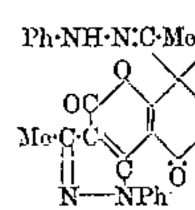
which is confirmed by its hydrolysis by alcoholic hydrogen chloride to acetic acid and the *substance*,

CH:C(OH)·CMeAc
CO——CAc:C·OH

m. p. 168°. Usnetol methyl ether is ozonised to a *peroxide*(?), $C_{14}H_{16}O_7$, m. p. 124—126°, which is hydrolysed with difficulty by alkali and zinc dust to *substances*, $C_{12}H_{14}O_5$, m. p. 97—99°, and $C_{10}H_{12}O_4$, m. p. 195—197°, the constitutions of which are discussed. Usnetic acid is thus usnetol-5-carboxylic acid (*methyl* ester, m. p. 190—192°, and its *methyl ether*, m. p. 117—118°) and usnic acid (*phenylbenzylhydrazide*, m. p. 195°) has formula (III). Alternative *o*-quinonoid formulæ for usnetol and the corresponding structures for usnic acid are not excluded, but analogy with other naturally occurring phloroglucinol derivatives suggests that (III) is the most probable.



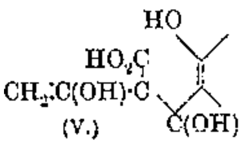
(III.)



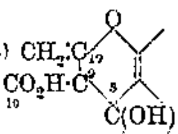
(IV.)

The 7- and 9-acetyl radicals in usnic acid and its derivatives react readily in the enolic form; accordingly, with pyridine and acetic anhydride an 11 : 12-*diacetate*, m. p. 199—200° (d-*form*, m. p. 199—200°; $[\alpha]_D$ +205°), is formed. This is a monobasic acid, which shows that the 8-hydroxyl has remained unattacked. The anhydrobisphenylhydrazone, m. p.

265° (Widman, *loc. cit.*), is a pyrazole derivative (IV), and the monoxime anhydride is an *iso*oxazole of similar constitution. Unlike that of usnic acid, the lactone ring of the latter is opened by sodium methoxide giving 4′-carbomethoxy-3′-methyl-5 : 5′-*iso*oxazolylusnetol, m. p. 147° (A., 1900, i, 235). *i-anti*-Usnic acid oxime (A., 1903, i, 96) appears to be the corresponding carboxylic acid, whilst the monoxime, m. p. 243—244°, which shows no tendency to anhydride formation, is probably the 11-oxime. The isomerisation of usnic acid to usnolic acid (Stenhouse and Grove, J.C.S., 1881, **39**, 234), a dibasic, β-ketonic acid, is formulated as (III)⟶(V)⟶(VI). The formula (VI) is shown to explain a large number of its reactions.



(V.)



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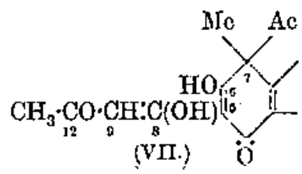


(VII.)

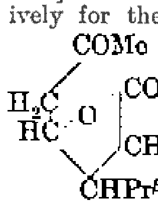
The constitution of decarbousnic acid (VII) follows from its mode of formation. It is confirmed by the hydrolysis and decarboxylation of diacetylusnic acid to 11 : 12-*diacetyldecarbousnic acid*, m. p. 112°. When decarbousnic acid or its diacetyl derivative is acetylated in presence of pyridine, 6 : 8 : 11 : 12-*tetraacetyldecarbousnic acid*, m. p. 189°, and a little of the 6 : 8 : 11-*triacetyl* derivative, m. p. 166°, are formed. The anhydrobisphenylhydrazone (1′-phenyl-3′-methyl-5 : 5′-pyrazolylusnetol-11-phenylhydrazone) and oxime anhydride (3′-methyl-5 : 5′-*iso*oxazolylusnetol) of decarbousnic acid and decarbousnol (9-decarboxyusnolic acid) are exactly analogous to the corresponding usnic acid derivatives. The formulæ given above are also supported by the behaviour of these derivatives with alkali and with ferric chloride and by many other reactions quoted from previous papers. The analogies between usnic acid and other naturally occurring phloroglucinol derivatives, *e.g.*, bergaptene (A., 1913, i, 192), albaspidin, lupulone, and cyanidin, are pointed out and their synthesis in the organism from simple aldehydes by means of aldol condensation, dehydration, and reduction is discussed. H. E. F. NOTTON.

Yeast ergosterol. II. F. REINDEL and E. WALTER (Annalen, 1928, **460**, 212—224).—α-Ergostanol (A., 1927, 241) contains an ethylenic linking and is therefore re-named α-ergostenol (tetrahydroergosterol). Owing to the ease with which oxidation occurs, neither the iodine value nor any other similar figure could be determined. Catalytic hydrogenation was unsuccessful. A method is given for the preparation of ergosterol from yeast fat. Ergosteryl acetate undergoes hydrogenation in ethereal solution in presence of platinum-black to give α-tetrahydroergosteryl acetate (formerly called α-ergostanyl acetate), which on hydrolysis affords α-ergostenol. Using platinum-black (Adam method) and ether, *α-ergostanyl acetate* (impure) results (the pure substance has m. p. 165—166°, $[\alpha]_D$ −7·5° in chloroform) and from this is obtained *α-ergostanol*, m. p. 150—151° practically inactive optically.

allo-α-Ergostanol (the former γ-ergostanol) is converted by phosphorus pentachloride into allo-*α-chloroergostan*, m. p. 119—120°, $[\alpha]_D$ +13·3° in chloroform, whilst the new α-ergostanol (m. p. 150—151°) similarly affords *α-chloroergostan*, m. p. 120—121°, $[\alpha]_D$ +22·8° in chloroform. Reduction of *allo*-α-chloroergostan with sodium in boiling amyl alcoholic solution gives a *hydrocarbon*, m. p. 84—85°, $[\alpha]_D$ +17° in chloroform, α-chloroergostan under similar conditions affording an isomeric *hydrocarbon*, m. p. 101—102°. Oxidation of the new α-ergostanol in glacial acetic acid solution at 70° with chromic oxide gives *α-ergostanone*, m. p. 174—175°, $[\alpha]_D$ +11·8° in chloroform [*ketazine*, m. p. 265° (decomp.); *oxime*, m. p. 225° (decomp.); *phenylhydrazone* m. p. 153—154°].

allo-α-Ergostanol similarly affords allo-*α-ergostanone*, m. p. 164°, $[\alpha]_D$ +34·9° in chloroform [*oxime*, m. p. 216°; *ketazine*, m. p. 155° (decomp.)]. *allo*-α-Ergostyl acetate, m. p. 144—145°, $[\alpha]_D$ +5·95°, produces no depression of the m. p. (144—145°) of γ-sitosyl acetate. Similarly, the above new hydrocarbon, m. p. 84—85°, $[\alpha]_D$ +17°, does not depress the m. p. of sitosan, m. p. 84—85°, $[\alpha]_D$ +28·5°. The m.-p. phenomena remain unexplained, but at the moment the two pairs of substances are not regarded as being identical. E. E. TURNER.

Action of Beckmann's chromic acid mixture on monocyclic terpenes. T. A. HENRY and H. PAGET (J.C.S., 1928, 70—81).—α-Terpinene is oxidised by Beckmann's chromic acid mixture mainly to dimethylacetonylacetone, only traces of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid being formed (J.C.S., 1921, **119**, 1714; 1923, **123**, 1878). *l*-Limonene is very slowly converted into 1 : 2 : 8-trioxyterpan and a ketolactone, $C_{10}H_{16}O_3$ (*semicarbazone*, m. p. 210°, $[\alpha]_D^{18}$ +1·28° in acetic acid), both of which have already been obtained by Wallach (Ann., 1893, **275**, 153) by the oxidation of terpineol, which therefore appears to be the first product of the action of chromic acid on limonene. α-Phellandrene is oxidised to *l*-α-*iso*propylsuccinic acid, thymoquinol, thymoquinone, and two *ketolactones*, $C_{10}H_{16}O_3$, b. p. 155—160°/1 mm., $[\alpha]_D^{20}$ +73·67° in water, +54·79° in benzene [*semicarbazone*, m. p. 183°, $[\alpha]_D^{13}$ +55·47° in acetic acid], and $C_9H_{14}O_3$, m. p. 48—50°, $[\alpha]^{20}$ +37·1° in water, −43·13° in benzene [*semicarbazone*, m. p. 187° (corr.) $[\alpha]_D^{20}$ +28·9° in alcohol or acetic acid]. The formulæ (I) and (II) are proposed respectively for these last-named compounds. The keto-



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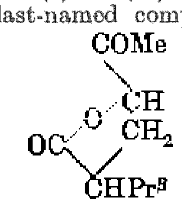

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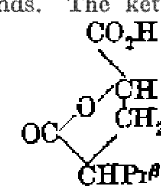


(III.)

lactone (I) is oxidised by sodium hypobromite to a *dibasic acid*, $C_9H_{14}O_4$, m. p. 138°, $[\alpha]^{19}$ +15·99 in aqueous sodium hydroxide [*silver* salt; *ethyl* ester, b. p. 168—170°/17 mm., d_{18}^{18} 1·0046, $[\alpha]_D^{18}$ +18·05° in alcohol, n_D^{20} 1·4530], which undergoes further oxidation with potassium permanganate, giving *l*-α-*iso*-

propylsuccinic acid. The dibasic acid is alternatively formulated as β-*iso*propyl-αβ-dihydromuconic acid or 1-carboxy-2-*iso*propyl-*cyclo*propylacetic acid, the former structure being supported by molecular refraction of the diethyl ester, the latter by absence of reactivity with bromine. Oxidation of the keto-lactone (II) with sodium hypobromite gives bromoform, a small quantity of *substance*, m. p. 225° (decomp.), containing 31% of bromine, and a *lactone acid* (III), $C_8H_{12}O_4$, m. p. 58—60° (*silver* and *lead* salts), which undergoes further oxidation with potassium permanganate, giving *l*-α-*iso*propylsuccinic acid. Confusion exists in previously published data with regard to the physical constants of the optically active forms of the last-named acid. The *dl*-acid, m. p. 117° (anilic acid, m. p. 144°), is partly resolved by quinine (less soluble fraction of *quinine* salt has m. p. 206°) and by quinidine. Complete resolution is effected by fractionation of the easily dissociated *strychnine* salt, followed by conversion into the *brucine* salt, m. p. 144°, $[\alpha]^{20}$ −15·9° in chloroform. The pure *l*-acid has m. p. 94°, $[\alpha]_D^{20}$ −23·46° in water (anilic acid, m. p. 129°). Thymoquinone reacts with 1 mol. of semicarbazide, giving 4-hydroxy-3-methyl-5-*iso*propylbenzeneazoformamide (J.C.S., 1913, **103**, 1419) and, in addition, a *disemicarbazone*, existing in two stable yellow modifications, m. p. 237° and 257°, and one colourless labile form, m. p. 237°. The yellow modification, m. p. 237°, is obtained from each of these by crystallisation from boiling acetic acid.

p-Cymene, present as impurity in commercial phellandrene, is attacked exceedingly slowly by Beckmann's chromic acid mixture, yielding minute quantities of *p*-methylacetophenone. The mechanism of chromic acid oxidation of α-terpinene, *l*-limonene, and α-phellandrene is discussed. M. CLARK.

Crystalline dihalogen derivatives of pinene. G. BRUS (Compt. rend., 1928, **186**, 87—89).—Neither the (orthorhombic) pinene dichloride, m. p. 173—174°, of Aschan nor the (monoclinic) dichloride of the author is isomorphous with (hexagonal) tricyclene dibromide. The constitutions of the two dichlorides thus remain unknown. B. W. ANDERSON.

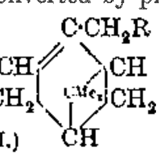
Products of the addition of chlorine and bromine to pinene and their de-chlorination. O. ASCHAN (Ber., 1928, **61**, [*B*], 38—45).—Dry chlorine is led over the surface of well-stirred pinene kept below 0°, whereby a mixture of pinene hydrochloride and 2 : 6-*dichlorocamphane* (*pinene-2 : 6-dichloride*), rhombic-bipyramidal crystals, *a* : *b* : *c*= 0·8587 : 1 : 1·9320, m. p. 173—174°, is obtained. The latter substance is stable towards zinc dust and alcohol but is slowly converted by sodium in boiling ether into cyclene, m. p. 62°. Similarly, 2 : 6-dibromocamphane is prepared in 15% yield by passing carbon dioxide charged with bromine vapour over pinene cooled in a mixture of ice and salt. The chloride or, preferably, the bromide is slowly converted by freshly-prepared silver acetate in boiling glacial acetic acid into the unsaturated *ester*, $C_{10}H_{15}$·OAc, b. p. 120—122°/15 mm., d_4^{20} 0·9894, n_D^{20} 1·47740 (corresponding *alcohol*, $C_{10}H_{16}O$, b. p. 212°), and a substance hydrolysed by alcoholic potassium hydroxide to the *glycol* or *ketol*, $C_{10}H_{18}O_2$, m. p. 132—133°.

Chlorine reacts violently with molten pinene hydrochloride or with the warm substance in the presence of antimony pentachloride, carbonisation occurring. In carbon tetrachloride a mixture of di- and tetrachlorocamphanes, m. p. 127—128°, appears to result, whereas when treated almost to saturation with chlorine in chloroform and carbon tetrachloride successively pinene hydrochloride gives a tetrachlorocamphane, m. p. 150—152°. With 1 mol. of chlorine in carbon tetrachloride a trichlorocamphane, m. p. 130°, results. The homogeneity of these chloro-compounds is not regarded as established. H. WREN.

Action of chlorine and bromine on nopinene. G. BRUS (Compt. rend., 1928, **186**, 240—242).—The action of chlorine and bromine on nopinene at −15° to −20° produces no crystalline compounds other than bornyl chloride and bromide, respectively, the mixture of optically active stereoisomeric dihalogen derivatives simultaneously formed being uncrystallisable. The different behaviour of pinene (cf. A., 1925, i, 821) may be ascribed to the fact that in nopinene a third centre of asymmetry is formed on the first addition of 2 halogen atoms to the molecule.

B. W. ANDERSON.

Influence of constitution on the rotatory power of optically active substances. XIX. H. RUPE and A. HÉRITIER (Annalen, 1927, **459**, 171—194).—Myrtenol (I, R—OH), obtained by an improved process from French myrtle oil (yield 25%), is readily converted by phosphorus tribromide in ethereal solution into *myrtenyl bromide* (I, R=Br), b. p. 93°/9 mm., $[\alpha]_D$ +32·31°. The latter does not afford a magnesium derivative, but when the preparation of the latter is attempted, an 80% yield of *dimyrtenyl*, b. p. 173—174°/10 mm., d_4^{20} 0·9521, $[\alpha]_D^{20}$ +13·793°, is obtained.



(I.)

This property of myrtenyl bromide, however, allows of the ready substitution of bromine by hydrocarbon radicals. Thus, magnesium methyl iodide converts myrtenyl bromide into *methylmyrtenyl* (*homopinene*) (I R=Me), b. p. 95·5—96°/62 mm., d_4^{20} 0·8697, $[\alpha]^{20}$ +33·962°. *Ethylmyrtenyl*, b. p. 73—73·5°/10 mm., d_4^{20} 0·8663, $[\alpha]_D^{20}$ +21·970°, n-*propylmyrtenyl*, b. p. 88—89°/10 mm., d_4^{20} 0·8624, $[\alpha]^{20}$ +21·632°, *phenylmyrtenyl*, b. p. 138—141°/12 mm., d_4^{20} 0·9712, $[\alpha]_D^{20}$ +29·486°, *benzylmyrtenyl*, b. p. 151—152°/10 mm., d_4^{20} 0·9633, $[\alpha]_D^{20}$ +16·182°, β-*phenylethylmyrtenyl*, b. p. 166—167°/10 mm., $[\alpha]_D^{20}$ −15·276°, or b. p. 167·5—168°/10·5 mm., $[\alpha]_D^{20}$ −4·5787°, n_α 1·52715, n_D 1·53116, n_β 1·54119, d_4^{20} 0·9574 (the second b. p. and [α] are probably the more accurate), and γ-*phenylpropylmyrtenyl*, b. p. 182·5—183·5°/10 mm., d_4^{20} 0·9522, $[\alpha]_D^{20}$ +4·957°, were prepared in a similar manner.

Magnesium phenylethinyl bromide (obtained from phenylacetylene and magnesium ethyl bromide) and myrtenyl bromide afford *phenylethinylmyrtenyl* (I, R= ·C:CPh), a yellow oil, b. p. 177·5—178·5°/10 mm. or 89—90° in a vacuum. It rapidly polymerises, has $[\alpha]_D^{20}$ +18·725°, n_α 1·55804, n_D 1·56336, n_β 1·57735, and d_4^{20} 0·9896. Phenylethinylmyrtenyl is reduced in boiling aqueous alcoholic solution by zinc–copper

couple to *phenylethenylmyrtenyl* (I, R=·CH:CHPh), b. p. 167·5—168·5°/10 mm., d_4^{20} 0·9683, $[\alpha]_D^{20}$ +13·050, n_α 1·54074, n_D 1·54534.

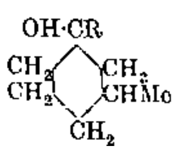
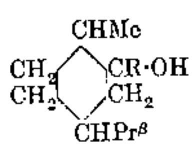
Myrtenyl bromide converts ethyl sodioacetoacetate into *ethyl myrtenylacetoacetate* (I, R=·CHAc·CO_2Et), b. p. 162—163·5°/11 mm. (*semicarbazone*, m. p. 122·2°, regenerating the pure ester when distilled in steam with oxalic acid). The ester, when hydrolysed with alcoholic sodium hydroxide, affords *homomyrtenyl methyl ketone* (I, R=·CH_2Ac) (isolated first as the *semicarbazone*, m. p. 173°), b. p. 127—129°/12·5 mm., d_4^{20} 0·9516, $[\alpha]_D^{20}$ +26·719°.

Myrtenal (I, R=·CHO), b. p. 91·75—92°/12·5 mm., d_4^{20} 0·9898, has $[\alpha]_D^{20}$ +15·682 (cf. Semmler and Bartelt, A., 1907, i, 429).

It was shown previously (Annalen, 1915, **409**, 327) that the esters of myrtenol with aliphatic and aromatic acids showed great regularities in their optical constants. Calculation from these results by Lowry and Dickson's method shows the esters to have anomalous rotatory dispersion. Adopting a new mode of calculation (the "end term formula"), however, the present authors find no anomaly (see original for mathematical part). Methyl-, ethyl-, *n*-propyl-, and phenyl-myrtenyl similarly exhibit normal rotation dispersion, but whilst benzylmyrtenyl is slightly anomalous, the phenylethyl and still more so the phenylpropyl derivative, exhibit marked anomaly of dispersion. This effect, due to the increasing distance of the phenyl group from the main nucleus, is intensified by unsaturation (phenylethenyl- and phenylethinyl-myrtenyl). Myrtenal has anomalous rotatory dispersion, but homomyrtenyl methyl ketone is normal.

The application of the new mode of calculation of rotatory dispersion to the case of pulegone shows that whilst pulegyl methyl ketone is an individual, pulegone is not (cf. Grignard and Savard, A., 1926, 408). E. E. Turner.

Influence of constitution on the rotatory dispersion of optically active substances. XX. H. Rupe and E. Kambli (Annalen, 1927, **459**, 195—217).—An improved method is given for the preparation of optically active 3-methyl*cyclo*hexanone from pulegone. Sodamide, followed by acetylene, converts the methyl*cyclo*hexanone into *3-methyl-1-ethinyl*cyclo*hexanol* (I, R=·C:CH), b. p. 76—78°/10 mm. The latter is a mixture of solid and liquid

(I.)   (II.)

isomerides (proportions about 3—5 to 1). The solid has m. p. 47·5°, b. p. 79°/11 mm., $[\alpha]_D^{20}$ −12·46°, d_4^{20} 0·8826. The liquid, probably not free from the solid form, has b. p. 77—78°/10 mm., d_4^{20} 0·9439, and $[\alpha]_D$ −2·84°. A *tetrabromide* was obtained from the solid form, which, when reduced with zinc-copper couple in alcoholic solution, gave *3-methyl-1-ethenyl*cyclo*hexanol* (I, R=·CH:CH_2), b. p. 77°/11 mm., m. p. 32°, d_4^{20} 0·9238, $[\alpha]_D^{20}$ 1·04°. *3-Methyl-1-ethyl*cyclo*hexanol* (I, R=Et), obtained from methyl*cyclo*hexanone and magnesium ethyl bromide has b. p. 75·5—76·5°/13 mm., d_4^{20} 0·9098, and $[\alpha]_D^{20}$ −2·68°.

Carvone is readily converted into tetrahydrocarvone in presence of alcohol, hydrogen, and nickel. The tetrahydro-compound, with sodamide and acetylene, gives *2-ethinyl*-p-*menthan-2-ol* (II, R=·C:CH), b. p. 104°/10 mm., d_4^{20} 0·9270, $[\alpha]^{20}$ −21·10° (*silver* derivative described). When reduced, the carbinol affords *2-ethenyl*-p-*menthan-2-ol* (II, R=·CH:CH_2), b. p. 103°/10 mm., d_4^{20} 0·9059, $[\alpha]_D^{20}$ −14·26°. *2-Ethyl*-p-*menthan-2-ol*, from magnesium ethyl bromide and tetrahydrocarvone, has b. p. 106·5—107·5°/11 mm., d_4^{20} 0·9082, and $[\alpha]^{20}$ −29·07°. *2-Phenylethinyl*-p-*menthan-2-ol* (II, R=·C:Ph), from tetrahydrocarvone and magnesium phenylethinyl bromide, has b. p. 185—186°/10 mm., or 105° in a vacuum, d_4^{20} 0·9920, $[\alpha]_D^{20}$ −12·62°, and on reduction affords *2-styryl*-p-*menthan-2-ol*, b. p. 173—174°/9 mm. or 102° in a vacuum, d_4^{20} 0·9601, and $[\alpha]_D^{20}$ −12·35°. When ω-bromostyrene, magnesium, ether, and tetrahydrocarvone were caused to interact, an *isomeric* styrylcarbinol, b. p. 103° in a vacuum, d_4^{20} 0·9695, $[\alpha]_D^{20}$ −36·19, and diphenylbutadiene were formed. *2-β-Phenylethyl*-p-*menthan-2-ol* (II, R=·CH_2·CH_2Ph), from magnesium β-phenylethyl bromide and tetrahydrocarvone, has b. p. 175—176·5°/10 mm., d_4^{20} 0·9585, and $[\alpha]_D^{20}$ −5·60°.

Boiling formic acid or a mixture of glacial acetic and concentrated sulphuric acid converts the above phenylethinylmenthanol into *2-phenacylidene*-p-*menthane*, b. p. 179—181°/10 mm. or 104° in a vacuum, d_4^{20} 0·9926, $[\alpha]^{20}$ −39·39° (*semicarbazone*, m. p. 156°).

The above 3-methyl-1-ethinyl*cyclo*hexanol, when boiled with mercuric oxide and dilute sulphuric acid, was converted into *1-acetyl-3-methyl*cyclo*hexanol* (I, R=Ac), b. p. 105°/10 mm., d_D^{20} 0·9991, $[\alpha]_D^{20}$ 4·58° [*semicarbazone*, m. p. 210°, (decomp.)]. The similarly prepared *2-acetyl*-p-*menthan-2-ol* (II, R=Ac) has b. p. 126°/11 mm., d_4^{20} 0·9662, and $[\alpha]_D^{20}$ −21·59° [*semicarbazone*, m. p. 212° (decomp.)].

The optical rotatory dispersion of most of the above-named substances was measured (6 lines). Methyl*cyclo*hexanone has the exceptionally high dispersion quotient of 3·42, and shows no appreciable anomaly. Tetrahydrocarvone (quotient 2·504) is also not anomalous. Of all the other compounds now described, only the β-phenylethylmenthanol exhibits anomalous dispersion. E. E. Turner.

Higher terpene compounds. XXXII. Addition reactions and the gentle permanganate oxidation of *d*-pimaric acid. L. Ruzicka and F. Balas (Annalen, 1928, **460**, 202—212).—The view previously held that *d*-pimaric acid contains one reactive and one only feebly reactive ethylenic linking is borne out by further work.

When potassium *d*-pimarate is oxidised with dilute potassium permanganate in aqueous solution, *dihydroxydihydro*-d-*pimaric acid*, $C_{20}H_{32}O_4$, m. p. 224° (decomp.), is formed (*diacetate*, m. p. 235°), together with a small quantity of an *isomeride*, m. p. 239° (decomp.). Using hydrochloric instead of acetic acid to precipitate the oxidation product, a third *substance*, m. p. 220—221°, is obtained.

d-Pimaric acid could not be caused to give a crystalline additive compound with bromine, but a *nitrosite*, pale greenish-yellow, m. p. 79—80° (decomp.), was obtained. Hydrogen chloride converts *d*-pimaric acid in cold dilute acetic acid solution into a mixture of three *hydrochlorides*, $C_{20}H_{31}O_2Cl$, respectively, melting at 232° (decomp.), 184° (decomp.), and 125° (decomp.), together with some other ill-defined derivatives containing chlorine. Repetition of the addition of hydrogen chloride to the acid, apparently under similar conditions, gave only the hydrochloride melting at 125°. At 100°, hydrogen chloride converts *d*-pimaric acid in glacial acetic acid solution rapidly into the hydrochloride melting at 184° (crystallographic data by Ulrich). Continued action of hydrogen chloride did not cause addition to the second ethylenic linking. The hydrochloride, m. p. 184°, was heated at 250° in quinoline solution; only *d*-pimaric acid was isolated from the product formed.

E. E. Turner.

Higher terpene compounds. XXXIII. Sesquiterpene compounds from camomile and milfoil oils. L. Ruzicka and E. A. Rudolph (Helv. Chim. Acta, 1928, 11, 253—261; cf. Ruhemann and Lewy, B., 1928, 147).—There is obtained from camomile oil after removal of chamazulene (A., 1926, 299) a distillate of b. p. 110—140°/11 mm., which contains a monocyclic *hydrocarbon*, $C_{15}H_{24}$, having three double linkings. The constants of a fraction of b. p. 123—125°/12 mm., are d_4^{18} 0·8770, n_1^{19} 1·4941, α_D +3·6°. Treatment of six fractions of b. p. 105—118°/12 mm. to 125—130°/12 mm., from the above distillate, with hydrogen chloride in ether affords a small amount of a *trihydrochloride*, $C_{15}H_{27}Cl_3$, m. p. 55° (cf. Ruhemann and Lewy, *loc. cit.*) together with a liquid portion, which with alcoholic potassium hydroxide regenerates the hydrocarbon. This is dehydrogenated by sulphur into cadalene.

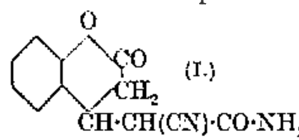
The alcohol fraction, b. p. 140—170°/11 mm., is treated successively with alcoholic potassium hydroxide, and phthalic anhydride in benzene. Decomposition of the hydrogen phthalate formed gives a small quantity of a compound, b. p. 150—160°/15 mm., probably $C_{15}H_{26}O$, and essentially a tricyclic alcohol. After removal of a further quantity of alcoholic substances by treatment with phthalic anhydride at 130°, the residue yielded a distillate, b. p. 150—160°, containing dicyclic alcohols, dehydrogenated into cadalene.

The sesquiterpenes, b. p. 115—125°/11 mm., from oil of milfoil do not give a crystalline hydrochloride, but are dehydrogenated into cadalene. The sesquiterpene alcohol fraction, b. p. 150—170°/11 mm., yields on treatment with phthalic anhydride in benzene a product, b. p. 155°/11 mm., probably a bicyclic alcohol mixture, dehydrated by formic acid into a *hydrocarbon*, $C_{15}H_{24}$, b. p. 120—125°/11 mm., d_4^{14} 0·9366, n_1^{14} 1·5045, which is tricyclic and contains one double linking. The remainder of the alcohol fraction, b. p. 160—165°/11 mm., consists of bicyclic alcohols, dehydrogenated into cadalene.

H. Burton.

Determination of valency requirements of alkyl groups. K. von Auwers and H. Dusterdiek.—See this vol., 305.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds. I. Addition of cyanoacetamide to coumarins. T. R. Seshadri (J.C.S., 1928, 166—172).—The reactivity of the double linking in the hetero-ring of coumarin is exemplified by the ease with which addition of cyanoacetamide takes place with those coumarin derivatives which have no alkyl or halide substituent in the hetero-ring, but may have substituents in the benzene nucleus. The products of the reaction, which is carried out in hot alcoholic solution in the presence of a little piperidine, are 3 : 4-dihydrocoumarin-4-cyanoacetamides (I). The reactivity is ascribed to the presence of the double linkation of the ketonic properties of the carbonyl group by attachment to the singly-bound oxygen atom.



(I.)

The additive products may be hydrolysed to give a variety of compounds, the nature of which depends on the conditions. 3 : 4-*Dihydrocoumarin-4-cyanoacetamide*, m. p. 219—220°, yields with cold, concentrated hydrochloric acid, 3 : 4-*dihydrocoumarin-4-cyanoacetic acid*, m. p. 226—227°. With boiling, concentrated hydrochloric acid or potassium hydroxide solution, 3 : 4-*dihydrocoumarin-4-acetic acid*, m. p. 113—114°, is obtained. The last-named acid is further hydrolysed on keeping in cold, faintly acid, aqueous solution to β-o-*hydroxyphenylglutaric acid*, m. p. 160° (*disilver* salt), reconverted on heating or on boiling with hydrochloric acid into 3 : 4-dihydrocoumarin-4-acetic acid. Using similar experimental conditions, 7-*methyl*-3 : 4-*dihydrocoumarin-4-cyanoacetamide*, m. p. 245°, yields 7-*methyl*-3 : 4-*dihydrocoumarin-4-cyanoacetic acid*, m. p. 230—232°, and 7-*methyl*-3 : 4-*dihydrocoumarin-4-acetic acid*, m. p. 111—112°. This lactone acid is hydrolysed on keeping in cold, faintly acid solution to β-p-*methyl*-o-*hydroxyphenylglutaric acid*, m. p. 148—149°, reconverted into the parent lactone on fusion. 6-Nitro-3 : 4-dihydrocoumarin-4-cyanoacetamide, m. p. above 300°, yields with boiling hydrochloric acid, 6-*nitro*-3 : 4-*dihydrocoumarin-4-acetic acid*, m. p. 205° (decomp.), which with cold alkalis, gives yellow solutions containing salts of β-*m*-nitro-*o*-hydroxyphenylglutaric acid (*disilver* salt). 6-*Amino*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*, m. p. 270° (*benzoyl* derivative, m. p. 300°), may be diazotised, and with boiling hydrochloric acid, gives the *hydrochloride*, m. p. 225° (decomp.), of 6-*amino*-3 : 4-*dihydrocoumarin-4-carbamylacetic acid*, m. p. 170—171°.

M. Clark.

3-Nitrodiphenylene oxide. H. Ryan, J. Keane, and J. C. M'Gahon (Proc. Roy. Irish Acad., 1927, 37, 368—372).—2 : 4-Dinitrodiphenyl ether is reduced to 4-*nitro-2-aminodiphenyl ether*, m. p. 107° (*acetyl* derivative, m. p. 118°), by a glacial acetic acid solution of stannous chloride containing hydrogen chloride. The nitroamine, when diazotised and heated with 50% sulphuric acid, gives, in 20—25% yield, 3-*nitrodiphenylene oxide*, m. p. 141°, which may be further nitrated to a *dinitrodiphenylene oxide*, m. p. 295°. The nitrodiphenylene oxides described

by Ryan and Cullinane (A., 1924, i, 534) and by Borsche and Schacke (A., 1924, i, 161) are probably the 2- and the 1-nitro-compounds, respectively.

G. A. C. GOUGH.

Odour and structure of certain cyclic acetals [alkylidene ethers]. R. R. READ, H. LATHROP, and H. L. CHANDLER (J. Amer. Chem. Soc., 1927, **49**, 3116—3119).—The following cyclic acetals were prepared by heating together equimolecular proportions of the appropriate αβ-diols and aldehydes under reflux for 6 hrs. on the steam-bath, with agitation and in presence of 5 drops of 40% sulphuric acid (cf. Fischer and Giebe, A., 1898, i, 167). *Methylene ethers*: of γ-phenoxypropane-αβ-diol, m. p. 40—43°, b. p. 138—139°/11 mm.; of α-phenylpropane-αβ-diol, b. p. 105—107°/12 mm.; of γ-phenylpropane-αβ-diol, b. p. 125—128°/16 mm., d_4^{20} 1·098; and of γ-*m*-tolylpropane-αβ-diol, b. p. 128—130°/15 mm., d_4^{20} 1·032. *Ethylidene ethers*: of γ-phenoxypropane-αβ-diol, m. p. 24°, b. p. 152—154°/11 mm.; of α-phenylpropane-αβ-diol, b. p. 116—118°/19 mm., d_4^{20} 1·032; of γ-phenylpropane-αβ-diol, b. p. 120—124°/16 mm.; of γ-*m*-tolylpropane-αβ-diol, b. p. 123—125°/13 mm., d_4^{20} 1·028; and of γ-*p*-tolylpropane-αβ-diol, b. p. 135—142°/17 mm., d_4^{20} 1·032. n-*Heptylidene ether* of γ-phenoxypropane-αβ-diol, b. p. 201—203°/12 mm. Few of the above possess any markedly agreeable odour, and none has an odour resembling that of jasmine.

F. G. WILLSON.

Stereoisomerism of disulphoxides and related substances. II. Derivatives of 1 : 4-dithian. E. V. BELL and G. M. BENNETT (J.C.S., 1928, 86—92).—The stereoisomerism of the α- and β-dithian dioxides (A., 1927, 958) is further confirmed by a study of their reactions and of their derivatives, including in each case a *hydrochloride*, unstable *hydrobromide*, *mercurichloride*, *tetrabromide*, and *hexabromide*. The action of potassium sulphide on ββ′-dichlorodiethyl sulphone yield the structural isomeride, dithian monosulphone (Fromm and Ungar, A., 1924, i, 68), m. p. 203°, dimorphous. The corresponding reaction with ββ′-dichlorodiethyl sulphoxide yields *dithian monoxide*, m. p. 125° (*chloroplatinate*; *chloroaurate*), more conveniently prepared by controlled oxidation of dithian. This monosulphoxide gives rise to stereoisomeric *methyl sulphonium* salts, $SO{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}S\cdot Me\}X$ (α-*picrate*, m. p. 187°, and β-*picrate*, m. p. 137°; α- and β-*chloroplatinates*; α-*iodide*) and to two *sulphoxide-sulphilimines*, $SO{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}S\cdot N\cdot SO_2\cdot C_7H_8$ (α-, m. p. 230—234°, and β-, m. p. 176—177°). The bis-sulphilimine of dithian, $C_7H_8\cdot SO_2\cdot N\cdot S{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_8$ (Mann and Pope, J.C.S., 1922, 1052), has also been separated into two crystalline *isomerides* (α-, decomp. 250—255°, and β-, decomp. 200—210°).

M. CLARK.

Pyrrolones. R. LUKEŠ (Chem. Listy, 1928, **22**, 1—12).—The action of Grignard reagents on various *N*-substituted succinimides leads to the production of pyrryl derivatives according to the following scheme:

$$\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}{>}NR \rightarrow \begin{matrix}CH_2\text{———}CO\\ |\\ CH_2\cdot CR'(OH)\end{matrix}{>}NR \rightarrow \begin{matrix}CH_2\cdot CO\\ |\\ CH{:}CR\end{matrix}{>}NR$$

Thus magnesium methyl bromide converts *N*-methylsuccinimide into 2-*hydroxy*-1 : 2-*dimethyl*-4-*pyrrolone*, m. p. 70°, and 1 : 2-*dimethyl*-4-*pyrrolone*, m. p. 62—63°, the latter product being identical with that obtained by the distillation of methylammonium lævulate. Similarly are prepared 1-*phenyl*-2-*methyl*-4-*pyrrolone*, m. p. 101°, 1-*ethyl*-2-*methyl*-4-*pyrrolone*, m. p. 33—34°, 1-*methyl*-2-n-*propyl*-4-*pyrrolone*, b. p. 145°/52 mm., and 1-*methyl*-2-n-*butyl*-4-*pyrrolone*, b. p. 148°/33 mm. The action of organic zinc derivatives is similar to that of magnesium; thus ethyl bromoacetate and *N*-methylsuccinimide in the presence of zinc yield the *ethyl* ester of 1-*methyl*-4-*pyrroloneacetic acid*, m. p. 123°.

R. TRUSZKOWSKI.

Aliphatic β-aminoketones and related amino-alcohols. C. MANNICH and W. HOF (Arch. Pharm., 1927, **265**, 589—598).—The benzoate of δ-dimethylaminobutan-β-ol, b. p. 60—62°/11 mm. (α-dimethylaminobutan-γ-ol, cf. Fourneau and Ramart-Lucas, A., 1919, i, 435), which has now been obtained by reducing δ-dimethylaminobutan-β-one (Mannich, A., 1917, i, 634), possesses pronounced anæsthetic properties. The reduction of the aminoketone to the amino-alcohol takes place smoothly by interaction with aluminium amalgam in moist ether. Analogues of the commercial product "Tutocaine" can be very simply prepared in this way, and the following is an account of results of further investigation. Acetone, paraformaldehyde, and piperidine hydrochloride, boiled together in alcohol solution, yield α-*piperidinobutan*-γ-*one*, b. p. 100—101°/11 mm. (*hydrochloride*, m. p. 167°; *picrate*, m. p. 107°; *oxime hydrochloride*, m. p. 201°). The ketone is reduced as described to α-*piperidinobutan*-γ-*ol*, an oil with a mouse-like odour, b. p. 102—103°/11 mm. (*hydrochloride*, m. p. 145°), the *benzoate hydrochloride* (m. p. 192°) of which is only weakly anæsthetic. By treating α-piperidinobutan-γ-one with magnesium methyl iodide, α-*piperidino*-γ-*methylbutan*-γ-*ol*, b. p. 115—116°/14 mm. (*hydrochloride*, m. p. 196°), is obtained, but the yield is poor.

Methyl ethyl ketone condenses with paraformaldehyde and dimethylamine (hydrochloride) to yield two products. Thus, condensation at the methyl group of the ketone gives α-*dimethylaminopentan*-γ-*one*, b. p. 103—104°/12 mm. (*chloroaurate*, m. p. 128°), and this compound forms about one fifth of the product; the remaining four fifths are the result of condensation at the methylene group, and so are composed of γ-dimethylaminomethylbutan-β-one (cf. Mannich and Curtaz, A., 1927, 231). This compound is readily reduced to γ-*dimethylaminomethylbutan*-β-*ol*, b. p. 65—67°/14 mm., of which the *hydrochloride* is very hygroscopic and the *benzoate hydrochloride*, m. p. 131°, is powerfully anæsthetic. The corresponding aminobenzoate hydrochloride is "Tutocaine," already referred to. When the same aminoketone is exhaustively methylated with methyl sulphate and the product, as quaternary base, distilled with steam, iso*propenyl methyl ketone*, b. p. 60—65° (*semicarbazone*, m. p. 176·5°), is obtained.

Methyl ethyl ketone, paraformaldehyde, and piperidine hydrochloride similarly yield γ-piperidinomethylbutan-β-one (Mannich and Curtaz, *loc. cit.*),

the *oxime hydrochloride* of which has m. p. 167° (the m. p. of the hydrochloride of the aminoketone itself is now given as 150°). This aminoketone is reduced to *γ-piperidinomethylbutan-β-ol*, b. p. 112—114°/14 mm., which yields very hygroscopic salts and a *benzoate hydrochloride*, m. p. 178°, which is a potent anæsthetic.

Methyl propyl ketone, paraformaldehyde, and dimethylamine hydrochloride yield chiefly γ-dimethylaminomethylpentan-β-one (*picrate*, m. p. 123°; cf. Mannich and Bauroth, A., 1924, i, 947). *γ-Dimethylaminomethylpentan-β-ol*, b. p. 75—76°/13 mm., is obtained from the foregoing on reduction.

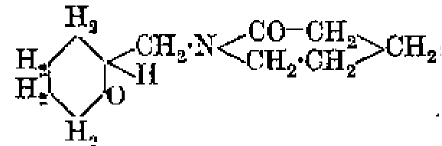
Pinacolin similarly condenses with paraformaldehyde and piperidine hydrochloride to give *α-piperidino-δδ-dimethylpentan-γ-one*, b. p. 116—119°/12 mm. (*hydrochloride*, m. p. 192°; *picrate*, m. p. 133°; *oxime hydrochloride*, m. p. 210°), which is reduced to *α-piperidino-δδ-dimethylpentan-γ-ol*, b. p. 121—123°/14 mm., of which the *hydrochloride*, m. p. 179—180°, and the *benzoate hydrochloride*, m. p. 186°, are described. The latter is a strong, persistent anæsthetic.

Allylacetone undergoes a similar condensation (with piperidine) to give γ-piperidinomethyl-Δ^{ϵ}-hexen-β-one (Mannich and Curtaz, *loc. cit.*), the hydrochloride of which is easily soluble in acetone, together with, in superior yield, a compound giving a hydrochloride sparingly soluble in acetone. This is *α-piperidino-Δ^{ζ}-hepten-γ-one*, b. p. 136°/16 mm. The *hydrochloride*, m. p. 157°, and the *hydrobromide*, m. p. 161°, are described. The aminoketone is reduced, like its congeners, to the carbinol, *α-piperidino-Δ^{ζ}-hepten-γ-ol*, b. p. 138°/14 mm., which is presumably a mixture of stereoisomerides, but yields a crystalline *benzoate hydrochloride*, m. p. 138°. This is almost devoid of anæsthetic properties.

Cocaine being derived, not from a simple amino-alcohol, but from the ester of an aminohydroxy-carboxylic acid, an attempt was made to prepare an analogous compound along the above lines. Thus, ε-piperidino-γ-ketohexoic acid (Mannich and Bauroth, *loc. cit.*) was converted into the *ethyl* ester, b. p. 113—114°/14 mm. (*hydrochloride*, m. p. 117—118°). Unfortunately, when the compound is reduced with aluminium amalgam, it does not yield the ester of the corresponding hydroxy-acid, but the ethyl group is simultaneously removed, and the lactone, *ε-piperidino-γ-hydroxyhexoic lactone*, b. p. 174—176°/13 mm., *hydrochloride*, m. p. 213°, is obtained.

W. A. Silvester.

2-ω-Piperidinomethyl*cyclo*hexanone and related compounds. C. Mannich and P. Honig (Arch. Pharm., 1927, **265**, 598—610).—The work of Mannich and Braun (A., 1920, i, 851; 1927, 659) has been extended in an attempt to obtain products with anæsthetic but not irritating properties. This has not been achieved. Diethylamine hydrochloride, formaldehyde, and *cyclo*hexanone readily yield 2-ω-*diethylaminomethyl*cyclo*hexanone*, b. p. 117°/24 mm. (*hydrochloride*, m. p. 105—107°), which is reduced by aluminium amalgam in moist ether to 2-ω-*diethylaminomethyl*cyclo*hexanol*, b. p. 119°/15 mm. This is presumably, like its lower homologue (*loc. cit.*), a mixture of stereoisomerides, but the *benzoate hydrochloride* can be purified without difficulty and then has m. p. 188—189° and is a powerful anæsthetic. 2-ω-*Piperidinomethyl*cyclo*hexanone*, b. p. 130°/20 mm. (*picrate*, m. p. 127°), is prepared in a similar way. It is unstable and its behaviour has been examined in some detail. The *hydrochloride* crystallised from *iso*propyl alcohol has m. p. 161°, but then solidifies again at 165°, and melts at 227°. Actually a decomposition takes place: when the hydrochloride is heated for some time at 170°, it is converted into 2-methylene*cyclo*hexanone and piperidine hydrochloride. 2-ω-Piperidinomethyl*cyclo*hexanone yields normally a *cyanohydrin*, m. p. 67°, and an *oxime*, m. p. 113°. When it is oxidised with cold dilute potassium permanganate solution it yields adipic acid and a small proportion of a *compound*, $C_{12}H_{19}O_2N$, m. p. 75° (*semicarbazone*, m. p. 210—212°), which is not the piperidide of an acid and so is considered to have the constitution:



When 2-ω-piperidinomethyl*cyclo*hexanone is exhaustively methylated and distilled with steam it yields *N*-methylpiperidine and a *compound*, $C_{14}H_{20}O_2$, b. p. 163—165°/14 mm., which is not a diketone, for it yields a mono-*oxime*, m. p. 123°, and a *semicarbazone*, m. p. 206°. 2-ω-Piperidinomethyl*cyclo*hexanone is decomposed when heated with an excess of phenylhydrazine at 150—170°; ammonia, aniline, and piperidine are formed, and the residue contains tetrahydrocarbazole. Reduction in the usual way affords 2-ω-*piperidinomethyl*cyclo*hexanol*, b. p. 141°/12 mm. (*picrate*, m. p. 127°), which is a mixture of two stereoisomerides, for the *benzoate hydrochloride*, originally of m. p. 175°, is separated by repeated recrystallisation into a product of m. p. 215° and a more soluble compound. It is a powerful anæsthetic. 2-ω-*Tetrahydro*iso*quinolinomethyl*cyclo*hexanone* (*hydrochloride*, m. p. 161°), is obtained in a similar manner to its congener and on reduction yields 2-ω-*tetrahydro*iso*quinolinomethyl*cyclo*hexanol*, b. p. 215—217°/14 mm. The *benzoate hydrochloride*, m. p. 205—206°, is a mixture of stereoisomerides with scarcely any anæsthetic potency. 2-ω-*Dimethylaminomethyl-4-methyl*cyclo*hexanone*, b. p. 123—125°/30 mm. (*hydrochloride*, m. p. 145—146°), similarly yields 2-ω-*dimethylamino-4-methyl*cyclo*hexanol*, b. p. 115—125°/20 mm., separable, as *hydrochloride*, into two isomerides, only one of which was obtained pure (m. p. 168—170°). The *benzoate hydrochloride* similarly gave a small sparingly soluble pure fraction, m. p. 212—214°, which was strongly anæsthetic. 2-ω-*Piperidinomethyl-4-methyl*cyclo*hexanone*, b. p. 115°/15 mm., gives a *hydrochoride* which behaves like its lower homologue described above, *i.e.*, it melts at 155°, solidifies again at 162°, and melts again at 230°. 2-ω-*Piperidinomethyl-4-methyl*cyclo*hexanol*, b. p. 147°/20 mm., is a mixture of isomerides. From menthone *dimethylaminomethylmenthone*, b. p. 120—135°/14 mm., is obtained. This can evidently be a mixture of structurally different isomerides and the *dimethylaminomethylmenthol*, b. p. 135—145°/18 mm.,

obtained by reduction must be a quite complex mixture. A *nitrate* is described, and the *benzoate hydrochloride* is eventually separated, by repeated recrystallisation, to give a pure sparingly soluble fraction of m. p. 239—241°, which is a powerful anæsthetic. W. A. SILVESTER.

Synthesis of unsaturated γ-ketonic amines and their reduction products. C. MANNICH and M. SCHÜTZ (Arch. Pharm., 1927, **265**, 684—695; cf. A., 1920, i, 851, and preceding abstract).—Styryl methyl ketone and its derivatives are now found to behave like other ketones in condensing with formaldehyde and secondary amines to give aminoketones. The yields are about 60% of the theoretical. The condensation takes place normally, *viz.*, at the terminal methyl group, and not in the aromatic nucleus (cf. Einhorn, A., 1906, i, 245). Piperidine hydrochloride, paraformaldehyde, and styryl methyl ketone yield *ε-piperidino-α-phenyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 180·5°; *phenylhydrazone hydrochloride*, m. p. 188°, decomp.), which, like its analogues described below, is unstable in the free state, and, although solid when isolated, undergoes rapid change into a glue. Its constitution is proved by its giving benzoic acid when oxidised and also by its giving, on hydrogenation, a saturated ketone different from the branched chain isomeride described by Mannich and Curtaz (A., 1927, 231). This hydrogenation, in which palladised charcoal is used, yields in fact *ε-piperidino-α-phenylpentan-γ-one*, b. p. 170—180°/20 mm. The *hydrochloride*, m. p. 145°, the *oxime hydrochloride*, m. p. 159°, and the *phenylhydrazone hydrochloride*, m. p. 151°, are described. This ketonic amine is reduced by aluminium amalgam in moist ether to *ε-piperidino-α-phenylpentan-γ-ol*, b. p. 210—220°/25 mm. The *hydrochloride* has m. p. 108°. The *benzoate hydrochloride*, m. p. 174°, and the p-*nitrobenzoate hydrochloride*, m. p. 204°, are also described, and the first of these is a potent, persistent anæsthetic. The piperidinophenylpentenone is also converted by the action of bromine in chloroform solution into *β-bromo-ε-piperidino-α-phenyl-Δ$^{\alpha}$-penten-γ-one*, of which the *hydrochloride* (m. p. 171°) and the *nitrate* (decomp. 102°) are described.

The following bases are prepared in a similar way to their analogues described above. *ε-Diethylamino-α-phenyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 116·5°; *phenylhydrazone hydrochloride*, m. p. 168°), which gives first *ε-diethylamino-α-phenylpentan-γ-one* (*hydrochloride*, m. p. 72°; *phenylhydrazone hydrochloride*, m. p. 149°) and then *ε-diethylamino-α-phenylpentan-γ-ol*, b. p. 168—170°/15 mm., the *benzoate hydrochloride* (m. p. 128°) of which is a persistent anæsthetic. *ε-Piperidino-α-3 : 4-methylenedioxyphenyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 185°; *phenylhydrazone hydrochloride*, m. p. 193°) is hydrogenated in glacial acetic acid by palladised charcoal to *ε-piperidino-α-3 : 4-methylenedioxyphenylpentan-γ-one* (*hydrochloride*, m. p. 155°; *oxime hydrochloride*, m. p. 169·5°), and this yields *ε-piperidino-α-3 : 4-methylenedioxyphenylpentan-γ-ol*, b. p. 235—240°/18 mm. (*hydrochloride*, m. p. 119°), of which the *benzoate hydrochloride* (m. p. 175—176°) is a weak anæsthetic with a bitter taste. *ε-Piperidino-α-3 : 4-dimethoxyphenyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 188°; *phenylhydrazone hydrochloride*, m. p. 195°) gives *ε-piperidino-α-3 : 4-dimethoxyphenylpentan-γ-one* (*hydrochloride*, m. p. 133°) and then *ε-piperidino-α-3 : 4-dimethoxyphenylpentan-γ-ol*, m. p. 69°, b. p. 240—245°/18 mm., the *benzoate hydrochloride*, m. p. 188°, of which is also very weakly anæsthetic and bitter to the taste. *ε-Diethylamino-α-3 : 4-methylenedioxyphenyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 165°) gives likewise the corresponding saturated ketone which was reduced without purification to *ε-diethylamino-α-3 : 4-methylenedioxyphenylpentan-γ-ol*, b. p. 222—228°/18 mm., the *hydrochloride* (m. p. 125°) and *benzoate hydrochloride* (m. p. 98°) of which are described. *ε-Piperidino-α-*p*-anisyl-Δ$^{\alpha}$-penten-γ-one* (*hydrochloride*, m. p. 186°) gives *ε-piperidino-α-*p*-anisylpentan-γ-one* (*hydrochloride*, m. p. 140°) and so *ε-piperidino-α-*p*-anisylpentan-γ-ol*, b. p. 270—275°/25 mm. (*hydrochloride*, m. p. 117°), of which the *benzoate hydrochloride*, m. p. 162°, is a weak anæsthetic. *ε-Diethylamino-α-3 : 4-dimethoxyphenyl-Δ$^{\alpha}$-penten-γ-one hydrochloride*, m. p. 134°, was obtained in very poor yield, accompanied by a gummy by-product. W. A. SILVESTER.

Purification of pyridine and α-picoline [2-methylpyridine] by fractional distillation. A. L. WILKIE and B. D. SHAW (J.S.C.I., 1927, **46**, 469—471T).—Purification is effected by distilling the crude bases, after dehydration, through two fractionating columns of the Dufton type; the top portion of the first column and the whole of the second, being encased in hot-air jackets, may be maintained at any desired temperature. 500 c.c. of crude bases, after two distillations, yielded more than 270 c.c. of pure pyridine, b. p. 115·3°/760 mm., d_4^{25} 0·9778 (cf. Heap, Jones, and Speakman, B., 1922, 49A); the methiodide prepared without purification from this product had m. p. 116—117° (decomp.), whilst that from pyridine mixed with 5% of α-picoline softened at 100° and melted completely at 114°. α-Picoline, purified in the same manner, has b. p. 128—128·6°/760 mm., d_4^{25} 0·9401, methiodide, m. p. 226—228°. W. J. POWELL.

Quadrivalent vanadium. II. Co-ordination number of vanadium in complex vanadyl salts. E. PARISI (Gazzetta, 1927, **57**, 859—862; cf. A., 1927, 122).—The green compound, vanadyl benzoylacetonate (cf. Morgan and Moss, J.C.S., 1913, **103**, 87) gives, when washed with pyridine, a crystalline yellow compound, *pyridine vanadyl bisbenzoylacetonate*, $C_{25}H_{23}O_5NV$, m. p. 163°. Since the Werner co-ordination number of vanadium in the green compound is already six, it is suggested that the molecule of pyridine which is acquired " forms part of the external sphere ": $[V(:O)(-O\cdot CMe:CH\cdot CPh:O\cdots)_2]C_5H_5N$, the co-ordination number remaining unaltered; cf. copper acetylacetonate (Ley, A., 1915, i, 453). Similar *picoline* (m. p. 146°), *piperidine*, *quinoline* (greenish yellow, m. p. 184°), and *aniline* (greenish-grey, m. p. 212°) compounds are obtained. E. W. WIGNALL.

Nitro-2-acetamidopyridines. A. E. TSCHITSCHIBABIN and A. W. KIRSSANOV (Ber., 1928, **61**, [*B*], 206—207).—*3-Nitro-2-acetamidopyridine*, m. p. 135—136°, prepared by the action of boiling acetic anhydride on the base, is very readily hydrolysed by

warm, dilute acids. Like 5-nitro-2-acetamidopyridine (Tschitschibabin and Pozdniakov, A., 1926, 845) it dissolves in dilute alkali hydroxide with formation of coloured, quinonoid salts. H. WREN.

Tautomerism in pyridine compounds. V. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1927, 59, 477—491).—See A., 1926, 1153.

Syntheses in the indole series. II. 5 : 6-Benz-4-carboline and its derivatives. W. O. KERMACK and R. H. SLATER (J.C.S., 1928, 32—45).—*o*-Nitrobenzyl chloride condenses with ethyl acetoacetate giving the compound $CO_2Et{\cdot}CAc(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$ (Ber., 1896, **29**, 637) and a *substance*, m. p. 183° (decomp.), probably $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NO_2){\cdot}CHAc{\cdot}CO_2Et$. When dry hydrogen chloride is passed into an alcoholic solution of the phenylhydrazone, m. p. 153·5° (decomp.) (lit. 148—149°), of *o*-nitrophenylpyruvic acid, m. p. 130° (lit. 121°), both 3-o-*nitrophenylindole*-2-*carboxylic acid* (I), m. p. 276° (decomp.) [*potassium, calcium, barium, magnesium, lead*, and *zinc* salts; *brucine* salt, m. p. 230°, $[\alpha]_D^{18}$ −50·5° in chloroform], and 3-o-*nitrophenylindole* (II), m. p. 119°, may be isolated from the reaction product, the proportions depending on reaction conditions. The *ammonium* salt of (I) is decomposed at 270—280°, giving the compound (II). Reduction of (II) in alcoholic solution by iron filings and hydrochloric acid yields 3-o-*aminophenylindole*, m. p. 82° [*hydrochloride*, m. p. 288° (decomp.); *picrate*, m. p. 190°]. The formyl derivative of this base was not isolated but treated directly with phosphorus oxychloride in toluene solution, when 5 : 6-*benz*-4-*carboline* (III), m. p. 245°, was obtained. The compound (II) is reduced by zinc dust in acetic acid solution, giving a non-basic *substance*, m. p. about 265°. The compound (I) is reduced by zinc dust in acetic acid solution, giving 3-*keto*-2 : 4-*dihydro*-5 : 6-*benz*-4-*carboline*, m. p. above 316°, which is further reduced by zinc [illegible] rent of hydrogen to give the compou[illegible] *Acetamidophenylindole*, m. p. about 15[illegible] by treatment with phosphorus oxychloride in toluene solution into 3-*methyl*-5 : 6-*benz*-4-*carboline*, m. p. 204—205° (*hydrochloride*; *picrate*; *chloroplatinate*). 3-o-*Propionamidophenylindole* is converted by a similar method into 3-*ethyl*-5 : 6-*benz*-4-*carboline*, m. p. 158° (decomp.). The phenylmethylhydrazone of *o*-nitrophenylpyruvic acid undergoes the Fischer indole reaction even in presence of dilute hydrochloric acid giving 3-o-*nitrophenyl*-1-*methylindole*-2-*carboxylic acid*, m. p. 234° (*calcium, barium, lead, zinc*, and *magnesium* salts), whence the following compounds were prepared: 3-*keto*-1-*methyl*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline*, m. p. 302°; 3-o-*nitrophenyl*-1-*methylindole*, m. p. 98°; 3-o-*aminophenyl*-1-*methylindole*, m. p. 129° [*hydrochloride*, m. p. 246° (decomp.); *picrate*, m. p. 196°]; 3-o-*acetamido*-1-*methylindole*, m. p. 159°; 1 : 3-*dimethyl*-5 : 6-*benz*-4-*carboline*, m. p. 154°. An improved method of preparation for *o*-nitrophenylpyruvic acid is described.

M. CLARK.

Oxidation of quinoline-8-sulphonic acid. E. SUCHARDA (Kosmos, Bull. Soc. pol. Nat. Leopol, 1920—1921, 18 pp.; Chem. Zentr., 1927, i, 3005—3006).—Oxidation of quinoline-8-sulphonic acid with potassium permanganate yields potassium isatin-7-sulphonate and a *potassium* salt, ($+H_2O$), m. p. 248°, of an additive compound of quinoline-8-sulphonic acid and 2-amino-3-sulphobenzoic acid; the latter acid has m. p. 263°. Its solution in concentrated sulphuric acid yields with potassium nitrite the internal anhydride of 2-diazo-3-sulphobenzoic acid, $CO_2H{\cdot}C_6H_3{\cdot}N{<}\overset{N}{\underset{SO_3}{|}}$ m. p. 150°, from which 2-hydroxy-3-sulphobenzoic acid ($+2H_2O$), m. p. 213° [barium ($+H_2O$) and sodium ($+2{\cdot}5H_2O$) salts] is produced by treatment with hydrochloric acid. With formamide, 2-amino-3-sulphobenzoic acid yields 4-hydroxy-8-sulphoquinazolin. Isatin-7-sulphonic acid has m. p. 80° ($+4H_2O$), 197° (anhyd.).

A. A. ELDRIDGE.

2-Methylquinoline oxide and *s*-di-*o*-aminobenzhydrazide. G. HELLER, W. DIETRICH, and G. REICHARDT (J. pr. Chem., 1928, [ii], **118**, 138—148).—2-Methylquinoline-*N*-oxide, previously regarded as 4-keto-2-methyl-1 : 4-dihydroquinoline (cf. Heller and Sourlis, A., 1908, i, 913; Meisenheimer and Stotz, A., 1926, 77), yields with a mixture of phosphorus trichloride and phosphoryl chloride mainly a new *chloro-2-methylquinoline*, m. p. 39—40° (*picrate*, m. p. 158—159°; *hydrochloride*, decomp. 190—195°). The constitution of this oxide is further confirmed by the formation from 4-chloro-2-methylquinoline and perbenzoic acid of 4-*chloro*-2-*methylquinoline*-N-*oxide*, m. p. 135° (*picrate*, m. p. 145·5°; *hydrochloride*, m. p. 173—174°), for which a corresponding alternative formula is not possible. When phenazine-*N*-oxide is heated with phosphorus pentachloride and phosphoryl chloride at 160—165° it gives a mixture of chloro-derivatives from which fractions of m. p. 110°, 147°, and 237° were isolated, the last being apparently identical with the dichlorophenazine oxide of Bam[illegible]nd Ham (A., 1911, i, 684). [illegible] compound previously regarded as 1 : 2-di[illegible]3-ketodihydroindazole (Heller and Kohler, A., 1923, i, 850) is shown by analysis and mol. wt. determination to be 3 : 3′-*bisbenzazimide*. It is hydrolysed by acetic and sulphuric acids to disalicylylhydrazide, and by alcoholic potassium hydroxide to a *substance*, m. p. 147°. The "3-hydroxyindazole" from which this is derived must, therefore, be *s*-*di*-o-*aminobenzhydrazide* [*hydrochloride*, m. p. 258° (decomp.), *diacetyl* derivative, m. p. 188°]. It is formed by reducing *s*-di-*o*-nitrobenzhydrazide with zinc dust and acetic acid.

H. E. F. NOTTON.

Quinoline derivatives. H. JOHN [with F. KAHL]. **V. Synthesis of furfurylidene- and cinnamylidene-2-methylquinoline-4-carboxylic acids. VI. Synthesis of 2-styryl-3-alkylquinoline-4-carboxylic acids** (J. pr. Chem., 1928, [ii], **118**, 14—16, 17—19; cf. A., 1927, 1200)—V. Isatin is condensed with furfurylideneacetone [β-2-furylvinyl methyl ketone] to give 2-(β-2-*furylvinyl*)*quinoline*-4-*carboxylic acid*, m. p. 249° (19 *salts* described), and with cinnamylideneacetone (δ-phenylbutadienyl methyl ketone) to give 2-(δ-*phenylbutadienyl*)*quinoline*-4-*carboxylic acid*, m. p. 245—247° (*methyl* ester, m. p. 90—91°; *ethyl* ester, m. p. 70°; 20 *salts* described), reducible to

the 2-δ-*phenylbutyl* compound, m. p. 142° (20 salts described). 6-*Bromo-2-(δ-phenylbutadienyl)quinoline-4-carboxylic acid*, m. p. 255—256° (20 *salts* described), is similarly obtained from 5-bromoisatin.

VI. 2-*Styryl-3-methylquinoline-4-carboxylic acid*, m. p. 274° (decomp.; *methyl* ester, m. p. 131°; 20 salts described), the 6-*bromo*-derivative, m. p. 248—250° (decomp.; 20 *salts* described), and 2-o-*hydroxystyryl-3-methylquinoline-4-carboxylic acid*, m. p. above 300° (20 *salts* described), are obtained from isatin or ɔ-bromoisatin and styryl ethyl ketone or o-hydroxystyryl ethyl ketone. C. HOLLINS.

Amides of α-phenylcinchoninic acid. S. WEIL and A. KONÓWNA (Rocz. Chem., 1927, **7**, 467—469).—The following amides have been prepared by the action of α-phenylcinchoninyl chloride on various amines: with o-*phenetidine*, m. p. 138°, with *aminodimethylphenylpyrazolone*, m. p. 249°, with *piperazine*, m. p. 280°, and with *lysidine*, m. p. 160°.

R. TRUSZKOWSKI.

Carbazine syntheses. IV. H. GOLDSTEIN and J. VAYMATCHAR (Helv. Chim. Acta, 1928, **11**, 245—249; cf. A., 1927, 1201).—Magnesium phenyl bromide and methyl 4 : 6 : 4′-triaminodiphenylamine-2-carboxylate react to give 1 : 3 : 7-triamino-5 : 5-diphenyldihydroacridine (not isolated), which is oxidised by ferric chloride into 1 : 7-diamino-5 : 5-diphenyldihydroacridine-3-imine (Kehrmann, Goldstein, and Tschudi, A., 1919, i, 552). Similarly methyl 4-amino-4′-hydroxydiphenylamine-2-carboxylate yields 7-amino-5 : 5-diphenyl-3-carbazone (Kehrmann and Brunner, A., 1926, 526). 7 : 9-*Diamino-*5 : 5-*diphenyl*-3-*carbazone*, violet, m. p. 227°, is obtained from methyl 4 : 6-diamino-4′-hydroxydiphenylamine-2-carboxylate. The diamino-compound described by Kehrmann and Tschui (A., 1925, i, 430) is probably 1 : 7-diamino-5 : 5-diphenyl-3-carbazone.

H. BURTON.

Stereochemistry of carbonyldiamino-acids. C. GRANACHAR and G. WOLF (Helv. Chim. Acta, 1928, **11**, 172—179).—When ethyl α-aminopropionate is treated with carbonyl chloride there are formed racemic- and meso-ethyl carbonyldi-α-aminopropionates, $CO(NH\cdot CHMe\cdot CO_2Et)_2$, having m. p. 153° (this vol. 74), and 85°, respectively. The meso-ester when treated with hydrochloric acid and ether yields α-5-*methylhydantoin-3-propionic acid*, m. p. 158—160°. Hydrolysis of the racemic- and meso-esters with alcoholic potassium hydroxide gives two *carbonyldi-α-aminopropionic acids*, m. p. 192—193° (decomp.) and 189—190°, which are probably identical, since treatment of both with diazoethane gives the racemic-ester. Resolution of the acid of m. p. 192—193° is effected through the *strychnine* salt, $[\alpha]_D$ −20·6° in water, from which l-*carbonyldi-α-aminopropionic acid*, m. p. 189—190°, $[\alpha]_D$ −21·0°, is obtained. H. BURTON.

Condensation products of benzylideneacetophenone [phenyl styryl ketone] and some of its derivatives. L. C. RAIFORD and H. L. DAVIS (J. Amer. Chem. Soc., 1928, **50**, 156—162).—Bromination of 4-acetamidoacetophenone in aqueous acetic acid affords 3-*bromo-4-acetamidoacetophenone*, m. p. 138—138·5°, from which 3-*bromo-4-aminoacetophenone hydrochloride*, m. p. 155—156°, and 3-*bromo-4-acetamidobenzoic acid*, m. p. 226—229°, were obtained by hydrolysis and oxidation respectively. Treatment of 4-acetamidoacetophenone with benzaldehyde in aqueous alcoholic sodium hydroxide yields 4-acetamidophenyl styryl ketone, m. p. 160—161° (cf. Giua and Bagiella, A., 1921, i, 730). 3-*Bromo-4-aminophenyl styryl ketone*, yellow, m. p. 146—147° (*diacetyl* derivative, m. p. 130—131°), and 3 : 5-*dibromo-4-aminophenyl styryl ketone*, m. p. 133—134° (*diacetyl* derivative, m. p. 173—174°), were prepared analogously. Treatment of phenyl styryl ketone with phenylhydrazine in glacial acetic acid affords the *phenylhydrazone*, m. p. 117—120°, which is converted into the corresponding pyrazoline, yellow, m. p. 135—136°, when boiled in glacial acetic acid (cf. Auwers and Voss, A., 1910, i, 70), the latter being also obtained if the phenylhydrazone is not separated from its reaction mixture immediately after its formation. The phenylhydrazone has a severe vesicant action on the skin. Treatment of 4-chlorophenyl styryl ketone with phenylhydrazine in cold glacial acetic acid yields directly 1 : 5-*diphenyl*-3-p-*chlorophenylpyrazoline*, orange, m. p. 129—130°. 1 : 5-*Diphenyl*-3-p-*acetamidophenylpyrazoline*, yellow, m. p. 241—242°, 1 : 5-*diphenyl*-3-(3′-*bromo*-4′-*aminophenyl*)-*pyrazoline*, m. p. 200·5°, 1 : 5-*diphenyl*-3-(3′ : 5′-*dibromo*-4′-*aminophenyl*)*pyrazoline*, orange, m. p. 180—181°, and 3-*phenyl*-5-p-*chlorophenyl*-1-p-*bromophenylpyrazoline*, m. p. 142—143°, are obtained analogously. Straus' conclusion that halogens have a stabilising effect on these hydrazones (cf. A., 1919, i, 41) is thus not confirmed. F. G. WILLSON.

Binary system "bromural pyramidone." H. SANDQVIST and W. HOK (Arch. Pharm., 1927, **265**, 705—707).—The m.-p. diagram for "bromural "pyramidone" mixtures has been constructed, using Rheinboldt's "thaw-melt" method (A., 1926, 25). No evidence of compound formation was obtained. The eutectic is at 75° (41% of "bromural"). W. A. SILVESTER.

Condensation of glycine anhydride with o-, m-, and p-nitrobenzaldehyde; formation of 3-aminohydrocarbostyryl and 2 : 5-diketo-3 : 6-di-o-nitrobenzylidenepiperazine. H. UEDA (Ber., 1928, **61**, [*B*], 146—151).—Glycine anhydride is converted by o-nitrobenzaldehyde in the presence of acetic anhydride and anhydrous sodium acetate at 115—125° into 2 : 5-*diketo*-3 : 6-*di*-o-*nitrobenzylidenepiperazine*, $NO_2\cdot C_6H_4\cdot CH{:}C{<}{\genfrac{}{}{0pt}{}{NH\cdot CO}{CO\cdot NH}}{>}C{:}CH\cdot C_6H_4\cdot NO_2$, decomp. about 334—336°, which is reduced by red phosphorus and hydriodic acid (d 1·7) to 3-*amino-2-hydroxy-3 : 4-dihydroquinoline*, m. p. 149—150° [*hydriodide*, m. p. 291° (decomp.); *hydrochloride*, m. p. about 310° (decomp.); *picrate* (+$2H_2O$), m. p. 214° (decomp.); *benzoyl* derivative, m. p. 205°]. The base is converted by nitrous acid into 2-hydroxyquinoline. Similarly, glycine anhydride and m-nitrobenzaldehyde afford 2 : 5-*diketo*-3 : 6-*di*-m-*nitrobenzylidenepiperazine*, decomp. about 313°, converted by phosphorus and hydriodic acid into m-*aminophenylalanine*, decomp. 260° [*dihydriodide*; *copper* salt, m. p. 245 (decomp.); *compound*, $C_{23}H_{22}O_4N_4$, decomp. 204, with phenylcarbimide]. Nitrous acid converts m-

aminophenylalanine into *dl-m*-hydroxyphenylalanine. Analogously, 2 : 5-*diketo*-3 : 6-*di*-p-*nitrobenzylidene-piperazine* is reduced to *dl-p*-aminophenylalanine [$+H_2O$, m. p. 256° (decomp.)], identical with the product of the nitration and subsequent reduction of phenylalanine; with phenylcarbimide it gives the *substance* $C_{22}H_{22}O_4N_4$, m. p. 236° (decomp.).

H. WREN.

Racemisation. VI. Action of alkali on peptides and on diketopiperazines. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1928, **76**, 299—318).—The previously observed (A., 1926, 852) racemisation of diketopiperazines in presence of alkali does not occur when the asymmetric carbon atom is tertiary (*e.g.*, in glycyl-*d-iso*valine anhydride) and must therefore be dependent on enolisation on this carbon atom. Such diketopiperazines show also greater resistance to hydrolysis. *Glycyl*-d-iso*valine* has $[\alpha]^{27}_{D}$ +1·7° in water; *glycyl*-d-iso*valine anhydride*, m. p. 269—270°, $[\alpha]^{27}$ +25° in aqueous pyridine. *Glycyl*-l-*phenylmethylaminoacetic acid* has $[\alpha]^{27}_{D}$ −82·8° in water; *glycyl*-d-*phenylmethylaminoacetic acid anhydride*, m. p. 297—298°, $[\alpha]^{28}_{D}$ +9·3 in aqueous pyridine.

C. R. HARINGTON.

Stereochemistry of reduced quinoxalines. III. Resolution of externally compensated α- and β-2 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines. C. S. GIBSON, J. H. NUTLAND, and J. L. SIMONSEN (J.C.S., 1928, 108—116).—Reduction of 2 : 3 : 7-trimethylquinoxaline by the method described in A., 1927, 366, affords a mixture, separated by fractionation from light petroleum solution into dl-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 97—98° (*oxalate*, m. p. 138—140°; *diacetyl* derivative, m. p. 131°), and dl-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 71° (*diacetyl* derivative, m. p. 147°). The racemic *a*-compound yields a less soluble d-*base*-d-*tartrate* $+2H_2O$, +51·1°, whilst from the mother-liquors of this salt, the l-*base*-l-*tartrate* $+2H_2O$, $[\alpha]^{20}_{5461}$ −51·6°, is obtained. d-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 61·5—62·5°, $[\alpha]^{20}_{5461}$ +117·5° (*di*-1 : 4-m-*nitrobenzoyl* derivative, −98·4°), and l-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 61·5—62·5°, $[\alpha]^{20}_{61}$ −117·5° (*diacetyl* derivative, m. p. 164·5—165·5°, $[\alpha]^{20}_{61}$ +164·3°, *hydrate*), are obtained from the tartrates. Resolution of the externally compensated β-compound is effected by the formation of the *d*-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-d-*methylenecamphor*, m. p. 243—244°, $[\alpha]^{20}$ +1312°, +1044°, and l-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-l-*methylenecamphor*, m. p. 243—244°, $[\alpha]^{20}_{61}$ −1307°, $[\alpha]^{20}_{5780}$ −1045°. Hydrolysis of these compounds with hydrochloric acid causes extensive racemisation of the bases, which were not obtained optically pure. Fractionation of the *oxalate*, m. p. 138—144° (decomp.), of the impure *d*-base and subsequent basification gave a dextrorotatory specimen of the *base*, m. p. 105—107°, $[\alpha]^{20}_{5461}$ +4·1°, whilst in a similar way, impure l-*base*, m. p. 105—108°, $[\alpha]^{20}_{61}$ −3·6°, was obtained. The methylene camphor derivatives are not decomposed smoothly by titration in alcoholic solution with bromine.

M. CLARK.

Contrast between iodine and bromine in glyoxaline substitution. H. PAULY and E. ARAUNER (J. pr. Chem., 1928, **118**, 33—52; cf. Pauly and Gundermann, A., 1909, i, 71; Pauly, A., 1910, i, 638).—The glyoxaline ring is peculiar in that bromination, like nitration and sulphonation, attacks the 4(5)-position, whilst iodination, like coupling with diazo-compounds, attacks the 2-position.

2-*Iodoglyoxaline*, m. p. 135—136° [*hydrogen oxalate*, m. p. 220°; *nitrate*, m. p. 136° (decomp.); *picrate*, m. p. 185°], prepared by reduction of di- or tri-iodoglyoxaline with boiling aqueous sodium sulphite, gives by bromination in alkali 4-*bromo*-2-*iodoglyoxaline*, m. p. 174°, and in chloroform with more bromine, 4 : 5-*dibromo*-2-*iodoglyoxaline*, m. p. 215·5°, isomeric with the 2 : 4-*dibromo*-5-*iodoglyoxaline*, m. p. 181° (*hydrochloride* and *nitrate* described), obtained by iodination of 2 : 4-dibromoglyoxaline. Pauly and Gundermann's "monoiodo-4-methylglyoxaline," m. p. 157° (*loc. cit.*), is an equimolecular mixture of the mono- and di-iodo-compounds. 2-Iodo-4-methylglyoxaline, m. p. 170—171° (*hydrogen oxalate*, m. p. 207°; *picrate*, m. p. 171°), is obtained pure by using half the theoretical amount of iodine, and 2 : 5-*di-iodo*-4-*methylglyoxaline*, m. p. 191—192° (*hydrochloride*, m. p. 220—222°), by using excess of iodine in dilute solution; the di-iodo-compound gives only the 2-iodo-compound on reduction with sodium sulphite. 5-*Bromo*-2-*iodo*-4-*methylglyoxaline*, m. p. 147—148° (*hydrochloride*, m. p. 211°), results from the bromination of 2-iodo-, or iodination of 5-bromo-4-methylglyoxaline. 4-*Iodo*-2-*methylglyoxaline*, m. p. 144—145°, cannot be obtained by direct iodination but is prepared from the di-iodo-derivative (Pauly, *loc. cit.*) and sodium sulphite. Pilocarpidine gives by iodination a mono*iodo*-compound, m. p. 161°, and a *di-iodo*-compound, m. p. 192°.

C. HOLLINS.

Glyoxaline-4(5)-formaldehyde. W. HUBBALL and F. L. PYMAN (J.C.S., 1928, 21—32).—The following derivatives of glyoxaline-4(5)-formaldehyde (J.C.S., 1916, **109**, 186) have been prepared: *nitrate*, m. p. 165° (corr.); *hydrochloride*, m. p. 169—170° (corr.), hygroscopic; *anil*, m. p. 142—143° (corr.); *oxime*, m. p. 183—184° (corr.); *semicarbazone*, m. p. 223—224° (corr.) ($+H_2O$), and *sodium hydrogen sulphite compound*. The aldehyde fails to condense with acetone. With acetophenone it gives a poor yield of glyoxaline-4(5)-methylideneacetophenone isolated as picrate. With ethyl acetate, the *picrate* of *ethyl urocanate*, decomp. 250° (sintering from 230°), was isolated in a single instance. The aldehyde condenses readily with pyruvic acid and β-naphthylamine, giving 2-[*glyoxalinyl*-4(5)]-β-*naphthacinchoninic acid*, decomp. 300°, and with dimethylaniline, giving pp'-*tetramethyldiaminodiphenyl* [*glyoxalinyl*-4(5)]-*methane*, m. p. 190° (corr.), which, on oxidation, yields a dye closely resembling malachite-green. The aldehyde, like *o*- and *p*-hydroxybenzaldehydes and pyrrole-2-aldehyde, fails to undergo many of the reactions characteristic of benzaldehyde. This behaviour is attributed either to the presence of an acidic group (·OH or :NH) or to stability in the tautomeric hydroxymethylene form. The preparation of *N*-methyl derivatives, in which conformity

to the benzaldehyde type might be expected, was therefore attempted. Methylation of glyoxaline-4(5)-formaldehyde gives a very poor yield of 1-*methylglyoxaline-5-formaldehyde* (I) [*picrate*, m. p. 170° (corr.); *nitrate*, m. p. 175° (corr., decomp.)] unaccompanied by the isomeric 1-methylglyoxaline-4-formaldehyde. Reduction of the compound (I), which shows a normal Cannizzaro reaction, gives 1 : 5-dimethylglyoxaline, whilst the products of oxidation and of reaction with potassium hydroxide solution are isolated respectively as the *picrate* of 1-*methylglyoxaline-5-carboxylic acid*, m. p. 198—199° (corr., decomp.), and 1-*methyl-5-hydroxymethylglyoxaline picrate*, m. p. 166° (corr.). Methylation of methyl glyoxaline-4(5)-carboxylate gives *methyl* 1-*methylglyoxaline-5-carboxylate*, m. p. 68—70° (corr.) [*picrate*, m. p. 171° (corr.)], together with a very small quantity of *methyl* 1-*methylglyoxaline-4-carboxylate*, m. p. 171—172° (corr.), and of the dimethylated quaternary base isolated as 4(5)-*carboxy*-1 : 3-*dimethylglyoxalinium picrate*, m. p. 220—221° (corr.). Oxidation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline by nitric acid yields 4(5)-*methylglyoxaline*-5(4)-*formaldehyde* (II), m. p. 167° (corr.) [*picrate*, m. p. 180—181° (corr.)], with 4(5)-methylglyoxaline-5(4)-carboxylic acid as by-product. Methylation of (II) gives 1 : 4-*dimethylglyoxaline-5-formaldehyde* (III), m. p. 70° (corr.) ($+H_2O$) [*picrate*, m. p. 212—213° (corr.)], alternatively obtained by oxidation of 1 : 4-dimethyl-5-hydroxymethylglyoxaline. Oxidation of (III) gives 1 : 4-*dimethylglyoxaline-5-carboxylic acid*, m. p. 205—206° (corr., decomp.) [*picrate*, m. p. 186—187° (corr.) ($+H_2O$)], which is converted by decarboxylation into 1 : 4-dimethylglyoxaline. The carbonyl group thus behaves like the nitro-group in directing the formation predominantly of substances in which the carbonyl and methyl groups are in the 5 : 1-position (A., 1924, i, 1112). M. CLARK.

Formation of 2-methylbenziminazoles. M. A. PHILLIPS (J.C.S., 1928, 172—177).—Nitration of diacetyl-*o*-phenylenediamine yields 4-nitrodiacetyl-*o*-phenylenediamine (I), m. p. 255° (Ladenburg, Ber., 1884, **17**, 150, gives m. p. 227°), oriented by reduction and acetylation to 1 : 2 : 4-triacetamidobenzene (II) Reduction of the compound (I) and of 2-nitrodiacetyl-*m*-phenylenediamine with iron powder and acetic acid yields 4-*aminodiacetyl*-o-*phenylenediamine*, m. p. 205° (which reacts normally with nitrous acid), and 2-*aminodiacetyl*-m-*phenylenediamine*, m. p. 250°, respectively. Derivatives of mono- or di-acetyl-*o*-phenylenediamine are converted by boiling with 3*N*-hydrochloric acid into substituted 2-methylbenziminazoles. The monoacetyl derivative appears to be formed as an intermediate in the formation of the ring compound from the diacetyl derivative, since *o*-aminoacetanilide may be isolated as well as 2-methylbenziminazole when diacetyl-*o*-phenylenediamine is hydrolysed in this way. 2-Methylbenziminazole is formed when *o*-phenylenediamine is boiled with 3*N*-hydrochloric acid and acetic anhydride, whereas the diacetyl derivative only is produced in the absence of the mineral acid. Compound (I) yields 5-nitro-2-methylbenziminazole with boiling sodium hydroxide solution as well as with hydrochloric acid. Compound (II) on treatment with hydrochloric acid followed by addition of acetic anhydride gives 5-acetamido-2-methylbenziminazole (*hydrochloride*, m. p. 325°, dimorphous, described as the base by Gallinek (Ber., 1897, **30**, 1912), also formed by reduction and subsequent acetylation of 5-nitro-2-methylbenziminazole. When the compound (II) is treated with hydrochloric acid alone, it yields the dihydrochloride of 5-amino-2-methylbenziminazole. M. CLARK.

Determination of valency requirements of alkyl groups. K. VON AUWERS and H. DUSTERDIEK (J. pr. Chem., 1928, **118**, 53—66; cf. von Auwers and Wegener, A., 1924, i, 534).—The scission of (mono)semicarbazones of 4-methyl-1-alkylcoumaranones by semicarbazide is a better criterion of the valency requirements of the 1-alkyl groups than the experiments previously described (*loc. cit.*). The order of decreasing "unsaturation" as now determined is Me, Et, Bu^a, Pr^a (cf. Me, Pr^a, Bu^a, Et, *loc. cit.*). The preparation of monosemicarbazones of the 1-methyl and 1-ethyl compounds presents no difficulty. 4-*Methyl*-1-*propylcoumaranone semicarbazone*, m. p. 179°, and the corresponding 1-*butyl* compound, m. p. 204°, on the other hand, are not easily obtained, fission of the ring occurring before formation of the monosemicarbazone. For the same reason, direct formation of the disemicarbazone is no indication of relative valency requirements of the alkyl substituents, but the conclusions previously reached as to the effect of position and number of substituent groups on the stability of the coumaranone ring are not invalidated.

The interaction of silver anthranilate with alkyl halides (Karrer, A., 1919, i, 339) might be expected to give alkyl esters or *N*-alkylated acids according to the degree of unsaturation of the alkyl group. Exactly similar results, however, are obtained with methyl, ethyl, propyl, and allyl iodides, the *N*-alkylated acid being the main product.

When indazole and an alkyl halide are heated together, the 2-derivative is formed almost exclusively; the silver salt method gives almost exclusively the 1-derivative. In presence of alkali, 1- and 2-isomerides are obtained, usually in about equal proportions; with *iso*propyl, allyl, and benzyl bromides, however, the 1-derivative predominates (A., 1921, i, 806; 1924, i, 992; 1925, i, 73). Extension of these observations to ethylene bromohydrin, γ-phenylallyl bromide and iodide, *n*-butyl bromide and iodide, *iso*amyl bromide, and *o*- and *p*-nitrobenzyl chlorides and iodides, confirms the dependence of the behaviour of indazole towards alkyl halides on the degree of unsaturation of the alkyl group. Alkylation in presence of alcoholic alkali at 80—100° gives 1- and 2-isomerides in the ratios: *n*-butyl, 1 : 1; *iso*amyl, 1 : 1; γ-phenylallyl, 3 : 1; *o*- or *p*-nitrobenzyl, 5 : 3. The following compounds are described: 2-butylindazole methiodide, m. p. 176—177°; 2-*isoamylindazole methiodide*, m. p. 155°; 2-methylindazole *iso*amyliodide, m. p. 125°; 2-β-*hydroxyethylindazole*, m. p. 102° (*methiodide*, m. p. 139°); 2-β-*iodoethylindazole*, m. p. 70° [reducible to 2-ethylindazole (picrate, m. p. 154°)]; 2-γ-*phenylallylindazole*, m. p. 103° (*picrate*, m. p. 167°); 1-γ-*phenylallylindazole*, m. p. 86—87° (*picrate*, m. p.

127·5—128·5°; *methiodide*, m. p. 172°); 1-o-*nitrobenzylindazole*, m. p. 80—82°; 1-p-*nitrobenzylindazole*, m. p. 122° (*picrate*, m. p. 133°). C. Hollins.

Indazole derivatives. K. von Auwers and H. Kleiner (J. pr. Chem., 1928, **118**, 67—90).—Some miscellaneous observations are recorded. 5-Nitroindazole, m. p. 207°, is obtained almost quantitatively from indazole and cold fuming nitric acid. Sulphonation is best performed with 5 parts of 20% oleum at 100° and gives a 46·5% yield of *indazole*-5(?)-*sulphonic acid*, m. p. 269—270° (*sulphonyl chloride*, m. p. 90—94°), which is converted by alkaline fusion into 5(?)-*hydroxyindazole*, m. p. 177—179° (*diacetate*, m. p. 91—91·5°). 5- and 7-Diazoindazoles could not be converted into the corresponding hydroxy-compounds.

By interaction with β-halogenoaliphatic esters indazole yields mainly 3-indazyl derivatives. *Ethyl* β-2-*indazylpropionate*, b. p. 206—207°, $d_4^{15\cdot2}$ 1·1453 (*picrate*, m. p. 126·5—127°; free acid, m. p. 148—149°), and β-1-*indazylpropionic acid*, m. p. 105·5—106·5°, are obtained from ethyl β-chloropropionate; β-2-indazylpropionic acid is also synthesised from 2-β-hydroxyethylindazole by way of the 2-β-*bromoethyl* (m. p. 60—60·5°) and 2-β-*cyanoethyl* derivatives. From indazole and ethyl α-bromobutyrate an ester, b. p. 170—180°/14 mm., is obtained, hydrolysable to α-2-*indazylbutyric acid*, m. p. 143—145°, which by decarboxylation yields 2-propylindazole (picrate, m. p. 151—152°). α-2-*Indazylphenylacetic acid*, m. p. 177° (decomp.), similarly gives 2-benzylindazole. By heating indazole with ethyl α-bromo-β-phenylpropionate at 200° there results 2-β-phenylethylindazole, m. p. 73° (*picrate*, m. p. 158—159°; *methiodide*, m. p. 171·5—172·5°), which is also obtained from indazole and β-phenylethyl bromide at 195°, or, with the 1-*isomeride*, m. p. 77—78° (*picrate*, m. p. 115—116°; *methiodide*, m. p. 184°), from the same components in presence of hot alcoholic alkali; from silver indazole and phenylethyl iodide the 1-isomeride only is obtained. 2-γ-*Phenylpropylindazole*, b. p. 227°/16 mm. (*picrate*, m. p. 121—122°; *methiodide*, m. p. 128—129°), and the 1-*isomeride*, m. p. 45—46° (*picrate*, m. p. 91—92°; *methiodide*, m. p. 141—143°), are formed in equal amounts from indazole, sodium ethoxide, and γ-phenylpropyl bromide; *p*-methylbenzyl bromide, b. p. 110°/15 mm., gives 2-p-*methylbenzylindazole*, m. p. 90—91° (*picrate*, m. p. 157—158°; *methiodide*, m. p. 165—166°), and a smaller quantity of the 1-*isomeride*, m. p. 43—44° (*picrate*, m. p. 127—129°; *methiodide*, m. p. 165°), the mixed oils distilling at 210—220°/15 mm. From 2-β-bromoethylindazole by the action of alcoholic alkali there is obtained 2-*vinylindazole*, b. p. 138°/15 mm., d_4^{20} 1·1065 (*picrate*, 128·5—129°; *methiodide*, m. p. 167°). Ethyl 1-indazylacetate yields a *methiodide*, m. p. 121—122°.

o-Toluoyl chloride reacts with indazole in well-cooled ether to give the 1-*derivative*, m. p. 91—92°, completely converted by heating for 2 hrs. into the 2-*isomeride*, m. p. 64—66°, also obtained directly at 110°; the former, but not the latter, is hydrolysed at once by hydrogen chloride in dry ether. 1-m-*Toluoylindazole*, m. p. 70—71°, 1-p-*toluoylindazole*, m. p. 92·5°, and 2-p-*toluoylindazole*, m. p. 87—88°, are described. 1(or 2)-*Indazylphenylthiocarbamide*, m. p. 102—103° (*methyl ether*, m. p. 59—60°; *acetyl* derivative, m. p. 117°) is obtained from indazole and phenylthiocarbimide. Indazole does not react with carbon disulphide.

From 6-nitroindazole, ethyl chloroacetate, and sodium ethoxide *ethyl* 6-*nitro*-1(or 2)-*indazylacetate*, m. p. 117—118° (free *acid*, m. p. 217—218°), is obtained. 6-Nitroindazole reacts with benzyl chloride at 130—180° to give 6-*nitro*-1(or 2)-*benzylindazole*, m. p. 124—125° (no methiodide), reducible to a diazotisable *amine*, m. p. 136—137°.

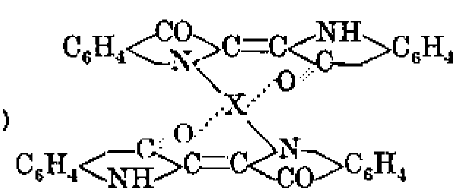
C. Hollins.

Tenacity of organic radicals towards nitrogen. K. von Auwers, H. Dusterdiek, and H. Kleiner (Ber., 1928, **61**, [*B*], 100—103; cf. A., 1925, i, 1100).—The decomposition of indazolium salt, $\left[C_6H_4{<}{\overset{CH}{\underset{NM}{}}}{>}NR\right]I$, has been studied, the percentage of the corresponding 2-alkylindazole produced being placed in parentheses after the name of the radical *R*: methyl (8); β-phenylethyl (30); ethyl (34); γ-phenylpropyl (37); β-hydroxyethyl (43); *iso*propyl (52); *n*-butyl (54); *n*-propyl (55); *iso*amyl (57); vinyl (0); Δ^{β}-propenyl (0); benzyl (0); *p*-methylbenzyl (0); *o*-chlorobenzyl (0); *p*-chlorobenzyl (0). The similar series for the production of 1-alkylindazoles from salts, $\left[C_6H_4{<}{\overset{CH}{\underset{NR}{}}}{>}NMe\right]I$, is as follows: ethyl (100); *n*-propyl (100); *iso*propyl (100); *iso*amyl (100); β-phenylethyl (100); γ-phenylpropyl (100); *p*-chlorobenzyl (93); methyl (92); Δ^{β}-propenyl (83); benzyl (77); *p*-methylbenzyl (75); *o*-chlorobenzyl (71); styryl (? 33). The relatively feeble union of methyl is remarkable; beyond propyl, increase in weight of the radical does not appear to be accompanied by increased tenacity. The relative tenacities of the benzyl, β-phenylethyl, and γ-phenylpropyl groups does not appear to be explicable by the accepted theories of valency demand of the component atoms. Contrary to previous observations (*loc. cit.*), 2-ethylindazole is not produced by decomposition of 1 : 2-diethylindazolium iodide.

H. Wren.

Constitution of the metallic complexes of indigotin. R. Kuhn and H. Machemer (Ber., 1928, **61**, [*B*], 118—127).—Indigotin, when treated with magnesium methyl iodide according to Zerewitinov, evolves 2 mols. of methane; hence the hydrogen atoms of both imino-groups are active. The copper and zinc compounds of indigotin, on the other hand, contain only two active hydrogen atoms for each atom of metal and therefore for two indigotin residues. Complex formation occurs therefore in such a manner that the bivalent metal replaces two active hydrogen atoms. These observations are incom-

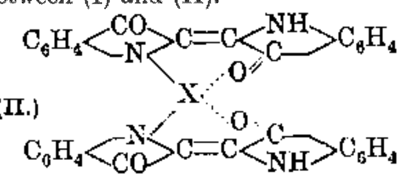
(I.)



patible with the constitution assigned to these compounds by Kunz and co-workers (A., 1923, i, 155,

1134; 1925, i, 1318; 1927, 366) and leave only a choice between (I) and (II).

(II.)



These structures are in harmony with the observations that the zinc and copper compounds afford indigotin and the metal as ion without evolution of gas when acted on by warm 5% hydrochloric acid and that the sodium derivative gives sodium hydroxide, indigotin, and no gas when treated with water. Similarly the red silver salt of 2-methylindolyl-2'-methylindolidenemethane has the composition $C_{19}H_{15}N_2Ag$ instead of $C_{19}H_{16}N_2Ag$ ascribed by Kunz (*loc. cit.*), since it evolves one mol. of methane whereas the free base evolves two. The applicability of magnesium methyl iodide to the elucidation of structural problems with complex salts is established by experiments with diacetyldioxime and its nickel derivative, cupferron and its copper and iron salts.

The production of metallic compounds from indigotin and the acetates of heavy metals involves, according to Kunz, a complicated decomposition of the salt according, for example, to the equation $2Ac{\cdot}OCu{=}2Cu{+}3Ac{\cdot}OH{+}C{+}CO_2$. This change has not been observed at temperatures at which complex formation occurs and, further, the amount of acetic acid produced is equivalent to that of the dye taken and not to that of the excess of acetate employed. Thus ethyl indigotinmalonate readily affords the *copper* compound, $C_{42}H_{26}O_8N_4Cu$, and the corresponding *cobalt* and *silver* derivatives, in each of which the imino-hydrogen atom is replaced by metal. The production of the zinc and copper complexes from the metal and indigotin in solvents of high b. p. is confirmed but the change occurs only when a large excess of metal containing oxide or carbonate is used, when air is present or the solvent takes part in the change. Pyrophoric copper does not react with solutions of indigotin or ethyl indigotinmalonate in pyridine or xylene at 100°, 125°, 150°, or 175° if oxygen is completely excluded. H. WREN.

2 : 2'-Dipyridylamine and its nitro-derivatives. A. E. TSCHITSCHIBABIN and W. A. PREOBRASHENSKY (Ber., 1928, **61**, [*B*], 199—206; cf. Tschitschibabin and Zeide, A., 1915, i, 590; Steinhäuser and Diepolder, A., 1916, i, 740).—2 : 2'-Dipyridylamine is prepared in 45% yield by heating a mixture of equivalent amounts of 2-aminopyridine and its hydrochloride for 40—50 hrs. with exclusion of atmospheric moisture. It exists in two polymorphic forms, m. p. 95° and 84°, obtained by crystallisation from water and anhydrous ether, respectively. The latter form is usually obtained by sublimation of either variety and generally passes into the former when melted and allowed to solidify. Nitration of 2 : 2'-dipyridylamine in concentrated sulphuric acid usually affords a mixture of nitro-derivatives, but by suitably controlling the quantity of nitric acid and the temperature the following compounds may be made the main products of the change : (1) 5-*nitro*-2 : 2'-*dipyridylamine*, m. p. 196—197°, obtained by use of a 10% excess of nitric acid at 0° and synthesised from 2-aminopyridine and 2-chloro-5-nitropyridine at 67—80° ; (2) 5 : 5'-*dinitro*-2 : 2'-*dipyridylamine*, by use of a 10% excess of nitric acid at 0° and from 2-chloro-5-nitro- and 5-nitro-2-aminopyridine ; (3) 3 : 5 : 5'-*trinitro*-2 : 2'-*dipyridylamine*, m. p. 197°, from 5-nitro- or 5 : 5'-dinitro-2 : 2'-dipyridylamine and the calculated quantity of nitric acid in hot sulphuric acid solution ; 3 : 5 : 3' : 5'-*tetranitro*-2 : 2'-*dipyridylamine*, m. p. 140—141°, not obtained in any of the processes described above but prepared by prolonged nitration of 2 : 2'-dipyridylamine at 100° or from 3 : 5 : 5'-trinitro-2 : 2'-dipyridylamine. 3 : 3'-*Dinitro*-2 : 2'-*dipyridylamine*, m. p. 179—180°, is obtained from the mother-liquors of the preparation of trinitrodipyridylamine and from 2-chloro-3-nitropyridine and 3-nitro-2-aminopyridine. Introduction of a fifth nitro-group could not be effected. The ease with which the nitro-compounds, even if containing only a single nitro-group, dissolve in solutions of alkali hydroxide with the formation of deeply-coloured salts shows that the pyridine has a much greater tendency than the benzene nucleus to pass into the quinonoid form. The dinitrodipyridylamine of Wibaut and La Bastide (this vol., 75) appears to be a mixture of isomerides.

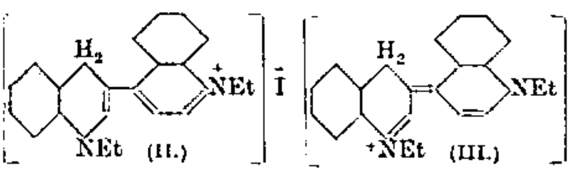
H. WREN.

ψ-Cyanine condensation. F. M. HAMER (J.C.S., 1928, 206—215).—The preparation of 2 : 2'-cyanines (ψ-cyanines) by condensation of 2-methylquinoline alkiodide with 2-iodoquinoline alkiodide is effected by addition of alkali to an aqueous or, better, to an absolute-alcoholic solution. The recommendation in the literature, that dilute hydrochloric acid be used as solvent with the object of increasing the stability of 2-iodoquinoline alkiodide, is based on a misapprehension, since this solvent decreases its stability. By use of 4-methylquinoline alkiodide, or 2-methylbenzthiazole alkiodide, instead of 2-methylquinoline, *iso*cyanines and thio-ψ-cyanines, respectively, are obtained. This method of preparation confirms the formulæ previously assigned to these compounds. By use of substituted indolenine quaternary salts containing a reactive 2-methyl group, dyes of a new type, the indo-ψ-cyanines, are prepared. The ψ-cyanines, like the other cyanines, act as photographic sensitisers. Their nomenclature is discussed. The following are described : 2-iodoquinoline ethiodide, m. p. 205° (decomp.) (lit. 220°) ; 1 : 6-dimethyl-2-quinolone, m. p. 82—84°, b. p. 205°/15 mm. (lit. m. p. 90°) ; 2-*iodo*-6-*methylquinoline methiodide*, m. p. about 225° (decomp.) ; 1 : 1'-dimethyl-ψ-cyanine iodide, m. p. 245—246° (decomp.) ; 1(1')-*methyl*-1'(1)-*ethyl*-ψ-*cyanine iodide*, m. p. 261—262° (decomp.) ; 1 : 1': 6- and 1 : 1' : 6'-*trimethyl*-ψ-*cyanine iodides*, m. p. about 220° (decomp.) and 183° (decomp.) ; 1 : 6 : 1' : 6'-*tetramethyl*-ψ-*cyanine iodide*, m. p. about 250° (decomp.) ; 1 : 1'-*diethyl*-ψ-*cyanine iodide*, m. p. 277° (decomp.) ; 6(6')-*methyl*-1 : 1'-*diethyl*-ψ-*cyanine iodide*, m. p. 258° (decomp.) ; 1 : 1'-*diethyl*-5 : 6(5' : 6')-*benz*-ψ-*cyanine iodide*, m. p. 273° (decomp.) ; 1 : 1'-*dimethyl*-5 : 6-(5' : 6')-*benz*-ψ-*cyanine iodide*, m. p. about 266 (decomp.) ; 1' : 2-*dimethylthio*-ψ-*cyanine iodide*, m. p. about 272—276° (decomp.) ; 1'-*methyl*-2-*ethylthio*-ψ-

cyanine iodide, m. p. about 266° (decomp.); *2-methyl-1'-ethylthio-ψ-cyanine iodide*, m. p. about 261—264° (decomp.); *1 : 3 : 3 : 1'-tetramethylindo-ψ-cyanine iodide*, m. p. 247° (decomp.); *3 : 3-dimethyl-1 : 1'-diethylindo-ψ-cyanine iodide*, m. p. about 222° (decomp.). Photographic data are given.

M. CLARK.

Cyanine dyes. X. Constitution of the *apo*-cyanines. W. H. MILLS and H. G. ORDISH (J.C.S., 1928, 81—86).—Oxidation of diethylerythro*apo*cyanine quaternary salts (G.P. 154,448) with iodine or potassium permanganate yields the corresponding salts of 3 : 4'-diquinolyl [diethiodide, m. p. 198°; dichromate, m. p. 211° (cf. Kaufmann and others, A., 1911, i, 721); *diethochloride* (I), m. p. 121°, deliquescent]. When the compound (I) is heated in a vacuum, ethyl chloride is eliminated with formation of *3 : 4'-diquinolyl*, m. p. 83—84° (*picrate*, m. p. 244°). Ethyl 4-quinolylpyruvate condenses with *O*-aminobenzaldehyde at 150—160°/12—15 mm., giving after hydrolysis of the ester, *3 : 4'-diquinolyl-2-carboxylic acid*, m. p. 204° (decomp.) ($+1\frac{1}{2}H_2O$), which is converted by heat into the corresponding diquinolyl, m. p. 83—84°, identical with that obtained from diethylerythro*apo*cyanine diethiodide. The tautomeric formulæ (II and III) must, therefore, represent the constitution of the last-named compound (cf. König, A., 1922, i, 1188), since only the 4-position


(II.) (III.)

for the last hydrogen atom will leave a conjugated chain of unsaturated linkings between the two nitrogen atoms. Ethyl 2-quinolylpyruvate condenses with *o*-aminobenzaldehyde yielding, after hydrolysis of the ester, *2' : 3-diquinolyl-2-carboxylic acid*, m. p. 175° (decomp.), converted by heat into 2' : 3-diquinolyl. The constitution of the last-named compound, advanced by Carlier and Einhorn (cf. A., 1891, 93) is thus confirmed.

M. CLARK.

Triazole compounds. II. Methylation of 1-hydroxy-1 : 2 : 3-benztriazoles. O. L. BRADY and C. V. REYNOLDS (J.C.S., 1928, 193—202).—1-Hydroxy-1 : 2 : 3-benztriazole (I) (*acetyl* derivative, m. p. 98°; *benzoyl* derivative, m. p. 77°) is prepared by boiling *sodium-o-nitrophenylhydrazine sulphonate* with potassium hydroxide or by the action of hydrazine on *o*-bromonitrobenzene. It yields 1 : 2 : 3-benztriazole when reduced with phosphorus and hydriodic acid, or when boiled with excess of hydrazine. Methylation of (I) with methyl sulphate and aqueous alkali, or with methyl iodide and sodium ethoxide, yields a mixture of *1-methoxy-1 : 2 : 3-benztriazole*, m. p. 89°, and *1-methyl-1 : 2 : 3-benztriazole-1-oxide* (II), m. p. 145°.

The proportion of *O*-methyl ether, the predominating product in either method of preparation, is greater in the second of these. Compound (II) is obtained alone by the action on (I) of methyl sulphate or methyl iodide followed by hydrolysis. Reduction of (II) with phosphorus and hydriodic acid gives 1-methyl-1 : 2 : 3-benztriazole, identical with that obtained by the action of nitrous acid on methyl-*o*-phenylenediamine. *o*-Nitromethylaniline was prepared by the action of nitric acid on methylacetanilide in acetic anhydride solution, with subsequent hydrolysis of the acetyl grouping. Reduction of the nitro-group to give methyl-*o*-phenylenediamine is conveniently effected by sodium hyposulphite. 1-Hydroxy-6-methyl-1 : 2 : 3-benztriazole (III) (*acetyl* derivative, m. p. 138°; *benzoyl* derivative, m. p. 129—130°), prepared by methods analogous to those described for (I), gives, on reduction, 6-methyl-1 : 2 : 3-benztriazole. Methylation of (III) with methyl sulphate and aqueous alkali or with methyl iodide and sodium ethoxide yields a mixture of *1-methoxy-6-methyl-1 : 2 : 3-benztriazole*, m. p. 50°, and *1 : 6-dimethyl-1 : 2 : 3-benztriazole-1-oxide* (IV), m. p. 169°, the proportion of *O*- to *N*-derivative being less in this case than in methylation of the compound (I). The variation in the *O*/*N* ratio is ascribed to the weaker acidity of (III), caused by introduction of the methyl group into the benzene nucleus and by the fact that *O*-methylation is ionic, whereas *N*-methylation is molecular in type (cf. A., 1926, 1142). By heating (III) with methyl sulphate, only (IV) is obtained. Compound (IV) yields on reduction *1 : 6-dimethyl-1 : 2 : 3-benztriazole*, m. p. 75°. To confirm the supposition that methylation of (I) and (III) causes the formation of the 1-*N*-methyl derivative, 1 : 6-dimethyl-1 : 2 : 3-benztriazole was synthesised from 4-nitro-*m*-tolylmethyl ether (for which an improved method of preparation is described). The ether, when heated with methylamine, yields 4-nitro-3-methylaminotoluene, which gives 4-amino-3-methylaminotoluene on reduction with sodium hyposulphite. Reaction of the diamine with nitrous acid gives 1 : 6-dimethylbenztriazole, identical with that formed by reduction of (IV). To eliminate the possibility of tautomerism, *3 : 6-dimethyl-1 : 2 : 3-benztriazole*, m. p. 50°, was prepared from 3-nitro-4-methylaminotoluene by reduction and diazotisation. It is distinct from 1 : 6-dimethyl-1 : 2 : 3-benztriazole.

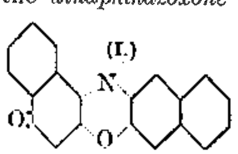
M. CLARK.

Sulphoxytriazines [ketothiontetrahydro-1 : 2 : 4-triazines]. J. BOUGAULT and L. DANIEL (Compt. rend., 1928, 186, 151—152).—Thiosemicarbazones of α-ketonic acids readily undergo cyclisation with loss of water under treatment with alkalis forming ketothiontriazines analogous to the diketotriazines similarly obtained (cf. Bougault, A., 1915, i, 598), the yields being almost theoretical. *6-Phenyl-*, m. p. 256°, *6-benzyl-*, m. p. 194°, and *6-β-phenylethyl-5-keto-3-thion-2 : 3 : 4 : 5-tetrahydro-1 : 2 : 4-triazine*, m. p. 210°, have been thus prepared. Ketothiontriazines have a stronger acid reaction than diketotriazines, and, like these, give mono- and di-esters (only the latter have been obtained in a pure condition). Whilst diketotriazines, treated with sodium hypobromite, yield a dibromo-derivative of the amide of the parent α-ketonic acid, with evolution of nitrogen, ketothiontriazines give a different (unidentified) product, without evolution of gas; but they are decomposed with effervescence by alkali hypochlorites, the benzylketothiontriazine yielding

phenylacetic acid, and the β-phenylethyl compound β-phenylpropionic acid. B. W. ANDERSON.

isoOxazoline oxides. E. P. KOHLER (J. Amer. Chem. Soc., 1928, **50**, 221—228; cf. A., 1927, 262).—Treatment of the lower-melting isomeride of α-bromo-γ-nitro-β-phenylpropiophenone with a methyl-alcoholic suspension of sodium carbonate affords three isomeric 1-*nitro*-2-*benzoyl*-3-*phenyl*cyclo*propanes*, m. p. 95° (cf. Kohler and Engelbrecht, A., 1919, i, 582), 88°, and 142°, respectively. The higher-melting isomeride of the first-named substance yields similarly, in addition to the *cyclo*propane derivatives, *α-hydroxy-γ-methoxy-γ-oximino-β-phenylpropiophenone* ($+1Me_2CO$), m. p. (solvent-free) about 190° (decomp.) [*acetate*, m. p. 185° (decomp.)] (I), from which the corresponding *hydroxamic acid*, m. p. 160° (decomp.), is obtained by treatment with cold aqueous alkali. The latter is isomerised in solution to β-hydroxy-γ-oximino-αγ-diphenyl-*n*-butyric acid (*loc. cit.*), whilst potassium acetate and acetic acid in methyl alcohol convert (I) into the corresponding methyl ester, the mechanism of the formation of this ester from the bromonitroketone, previously reported, being thus explained. When either of the above oximino-derivatives is heated with methyl alcoholic hydrochloric acid, trans-β-*benzoyl-α-phenylacrylic acid*, m. p. 202°, is obtained. This was synthesised as follows: bromination of β-benzoyl-α-phenylpropionic acid yields two isomeric β-*bromo*-derivatives, m. p. (decomp.) 195° and 208°, respectively, the former containing ether of crystallisation, and yielding, on treatment with aqueous sodium carbonate, the above benzoylphenylacrylic acid, together with an indifferent *compound*. F. G. WILLSON.

Azoxines. IV. H. GOLDSTEIN and A. WARNÉRY (Helv. Chim. Acta, 1928, **11**, 250—253; cf. A., 1926, 1159; 1927, 63).—Condensation of 3-amino-β-naphthol with 2-hydroxy-1 : 4-naphthaquinone yields the *dinaphthazoxone* (I), m. p. 276—277°, together with 2-(3-*hydroxy*-β-*naphthyl*)-*amino*-1 : 4-*naphthaquinone*, m. p. 205°. With the same aminonaphthol and 2-hydroxy-1 : 4-naphthaquinone-4-imine, there is formed a *dinaphthoxazime* (I; O:=NH:), chars at 238—240° (*acetyl* derivative, m. p. 238°; N-*phenyl* derivative, m. p. 257°, obtained from 2-hydroxy-1 : 4-naphthaquinone-4-anil).



H. BURTON.

2-(Aminophenyl)benzthiazoles. H. HAUSER (Helv. Chim. Acta, 1928, **11**, 198—209).—Reduction of 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl disulphide with aqueous sodium sulphide yields 4-chloro-*o*-aminothiophenol. Treatment of this with *p*-nitrobenzoyl chloride and subsequent reduction of the nitrothiazole produced with iron and hydrochloric acid gives 5-*chloro*-2-p-*aminophenylbenzthiazole*, m. p. 183—184° (all m. p. are corr.). Similarly, there have been prepared 5-*chloro*-2-m-*aminophenyl*-, m. p. 158—159°; 5-*chloro*-2-o-*aminophenyl*-, m. p. 161—162°; 5-*bromo*-2-p-*aminophenyl*-, m. p. 188—189°; 6-*chloro*-2-p-*aminophenyl*-4-*methyl*-, m. p. 150—151°; 6-*chloro*-2-p-*aminophenyl*-4-*methoxy*-, m. p. 220—221°; 6-*ethoxy*-2-p-*aminophenyl*-, m. p. 199·5—200·5°; 4 : 6-*di*-*chloro*-2-p-*aminophenyl*-, m. p. 198°; 4 : 6 : 7-*tri*-*chloro*-2-p-*aminophenyl*-, m. p. 224—225°; 5-*chloro*-2-(2′-*chloro*-5′-*aminophenyl*)-, m. p. 176—177°, and 5-*chloro*-2-(4′-*chloro*-3′-*aminophenyl*)-*benzthiazoles*, m. p. 164·5—165·5°.

With Epsilon acid as the secondary component *dyes* have been prepared from the above bases and 2-*p*-aminophenylbenzthiazole. The positions of the absorption bands for aqueous solutions of the dyes are given. Introduction of chlorine into the aminophenylbenzthiazole molecule has no effect on the depth of shade of the dye as is the case with methyl-substituted compounds (Bogert and Allen, A., 1927, 679). H. BURTON.

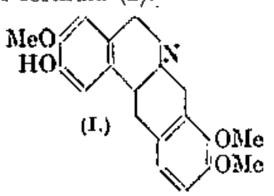
Nor-*d*-ψ-ephedrine, an alkaloid from *Ephedra* species. S. SMITH (J.C.S., 1928, 51—53; cf. A., 1927, 1094).—The Chinese drug Ma Huang contains, in addition to and *l*-ephedrines and *l*-methylephedrine, a fourth alkaloid, *nor*-d-ψ-*ephedrine*, $OH\cdot CHPh\cdot CHMe\cdot NH_2$, m. p. 77—78° (corr.), $[\alpha]^{20}$, +32·2° in methyl alcohol [*sulphate*, m. p. 295° (corr., decomp.), dependent on the rate of heating, +42·9° in water; *hydrochloride*, m. p. 178—179° (corr.); *hydrogen tartrate*, m. p. 149—151° (corr.), $[\alpha]^{20}_{5461}$ +43° in water; *dibenzoyl* derivative, m. p. 156—157° (corr.), $[\alpha]^{20}{}_{61}$ +28° in methyl alcohol]. The constitution follows from formation of *d*-ψ-methylephedrine methiodide on treatment with methyl iodide. N-*Benzoylnor*-d-ψ-*ephedrine*, m. p. 132° (corr.), $[\alpha]^{20}_{5461}$ +58·3° in methyl alcohol, obtained by partial hydrolysis of the dibenzoyl derivative, yields, when warmed with dilute hydrochloric acid and alcohol, or kept for some time in acetone solution with hydrogen chloride, O-*benzoylnor*-d-ψ-*ephedrine hydrochloride*, m. p. 244—245° (corr., decomp.), $[\alpha]^{20}{}_{61}$ −32·5° in water, from which the original *N*-benzoyl derivative is regenerated on treatment with alkali. M. CLARK.

Preparation of coniine and conhydrine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 25—28).—The finely-ground hemlock seeds (0·4—0·5% total alkaloids), mixed with wood-wool, are moistened with 15% aqueous sodium hydroxide and extracted four times with warm ether in a copper vessel. The concentrated extract is acidified with 50% acetic acid and the solvent is distilled off. After cooling the residues, solidified fat is removed from the surface and rejected after extraction of traces of alkaloids with 10% acetic acid. The total acetic acid solutions are shaken with ether to remove colouring matter, excess of 35% sodium hydroxide solution is added, and the alkaloids extracted with ether are fractionally distilled, using a wide condenser tube. The fraction up to 165° is converted into coniine salts, at 166—174° "coniine purum" of commerce distils, and the distillate above 174° is refractionated for coniine purum and conhydrine. Coniine hydrochloride, m. p. 220°, and hydrobromide, m. p. 211°, are obtained by the action of alcoholic acid on the base in alcohol, precipitation with ether, and recrystallisation from alcohol–ether. C. HOLLINS.

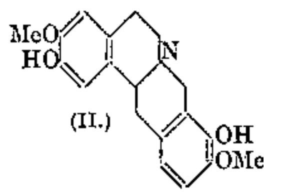
Preparation of pilocarpine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 20—24).—Crude pilocarpine,

extracted from *Pilocarpus pinnatifolius* (which should give by analysis at least 0·4% total alkaloids), is purified by crystallisation of the nitrate, m. p. 175°, from 90% alcohol. The pure base, m. p. 34°, gives a hydrochloride, m. p. 200°, neutral sulphate, salicylate, and valerate. C. HOLLINS.

Two new alkaloids from *Corydalis cava*. J. GADAMER, E. SPÄTH, and E. MOSETTIG (Arch. Pharm., 1927, **265**, 675—684).—Knörck (Dissertation, Marburg, 1926) isolated two new alkaloids from *Corydalis cava*. The first of these (0·01 g. was available for examination) has m. p. 240—241° (new determination, in evacuated tube, as are all the other m. p.'s recorded below); it also contains three methoxyl groups, and resembles, but is not identical with, corybulbine or corypalmine. These properties suggest that the compound in question is the hitherto unknown iso*corypalmine* (d-*tetrahydrocolumbamine* or 2-*hydroxy*-3 : 9 : 10-*trimethoxytetrahydroprotoberberine*) of formula (I).



(I.)



(II.)

The base (cf. Spath and Mosettig, A., 1927, 368) obtained from *d*-canadine (cf. Gadamer and Voss, A., 1910, i, 415) was methylated by treatment with diazomethane, and by working more carefully than previously (Spath and Mosettig, *loc. cit.*) a higher proportion of trimethoxy-compound was obtained. The *d*-tetrahydrocolumbamine eventually isolated had m. p. 239—241° and was identical with Knorck's product. The identity was confirmed by preparing l-*tetrahydrocolumbamine*, m. p. 241—242°, in a similar way from the *lævo*-isomeride of the dihydroxy-compound. In this preparation, *l*-corypalmine, m. p. 235—237°, was isolated as the second product. An equimolecular mixture of *d*- and *l*-tetrahydrocolumbamine reproduced the *racemic* compound, m. p. 221—222°, of natural origin.

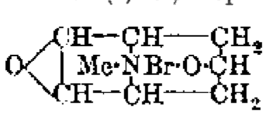
Knorck's second base had m. p. 192—193° and actually contained only two methoxyl groups, not three as originally supposed. It was smoothly and completely methylated with diazomethane to give *d*-tetrahydropalmatine. The compound was ethylated with diazoethane and the product oxidised without isolation. Mild oxidation gave 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, together with (from the liquors after further oxidation) 5-methoxy-4-ethoxyphthalic acid (isolated as its ethyl imide). More drastic oxidation gave two acids, which were isolated, and separated as their ethyl imides, viz., 5-methoxy-4-ethoxy- and 4-methoxy-3-ethoxy-phthalic acids. Knorck's second base is therefore 2 : 9-dihydroxy-3 : 10-dimethoxy-tetrahydroprotoberberine (II). Efforts to synthesise this compound have as yet been unsuccessful.

W. A. SILVESTER.

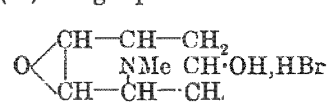
ψ-Scopine and scopoline. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1928, **186**, 147—149).—ψ-Scopine is oxidised by chromic acid giving methylamine, *m*-hydroxybenzaldehyde, and an amorphous phenolic *substance*. As the former two compounds are degradation products of scopinium bromide (cf. Polonovski, A., 1927, 888), ψ-scopine is probably first oxidised to a scopinone salt, which at once alters to the tautomeric scopinium form, which then breaks down into the products mentioned. Scopoline does not form these oxidation products; moreover, it is not affected by the action of sulphuric and acetic acids at 160°, whereas ψ-scopine thus treated undergoes partial conversion into scopoline, and in addition yields an amorphous *substance*, analogous to that mentioned above. The following compounds are described: *benzoyl-ψ-scopine*, m. p. 142° (*hydrochloride*, m. p. 216°; *picrate*, m. p. 104°; *chloroaurate*, m. p. 220°); *acetyltropyl-ψ-scopine*; *tropyl-ψ-scopine* (amorphous *picrate* and *chloroaurate*); Nor-*ψ-scopine*, m. p. 184° (*hydrochloride*, m. p. 262°; *picrate*, m. p. 225°; *chloroaurate*, m. p. 220°); and *ψ-scopylphenylurethane*; m. p. 229°, neutral to litmus (*hydrochloride*, m. p. 244°; *chloroaurate*, m. p. 210°). The corresponding isomeric *scopolinylphenylurethane* is alkaline to litmus, and has a *hydrochloride*, m. p. 226°.

B. W. ANDERSON.

Amino-oxides of alkaloids. IV. Transformation of a derivative of the *N*-oxide of scopolamine into a quaternary scopinium derivative. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1928, [iv], **43**, 79—97).—The formation of the amine-oxide, O:N:R·O·CO·R′, is the main result of the action of hydrogen peroxide on alkaloids of the tropan group (cf. A., 1925, i, 828; 1926, 1160), but hydrolysis with formation of the linkings N·R·OH, and, secondarily, O:N:R·OH, may also occur. Thus the mother-liquors after the separation of the hydrobromide of scopolamine *N*-oxide afford a quaternary *bromide*, m. p. 209—210°, in which the basic nitrogen atom is linked with three carbon atoms and an ether oxygen atom, :NBr·O·. For the new base which could not be isolated on account of its instability, the name *scopinium* is proposed; the *nitrate*, m. p. 213°, and *chloride*, m. p. 187°, are also described. Scopinium bromide is not reduced by sulphurous acid, but with zinc and hydrochloric acid or with sodium amalgam is converted (+2H) into a tertiary base, *ψ-scopine*, $C_8H_{13}O_2N$, m. p. 125—126°. The *hydrochloride*, m. p. 257—258°, *hydrobromide*, m. p. 250°, *picrate*, m. p. 234°, *chloroaurate*, m. p. 239—240°, *chloroplatinate*, m. p. 223°, d-*hydrogen tartrate*, m. p. 181°, $[\alpha]_D$ +13·5°, *methiodide*, m. p. 249° (decomp.), and N-*oxide*, m. p. 213° (decomp.) (*hydrobromide*, m. p. 192°, *hydrochloride*, m. p. 185°, and *picrate*, m. p. 210°), are described. The *acetyl* derivative, a basic *oil* gives a *picrate*, m. p. 187°, and *chloroaurate*, m. p. 203°. The above properties of ψ-scopine, its stability in acid and alkali media (the base is recovered unchanged after boiling for 6 hrs. with sodium in amyl alcohol), and its optical inactivity agree with a scopic rather than a scopoline formula, the reduction of scopinium bromide (I) to ψ-scopine (II) being represented:



(I.)



(II.)

Further support for the scopic structure for scopinium bromide is afforded by its degradation with silver oxide or sodium hydroxide or sodium carbonate into methylamine and *m*-hydroxybenzaldehyde, neither *o*- nor *p*-hydroxybenzaldehyde being formed, whereas a scopolinium structure should afford *p*-hydroxybenzaldehyde. ψ-Scopine is thus regarded as a diastereoisomeride of scopine, and its formation from scopolamine *N*-oxide is analogous to the transformation of tropine into ψ-tropine through tropinone. Scopoline chloroaurate has m. p. 235·7°, its *N*-oxide (anhydrous), m. p. 244° (hydrochloride, m. p. 191°, hydrochloride, m. p. 192°, picrate, 204—205°). R. BRIGHTMAN.

Preparation of colchicine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 29—32).—Details are given for the extraction of colchicine and colchiceine from the seeds or other parts of meadow saffron.

C. HOLLINS.

Occurrence of harmine in a South American liane (yage). F. ELGER (Helv. Chim. Acta, 1928, **11**, 162—166).—Harmine, m. p. 263—264° (lit. 257—259°), is extracted from the bark (1·7%) and the wood (0·8%) of the yagé. Telepathine (Hamet, Compt. rend., 1927, **184**, 1266) and yageine are identical with harmine. H. BURTON.

Determination of morphine in opium. R. EDER (Festschr. A. Tschirch, 1926, 392—409; Chem. Zentr., 1927, i, 3213).—The opium (1 part) is extracted by Helfenberger's method with water (8—10 parts), and the total alkaloids (except narceine) in the extract are precipitated with so much alkali (*e.g.* 0·2617 g. of sodium carbonate) as leaves the least possible amount of morphine in solution. If much calcium is present, ammonia solution is employed. The other alkaloids are separated from morphine by shaking the alkaline liquid with benzene. The results are identical with those obtained by Helfenberger's method. A. A. ELDRIDGE.

Vanillin and piperonal as reagents for alkaloids. L. VAN ITALLIE and A. J. STEENHAUER (Arch. Pharm., 1927, **265**, 696—698).—Vanillin and piperonal behave like other aldehydes in giving sensitive colour reactions with certain alkaloids, viz., *apo*morphine, aspidospermine, cevadine, codeine, and morphine. Reddish-violet or blue colours are produced when a small quantity of the alkaloid in warm alcohol is treated, *e.g.*, with the aldehyde and dilute sulphuric acid. W. A. SILVESTER.

Analogous organic compounds of phosphorus and arsenic. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 92—99).—Phenylmethylphosphinic acid readily forms the *acid chloride*, b. p. 155°/11 mm., 167°/22 mm., *methyl* ester, b. p. 137°/11 mm., *ethyl* ester, b. p. 143°/11 mm. (the parachor corresponds with the existence of a semipolar double linking), and *anilide*, m. p. 142°. Phenylmethylphosphinyl chloride reacts with benzoic acid giving benzoyl chloride. With *o*-ethylaminobenzoic acid, it gave in one instance a *compound*, m. p. 186°, containing nitrogen and phosphorus, and, in another instance, an unstable *compound*, m. p. 168°, reverting to the acid. The arsinic acid grouping in phenylmethylarsinic acid (for which a new method of preparation is described) behaves differently. The ethyl ester is not obtained by treatment of the silver salt with ethyl iodide. With thionyl chloride, the acid yields phenyldichloroarsine and probably methyl chloride. Phenylmethylchloroarsine also reacts with thionyl chloride giving phenyldichloroarsine. Diphenylchloroarsine and diphenylarsinic acid give definite crystalline additive *compounds*, $Ph_2AsCl,SOCl_2$ and $Ph_2AsO\cdot OH,SOCl_2$, respectively. These are decomposed, when heated under reduced pressure, with formation of phenyldichloroarsine and chlorobenzene in either case. The mechanism of the action of thionyl chloride on secondary arsinic acids is discussed. M. CLARK.

Guaiacol cacodylate. A. ANGELETTI (Giorn. Farm. Chim., 1927, **76**, 165—172; Chem. Zentr., 1927, ii, 1346).—Besides the compound, $AsMe_2O\cdot OH,OH\cdot C_6H_4\cdot OMe$, which is completely decomposed in aqueous solution, there is a eutectic, m. p. 18°, containing 87·3% of guaiacol. A. A. ELDRIDGE.

Constitution of the supposed *N*-methylenesulphurous acid derivatives of amines. I. Oxidation by an alkaline solution of iodine. G. NEWBERY and M. A. PHILLIPS (J.C.S., 1928, 116—126).—Reduction of a mixture of sodium 4-aminophenylarsinate and sodium phenylarsinate with sodium hyposulphite affords *4-aminoarsenobenzene* (*hydrochloride*), whilst similar treatment of the former salt gives 4 : 4′-diaminoarsenobenzene. The solubility of this base in hydrochloric acid differs from that prepared by Kashima (A., 1925, i, 1195) using hypophosphorous acid reduction. Nitration of ethenyl-*o*-aminophenol in sulphuric acid at 10—20° yields crude *5-nitroethenyl-*o*-aminophenol*, m. p. 150—151°, which is hydrolysed by boiling hydrochloric acid giving 5-nitro-*o*-aminophenol together with a small amount of the 4-nitro-isomeride, and is reduced by iron powder and aqueous acetic acid, forming *5-aminoethenyl-*o*-aminophenol*, m. p. 147°. Details are given for the preparation of 3-amino-4-hydroxyarsenobenzene, 4-amino-2-hydroxyphenylarsinic acid (cf. Hewitt and King, A., 1926, 746), 5-amino-2-hydroxyphenylarsinic acid, 4-amino-3-hydroxyphenylarsinic acid, and 4 : 4′-diamino-3 : 3′-dihydroxyarsenobenzene. Sodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-*NN*′-dimethylenesulphite prepared by the action of excess of formaldehyde and sodium hydrogen sulphite on 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (cf. Christiansen, A., 1923, i, 1148; Voegtlin and Johnson, *ibid.*, 70) and its *isomeride* obtained from the diamino-compound and excess of sodium formaldehyde hydrogen sulphite, yield acids having different physical and pharmacological properties. *Sodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene*-N-*monomethylenesulphite* and *sodium 4 : 4′-diaminoarsenobenzenedimethylenesulphite* are described.

Treatment of an aqueous solution of the hydrochlorides of 19 bases (including the above) with aqueous formaldehyde (2 mols. for each amino-group) and sodium hydrogen sulphite, with subsequent determination of nitrogen, arsenic, total sulphur, and oxidisable sulphur by alkaline iodine (cf. Elvove, B., 1926, 27), shows that in the compounds containing

the *o*-aminophenol grouping the combined sulphur is not oxidised. It is suggested that in this class of compounds the grouping $NH\cdot CH_2\cdot SO_3Na$ is present, whilst in the oxidised compounds the grouping $NH\cdot CH_2\cdot O\cdot SO_2Na$ exists. H. BURTON.

Diphenylamine- and triphenylamine-arsenic acids. I. Action of arsenic acid on diphenylamine. H. LIEB and O. WINTERSTEINER [with W. FROST] (Ber., 1928, **61**, [*B*], 107—116).—Arsenic acid does not react smoothly when heated with pure diphenylamine, whereas controllable change occurs when a preserved specimen of the base is used. Previous boiling of the amine under atmospheric pressure or treatment with air at 100°, or addition of nitrobenzene, glacial acetic acid, concentrated hydrochloric acid, or water, but not of xylene, causes reaction to occur smoothly. Optimum conditions are found in the use of 12 g. of arsenic acid, 10 g. of diphenylamine, and 1·5 c.c. of water at 100° and finally at 140—145°. The products are (1) *p*-phenylaminophenylarsinic acid (diphenylamine-*p*-arsinic acid), decomp. 286° [Burton and Gibson (A., 1926, 419) record m. p. 265°]; the *ammonium*, *disodium* ($+8H_2O$), and *magnesium* salts are described: (2) *diphenylamine*-pp'-*diarsinic acid*, $NH[C_6H_4\cdot AsO(OH)_2]_2$, decomp. 330—340°; (3) occasionally *bisdiphenylaminearsinic acid*, $(NHPh\cdot C_6H_4)_2AsO\cdot OH$. Diphenylamine-*p*-arsinic acid cannot be acetylated; attempts to arsenate acetyldiphenylamine were unsuccessful. Reduction of diphenylamine-*p*-arsinic acid by hypophosphorous acid to *di*-p-*phenylaminoarsenobenzene* is best effected by rapid dissolution of the organic compound in an excess of 50% hypophosphorous acid on the water-bath and preservation of the rapidly cooled solution at the atmospheric temperature during some hours. Reaction very readily proceeds further with the production of polyarsenides. Similar reduction of diphenylamine-*pp'*-diarsinic acid affords pp'-*di-phenylaminoarsenobenzene*-p''p'''-*diarsinic acid*, $As_2[C_6H_4\cdot NH\cdot C_6H_4\cdot AsO(OH)_2]_2$, readily soluble in ammonia and sodium carbonate solutions; the *magnesium* salt is described. H. WREN.

Active hydrogen atoms of hæmin. R. KUHN and M. FURTER (Ber., 1928, **61**, [*B*], 127—131).—Hæmin from different sources and purified by different methods invariably evolves 3 mols. of methane when acted on by magnesium methyl iodide according to Zerewitinov at temperatures not exceeding 40° (cf. Kuhn and co-workers, A., 1927, 784; Fischer, A., 1926, 630; 1927, 1099). Dimethylhæmin contains only one active hydrogen atom. The third active hydrogen atom of hæmin which does not find expression in Fischer's formula, is due to a hydrogen atom which, with the chlorine atom of the FeCl group, is lost as hydrogen chloride. Under the influence of Grignard's reagent in pyridine, hæmin loses all its chlorine which is quantitatively found in the ionised condition after addition of water. Pyridine in the absence of magnesium methyl iodide does not cause a similar change and iron is only replaced in traces. The compound, $C_{34}H_{31}O_4N_4Fe$, obtained by the action of aniline on hæmin contains only two active hydrogen atoms. H. WREN.

Action of aniline dyes on albumin, caseinogen, and gelatin. M. A. RAKUSIN (Biochem. Z., 1928, **192**, 167—171).—Proteins form compounds with both acid and basic dyes which are irreversible in boiling water. The compounds of protein with basic dyes are reversible in alcohol. Albumin (different from caseinogen) gives with acid dyes compounds which are irreversible in boiling alcohol and are often true chemical compounds. Caseinogen behaves as an amphoteric body. In the dyeing of albumin both the biuret complex and the free NH_2 groups take part. P. W. CLUTTERBUCK.

Rapid determination of carbon and hydrogen in organic compounds. II. E. BERL, A. SCHMIDT, and K. WINNACKER (Ber., 1928, **61**, [*B*], 83—91; cf. A., 1926, 749).—The lead chromate employed must be dried at 550—600° to ensure complete removal of water; the dry substance is extraordinarily hygroscopic. Complete desiccation of some varieties of lead chromate is not effected at 200°.

The formation of higher oxides of nitrogen during the combustion of nitrogenous compounds appears to depend, not on the state of oxidation of nitrogen in the compound, but on the ratio, C : N. It is not observed with nitrobenzene, nitroacetanilide, chlorodinitrodiphenylamine, or thiocarbanilide, but occurs with thiocarbamide and guanidine nitrate. The apparatus described previously (*loc. cit.*) is modified by lengthening the combustion tube and introducing a layer of lead peroxide heated at 180° in an air bath. If carbon dioxide is determined volumetrically, the gas burette must be cleansed frequently from traces of grease; this can be obviated by adding a few drops of "Nekal" solution to the acidified, saturated salt solution or by using a 20—25% solution of glycerol saturated with sodium chloride (the vapour tension of these solutions is 80% of that of water).

The combustion of liquids of relatively low b. p. is described in detail. H. WREN.

Pregl's micro-analytical method for determination of carbon and hydrogen. H. D. K. DREW and C. R. PORTER (J.S.C.I., 1928, **47**, 17—21T).—Calcium chloride is shown to be unsuitable as a drying or an absorbing agent in the combustion apparatus of Pregl. Phosphorus pentoxide mixed with glass wool is found to be ideal for the purpose (cf. Kemmerer and Hallett, A., 1927, 269; B., 1927, 958). Details of procedure are given for the filling of the drying and absorbing tubes and for carrying out analyses. Possible sources of error are examined experimentally. It is established that each filled combustion tube is characterised by a "normal" blank value and a "permanent" blank value, these values being the amounts of moisture delivered to the absorption tubes during blank runs when the tube is in a condition for carrying out analyses and when it is at maximum desiccation, respectively. A simple method of obtaining the normal state is given. The new carbon dioxide-absorbing tube lasts for about twenty analyses, as against about four for Pregl's tube. The results of analyses are exact and are free from fluctuations.

Direct Nesslerisation of Kjeldahl digestions. H. M. CHILES (J. Amer. Chem. Soc., 1928, **50**, 217—

221).—The ammonia in Kjeldahl digestions, up to a concentration of 20 mg. nitrogen per 100 c.c., can be determined colorimetrically by direct Nesslerisation, in presence of up to 5—8 g. of sodium or potassium sulphate, provided 5 c.c. of gum arabic solution, prepared as follows, be added per 100 c.c. of solution to be tested. Powdered gum arabic (10 g.) is stirred into ammonia-free water (190 c.c.) and the solution shaken for 10 min. with Permutite powder (4 g.). The slightly turbid liquid is decanted, and the treatment with Permutite repeated if it gives more than a faint coloration with Nessler solution. If reduction of the Nessler reagent is observed, the gum arabic solution is treated with about one tenth of its volume of the reagent, kept until clear, and decanted. Standard solutions for comparison should be prepared with salt contents as nearly as possible equal to those of the solutions to be determined. F. G. WILLSON.

Volumetric determination of amino-nitrogen. K. LINDERSTRØM-LANG (Compt. rend. Lab. Carlsberg, 1927, **17**, No. 4, 1—17).—The methods of Van Slyke and Folin for determining amino-groups in amino-acids are uncertain. It is deduced theoretically that such groups can be accurately titrated if use is made of the correct indicator in an appropriate solvent. A satisfactory method is described, which consists of titrating the free amino-acids in aqueous acetone solution (200 c.c. of acetone, 10 c.c. of water) with tenth normal 90% alcoholic hydrochloric acid, using naphthyl-red (benzeneazo-α-naphthylamine) as indicator, preferably at its most acid colour change (corresponding with p_H 4·8 in water). All the nitrogen can be determined in this way in amino-carboxylic acids, diamino-carboxylic acids, amino-dicarboxylic acids, the corresponding hydroxy-acids, proline and hydroxyproline, two thirds in histidine, half in asparagine, arginine, tryptophan, and dipeptides, and one third in creatine and guanidine, but the basic groups in aromatic amino-acids, amino-sulphonic acids such as taurine, and certain other weakly basic groups are not titrated. Incidentally the preparation of pure naphthyl-red, m. p. 124°, from diazoaminobenzene and α-naphthylamine is described in detail.

S. COFFEY.

Volumetric determination of organic substances completely oxidisable by sulphuric acid–chromic acid mixtures in presence of silver nitrate. H. CORDEBARD and V. MICHL (Bull. Soc. chim., 1928, [iv], **43**, 97—106; cf. Simon, A., 1922, ii, 593).—Owing to the stability of acetic acid towards oxidising agents application of the sulpho-chromic acid method to acetates and acetyl derivatives yields untrustworthy results. Fairly trustworthy values are, however, obtained in presence of silver chromate. The present method involves the volumetric determination of the excess of chromate and hence addition of silver chromate as such is not desirable. The substance is dissolved in a slight excess of a solution of potassium dichromate and silver nitrate equivalent to the amount of silver dichromate necessary for the oxidation of the acetic acid likely to be produced added. The mixture is boiled under a reflux condenser after addition of an equal volume of concentrated sulphuric acid. The excess of chromate is determined by titration with a solution of ferrous sulphate, after precipitation of the silver with sodium chloride. J. S. CARTER.

Analysis of brominated cresols. J. BUXTON and H. J. LUCAS (J. Amer. Chem. Soc., 1928, **50**, 249—252).—A slow reaction between alcohol and bromate in acid solution may affect the accuracy of Francis and Hill's method (A., 1925, ii, 163) of determining brominated cresols, and this source of error is eliminated by using aqueous acetic acid instead of alcohol as solvent. In the determination of total bromine by Robertson's method (J.C.S., 1912, **107**, 902), for which a modified apparatus is described, fading of the ferric thiocyanate end-point is avoided by boiling the solution with 1 c.c. of *N*-ferric nitrate solution before acidification, by which means the hydrogen peroxide is decomposed. A further 9 c.c. of ferric nitrate solution is added after acidification.

F. G. WILLSON.

Determination of aromatic aldehydes by titration with benzidine acetate solution. P. N. VAN ECK (Pharm. Weekblad, 1928, **65**, 82—84).—The aldehyde is dissolved in glacial acetic acid, an acetic acid solution of blood added as indicator, and the mixture titrated with the benzidine acetate solution. The end-point is determined by bringing a drop of the mixture on to filter-paper damped with hydrogen peroxide, the blue coloration of the blood–benzidine–peroxide reaction appearing only after all the aldehyde has reacted. Benzaldehyde does not give a good end-point, since it forms a green reaction product with benzidine. S. I. LEVY.

Determination of small quantities of benzoic and cinnamic acids, with some notes on the colorimetric determination of salicylic acid. J. R. NICHOLLS (Analyst, 1928, **53**, 19—29).—Benzoic acid may be determined by partial oxidation to salicylic acid by adding 1 c.c. of iron solution (50 c.c. of *N*-ferric chloride and 13 c.c. of *N*/10-sulphuric acid to 100 c.c.) to an aliquot part of a neutral solution containing not more than 4 mg. of benzoic acid to 15 c.c. of water, together with 1 c.c. of 0·1% hydrogen peroxide. After heating to boiling, 0·5 c.c. of *N*-sodium hydroxide solution is added, the whole filtered hot into a 50 c.c. Nessler tube, and the precipitate washed with hot water. The filtrate is cooled, diluted to the mark, and 1 drop of iron solution added; the colour is matched by adding a 0·01% solution of salicylic acid to a blank carried out in an identical manner. The salicylic acid may also be determined by Jorissen's test. Under these conditions a constant proportion (slightly more than 10%) of the benzoic acid is oxidised to salicylic acid, but appreciable quantities of salts other than nitrates must be absent. Cinnamic acid, if present, may be quantitatively oxidised to benzoic acid in neutral or alkaline solution with potassium permanganate.

D. G. HEWER.

Determination of mercury salicylate and lactate. A. JONESCO-MATIU and C. V. BORDEIANO (J. Pharm. Chim., 1927, **6**, 300—307).—A volumetric method for the analysis of mercuric salicylate and lactate is described, based on the oxidation of the salt with a mixture of 1 part of nitric acid and 2 parts of

sulphuric acid, and the subsequent titration of the mercury with sodium chloride solution, using the precipitate formed on adding a small quantity of sodium nitroprusside as an indicator. The method is accurate to 1%. E. A. LUNT.

Determination of the amino-group in nitroarylamines. II. Determination of nitrotoluidine, nitronaphthylamine, and nitroarsanilic acid. N. SEMIGANOVSKY (Z. anal. Chem., 1927, **72**, 295—298).—The amino-group content of nitrotoluidines, nitroacetotoluidides, nitroacetnaphthalides (other than *m*-nitroarylamines), and nitroarsanilic acid has been successfully determined by the author's method (A., 1927, 1062). Dinitroarylamines cannot thus be analysed; thus 3 : 4-dinitrophenol when boiled with alkali yields 7% of its nitrogen as ammonia. F. S. HAWKINS.

Morphine reaction of Pellagris and Vulpius. L. EKKERT (Pharm. Zentr., 1928, **69**, 1—6, 19—22).—The procedure may be much simplified; it is only necessary to heat the substance or its solution with a little concentrated sulphuric acid until the original red coloration deepens finally to brown, dilute with water, and extract separate portions with ether, chloroform, and ethyl acetate, respectively. The colour changes at various dilutions with water and these solvents are described; they are due to the formation and oxidation of *apo*morphine. The colour changes observed with several morphine derivatives and allied alkaloids are described. S. I. LEVY.

Alkaloid ferrocyanides and their analytical applications. M. GADREAU (J. Pharm. Chim., 1927, [viii], **6**, 145—151).—Methods for the quantitative determination of strychnine and of brucine, and for the separation and determination of mixtures of these two alkaloids are described. The methods are based on determinations as ferrocyanides and the difference in the time required to precipitate strychnine and brucine ferrocyanide is made the basis of the separation. It is suggested that owing to the solubility of certain alkaloid ferrocyanides, morphine, codeine, eserine, etc., hydroferrocyanic acid cannot be regarded as a specific reagent for tertiary amines. E. A. LUNT.

Biochemistry.

Effect of over-breathing and of breathing high concentrations of carbon dioxide on urinary excretion of water and chlorides. G. E. SIMPSON and A. H. WELLS (J. Biol. Chem., 1928, **76**, 171—184).—The urinary excretion of water and chlorides is increased by over-breathing and decreased by breathing air containing more than 4% of carbon dioxide. C. R. HARINGTON.

Respiratory proteins of blood. I. Copper content and minimum mol. wt. of hæmocyanin of *Limulus polyphemus*. A. C. REDFIELD, T. COOLIDGE, and M. A. SHOTTS. **II. Combining ratio of oxygen and copper in bloods containing hæmocyanin.** A. C. REDFIELD, T. COOLIDGE, and H. MONTGOMERY (J. Biol. Chem., 1928, **76**, 185—196, 197—205).—I. The hæmocyanin of *Limulus polyphemus* contains 0·173% of copper, which gives a minimum *M* of 36,700; since ultra-filtration experiments indicate that *M* lies between those of hæmoglobin and pseudoglobulin the true value of *M* is probably 73,400, and the substance contains two atoms of copper per molecule.

II. In the hæmocyanins of nine species, oxygen is combined with copper in the atomic ratio of 1 : 1. C. R. HARINGTON.

Hæmoglobin and iron in blood under tropical conditions. H. MENGERT-PRESSER (Med. dienst volksgezondh. Nederlandsch-Indie, 1926, 240—260; Chem. Zentr., 1927, ii, 277).—Higher values were obtained for natives than for Europeans. A. A. ELDRIDGE.

Composition of the blood of various human races and some analyses of pathological blood. W. F. DONATH (Med. dienst volksgezondh. Nederlandsch.-Indie, 1926, 261—277; Chem. Zentr., 1927, ii, 276).—The iron content of the blood of natives is higher than that of Europeans, which again is higher than that of Europeans in Europe. In general, lower values are observed in disease, particularly in tuberculosis. The iron of the blood is associated exclusively with the erythrocytes. A. A. ELDRIDGE.

Sulphur content of various proteins. E. KAISER (Biochem. Z., 1928, **192**, 58—66).—The sulphur content of the globin of the hæmoglobin of cat is 0·97—0·98%, of ox 0·59—0·60%, of horse (5 samples) 0·58—0·60% (1 sample), 0·49%, and of dog 0·50—0·73%. No sulphur is lost in elimination of the globin and the different sulphur contents of the different hæmoglobins obtained by Valer (this vol., 191) are thus confirmed. Globulins precipitated by Hammersten's method contain rather more sulphur than when precipitated by ammonium sulphate. P. W. CLUTTERBUCK.

Clinical methods for the determination of hæmoglobin. E. M. F. ITHURRAT and V. MORERA (Rev. asoc. med. Argentina, 1926, **39**, 401—426; Chem. Zentr., 1927, ii, 305).—Newcomer's method is recommended, although Bürker's method is more accurate. A. A. ELDRIDGE.

Methæmoglobin formation. I. Effect of certain gases, acids, and alkalis on the production of methæmoglobin by chemicals. II. Methæmoglobin production by chemicals *in vivo*. C. SUZUKI (Folia pharmacol. japon., 1927, **4**, 156—179, 180—194).—I. The production of methæmoglobin in fresh rabbit's blood *in vitro* by potassium chlorate, pyrogallol, hydroxylamine perchlorate, potassium nitrate, and aniline hydrochloride is promoted by carbon dioxide and acids, and inhibited by alkali. Except for pyrogallol, the effects are more marked in blood hæmolysed by water.

II. *In vivo* (mice), the effects are less pronounced. That of potassium chlorate and potassium nitrate is not influenced by acids. CHEMICAL ABSTRACTS.

Equilibria involving oxidation of hæmoglobin to methæmoglobin. J. B. Conant and N. D. Scott (J. Biol. Chem., 1928, **76**, 207—222).—The extent of oxidation of hæmoglobin to methæmoglobin by various reversible oxidising agents has been observed spectrophotometrically; the results confirm both the view (A., 1925, i, 455) that the hæmoglobin–methæmoglobin system is reversible and the value previously obtained for the oxidation–reduction potential of this system. Whereas the value of n in the electrochemical equation relating to the equilibrium should be 1 or 4 according as hæmoglobin has M 16,700 with 1 atom of iron or 66,800 with 4 atoms of iron, spectroscopic observations of the equilibrium between hæmoglobin and naphtholsulphonate-indophenol, and of that between carboxyhæmoglobin and potassium ferricyanide, indicate an actual value for n of 2. C. R. Harington.

Determination of methæmoglobin. J. B. Conant, N. D. Scott, and W. F. Douglass (J. Biol. Chem., 1928, **76**, 223—227).—The method of Conant and Fiesen (A., 1925, i, 456) has been modified by substituting titanous tartrate as a reducing agent for the β-anthraquinolsulphonate formerly employed. C. R. Harington.

Reduction of hæmin by cysteine. W. Cremer (Biochem. Z., 1928, **192**, 426—427).—When cysteine and hæmin are mixed in an atmosphere of carbon monoxide, 1 mol. of carbon monoxide is absorbed per mol. of hæmin. P. W. Clutterbuck.

Independence of the displacement of the absorption bands, and changes of absorption in hæmatoporphyrin solutions. Cause of the variability of the spectrum of acid hæmotoporphyrin with concentration of acid. A. Tethi (Biochem. Z., 1928, **192**, 105—117).—Absorption of light by hæmatoporphyrin dissolved in different media may be very different quantitatively even when the solutions behave similarly in respect to absorption maxima. The variation of the spectra of acid hæmatoporphyrin with the concentration of the acid depends on the fact that the spectrum of the less strongly acid solutions is additively composed of the spectra in neutral and in pure acid solution. P. W. Clutterbuck.

Independence of the displacement of absorption bands and of the changes of absorption of light in different solutions of pigments. V. Zilzer (Biochem. Z., 1928, **192**, 118—122).—The displacement of the absorption bands and changes in the degree of absorption of light by pigments in media of different chemical nature can be quite independent of one another. Using various pigments (hæmatoporphyrin, rhodamine-B, patent-blue, phloxin, quinoline-blue) and alcohol and 0·1N-potassium hydroxide as media, it is shown that the region of maximum absorption can be different with almost identical strength of absorption, or inversely the maximum may have the same position and yet the absorption be different or both the position of the maximum and the degree of absorption may be different. P. W. Clutterbuck.

Phosphorus in the metabolism of blood-sugar. G. Florence and T. Zola (Bull. Soc. Chim. biol., 1927, **9**, 1244—1252).—High levels of blood-sugar are associated with a concentration of organic phosphorus higher, and of inorganic phosphorus lower than normal. W. O. Kermack.

Blood-sugar after vagus irritation. J. Lehmann (Skand. Arch. Physiol., 1927, **52**, 169—186; Chem. Zentr., 1927, ii, 1362).

Effect of brewers' yeast extract on the combined sugar of the blood. M. Bufano (Arch. Farm. sperim., 1927, **44**, 22—31).—The proportion of total sugar in the blood of rabbits to which extract of brewers' yeast is administered subcutaneously shows no uniform variation, any increase observed being in the free sugar and any decrease in the combined sugar. The amount of the free sugar may either diminish or increase slightly. In some cases the combined sugar gradually but completely disappears, whilst in others it tends after a time to revert to its original quantity. The amount of the extract administered is without influence on the results. The observations made emphasise the excessive lability of combined sugar *in vivo* towards the enzymes of brewers' yeast and seem to justify the conclusion that similar lability of the sugar in presence of the little-known endogenous enzymes may be the cause of the variations occurring in the combined sugar content of the blood of both healthy and diseased organisms. T. H. Pope.

Determination of the reducing substance in blood. S. Jonsell, E. Jorpes, and N. Sikstrom (Acta med. Skand., 1926, **63**, 446—477; Chem. Zentr., 1927, ii, 305).—Hagedorn and Jensen's method, in which the error is 1·58%, is preferred. A. A. Eldridge.

Determination of protein-sugar. H. Bierry (Compt. rend. Soc. Biol., 1927, **96**, 606—609; Chem. Zentr., 1927, i, 2759).—Plasma (10 c.c.), distilled water (14 c.c.), and sulphuric acid (d 1·84, 2 c.c., diluted 1 : 4) are heated at 120° in an autoclave for 30 min.; when cold, the mixture is treated with sodium carbonate and mercuric chloride (dropwise), then sodium carbonate to a violet coloration of purple bromocresol paper, filtered, and the mercury removed with zinc powder or copper borings, and the sugar determined by Bertrand's method. A. A. Eldridge.

Determination of sugar, uric acid, urea, and creatinine in 1 c.c. of blood. E. S. Rose (J. Amer. Pharm. Assoc., 1928, **17**, 41—42).—The blood is freed from protein and the sugar, uric acid, and urea are determined in the filtrate by slight modifications of the Folin–Wu methods. Creatinine is determined colorimetrically by the reduction of alkaline sodium picrate solution. E. H. Sharples.

Blood-ammonia, its formation and physiological behaviour. J. K. Parnas (XII Int. Cong. Physiol., 1926, 124—126; Chem. Zentr., 1927, i, 2918—2919).—The non-colloidal nitrogenous substance which, by ferment action, yields ammonia directly the blood is withdrawn from the blood-vessels, is present in rabbit's blood to the extent of 2 mg. per 100 c.c., and in human blood to a much smaller extent. The formation of ammonia is independent of the content or addition of amino-acids or urea, but

is related to p_H, temperature, and dilution. For the uterine veins of pregnant rabbits the increase of ammonia content is significant. Only portal blood contains relatively much ammonia. Anoxæmia increases the ammonia content. During death blood-ammonia increases on account of anoxæmia; after death further increase is due to its production from its precursor. A. A. ELDRIDGE.

Ammonia of human blood. E. ADLER and K. SCHWERIN (Klin. Woch., 1927, **6**, 1188—1189; Chem. Zentr., 1927, ii, 709—710).—The ammonia content (actual) of human blood 5—6 min. after withdrawal is 0·02 mg. per 100 c.c., whilst that (virtual) of sterile blood kept at 37° for 24 hrs. is 2 mg. Violent muscular exercise has no effect on the values, but individuals with marked cyanosis or moribund give high actual values (0·091 mg.). Blood-ammonia values are independent of the variations in urinary ammonia elimination. Insulin does not influence the blood-ammonia value; in four of five cases of carcinoma low virtual and fairly high actual values were obtained. A. A. ELDRIDGE.

Test for ergothioneine and its determination in simple solution and in blood-filtrates. G. HUNTER (Biochem. J., 1928, **22**, 4—10).—When a solution of sodium carbonate and sodium acetate, mixed with a solution containing ergothioneine, is added under specified conditions to a diazotised sulphanilic acid solution, a clear yellow colour develops. On addition, after 30 seconds, of strong sodium hydroxide solution to this mixture a red colour with a purple tinge is produced. By this specific test ergothioneine can be detected in a dilution of about one in five millions. Quantitative results can be obtained by matching against standards made from known amounts of ergothioneine or against phenol-red standards. Determinations of ergothioneine have been carried out on bloods from various animals. The protein-free blood-filtrates are prepared by the tungstic acid method of Folin and Wu. S. S. ZILVA.

Micro-determination of adenine nucleotide content of blood. M. V. BUELL and M. E. PERKINS (J. Biol. Chem., 1928, **76**, 95—106).—Whole blood is freed from proteins with tungstic acid; adenine nucleotide is precipitated from the filtrate with excess of uranyl nitrate; the precipitate is hydrolysed with dilute sulphuric acid, the solution freed from uranium, and the adenine precipitated as the silver compound in presence of gelatin; the resulting solution is compared nephelometrically with a similarly treated standard solution of adenine. The error of the method is 2—3%. Figures are given for the adenine nucleotide content of the bloods of various species, the amounts ranging from 2—3 mg.% for ox blood to 60—90 mg.% for pigeon blood. C. R. HARINGTON.

Determination of amino-acids in blood: Folin's method. S. H. EDGAR (Biochem. J., 1928, **22**, 162—167).—Figures have been obtained with Folin's colorimetric method (A., 1922, ii, 540) which varied according to the alkalinity of the solutions. The relative rates of change have been investigated. The rate of increase of the amino-acid-nitrogen falls gradually to give a constant value at an alkalinity higher than that used by Folin. S. S. ZILVA.

Determination of oxalic acid in blood, urine, etc. J. KHOURI (Bull. Soc. Chim. biol., 1927, **9**, 957—960).—See A., 1927, 689.

Composition of the blood of children. G. DE TONI (Clin. pediatr., 1926, **8**, 449—493; Chem. Zentr., 1927, ii, 276).—A system of analytical methods is described. A. A. ELDRIDGE.

Inorganic substances in human blood. I. Cation and anion content of normal serum. W. H. JANSEN and A. M. LOEW (Deuts. Arch. klin. Med., 1927, **154**, 195—220; Chem. Zentr., 1927, i, 3099).—Average, minimum, and maximum values (mg.%) for human blood are: (cations) sodium 320, 315, 350; potassium 20, 18, 22; calcium 10·2, 9·4, 11·0; magnesium 2·34, 1·8, 2·8; (anions) chlorine 360, 335, 370; phosphorus 13, 10·1, 14·5; sulphur 141·5, 117, 166·6; ratio sodium : potassium 16·5, calcium : magnesium 4·0—5·0; potassium : calcium 2·0. At an average carbon dioxide tension of 40 mm. the carbonic acid capacity is 118·6 mg.% CO_2. The chloride : hydrogen carbonate quotient is 2·2. A. A. ELDRIDGE.

Calcium, magnesium, and potassium content of muscular tissue and blood. M. CAHANE (Compt. rend. Soc. Biol., 1927, **96**, 1168—1169; Chem. Zentr., 1927, ii, 709).—In old animals (guinea-pigs, rabbits, dogs, cats) the calcium content of the muscular tissue and blood is subnormal, and that of magnesium less markedly so, whilst the potassium content undergoes no regular change. A. A. ELDRIDGE.

Variations in serum-calcium. P. MEGLITZKY (Z. ges. exp. Med., 1927, **55**, 13—16; Chem. Zentr., 1927, ii, 589).—In hunger, the serum-calcium of cats rises to 180% of the normal value, and later falls to subnormal values. Nephrectomy causes a rapid increase, followed by a premortal fall. Mercuric chloride poisoning and splenectomy cause a fall. A. A. ELDRIDGE.

Condition of serum-calcium and its pathological significance. K. KLINKE (Klin. Woch., 1927, **6**, 791—794; Chem. Zentr., 1927, i, 3203).—Calcium is present in serum in the following forms: ionised; soluble complex or molecular salt; salt adsorbed on protein. The three forms are not only in equilibrium, but also are related chemically. A. A. ELDRIDGE.

Condition of calcium in serum. A. NITSCHKE (Biochem. Z., 1928, **192**, 123—127).—The equilibrium constant of saturated solutions of calcium hydrogen carbonate, determined in dialysis experiments by application of the Donnan theory, is $K=[Ca^{\cdot\cdot}][HCO_3']/[H^{\cdot}]=2570$ at 37°. The ionised calcium at p_H 7·35, HCO_3' 67·2 vol.-% is therefore 14·5 mg.-%. The equilibrium constant for a similar solution of calcium phosphate at 37° is $K=[Ca^{\cdot\cdot}][HPO_4']/[H^{\cdot}]=67\times10^{-7}$. In serum at p_H 7·35, phosphorus content 3·7 mg.-%, and calcium content 10 mg.-%, the calcium is present 2·4 mg. as molecular calcium hydrogen phosphate, 5·6 mg. in the ionised form, and about 2 mg. as protein-calcium (cf. A., 1926, 422, 1051). P. W. CLUTTERBUCK.

Conductivity of aqueous salt solutions containing calcium hydrogen carbonate. A. NITSCHKE (Biochem. Z., 1928, **192**, 128—131).—Considerably greater ionisation is detected by conductivity measurements in aqueous solutions containing calcium hydrogen carbonate than appears from Rona's expression (A., 1913, i, 544). For such solutions the mean equilibrium constant at 37° is 3030, a value agreeing fairly well with that obtained by the use of the Donnan theory, 2570 (see preceding abstract).

P. W. CLUTTERBUCK.

Determination of the alkali reserve of the blood. S. P. SUNER (XII Int. Cong. Physiol., 1926, 135—136; Chem. Zentr., 1927, ii, 305).—The blood (10 c.c.) is centrifuged for 10 min. with potassium oxalate (20 mg.), and 4 c.c of plasma mixed with 16 c.c. of distilled water. The p_H is determined electrometrically before and after the addition of 0·1 c.c. portions of 0·1N-hydrochloric acid. A. A. ELDRIDGE.

Comparative buffering power of blood and body fluids. E. GELLHORN (Pflüger's Archiv, 1927, **216**, 253—266; Chem. Zentr., 1927, i, 2920—2921).—An examination of body fluids of echinoderms with respect to acid-neutralising and buffering power, and nitrogen content. A. A. ELDRIDGE.

Copper in human blood-serum. O. WARBURG (Klin. Woch., 1927, **6**, 1094—1095; Chem. Zentr., 1927, ii, 590).—Human blood serum contains loosely-combined copper in relatively large quantities (1—2 × 10^{-3} mg./c.c.), 0·2—0·4% of the total quantity of iron. The copper can be determined colorimetrically by means of ferrocyanide, or by measuring its catalytic effect on the oxidation of cysteine by atmospheric oxygen; by the latter method 10^{-5} mg. can be detected, and the effect due to copper can be readily differentiated from effects due to iron and manganese.

A. A. ELDRIDGE.

Micro-determination of chlorine and iron in blood and other liquids. F. H. SMIRK (Biochem. J., 1928, **22**, 201—207).—The determinations can be carried out by this method on 0·02—0·01 c.c. of the physiological fluid if the prescribed conditions are fulfilled. The principles of the methods are similar to those already described (*ibid.*, 1926, **21**, 31; Fowweather, A., 1926, 443). S. S. ZILVA.

Spreading into a unimolecular layer as a method for the determination of blood-fat. E. GORTER and F. GRENDEL (Biochem. Z., 1928, **192**, 431—456).—The usual Langmuir–Adam method is used for measurements of unimolecular layers of a variety of oils, sterols, phosphatides, and natural fats and is adapted for the determination of the total-blood-fat and of the fractions obtained after extraction with light petroleum. The total blood-fat may be determined with small quantities (0 1—0·2 c.c.) of blood with an accuracy of 1%, but the light petroleum extract from this amount of fat is too small to give a sufficiently large surface for measurement. The material extractable by light petroleum is therefore obtained by difference of the total fat and the fat remaining after light petroleum extraction.

P. W. CLUTTERBUCK.

Reaction of blood in the determination of sex. Importance of manganese mixtures in a reaction for the determination of sex. W. W. PRÁWDICZ-NEMINSKI (Biochem. Z., 1928, **192**, 303—323).—A study of the Manoilov reaction for the determination of sex shows that the reagents alone, without addition of blood, can give the whole series of results described as "male," "female," etc., reactions. Variation of the concentration of hydrochloric acid from 9·52% to 0·1N gives all these reactions, the rôle of the acid being not limited to the change of p_H but being chiefly that of forming ozone and chlorine by reaction with permanganate. The type of reaction obtained in the presence of organic substances then depends on their oxidisability. P. W. CLUTTERBUCK.

Influence of X-rays on certain blood constituents. A. GIGON and M. LUDIN (Schweiz. med. Woch., 1926, **56**, 814—816; Chem. Zentr., 1927, ii, 278).

Catalase value and catalase index of ox blood. T. RADEFF (Berlin tierarztl. Woch., 1926, **42**, 781—782; Chem. Zentr., 1927, ii, 277).—The normal catalase value is about 8·54; in disease it is reduced without reduction of the catalase index (catalase value/erythrocyte value). A. A. ELDRIDGE.

Action of arsenic on blood ferments. I. PARFENTJEV (Vestn. mikrobiol. epidemiol., 1926, **5**, 269—275; Chem. Zentr., 1927, ii, 446).—Amylase and peroxidase are not inhibited by arsenious oxide *in vitro*; catalase is markedly inactivated by 0·1%, but very dilute solutions stimulate the action of catalase and peroxidase. Only a high content is disadvantageous to lipase. In acute poisoning of rabbits *per os* there is no disturbance of fermentative processes.

A. A. ELDRIDGE.

Action of arsenic and related elements. I. Significance of oxygen for arsine-hæmolysis. R. LABES (Arch. exp. Path. Pharm., 1928, **127**, 125—147).—Hæmolysis of a suspension of red blood-cells by arsine does not occur, or takes place very slowly, if oxygen is removed from the corpuscles by a current of an inert gas (hydrogen or nitrogen) or carbon monoxide, or by reduction with sodium sulphite. The addition of a culture of paramœcia (as a reducing agent) to the red cell suspension has a similar effect. Arsine-hæmolysis thus requires the presence of oxygen and this is supplied by the oxyhæmoglobin. The significance of these findings is discussed but no definite conclusions can be reached. Within the limits c_H 4×10^{-7} to $0·25 \times 10^{-7}$ with phosphate buffers, c_H has no significant influence on arsine-hæmolysis, but high concentrations of phosphate tend to retard hæmolysis. A. WORMALL.

Hæmolysis. PIETTRE and CHRÉTIEN (J. Pharm. Chim., 1927, [viii], **6**, 5—20).—The mechanism of hæmolysis is discussed from the authors' results on the hæmolytic power induced in sheep's serum by the injection of stroma solutions prepared by dissolving dried, pulverised stroma from various animals in alkali. The action of sodium chloride as a hæmolytic factor is rejected, except with reference to its action on the proteins present, whilst the existence of a sensitiser is postulated as a definite substance which forms a stable compound with the stroma-protein.

E. A. LUNT.

Influence of hydrogen-ion concentration on saponin hæmolysis. L. Kofler and Z. Lazar (Arch. Pharm., 1927, **265**, 610—623).—There is disagreement between Mond (A., 1926, 856) and earlier workers regarding the influence of hydrogen-ion concentration on hæmolysis by saponins, but this disagreement is now found to be only apparent. Actually, different saponins are differently affected, and they can be classed in two groups. In the first group the hæmolytic index is at its lowest when the medium has p_H 8—9 and rises on each side of this point, at first slowly, later quickly, until at p_H 5·6 or p_H 10·48 acid hæmolysis or alkaline hæmolysis, respectively, supervenes. To this group belong "saponin pur. albiss.," digitonin, smilacin, cyclamin, horse-chestnut saponin (Merck), the saponins from *Primula veris* and *P. eliator*, quillaia saponin, and *Gypsophila* saponin. In the second group the hæmolytic index is the lower the higher the figure for p_H, *i.e.*, there is practically no hæmolytic action until just before alkaline hæmolysis takes place, whereas on the acid side the hæmolytic index is very high. To this group belong "saponin-gereinigt" (Kahlbaum), senegrin, and sapindus saponin (two commercial preparations). The behaviour of this second class is probably to be accounted for on chemical grounds. In some of the above tests parallel experiments were made with products specially purified by electro-dialysis. In all the experiments cow's corpuscles were used; they were washed, and the suspensions were made up with Jarisch's phosphate buffer solution. The hæmolytic action of saponins is different according as washed or unwashed blood corpuscles are used; moreover, the effect of the serum present depends on the saponin used, thus, when digitonin acts on washed blood corpuscles it is about 11% more active than when it acts on unwashed corpuscles, whereas the difference when *Gypsophila* saponin (purified by electro-dialysis) is used is 452%. This effect of serum is attributed to the presence of cholesterol and other compounds, and to the buffering action on the already slightly acid saponin solution. Experiments showed that surface activity of saponin solutions and their hæmolytic action bore no relationship to one another.

W. A. Silvester.

Pancreas as a source of the fibrin ferment in blood. W. N. Boldyrev and A. W. Boldyrev (XII Int. Cong. Physiol., 1926, 22—23; Chem. Zentr., 1927, i, 3015).—Total or partial extirpation of the pancreas increases the coagulation time. Later the blood regains its power of coagulation.

A. A. Eldridge.

Anticoagulant action of peptone *in vitro*. J. O. W. Barratt (Biochem. J., 1928, **22**, 230—235).—Peptone acts on fibrinogen in citrated blood-plasma, diminishing its amount. It is without action on thrombin.

S. S. Zilva.

Heparin. W. H. Howell (XII Int. Cong. Physiol., 1926, 80; Chem. Zentr., 1927, ii, 277).—Heparin, an anticoagulant prepared from liver, contains calcium and sulphate, but no protein, amino-acid, or phosphorus. It may be a conjugated glycuronic acid of glucosidic structure.

A. A. Eldridge.

Chemical changes in muscle. I. Methods of analysis. E. Boyland (Biochem. J., 1928, **22**, 236—244).—The minced muscle is extracted with cold alcohol. Glycogen is determined by a modified Pflüger's method in the alcohol-insoluble residue. After removing the alcohol from the filtrate, the fraction is cleared of lipins and protein by precipitation either with ammonium sulphate or with phosphotungstic acid. In the first procedure the solution is extracted with ether to remove the lactic acid and the sugars are determined by Hagedorn and Jensen's method (A., 1923, ii, 265) in the extracted solution after hydrolysis. In the second procedure the hexoses are removed from the solution by precipitation with copper sulphate and calcium hydroxide. For the determination of lactic acid a modified Clausen's method in which steam-distillation was combined with oxidation was employed.

S. S. Zilva.

Combination of potassium in muscle. E. Raab (Pflüger's Archiv, 1927, **216**, 540—548; Chem. Zentr., 1927, ii, 593).—The results of Neuschloss (*ibid.*, **213**, 19) are not confirmed. In frog gastrocnemius, toad, and rabbit muscle all th potassium was diffusible with sodium chloride solution.

A. A. Eldridge.

Vasodilator constituents of tissue extracts. Isolation of histamine from muscle. W. V. Thorpe (Biochem. J., 1928, **22**, 94—101).—Fresh ox muscle was thoroughly extracted with 60% alcohol and after removing the alcohol, the fat-free aqueous extract was cleared with basic lead acetate, and the phosphotungstates were prepared. The latter were extracted with acetone, whereby the active substance was removed. On further fractionation by the Kossel-Kutscher method the histamine was found in the histidine fraction. After allowing the carnosine nitrate which formed the bulk of this fraction to crystallise from an alcoholic solution, the mother-liquor was dried with baryta and extracted with alcohol. After removal of alcohol and barium a crystalline precipitate was produced by the addition of picric acid. From this precipitate histamine dipicrate was isolated by fractional crystallisation. The amount of active substance obtained at the end of each stage in the purification was estimated by the action on the cat's blood-pressure. The distribution of the depressor substances in sterile extracts, in which hydrolytic changes were avoided, from a number of organs of horse and ox has also been determined. The whole of the depressor activity of the alcoholic extract of muscle is most probably due to histamine.

S. S. Zilva.

Microchemical studies on the nervous system. I. R. M. May (Bull. Soc. Chim. biol., 1927, **9**, 970—981).—See A., 1927, 986.

Metallic lakes of the oxazines (gallamin-blue, gallocyanine), and cœlestin-blue as nuclear stain substitutes for hæmatoxylin. F. Proescher and A. S. Arkush (Stain Tech., 1928, **3**, 28—38).—The dyes are dissolved in 5% aqueous ferric ammonium sulphate solution. The solutions are boiled for 2—3 min., cooled, and filtered. The iron lakes stain nuclei a deep blue or bluish-black in 3—5 min. No differentiation with acid is required. Cœlestin-blue

gives the most stable solution and is recommended as a routine nuclear stain. The protoplasm remains practically colourless and counter-staining with acid dyes (ethyleosin, orange-G, fuchsin) gives results similar to a hæmatoxylin stain. Staining of fat with Sudan, scarlet-red, etc. does not interfere with nuclear staining by these dyes. They are superior to hæmatoxylin as stains for the central nervous system. The nature of the staining process is discussed.

H. W. DUDLEY.

Iodine content of thyroid in the Japanese fœtus, the new-born child, and at the age of puberty. T. NOSAKA (Folia endocrinol. japon., 1926, **2**, 1—17).

Adrenaline content of the suprarenals of various mammals. A. LEULIER and P. GOJON (Compt. rend. Soc. Biol., 1927, **96**, 547—548; Chem. Zentr., 1927, ii, 102).—The order is: rabbit (0·015%), sheep, pig, goat, cow, ox, horse, steer (0·246%). Keeping the tissue over sulphuric acid in a vacuum for 24 hrs. increases the adrenaline content. A. A. ELDRIDGE.

Unsaponifiable matter from the stomach oil of *Scymnorhinus lichia*. E. D. KAMM (Biochem. J., 1928, **22**, 77—79).—The unsaponifiable matter of the oil consists mainly (98%) of squalene, butyl alcohol (0·28%), and a residue (0·96%) which is chiefly selachyl alcohol. The bulk of the squalene was obtained by distilling the oil at 228—230°/2 mm. A much smaller yield of this compound was derived from the unsaponifiable fraction by distillation. Batyl alcohol crystallised on keeping from the fraction which distilled over from the unsaponifiable fraction at 190—225°/0·55 mm. The residue of the unsaponifiable fraction yielded batyl alcohol on hydrogenation. S. S. ZILVA.

Biological significance of unsaponifiable matter of oils. III. Fish-liver oils. H. J. CHANNON (Biochem. J., 1928, **22**, 51—59).—The liver oils of a number of fish were investigated. The oils of the *Selachii* differ from those of the *Teleostei* in that, in many cases, very large amounts of unsaponifiable matter occur in the former. In the liver oils of the *Selachii* the higher the percentage of unsaponifiable matter in a given oil, the lower is the percentage of sterol in that fraction. Squalene was not detected in the liver oils of any of the fish studied save in those from three members of the *Squalidæ* family. The origin of squalene is discussed. S. S. ZILVA.

Lipin distribution in normal and abnormal liver. I. Ox liver. E. R. THEIS (J. Biol. Chem., 1928, **76**, 107—114).—Normal ox liver contains 4·6% of total lipins, of which 55% are phospholipins and 45% fats; figures are given for the distribution of the various fatty acids, indicating a high proportion of acids with 4 double linkings. In liver showing the signs of fatty degeneration, both the total amount and the iodine number of the phospholipin fraction are much decreased. C. R. HARINGTON.

Composition of intraocular fluids. I. Ox and horse. E. TRON (Arch. Ophth., 1926, **117**, 677—692; Chem. Zentr., 1927, ii, 586).

Composition of human milk. G. D. ELSDON (Analyst, 1928, **53**, 78—82).—Maximum, minimum, and average figures for total solids, solids-not-fat, and fat are recorded for 529 samples of human milk from 86 subjects. The proteins gradually diminished from 2·2% for 1 day to 1·23% for 50 days to 9 months, and the ash from 0·37% to 0·2%, whilst the fat increased. Average compositions based on recorded figures are taken as: 1—7 days, fat 3·0, protein 2·1, lactose 6·8, ash 0·3; 7—28 days, 3·5, 1·6, 6·8, and 0·25; 1—9 months, 3·5, 1·3, 6·9, and 0·22%. Mixed fat from samples taken early in lactation had iodine value 35·9, Reichert–Meissl–Wollny value, 3·4, Polenske value, 1·9, and Kirschner value 2·0.

D. G. HEWER.

Milk composition and energy. O. R. OVERMAN and F. P. SANMANN (Illinois Sta. Rep., 1926, 91—92).—Formulæ are given for determining the energy value of milk. The true heats of combustion of butter fat, milk protein, and lactose probably lie between Anderson's and Abderhalden and Hammarsten's values. CHEMICAL ABSTRACTS.

Composition of milk of cows receiving cod-liver oil. E. C. V. MATTICK (Biochem. J., 1928, **22**, 144—149).—The addition of cod-liver oil to the diet of the cow changes the chemical composition of the milk. An increase in the percentage of total calcium and in the time of coagulation of the milk by rennet is particularly marked. This is not the case when arachis oil is added. S. S. ZILVA.

Effect of heat on milk. IV. Iodine content. H. E. MAGEE and A. E. GLENNIE (Biochem. J., 1928, **22**, 11—14).—Heat causes the disappearance by volatilisation of 20% or more, according to the duration of heating, of the total iodine of separated milk. In the case of boiled milk the evenness of the losses suggest that limit of loss produced by heat is nearly reached. The loss of iodine is due to volatilisation, since it does not occur after potassium hydroxide has been added to the milk. Of the iodine of cow's milk 83% is diffusible. This proportion is not disturbed by heating the milk. Milk-fat contains more iodine than an equal volume of separated milk. The iodine associated with the fat is most probably chemically bound with the unsaturated fats and is therefore not diffusible. S. S. ZILVA.

Elimination of yellow vegetable colouring matters in human milk. H. PAFFRATH and A. CONSTEN (Z. Kinderheilk., 1926, **42**, 51—59; Chem. Zentr., 1927, ii, 110).—Carotin and xanthophyll were separately determined in human milk by a colorimetric method. The use of vegetables containing carotin or xanthophyll increases the amount of those substances, respectively, in the milk. Both are present when white vegetables are employed, and must in this case originate from animal foods.

A. A. ELDRIDGE.

Nature of the protein surrounding fat globules of milk. R. W. TITUS, H. H. SOMMER, and E. B. HART (J. Biol. Chem., 1928, **76**, 237—250).—Determinations of nitrogen distribution, sulphur and phosphorus content, and optical rotation, and precipitin tests indicate that the protein of the envelopes of the fat globules of milk is probably caseinogen.

C. R. HARINGTON.

Determination of constituents of bile after injection and absorption of sodium hydrogen carbonate. P. Carnot and Z. Gruzewska (Compt. rend. Soc. Biol., 1927, **96**, 912; Chem. Zentr., 1927, ii, 590—591).—The only changes are an increase in the carbon dioxide and a decrease in the pigment content. A. A. Eldridge.

Surface activity of bile-acids. I. N. A. Krajevski and N. Vedenski (Biochem. Z., 1927, **191**, 241—249).—Curves showing the variation of surface tension of aqueous solutions of sodium glycocholate and taurocholate with temperature and concentration are obtained. The surface tension of these solutions in relatively high concentration decreases linearly with temperature, the temperature coefficient and also the total surface energy (E) being smaller than for pure water. The surface tension of sodium glycocholate in small concentration ($0{\cdot}012M$) decreases with the temperature according to a typical curve. The surface activity (G) of the sodium salts of both acids in small concentration is very large and decreases rapidly with increase of concentration. The adsorption limit is attained very rapidly for both solutions (cf. A., 1927, 1104). P. W. Clutterbuck.

Colorimetric determination of bile salts in duodenal fluid. M. Chiray and L. Cuny (J. Pharm. Chim., 1928, [viii], **7**, 97—106).—The method of Herzfeld and Haemmerli (A., 1925, i, 722) has been quantitatively studied and modified.

E. H. Sharples.

Nephelometric determination of trypsin and pepsin in gastric and intestinal juice. Stability of trypsin. P. Rona and H. Kleinmann (Klin. Woch., 1927, **6**, 1174—1177; Chem. Zentr., 1927, ii, 721).—The authors' method depends on the addition of very dilute ferment solutions to very dilute serum-albumin or sodium caseinate solutions brought to a suitable acidity by the addition of acids or buffers. The reaction takes place at 37°; samples are taken at intervals, the ferment action being immediately stopped by heating or by changing the p_H. A suitable reagent is then added to the solutions to produce a stable, homogeneous opalescence which is proportional to the albumin content. The samples are compared nephelometrically with that taken before the addition of ferment, due allowance being made for change of concentration. A. A. Eldridge.

Buffering power of urine. S. P. Suner (XII Int. Cong. Physiol., 1926, 135; Chem. Zentr., 1927, ii, 279).—The buffering power of urine, which is much greater than that of blood, is a function almost exclusively of the phosphate content. The buffering curve, a straight line, is constant for an individual, but varies among individuals. A. A. Eldridge.

Relation between colloids, surface tension, and p_H of urine. S. P. Suner (XII Int. Cong. Physiol., 1926, 135; Chem. Zentr., 1927, ii, 279).—On acidification of normal urine, the fall in surface tension runs parallel with that of p_H; with urine from which colloids have been removed with animal charcoal, the surface tension is unchanged by progressive acidification. A. A. Eldridge.

Urine analysis. A. Jolles (Arch. Pharm., 1927, **265**, 717—720).—Piorkowski's paper (*ibid.*, 1926, **264**, 460) is commented upon. When thymol is used as a preservative there is a risk that erroneous results will be obtained in the Obermayer, Jaffe, or Salkowski tests. The violet colour due solely to the thymol is, however, easily distinguished as being such (cf. Jolles, Z. physiol. Chem., 1913, **87**, **310**). Piorkowski recommends Spiegler's test for albumen, but this test sometimes gives a positive indication with normal urine, and sometimes fails to indicate albumin even when it is present, because there is a lack of sodium chloride in the urine. The author recommends a modified test, of which details are given, but suggests that reliance should not be placed on a single reagent. As confirmatory tests the ferrocyanide, acetic acid, sulphosalicylic acid, and Spiegler (as modified) are recommended; the last of these is the most sensitive.

W. A. Silvester.

Uric acid determination in urine as a test of kidney function. H. Lucke (Klin. Woch., 1927, 6, 1275; Chem. Zentr., 1927, ii, 1380).

Manganese in urine. R. F. McCrackan and E. Passamaneck (Arch. path. lab. med., 1926, **1**, 585—589; Chem. Zentr., 1927, ii, 279).—By colorimetric determination in the ash of normal urine evaporated with nitric acid, 0·02 mg. [% ?] of manganese was found. A. A. Eldridge.

Determination of hippuric and phenaceturic acids in urine. E. J. Wayne (Biochem. J., 1928, **22**, 183—187).—The urine is boiled with sodium hydroxide and hydrogen peroxide to liberate the benzoic and phenylacetic acids. After neutralisation and treatment with bromine the solution is filtered, the filtrate acidified with sulphuric acid and extracted with ether. The ethereal extract is washed with an acidified saturated solution of sodium chloride, transferred to a special apparatus in which the solvent is evaporated and the acids are sublimed and trapped in a cotton-wool plug. The sublimed acids after being weighed are washed out with 90% alcohol and titrated. The titration serves as a check on the weight if the pure acids are present alone and with mixtures of benzoic and phenylacetic acids it serves to determine the relative amount of each. Duplicate experiments on the different samples of urine by this method giving 0·2—0·3 g. of sublimate were found to agree to within 0·07 g. Using a dog's urine of known hippuric acid content an average of 97% of added hippuric acid was recoverable as benzoic acid.

S. S. Zilva.

Determination of urobilinogen in urine and fæces. A. Adler (Deuts. Arch. klin. Med., 1927, **154**, 238—248; Chem. Zentr., 1927, i, 3213).—Isolation of urobilinogen is necessary for its accurate determination; a suitable extraction apparatus has been constructed. A. A. Eldridge.

Kahn's albumin-*A* reaction in serum. K. Posener and W. Behrens (Klin. Woch., 1927, **6**, 853—854; Chem. Zentr., 1927, ii, 148).—A discussion of the diagnostic value of Kahn's reaction.

A. A. Eldridge.

Deposition of calcium and iron in the brain. E. C. Eaves (Brain, 1926, **49**, 307—332; Chem. Zentr.,

1927, ii, 273).—Certain pathological conditions lead to an excessive storage of calcium and iron in the brain. A. A. ELDRIDGE.

Lactic acid content of pathological discharges. R. SCHELLER (Munch. med. Woch., 1927, 73, 1879—1881; Chem. Zentr., 1927, i, 3100). A. A. ELDRIDGE.

Analysis of urethral calculus. E. LOBSTEIN (J. Pharm. Chim., 1927, [viii], 6, 156—159).—The calculus consisted principally of calcium phosphate and contained small amounts of ammonium magnesium phosphate, calcium carbonate, ammonium urate, and cystine. E. A. LUNT.

Activity of catalase in normal and neoplastic tissues. A. H. ROFFO and B. BARBARA (Bol. inst. med. exp., 1926, 2, 599—604; Chem. Zentr., 1927, ii, 446).—The catalase activity decreases in organs in the order liver, kidney, heart, lungs, spleen, and appears to be increased in the organs of cancerous animals. The oxidation–reduction relation is disturbed, the reduction phenomena being more marked in neoplasms. A. A. ELDRIDGE.

Occurrence and detection of arginine in cystinuria. F. A. HOPPE-SEYLER (Deut. Arch. klin. Med., 1927, 154, 97—106; Chem. Zentr., 1927, i, 3100).—Arginine was detected in the urine in cystinuria by precipitation with flavianic acid, decomposition of the precipitate with barium hydroxide, purification with phosphotungstic acid, and treatment of the filtrate with cupric carbonate, forming *d*-arginine-copper nitrate. A. A. ELDRIDGE.

Glycolysis. I. Glycolysis in blood of normal (non-diabetic) dogs. B. ROHNY (Biochem. Z., 1928, 192, 1—7).—Glycolysis in normal (oxalated) blood proceeds far more rapidly at 37° than at lower temperatures, but is inhibited at 56°. Glycolysis also takes place in serum, but is decreased or compensated for, especially in the first hour, by a parallel formation of sugar. Since the blood-sugar concentration is far greater in serum separated from clot than in serum in contact with clot, it is considered that clot contains a substance inhibiting increase of sugar concentration. P. W. CLUTTERBUCK.

Glycolysis. II. Glycolysis in the blood of diabetic (depancreatised) dogs. Z. ASZÓDI (Biochem. Z., 1928, 192, 8—13).—The processes of formation of sugar and of glycolysis (cf. preceding abstract) occur similarly in the blood of both normal and diabetic (depancreatised) dogs and the glycolytic enzyme remains active in presence of oxalate, its activity increasing at temperatures up to 37° and being inhibited at 56°. P. W. CLUTTERBUCK.

Quantitative variation of alloxuric substances in urine of diabetics in connexion with insulin therapy. G. GIORGI (Prob. nutriz., 1926, 3, 41—54; Chem. Zentr., 1927, ii, 279).—Administration of insulin causes an immediate increase in the excretion of alloxuric substances. A. A. ELDRIDGE.

Behaviour of the blood-sugar in diabetes after administration of various carbohydrate carriers *per os*, with and without insulin. H. MAUERHOFER (Z. klin. Med., 1927, 105, 641—660; Chem. Zentr., 1927, ii, 710).—Oatmeal appears to reduce glycosuria; the effect of barley is less marked and is followed by sugar excretion. A. A. ELDRIDGE.

Action of nickel and cobalt salts on the hypoglycæmic effect of insulin on diabetics. M. LABBE, H. ROUBEAU, and F. NEPVEUX (Compt. rend., 1928, 186, 181—183).—Injections of nickel and cobalt chlorides into diabetic and normal human subjects have no effect on the blood-sugar, nor do these salts increase the effect of insulin in human diabetics as they do with dogs and rabbits (cf. A., 1926, 869). B. W. ANDERSON.

Iodine–starch test of body fluids. Deductions from tests of external secretion of pancreas in diabetes, in diseases of the gall-bladder and pancreas, and in a normal condition. A. BASSLER (Arch. Int. Med., 1928, 41, 18—41).—Suggested modifications of the test proposed by the author (*ibid.*, 1925, 35, 162) for pancreatic activity are discussed. The results are given of the application of the test to many types of body-fluid and it is claimed that the test is valuable clinically. Emphasis is laid on the power of sugar and dextrin to combine with iodine and on the effect of this on the determination of diastase. W. O. KERMACK.

Coefficient of dysdeaminisation. Relation between certain non-protein nitrogenous substances of the blood as evaluation of ureogenetic function. P. CRISTOL, A. PUECH, and TRIVAS (Compt. rend. Soc. Biol., 1927, 96, 676—677; Chem. Zentr., 1927, i, 2749).—The "coefficient of dysdeaminisation" is the relation (polypeptide- + amino-acid - nitrogen)/(polypeptide - + amino - acid - + urea-nitrogen); its value (30—35%) is lowered in renal disease and raised in hepatic derangement. A. A. ELDRIDGE.

Lactic acid in blood, particularly in hepatic disease. G. NOAH (Klin. Woch., 1927, 6, 1465—1466; Chem. Zentr., 1927, ii, 1362).—The blood-lactic acid of rabbits is occasionally raised by the injection of a lethal quantity of phosphorus. In human liver disease the (fasting) value is normal, but high values were finally obtained in two cases of atrophy. Blood from a malignant tumour showed a high lactic acid and a low sugar value. A. A. ELDRIDGE.

Technique and interpretation of the van den Bergh test [for bilirubin]. R. E. STEEN (Irish J. Med. Sci., 1927, [vi], No. 21, 573—582).—A modified technique for the detection of hepatic bilirubin is described. CHEMICAL ABSTRACTS.

Iodine content of mussel shells [and its relation to] the goitre problem. II. E. WILKE-DORFURT (Biochem. Z., 1928, 192, 73—82).—The amount of iodine in the shells of a large number of different kinds of these animals is tabulated and discussed in relation to their source and to the goitre problem (cf. A., 1927, 642). P. W. CLUTTERBUCK.

Possible increase of guanidine in blood in hypertension. R. H. MAJOR and C. J. WEBER (Arch. Int. Med., 1927, 40, 891—899).—By the use of a modification of the colorimetric method previously described by the authors (cf. Bull. Johns Hopkins

Hosp., 1927, **40**, 85) small increases in the amount of guanidine in the blood have been found in cases of arterial hypertension and larger increases in cases of uræmia. W. O. Kermack.

Amino-acid content of blood of children in health and in disease. S. H. Edgar (Biochem. J., 1928, **22**, 168—172).—The amino-acid nitrogen in fasting bloods is consistently lower than in non-fasting. The mean difference is 0·74 mg.-%. In rheumatism and chorea with or without carditis there is no change, in nephritis, on the other hand, and still more in renal and coeliac infantilism there is a lowering in the amino-acid nitrogen. S. S. Zilva.

Changes in catalase, lipase, and amylase content of blood of infants in digestive disturbances. M. Manicatide, A. Dambaviceanu, and A. Rosianu (Compt. rend. Soc. Biol., 1927, **96**, 1243—1244; Chem. Zentr., 1927, ii, 707).—Infantile cholera and dyspepsia activate catalase, but do not affect lipase and amylase; athrepsia and dyspepsia with dystrophia reduce the activity of the lipase, the catalase and amylase remaining unaffected. During recovery the activity of the lipase and amylase is increased. A quinine-resistant lipase was found in the serum in infantile cholera. A. A. Eldridge.

Hydrogen-ion concentration of fæces of rachitic children. T. Redman (Biochem. J., 1928, **22**, 15—21).—There was no definite correlation between the different stages of rickets and the p_H values of the fæces of the patients under the conditions described. The p_H determinations were made by means of the quinhydrone electrode. S. S. Zilva.

Chlorides and inorganic constituents of serum and cerebrospinal fluid in meningitis. G. C. Linder and E. A. Carmichael (Biochem. J., 1928, **22**, 46—50).—The fall of chloride concentration in the cerebrospinal fluid in meningitis is dependent on a similar fall in the chloride concentration of the serum, the relative concentrations in the two remaining the same. The associated disturbances are an increase, sometimes large, of the hydrogen carbonate in both fluids and a small decrease in total base in the cerebrospinal fluid. Sometimes a greater depletion of base occurs in cerebrospinal fluid and in serum, and in such cases the hydrogen carbonate does not rise and may be low. S. S. Zilva.

Potassium and calcium in serum after ingestion of urea. R. E. Mark and E. Kohl-Egger (Zentr. inn. Med., 1927, **48**, 578—584; Chem. Zentr., 1927, ii, 710).—Normally the potassium content of dog's serum shows but slight changes after ingestion of urea, whilst the calcium value is raised and maintained for some time at a high level. In renal insufficiency the potassium content gradually rises and later falls, the calcium content exhibiting no marked change. A. A. Eldridge.

Cause of Andrewes' diazo-test for renal inefficiency. G. A. Harrison and R. J. Bromfield (Biochem. J., 1928, **22**, 43—45).—Andrewes' reaction (Lancet, 1924, i, 590) and Pauly's reaction are not identical. Histamine, tyramine, tyrosine, histidine, tryptophan, indole, and skatole do not give the former reaction. A cyclic amine such as histamine or tyramine cannot therefore be responsible for it (cf. Hewitt, A., 1925, i, 726). Evidence is produced that the substance in uræmic sera responsible for Andrewes' reaction is an indoxyl compound, presumably potassium indoxyl sulphate (indican) or possibly in part indoxyl glycuronate. S. S. Zilva.

Tuberculosis. I. Plasma proteins, cholesterol, and corpuscle volume. L. Eichelberger and K. L. McCluskey (Arch. Int. Med., 1927, **40**, 831—839).—As compared with normal the blood plasma of tuberculous patients shows an increase of fibrinogen and globulin and a decrease in albumin, the total protein being increased. The total cell volume is usually below normal, whilst the cholesterol content of the whole blood may be increased. An increasing or stationary hypercholesterolæmia indicates resistance to the disease. W. O. Kermack.

Glutathione content of organs of tuberculous guinea-pigs. P. Delore (Compt. rend. Soc. Biol., 1927, **96**, 974; Chem. Zentr., 1927, ii, 272).—The glutathione content of the organs of guinea-pigs is not constant, and is not definitely affected by experimental tuberculosis. As with dogs, the liver contains most and the lungs least glutathione. A. A. Eldridge.

Cystinuria in tuberculosis. R. Monceaux (Compt. rend. Soc. Biol., 1927, **96**, 323—324; Chem. Zentr., 1927, i, 3100).—The coefficient neutral/total sulphur is greatly increased in tuberculosis. Neutral sulphur appears in the urine as cystine; it is separated by clarification with lead acetate, removal of the lead with hydrogen sulphide, concentration, extraction with ammonia, concentration, and crystallisation. A. A. Eldridge.

Chlorine and sodium content of organs in uræmia. L. Blum and D. Broun (Compt. rend. Soc. Biol., 1927, **96**, 640—642; Chem. Zentr., 1927, i, 3014).—Uræmia is accompanied by chlorine retention; the sodium content is normal or increased with œdema, but reduced in absence of œdema. The brain and the musculature are particularly considered. A. A. Eldridge.

Basal metabolic rate of students in Sydney, N.S.W. E. M. Hindmarsh (Austral. J. Exp. Biol., 1927, **4**, 225—268).—The basal metabolic rate of 76 subjects has been determined by the gasometer method, by Benedict's oxygen absorption method, and by King's carbon dioxide output method. The methods gave respectively average reductions of 8·9, 9·6, and 6·0% for men and of 10·5, 10·9, and 7·3% for women, compared with the Du Bois standard values. It is suggested that these reductions are due to the more ready muscular relaxation of the students in the warm climate of Sydney. E. A. Lunt.

Regulation of metabolism. V. Hunger metabolism. Dependence of muscular glycogen deposition on the nervous system. VI. Neural regulation of glycogen deposition. E. Wertheimer (Pflüger's Archiv, 1927, **215**, 779—795, 796—803; Chem Zentr., 1927, i, 2570—2591).—Even in severe lack of glycogen, section of the ischiatic nerve or Achilles tendon is not accompanied by mobilisation of glycogen. Adrenaline acts directly

on the liver, but through the nervous system on muscle. In severe hunger the fat deposition in the popliteal space after section of the ischiatic nerve is unchanged. Results with dogs, cats, rabbits, and guinea-pigs are compared. A. A. ELDRIDGE.

Changes in blood and urine of starving puppies. G. W. PUCHER (J. Biol. Chem., 1928, **76**, 319—329).—New-born puppies were deprived of food and water, with the result that the body temperature fell, there was marked retention of carbamide and slight retention of chlorides in the blood, the oxygen and water content of the blood remained unchanged, and the blood-sugar fell to 30 mg.-% or less, without, however, the occurrence of hypoglycæmic convulsions. Puppies 6 weeks old showed similar, but much less marked reactions to starvation. No inanition fever, such as occurs in human infants and is associated with similar changes in the blood, was ever observed in these animals. C. R. HARINGTON.

Pentose metabolism. II. Disposal of *l*-arabinose and of *d*-xylose in the rabbit. R. C. CORLEY (J. Biol. Chem., 1928, **76**, 23—30).—Oral administration of *l*-arabinose, with or without dextrose, caused no change in the blood or urine; after intravenous injection, the excess of arabinose disappeared from the blood within 3 hrs. in the normal or insulin-treated rabbit, but was still marked after 4 hrs. in the rabbit suffering from tartrate nephritis. With oral doses of *d*-xylose up to 2 g. per kg. the maximum concentration attained in the blood and the rate of excretion in the urine was proportional to dosage; larger doses had no increased effect; simultaneous administration of dextrose, and, to a smaller extent, of lævulose, diminished the absorption of xylose. C. R. HARINGTON.

Metabolism of lactose. III. Galactose tolerance in the rabbit. R. C. CORLEY (J. Biol. Chem., 1928, **76**, 31—42).—Similar results were obtained with galactose to those already observed (cf. preceding abstract) with *d*-xylose. In presence of large amounts of dextrose, removal of galactose from the intestine can take place without corresponding increase in the blood; this process of removal is probably not bacterial. A dose of dextrose given subsequently to one of galactose reduced the concentration of the latter in the blood. C. R. HARINGTON.

Effect of muscular work on endogenous tissue catabolism. H. H. MITCHELL and J. H. KRUGER (J. Biol. Chem., 1928, **76**, 55—74).—The endogenous tissue catabolism of rats, as measured by the urinary excretion of creatinine, was not increased by muscular work when the diet contained much carbohydrate and little fat or much fat and little carbohydrate. It follows that, in the presence of sufficient non-nitrogenous food material to meet the energy requirements, tissue breakdown is not a necessary result of muscular work. C. R. HARINGTON.

Chemical changes in the proteins of muscular tissue when passing into rigor. H. R. HEWER, H. JAIRAM, and S. B. SCHRYVER (Biochem. J., 1928, **22**, 142—143).—The experiments were carried out with the gastrocnemius and sartorius muscles of the frog. When the muscle was thrown into boiling 20% hydrochloric acid for hydrolysis immediately after excision it gave a single twitch when coming into contact with the hot vapour or liquid. Under these conditions about 30% of diamino-nitrogen was obtained. If the preliminary twitch was abolished by previous treatment of the animal with either urethane or β-eucaine the figure fell to 26—27%. If, on the other hand, the muscles were allowed to pass into rigor by remaining in a moist chamber for about 20 min. at 40° the diamino-nitrogen rose to 36%. This sank to about 30—31% when the muscles were allowed to pass out of rigor by keeping for several hours at 40°. The results are very analogous to the results obtained by the treatment of gelatin with acids (cf. Knaggs, A., 1923, i, 1143; Schryver and Buston, A., 1927, 785; Thornley, this vol., 81). S. S. ZILVA.

Dehydrogenation of succinic acid. A. HAHN and W. HAARMANN (Z. Biol., 1928, **87**, 107—114).—Fumaric acid is primarily formed when succinic acid is dehydrogenated by muscle tissue in a vacuum in the presence of methylene-blue and is then converted into malic acid by enzymic action. Other products are also formed in smaller amounts, presumably by dehydrogenation of malic acid, but these have not been identified. The criticism by Bach and Michlin (A., 1927, 591) of the theory of dehydrogenation of succinic acid in the muscle-methylene-blue experiments is not supported. A method for determining fumaric acid in the presence of malic and succinic acids is described. A. WORMALL.

Cholesterol. III. Relation of the adrenal gland and the spleen to cholesterol metabolism. F. S. RANDLES and A. KNUDSON (J. Biol. Chem., 1928, **76**, 89—93).—Removal of the spleen or of the adrenal glands has no effect on the cholesterol content of the blood of the rat. C. R. HARINGTON.

Lipin metabolism and constitution. H. MUCH (Arch. Frauenk. Konstit., 1926, **12**, 353—367; Chem. Zentr., 1927, ii, 595).—A discussion. A. A. ELDRIDGE.

Lipin metabolism and generative glands. R. JAFFÉ (Arch. Frauenk. Konstit., 1926, **12**, 368—376; Chem. Zentr., 1927, ii, 282).—A survey. A. A. ELDRIDGE.

Fat metabolism. I. Influence of single foodstuffs on blood-lipins. C. W. MCCLURE and M. E. HUNTSINGER (J. Biol. Chem., 1928, **76**, 1—18).—The nitrogen and dextrose content of the blood were slightly diminished following ingestion of fat (oleic acid or olive oil); the cholesterol and fatty acid content was increased by all types of foodstuff. The iodine numbers of the cholesterol fraction showed a decrease after all types of food, suggesting qualitative variations in the sterols of the blood. The fatty acids of the blood were increased by all foods, whilst the lecithin-phosphorus was affected only by ingestion of oleic acid, which produced an increase. Changes in the iodine number accompanying increase in the fatty acid concentration after ingestion of oleic acid indicate that the increase is not due to the latter acid alone, and in general, the variations in blood-lipins observed in these experiments are ascribed to mobilisation of lipins from the tissues. C. R. HARINGTON.

Oxidation of phenyl-fatty acids in the animal organism. H. S. RAPER and E. J. WAYNE (Biochem. J., 1928, **22**, 188—197).—Normal phenylpropionic, phenylbutyric, phenylvaleric, and phenylhexoic acids when administered to dogs yield amounts of benzoic and phenylacetic acids, as the case may be, which indicate that the fatty acid side-chain is oxidised quantitatively in accordance with the theory of β-oxidation. Under the same conditions phenylnonoic and phenyldecoic acids yield smaller amounts of benzoic and phenylacetic acid, respectively, than would be expected if quantitative β-oxidation of the side-chain takes place, which suggests that some other mode of oxidation occurs, in addition, with phenyl-fatty acids containing side-chains approaching in length those of the higher fatty acids. Cinnamic and phenyl*iso*crotonic acids yield the same amounts of benzoic and phenylacetic acids, respectively, as the corresponding saturated acids.

θ-*Phenylnonoic acid*, m. p. 29—30°, was prepared by esterification and reduction from η-*benzoyloctoic acid*, m. p. 74·5—75° (*semicarbazone*, m. p. 151·5—152°), obtained from azelaic acid. The methods for the preparation of the other acids are given.

S. S. ZILVA.

Nutritive value of hydrogenated oils. S. UENO, M. YAMASHITA, Y. OTA, and Z. OKUMURA (J. Soc. Chem. Ind. Japan, 1927, **30**, 378—385).—Olive oil, cotton-seed oil, cod-liver oil, peanut oil, soya-bean oil, sesame oil, and deodorised coconut oil were hydrogenated at 120° under conditions which would not destroy vitamin-*A*. In each case the hydrogenated oil gave a result superior to that of the original oil. This is attributed to the fact that the hardened oil consists chiefly of the glycerides of the saturated acids and of the oleic acid series, which are stable to light and air, and also that toxic substances are eliminated during purification and hydrogenation.

Y. TOMODA.

Nutritive value of fat. III. J. OZAKI (Biochem. Z., 1928, **192**, 428—430).—The nutritive value of a variety of natural fats is determined using rats by the method previously described (A., 1926, 1272; B., 1926, 930; this vol., 86), vitamin-*A* being added to each in order to prevent disturbances due to vitamin deficiency. The nutritive values of the fats examined decrease in the following order: butter, rapeseed oil, arachis oil, olive oil, liver fat, herring oil, cotton-seed oil, triolein, beef fat, lard, whale oil, and sardine oil. Liver fat does not appear to have a specially high nutritive value and its therapeutic importance must depend on its vitamin content.

P. W. CLUTTERBUCK.

Digestion in the cockroach. III. Digestion of proteins and fats. V. B. WIGGLESWORTH (Biochem. J., 1928, **22**, 150—161).—The proteolytic enzymes of the cockroach consist of a tryptase and a peptidase. Peptase is absent. The tryptase resembles pancreatic trypsin in the products of digestion, the relative production of "free acidity" and "formaldehyde acidity" during digestion, the effect of salts, and in acting on proteins only on the alkaline side of their isoelectric point. Its range of activity, however, extends further in the acid direction. The peptidase is present in the intestinal secretion. It has been partly separated from the tryptase by adsorption and it appears to have an optimal zone of activity about p_H 8·5. Lipase as present in a crude emulsion of the cockroach gut is usually but not constantly activated by sodium glycocholate, but is not activated by phosphates apart from their influence as buffers. Its optimal zone is around p_H 8·0. It is almost inactive at the normal reaction of the crop.

S. S. ZILVA.

Digestibility of proteins of cotton seed. W. D. GALLUP (J. Biol. Chem., 1928, **76**, 43—53).—The coefficient of digestibility (for the albino rat) of the proteins of cotton-seed meal is lower than that of the seeds themselves; the digestibility of both is reduced by autoclaving. Addition of gossypol to the diet in sub-lethal amounts had no effect on the digestibility of these proteins. C. R. HARINGTON.

Value of whole potato in human nutrition. S. K. KON and A. KLEIN (Biochem. J., 1928, **22**, 258—260).—An experiment is described in which two adults, a man and a woman, lived over a period of 167 days in nitrogen equilibrium and in good health on a diet in which the nitrogen was practically solely derived from the potato. The daily nitrogen intake was on the average 5·7 g. for the man and 3·8 g. for the woman. S. S. ZILVA.

Nutritional value of tuberin, the globulin of potato. S. K. KON (Biochem. J., 1928, **22**, 261—267).—Tuberin appears to be a complete protein from the dietetic point of view. Its biological value as measured at an 8% level of intake by Mitchell's method is 71. When fed to rats according to Osborne, Mendel, and Ferry's method a maximal gain of 2 g. body-weight per g. of protein ingested was found at a 7—8% level of intake. S. S. ZILVA.

Relation of protein to mineral metabolism. S. LAUTER (Verh. deuts. Ges. inn. Med., 1926, 330—331; Chem. Zentr., 1927, ii, 283).—With a diet rich in carbohydrate and fat and poor in mineral matter, there was an increase in alveolar carbon dioxide tension and blood alkali reserve, without change in nitrogen excretion, and a decrease in chlorine, sodium, and potassium. Administration of hydrogen chloride (oral) and sodium dihydrogen phosphate (intravenous) reduces the alveolar carbon dioxide tension, the blood alkali reserve, and the p_H of the blood, but there is a marked increase in the ammonia and nitrogen elimination. A. A. ELDRIDGE.

Sodium chloride and protein content of the serum of pigs in feeding. T. RADEFF (Arch. wiss. prakt. Tierheilk., 1926, **55**, 300—305; Chem. Zentr., 1927, ii, 278).—The sodium chloride content of fish meal fed to pigs does not affect the sodium chloride content of the serum. A. A. ELDRIDGE.

Iron metabolism. II. Iron and hæmoglobin formation. III. Observations with animals kept in rarefied air. W. LINTZEL (Z. Biol., 1928, **87**, 97—106, 137—144).—II. Young rats from the same litter have been fed on a practically iron-free diet consisting of egg-white, filtered lard, refined crystalline sucrose, specially treated rice, and vitamins (milk and orange juice), with and without the addition of iron in the form of ferric chloride or diluted ox-blood.

The total iron content of the animal and the hæmoglobin-iron were determined by a method described. The results show that the inorganic iron of the food can be utilised for the formation of hæmoglobin and to increase the total body-iron, whereas equivalent amounts of hæmoglobin-iron are without significant effect. It is calculated that one half to two thirds of the total hæmoglobin present has been synthesised from inorganic iron. The effect of inorganic iron in stimulating growth is confirmed, but the view that inorganic iron stimulates the bone-marrow is unnecessary.

III. Rats were kept for 1—5 weeks in rarefied air of pressure 280 mm. (corresponding with a height of 8000 metres) and fed on a mixed diet. The body-weight shows a decrease, whilst the absolute amount of hæmoglobin-iron increases up to 100%, the total iron increases to a less extent, and the weight of the heart (fresh and dry matter) also increases. After 3 weeks at the low pressure, acclimatisation is complete and no further increases in the iron values occur. Similar experiments with rats on an iron-free diet indicate that no appreciable increase (up to 20% only) in the hæmoglobin-iron occurs at the expense of the rest of the body-iron. A. WORMALL.

Sulphur metabolism. H. FLURIN (Progr. méd., 1926, **54**, 1706—1713; Chem. Zentr., 1927, ii, 282).—A critical discussion. A. A. ELDRIDGE.

Purine metabolism. V. Nuclear-plasmic ratio of frogs. R. TRUSZKOWSKI (Biochem. J., 1928, **22**, 198—200).—From monthly determinations over a period of more than a year it is concluded that the nuclear-plasmic ratio of *Rana esculenta* has a value of approximately double that of mammals. It is highest from May to January, the value falling slightly during the periods of winter sleep, hunger, and sexual activity which follow. The existence of specific reserve protein in the cytoplasm of the frog is not confirmed. S. S. ZILVA.

Uricæmia in its relation to nucleoprotein metabolism. I. Uricæmic equilibrium and the place of origin of endogenous uric acid. II. Action of the liver on degradation products of nucleoproteins. L. GAROT (J. physiol. path. gen., 1926, **24**, 525—540, 556—571; Chem. Zentr., 1927, ii, 283).—Supply of nucleoproteins effects a reduction of the uric acid value of the blood independently of the endogenous blood uric acid content. There is more uric acid in venous than in arterial blood. Liver function in respect of purine derivatives is discussed. A. A. ELDRIDGE.

I. Influence of administration of active iron oxide and of radiothorium on the formation of blood and on metabolism in normal rabbits, in regard to the urinary C : N quotient. II. Influence of radiothorium on the urinary C : N quotient. III. Influence of narcosis on the urinary C : N quotient (dysoxidisable carbon in urine after narcosis). A. A. GOLDBLOOM (Biochem. Z., 1928, **192**, 250—271, 272—297, 298—302).—I. Attempts to increase the red cell count of the blood of normal rabbits having failed, similar attempts are made using simultaneous administration of active iron oxide and radioactive substances. With daily peroral administration of 5 mg. of active iron oxide and 75 units of radiothorium per kg., the C : N ratio is, but the red cell count is not increased. Increasing the dose of radiothorium to 150 units or more led, however, to an increase in the number of red cells.

II. Daily peroral administration of radiothorium (22—240 units per kg.) causes a rise of urinary C : N ratio and a single intravenous injection of radiothorium (150—5000 units) causes in rabbits a gradual rise of the ratio.

III. The urinary C : N ratios in dogs before, during, and 1—4 days after narcosis by morphine, ether, ether and morphine, chloroform and morphine, or chloroform, morphine, and atropine are tabulated. Morphine, morphine with chloroform, and morphine, chloroform, and atropine did not affect the ratio, but ether and ether with morphine caused considerable increase, but only on the day of narcosis.

P. W. CLUTTERBUCK.

Relation between (*a*) external hydrogen-ion concentration and (*b*) thallium salts and the rate of amphibian metamorphosis. J. BELEHRADEK, J. S. HUXLEY, and F. R. CURTIS (Biochem. J., 1927, **22**, 63—66).—The rate of metamorphosis induced by keeping frog tadpoles in weak thyroid extracts depends on the p_H of the medium, being, between p_H 6·8 and 8·0, greatest on the alkaline side and least on the acid side. This effect is not connected with variations of the internal p_H. In tadpoles treated with free iodine no definite effects of different external p_H could be detected. There is no antagonism between thallium and the metamorphosis-accelerating function of foreign thyroid or of the tadpoles' own thyroid under the conditions of this investigation.

S. S. ZILVA.

Changes of the liver during diminished atmospheric pressure and during autolysis. A. LOEWY and J. LEIBOWITZ (Biochem. Z., 1928, **192**, 67—72).—The previous experiments (A., 1927, 792) on the distribution of phosphorus between the ether extract and residue of the normal liver and of the liver after a period under reduced pressure are repeated using rabbits, guinea-pigs, and rats, this time care being taken to use reagents free from phosphorus. The results with rats and rabbits are indecisive, but with guinea-pigs an increase of ether-soluble phosphorus (phosphatides) during diminished pressure from 5% to 15—36% of the total phosphorus is obtained, thus confirming the former result. Autolytic changes, although not totally excluded, do not account for these results. P. W. CLUTTERBUCK.

Production of hyperglycæmia by subcutaneous injections of arsenious oxide in the rabbit. F. P. UNDERHILL and A. DIMICK (J. Biol. Chem., 1928, **76**, 163—170).—Injection of sub-lethal amounts of arsenious oxide into rabbits produces marked hyperglycæmia, accompanied by disappearance of glycogen from the liver but by practically no glycosuria.

C. R. HARINGTON.

Influence of arsenious acid on respiration and fermentation. II. K. DRESEL (Biochem. Z., 1928, **192**, 351—357).—In continuation of previous work

(A., 1927, 73) the effect of different concentrations of arsenious acid and the action of dextrose and metallic salts on the inhibition by arsenious acid of respiration and fermentation of yeast are investigated. Inhibition of fermentation by arsenious acid is always somewhat less than of respiration, but a concentration of 10^{-4} mol. considerably inhibits both. Increasing the concentration of dextrose decreases the inhibitory effect. Iron, manganese, cobalt, copper, zinc, and nickel sulphates all inhibit both respiration and fermentation of yeast. If respiration and fermentation are inhibited by 2×10^{-4} mol. of arsenious acid, addition of metallic salts then causes no change.

P. W. CLUTTERBUCK.

Action of arsenious acid on the respiration model, especially on the oxidation of tartaric acid in presence of iron. K. DRESEL (Biochem. Z., 1928, **192**, 358—368).—The influence of temperature on the oxidation of tartaric acid in presence of iron is investigated. The oxygen utilisation at 21° with concentrations of iron increasing from $M/4000$ to $M/1000$ after 60 min. is 0—14·9 mm.³ of oxygen, whereas at 37° it is 134 to >800 mm.³ The production of carbon dioxide is equal to the oxygen utilisation. Arsenious acid inhibits oxidation of tartaric acid at the ordinary temperature and at 37·5°, the greater the concentration of acid the greater the inhibition, and the inhibition increases with the time of reaction. Addition of iron counteracts the inhibition of oxidation by arsenious acid.

P. W. CLUTTERBUCK.

Value of cholesterol determinations in blood in lead poisoning. E. KÜHN (Zentr. Gewerbehyg., 1927, **14**, 117—129; Chem. Zentr., 1927, ii, 602).—In lead poisoning the cholesterol content of the total blood is frequently higher than that of the serum, whereas the reverse is normally the case. The frequency of the inversion, however, is not great enough to be regarded as specific for lead poisoning.

A. A. ELDRIDGE.

Aromatic nitro- and amino-compounds as blood-poisons. W. LIPSCHITZ (Zentr. Gewerbehyg., 1927, **14**, 11—14; Chem. Zentr., 1927, i, 2752).—In both cases the chief symptom is methæmoglobinæmia. Oxygen and quinine are antidotes.

A. A. ELDRIDGE.

Influence of tetrahydro-β-naphthylamine on tissue oxidation and some of its partial processes. U. VON EULER (Skand. Arch. Physiol., 1927, **51**, 129—135; Chem. Zentr., 1927, ii, 1365).—Decolorisation of methylene-blue in finely-minced muscle (rabbit, frog, and guinea-pig) takes place more rapidly in presence of 10^{-10} to 10^{-4} (max. 10^{-6}) parts of tetrahydro-β-naphthylamine, and more slowly in presence of 10^{-3} parts. Washed muscle reacts only in presence of succinate as donator.

A. A. ELDRIDGE.

Influence of parasympathetic poisons on blood-sugar concentration. I. S. LANG and M. VAS. **II.** S. LÁNG and L. RIGO (Biochem. Z., 1928, **192**, 137—143, 172—176).—I. The action of pilocarpine, physostigmine, muscarine, choline, and atropine on blood-sugar concentration is investigated. Substances which stimulate the parasympathetic system in small doses decrease, and in large doses increase, the blood-sugar concentration, whilst medium doses show a diphasic effect, at first increasing and then decreasing. Atropine behaves similarly, but choline in large doses tends to decrease rather than to increase the blood-sugar. The results cannot be explained in terms of variation in the water content of the blood.

II. Arecoline, acetylcholine, and scopolamine in small doses decrease and in large doses increase the blood-sugar concentration, whilst atropine inhibits the blood-sugar lowering effect of pilocarpine.

P. W. CLUTTERBUCK.

Pharmacological determination of atropine. J. DE D. FERNANDEZ (Arch. exp. Path. Pharm., 1928, **127**, 197—203).—The isolated heart of the grass- or water-frog, brought to a standstill by acetylcholine, has been used to determine the strength of atropine solutions. The time required for the latter to abolish the standstill is noted and compared with the effect of suitable standard atropine solutions. If the atropine solution is not too strong, the atropine can be washed out of the heart completely by Ringer solution and several successive determinations can be made on the same heart.

A. WORMALL.

Detection and determination of atropine in the smoke of *Stramonium* cigarettes. J. DE D. FERNANDEZ (Arch. exp. Path. Pharm., 1928, **127**, 204—211).—The smoke from cigarettes prepared from *Stramonium* leaves was drawn through acidified distilled water and the solution purified. The presence of atropine in these solutions was demonstrated by the chemical tests of Vitali and of Arnold, and pharmacologically by the effect on cat's-eyes and by the relaxation of isolated ox bronchial muscle contracted by pilocarpine. The determination of atropine was made by the frog's heart method (cf. preceding abstract) and by the antagonistic effect on the lowering of the blood-pressure of the cat by acetylcholine. The purified smoke solution from 1 g. of leaves, which contain about 3 mg. of alkaloid per g., contains 0·1 mg. of atropine, but this is a minimum figure, since much alkaloid is destroyed during purification.

A. WORMALL.

Detection of caffeine, morphine, and barbituric acid derivatives in the brain [following intravenous injection]. Problem of sleep. II. E. KEESER and I. KEESER (Arch. exp. Path. Pharm., 1928, **127**, 230—235).—Caffeine, after the injection of 0·1—100 mg. per kg. into the ear vein of a rabbit, can be detected by a sublimation method (cf. A., 1927, 1110) in all the parts of the brain examined when the animal is killed ½—5 hrs. after the injection. After the injection of morphine (0·005—0·12 g. per kg.), morphine can be detected similarly in relatively large amounts in the diencephalon and also in the great hemispheres; in no case did the mid-brain, the pons, medulla oblongata, or the cerebellum give positive results. Injection of barbituric acid derivatives (veronal, luminal, or diallylbarbituric acid) in amounts of 40—70 mg. per kg. led to a recovery of the narcotic in the diencephalon, principally in the thalamus, whilst the results were negative with the great hemispheres, mid-brain, medulla oblongata, pons,

and cerebellum. These results are discussed in relation to the problem of sleep. A. WORMALL.

System catalase—anticatalase in blood and various animal organs under different physiological and pathological conditions. E. D. GAGARINA and W. D. JANKOWSKY (Compt. rend. Soc. Biol., 1927, **97**, 481—482; Chem. Zentr., 1927, ii, 1353).—With animals poisoned by morphine there is an increase of catalase in all organs, especially the liver and muscle, but a considerable decrease in the blood catalase. The anticatalase content of all organs except muscle and lungs is reduced. With arsenic poisoning there is an increase of catalase and anticatalase in organs and a decrease in the blood; with alcohol poisoning there is a reduction of catalase and anticatalase in the liver and blood, and a small increase in the other organs. A. A. ELDRIDGE.

Alkaloid ferrocyanides. M. GADREAU.—See this vol., 314.

Chemical constitution and toxicity. E. WALKER (Biochem. J., 1928, **22**, 292—305).—The toxicity was measured against the unicellular organism *Colpidium colpoda* and also against *Glaucoma scintillans*. Most of the compounds investigated were arsenic derivatives, but some antimony, bismuth, and mercury compounds have also been examined. Aromatic arsenic compounds are more toxic than the aliphatic derivatives, the tervalent derivatives than the quinquevalent derivatives, the secondary derivatives than the primary and tertiary derivatives, and the primary derivatives than the tertiary derivatives. The most toxic arsenic compounds are the tervalent secondary derivatives and within this class compounds of the diphenylarsine type are the most toxic. There are indications that antimony compounds are more toxic than the corresponding arsenic compounds. Organisms which have ceased all movement under the influence of arsenic can be revived at once and continue to live for periods up to 2 hrs. by the addition of a suitable sulphydryl compound. Unicellular organisms afford only a measure of general protoplasmic toxicity. S. S. ZILVA.

***In vitro* tests of the toxicity of certain drugs for hydatid scolices.** I. C. ROSS (Austral. J. Exp. Biol., 1927, **4**, 283—288).—The action of acriflavine, trypan-blue, potassium antimony tartrate, and emetine on hydatid scolices has been examined *in vitro*. A 1 in 1000 solution of acriflavine proved fatal in 3 hrs. and a 1 in 10,000 solution in 8 hrs.; a 1 in 1000 solution of the tartrate killed all scolices in 6 hrs. Emetine and trypan-blue proved relatively ineffective, a large proportion of scolices remaining active after 14 hrs. with a 1 in 1000 solution of the former, and after 16 hrs. with a 1 in 200 solution of the latter. E. A. LUNT.

Acid penetration into living tissues. N. W. TAYLOR (J. Gen. Physiol., 1928, **11**, 207—219).—Evidence is obtained that acid penetration through a membrane occurs either in the form of the undissociated molecule or by the simultaneous passage of hydrogen ion and an anion, and that the sourest acids are those which penetrate most rapidly. Measurements have been made of the threshold concentrations for sourness of nine acids, and the relative concentration gradients of the undissociated acids across the cell membrane have been calculated for a series of acids having equal sourness. It is considered that a comparison of the data obtained, and the relative concentration gradients calculated from acid penetration experiments of other workers, with the results of adsorption experiments on charcoal, indicates that the acids are taken up by the tissues by adsorption processes. Polar groups (OH, Cl, and Br) reduce markedly the ability of organic acids to penetrate living tissues. The influence of the optical character of the acid on penetration is briefly discussed. A. WORMALL.

Cell physiology. V. Antagonism of cations in their actions on the protoplasm of *Amœba dubia*. P. REZNIKOFF (J. Gen. Physiol., 1928, **11**, 221—232).—By means of immersion and injection experiments (cf. Chambers and Reznikoff, A., 1926, 759) the antagonistic effects of the chlorides of calcium, lithium, sodium, and potassium for amœbæ have been determined. Lithium chloride has a much greater dispersing effect on the plasmalemma and liquefies the internal protoplasm even more markedly than sodium chloride. Both calcium and magnesium antagonise sodium in its action on the plasmalemma much better than they antagonise potassium, whilst the reverse occurs with the internal protoplasm. The antagonistic effect is greater with magnesium than with calcium against sodium in the immersion experiments and against potassium in the injection experiments. With higher and toxic concentrations of the salts, the combined solutions of antagonising salts are more rapidly toxic than either alone. The antagonistic action of these salts with the internal protoplasm differs from that with the surface membrane, and there appears to be no relationship between the degree of antagonising power and the solidifying or dispersing effect on protoplasm of each salt individually. A. WORMALL.

Penetration of methylene-blue into living cells. M. M. BROOKS (Proc. Nat. Acad. Sci., 1927, **13**, 821—823).—The influence of p_H in the range 5·4—9·0 on the rate of penetration of methylene-blue into the living cells of *Valonia* has been investigated. At 25° penetration is so rapid that no variation can be detected; at 22·5° the rate of penetration increases with increasing p_H. Spectrophotometric analyses indicate that this dye is absorbed as such and undergoes subsequent oxidation in the cell to trimethylthionine. E. A. LUNT.

Affinity of different types of enzyme for their substrates. J. B. S. HALDANE (Nature, 1928, **121**, 207).—The enzymes can be classified into three groups according to the values of the dissociation constants of the enzyme-substrate compounds: (*a*) of low affinity, including the hydrolytic enzymes acting on crystalloidal substrates, yeast carboxylase, and liver catalase, (*b*) of medium affinity, consisting of the enzymes which hydrolyse colloidal substrates, (*c*) of high affinity, consisting of the only oxidising–reducing enzymes other than catalase so far studied (plant peroxidase, milk xanthine-oxidase, yeast oxygenase). A. A. ELDRIDGE.

Structure and enzyme reactions. III. System polysaccharide–amylase–protein. S. J. Przylecki and H. Niedzwiecka (Biochem. J., 1928, **22**, 34—42; cf. Przylecki and others, A., 1927, 1113).—Ten g. of powdered caseinogen adsorbs 20% of starch from 50 c.c. of 1% solution of the latter. Alcohols reduce adsorption by 13—15%. Coagulated egg-white adsorbs from 30 to 40% of the starch under the above conditions and in this also the adsorption is reduced by the presence of alcohols by 20%. The action of the alcohols in both cases is elutive. Seventy to 95% of pancreatic amylase is adsorbed by coagulated egg-white. Alcohols affect the adsorption of the enzyme only to a small extent. Liver coagulum also adsorbs amylase. Although the enzyme cannot be removed from the residue by washing, the latter retains the activity for several months. Alcohols also do not remove the enzyme from this residue. Similar results of irreversible adsorption were obtained by treating amylase with carbohydrate-free liver coagulum. Glycogen causes a negligible elution of amylase from egg-white or from liver coagulum. The presence of coagulated egg-white or liver coagulum retards the velocity of the enzymic hydrolysis of starch in proportion to the degree of adsorption. The addition of alcohols to such systems leads to an acceleration of reaction proportional to the degree of elution of adsorbed polysaccharide. In the presence of fresh egg-white the reaction is scarcely retarded and the addition of small quantities of alcohols has no accelerating effect on the velocity of hydrolysis. The velocity of reaction in the system polysaccharide–amylase–protein gel is therefore regulated entirely by the concentration of unadsorbed substrate. S. S. Zilva.

Diastase. IV. Extractable and non-extractable α-diastase content of different kinds of cereals. V. Synievski (Biochem. Z., 1928, **182**, 457—462).—The α-diastase and nitrogen contents of samples of oats, wheat, rye, and barley are tabulated. The number of diastatic units per mg. of nitrogen decreases in the following order: wheat, barley, rye, oats. About one third of the diastase of wheat and barley, four fifths of that of rye, and the whole of that of oats can be extracted by water. The proportionality between the number of α-diastase units and the nitrogenous material rendered extractable by the action of papain is only slight. Agreement is approximate for barley and wheat but deviation is considerable with rye and oats (cf. A., 1925, i, 469; 1926, 93). P. W. Clutterbuck.

Conversion of α- into β-diastase. F. Polak and A. Tychovski (Biochem. Z., 1928, **192**, 463—478).—The optimal p_H for α-diastase is 5·10 and for β-diastase 4·30. A normal barley extract (20 g. of barley and 100 c.c. of distilled water) has a p_H of 6·30, its β-diastase action being increased 17 times by displacement of the to 4·30. An extract of barley after treatment of the grain with papain contains, at the optimal p_H, twice the amount of β-diastase as an ordinary aqueous extract. It is concluded that by changes of p_H conversion of α- into β-diastase occurs. P. W. Clutterbuck.

Enzymic decomposition of α- and β-glycerophosphoric acids. P. Karrer and R. Freuler (Festschr. A. Tschirch, 1926, 421—424; Chem. Zentr., 1927, i, 3064).—A comparison of the behaviour of synthetic racemic sodium α- and β-glycerophosphates towards glycerophosphatase. The hydrolysis is equally rapid in the two cases, and follows the same course; it proceeds best in strongly acid solution. A. A. Eldridge.

Biochemical synthesis of glycerides. Reversibility of enzymic action of the cytoplasm of the castor-bean. A. Morel and L. Velluz (Compt. rend., 1928, **186**, 43—46).—The active portion of the castor-bean is the cytoplasm, which, when activated by 0·1*N*-acetic acid in presence of olive oil by a special process, washed, dried, and pulverised, is capable of causing both hydrolysis of olive oil and the reverse process of esterification. B. W. Anderson.

Synthetic action of bacterial lipases. N. van der Walle (Zentr. Bakt., 1927, II, **70**, 369—373; Chem. Zentr., 1927, ii, 583).—*Bacillus pyocyaneus* esterifies oleic acid with propyl, *iso*butyl, amyl, hexyl, or octyl alcohol, methylnonylcarbinol, or glycerol, but not with methyl, ethyl or benzyl alcohol or ethylene glycol. Acetic acid was not esterified with methyl, ethyl or amyl alcohol or glycerol, nor butyric acid with glycerol. *Staphylococcus aureus* powder esterifies oleic acid with glycerol, but not with amyl alcohol. *B. prodigiosus* esterifies oleic acid with glycerol. *B. coli* ferment powder does not affect mixtures of oleic acid with *iso*butyl alcohol, amyl alcohol, or glycerol. The ferment powder from *B. dysenteriæ* (*a*) Shiga-Kruse and (*b*) Flexner was inactive for mixtures of oleic acid and amyl alcohol or glycerol. The synthesis is never quantitative. Possibly the unsaturated character of oleic acid is concerned with its reactivity. A. A. Eldridge.

Action of bile on the tributyrinolytic power of blood-serum. L. Avellone (Riv. pat. sperim., 1926, **1**, 395—399; Chem. Zentr., 1927, ii, 278).—In presence of bile, serum-lipase appears not to be inhibited by quinine. A. A. Eldridge.

Effect of rennin on caseinogen. II. Properties of casein. V. Pertzoff (J. Gen. Physiol., 1928, **11**, 239—253).—Purified casein preparations, obtained by the action of rennin on caseinogen (cf. A., 1927, 895), dissolve in combination with base to the extent of 1450 g. per mol. of sodium hydroxide at 21—37°, compared with a combining weight of 2100 g. for caseinogen under the same conditions; a comparison of the titration curves of the two proteins confirms the view that casein is a stronger acid than caseinogen. Casein is not a product formed by partial hydrolysis or by denaturation of caseinogen, nor is it identical with caseinogen modified by excess of alkali. A casein preparation which gave an abnormal base-combining capacity (1700 g. per mol. of sodium hydroxide) does not appear to be a mixture of casein and caseinogen, and no appreciable alteration in the combining capacity occurred on digestion with rennin. A. Wormall.

Peptic digestion of coagulated egg-white. E. G. Young and I. G. Macdonald (Trans. Roy.

Soc. Canada, 1927, [iii], **21**, V, 385—393).—Coagulation of egg-white by heating at 100° for 2—30 min. does not affect the rate at which it is digested *in vitro* by pepsin. W. O. Kermack.

Xanthine oxidase. X. Action of light. F. Bernheim and M. Dixon (Biochem. J., 1928, **22**, 113—124).—The reduction of methylene-blue by the xanthine oxidase system is markedly accelerated by light but only if traces of oxygen are present. Previous exposure of the oxidase solution or the methylene-blue to light in the presence of oxygen for short periods produces an acceleration of the reaction. Exposure for longer periods produces a destruction of the enzyme. Neither effect occurs on irradiation in the absence of oxygen. These phenomena are due to the formation of an active oxidising agent, probably hydrogen peroxide, by the action of light since the presence of $10^{-6}M$-hydrogen peroxide in general more than doubles the activity of the enzyme whilst a very definite acceleration is produced by $10^{-8}M$. In higher concentrations the peroxide destroys the enzyme. The nature of the effect produced by a peroxide solution of given strength and by methylene-blue which has been exposed to light and oxygen depends on the amount of oxidase present. The accelerating action of added hydrogen peroxide on the enzyme also takes place when aldehyde is substituted for hypoxanthine and nitrate for methylene-blue. In presence of peroxidase the peroxide formed during the aerobic irradiation of methylene-blue solutions is able to carry out secondary oxidations of nitrites. This oxidation does not occur in the absence of either peroxidase, oxygen, or light. S. S. Zilva.

Reduction of nitrates in animal tissues. F. Bernheim and M. Dixon (Biochem. J., 1928, **22**, 125—134).—The livers of all the animals studied but only the muscle of the rat and the guinea-pig reduced nitrate. Hydrogen donators did not increase the reduction of nitrate by washed muscle. The dehydrases of muscle are incapable of reducing nitrate. The properties of the nitrate-reducing system in muscle are described. The system appears to be enzymic and completely disappears on addition of $0{\cdot}002M$-cyanide. In the liver the nitrate-reduction is due to (*a*) a system having the same properties as that in muscle and (*b*) the aldehyde (xanthine) oxidase probably identical with that in milk. The two systems can be separated. No hydrogen donator other than the substrates of the oxidase has been found which will increase the reduction of nitrate in liver. S. S. Zilva.

Melanin formation. H. Schmalfuss (Naturwiss., 1927, **15**, 453—457; Chem. Zentr., 1927, ii, 713).—Most melanins are formed by a fermentative process, whereby a chromogen (*e.g.*, 3 : 4-dihydroxyphenylalanine), a suitable gas (*e.g.*, oxygen), and a suitable ferment are necessary. The formation of melanin under various conditions was examined. It is inhibited by sulphur dioxide, hydrogen sulphide, hydrogen cyanide, chlorine, bromine, and ammonia, and by a hydrogen-ion concentration greater than 5×10^{-5}. Light has no effect. The ferment is destroyed by heat, but a heat-resistant material produces melanin at high temperatures. A. A. Eldridge.

Crystalline urease. II. J. B. Sumner and D. B. Hand (J. Biol. Chem., 1928, **76**, 149—162; cf. A., 1926, 1061, 1176).—Inactivation of crystalline urease by dilution of its aqueous solution may be prevented by using 2% gum arabic as a diluent. A modification of the author's method for obtaining crystalline urease is described which may be applied to Jack beans of low enzymic content. The typical crystalline preparations described have never been obtained free from urease; urease is but slightly adsorbed on the crystalline proteins of the Jack bean; the enzymic activity of the preparations rises on re-crystallisation; the identity of the preparation with the enzyme itself is therefore regarded as established. C. R. Harington.

Effects of phloridzin and other substances on fermentations by yeast. W. J. Dann and J. H. Quastel (Biochem. J., 1928, **22**, 245—257).—Phloridzin shows a much higher retarding action on the normal rate of zymin fermentation of dextrose than salicin, æsculin, or amygdalin, especially when relatively small quantities of the substances are used; 10^{-4} g.-mol. of phloridzin effects a 31% retardation and 10^{-3} g.-mol. a 59% retardation of the rate of fermentation due to zymin. Phloretin shows a similar but somewhat less vigorous action than phloridzin. The rate of fermentation after addition of phloridzin is linear. Of the polyhydric phenols, phloroglucinol is the most effective in retarding the rate of fermentation of dextrose by zymin. The retarding action of phloridzin is not exhibited in the zymin fermentation of pyruvic acid or in the fermentations of dextrose and pyruvic acid by living yeast. Allyl alcohol and acrylic acid retard fermentation of dextrose by zymin and living yeast, the retardation increasing with time. Neither allylamine nor allylacetic acid has such an action. The rate of the evolution of carbon dioxide was measured by Tryhorn and Jessop's apparatus. S. S. Zilva.

Isolation of a second sterol from yeast-fat. I. Smedley-Maclean (Biochem. J., 1928, **22**, 22—26).—A sterol, *zymosterol*, $C_{27}H_{42}O$, m. p. 108—109° $[\alpha]_{5461}$ in ether, $+34{\cdot}1°$ (*acetate*, m. p. 112—113°) present in yeast is described. It can be separated from the less soluble ergosterol of the crude sterol fraction by recrystallisation from alcohol, ether, and acetone. The iodine value suggests the probable presence of three ethenoid linkings. It can be brominated. Specimens of zymosterol in a dilution in alcohol of 1 in 20,000 showed no selective absorption in the ultra-violet region. In lower dilutions the absorption bands characteristic of ergosterol in this region are visible. Like ergesterol it is precipitated by digitonin. S. S. Zilva.

Formation of fats by micro-organisms. G. Seliber (Mon. Sci. Inst. Lesgaft, Leningrad, 1926, 1—101).

Diffusion products of bacterial cells as influenced by the presence of various electrolytes. H. J. Shaughnessy and C. F. A. Winslow (J. Bact., 1927, **14**, 69—99). Chemical Abstracts.

Soluble specific substances of Friedländer's bacillus. III. Types *A* and *C*. W. F. Goebel

and O. T. Avery (J. Exp. Med., 1927, **46**, 601—607; cf. A., 1927, 1114).—The carbohydrate obtained from type *A* has α_D −100 to −105°, acid equivalent 430—445, C, 43·98, H, 6·00%, and gives 64—68% of reducing sugars (as dextrose) and a sugar acid on hydrolysis. The carbohydrate obtained from type *C* has α_D +100°, acid equivalent 680, yields about 75% of reducing sugar (chiefly dextrose) and a sugar acid.

Chemical Abstracts.

Nitrogen fixation by *Azotobacter chroococcum*. S. Ranganathan and R. V. Norris (J. Indian Inst. Sci., 1927, **10A**, 79—96).—An examination of the carbon metabolism of *A. chroococcum* is described. The decreased activity of cultures of the organism with age was more marked in mineral salts-mannitol-agar than in soil extract-mannitol-agar media. The amount of nitrogen fixed increases as the amount of sugar fermented. More than half of the total fixation of nitrogen occurs in the first few days of the fermentation. No definite relationship exists between the amount of nitrogen fixed and the concentration of sugar in the media. The acceleration of nitrogen fixation by phosphates is not accompanied by any reduction in the amount of sugar decomposed. During the fermentation of dextrose by *Azotobacter*, carbon dioxide, ethyl alcohol, aldehyde, and formic, acetic, lactic, and tartaric acids are formed. Ammonia is probably the first product of nitrogen fixation and is probably elaborated into complex substances through the intermediate stage of mono- and di-amino-acids. Cells contain about 30% of protein matter and considerable amounts of fat and phosphatides.

A. G. Pollard.

Certain cell constituents of acid-fast [bacteria] and their antigenic character. I. A. Korff-Petersen and W. Liese (Z. Immunitatsforsch., 1927, **51**, 87—114; Chem. Zentr., 1927, ii, 583—584).

A. A. Eldridge.

Reaction between toxin and antitoxin and the significance for the immune action of serum. S. Schmidt (Dansk Tidsskr. Farm., 1928, **2**, 25—40).—The rate of flocculation of toxin by antidiphtheritic sera of different individuals is very variable. The variations in the flocculability, however, show no relationship to the antitoxin titre and often a serum feeble in antitoxic power flocculates more rapidly than a serum rich in antitoxin. In general, a satisfactory agreement is found between the velocity of neutralisation and that of flocculation. Heating at 60° for 1 hr. sometimes destroys the flocculating power, but the neutralisation affinity between toxin and antitoxin is not affected. Salts have a marked influence on the rate of flocculation and also retard or prevent the formation of the toxin–antitoxin complex. The influence of sodium iodide on the latter process is very marked and suitable amounts may produce at least partial dissociation of the toxin–antitoxin complex, even when this is in the form of a precipitate. The instability of the complex supports the conception of Arrhenius and Madsen that there is a reversible reaction, toxin+antitoxin $\rightleftharpoons$ toxin–antitoxin complex.

A. Wormall.

"Kombucha." I and II. S. Hermann (Biochem. Z., 1928, **192**, 176—187, 188—199).—"Kombucha" is allied to fungi and contains besides *Bacterium xylinum* and *B. xylinoides* a previously unknown bacillus, *B. gluconicum*, which converts dextrose quantitatively to gluconic acid. Sucrose, on account of the presence of yeasts, is also quickly decomposed and from the invert-sugar large amounts of gluconic acid are obtained, whilst the alcohol formed by fermentation is oxidised to acetic acid. It is suggested that the therapeutic action of "Kombucha" is related to the presence of *B. gluconicum*.

P. W. Clutterbuck.

Decomposition of organic substances in the sea. J. Kořínek (Biochem. Z., 1928, **192**, 230—237).—Organic material in the neighbourhood of the coast is decomposed by sea-water bacteria, the fresh-water bacteria, swept down into the sea, taking no important part. In the mixing of sea- and fresh-water, that type of bacteria develops for which the salt concentration is optimal. Most soil bacteria have their optimum in fresh-water; the more sea-water added, the more is their growth inhibited. Sea- and fresh-water mixed in different proportions do not show proportional differences in p_H because of the difference in the type of bacteria finding their optimal conditions in the different mixtures. In general, the bacterial flora of brackish and sea-water causes greater acidification of a fluid containing dextrose than the flora of fresh-water. Sea-water appears to rid itself of fresh-water bacteria chiefly by their agglutination.

P. W. Clutterbuck.

Factors causing variable results with flagella stains. W. H. Wright (Stain Tech., 1928, **3**, 14—27).—A summary of the methods of staining flagella is given and the effects of varying such conditions as the reaction of the mordant and the temperature at which the staining is performed are discussed.

H. W. Dudley.

Preparation of agar culture media. A. R. Grace (Austral. J. Exp. Biol., 1927, **4**, 269—270).—A method is described for the preparation of clear agar jelly in which the dry agar is tied into a gauze bag suspended in the water in an Erlenmeyer flask in which the jelly is to be made. The flask is autoclaved for 25 min. at 120°, the bag raised out of the water, and the agar allowed to drain out of the bag for 10 min. at 110°, again in the autoclave. E. A. Lunt.

Respiration and glycolysis of the skin and the influence of hormones. E. Klopstock (Dermatol. Woch., 1926, **83**, 1468—1471; Chem. Zentr., 1927, i, 3015).

A. A. Eldridge.

[Action of various substances on the composition of the blood.] II. Thyroid gland. III. Tyramine. F. Rothschild and M. Jacobsohn. **IV. Adrenaline. V. Atropine. VI. Choline.** M. Jacobsohn and F. Rothschild (Z. klin. Med., 1927, **105**, 403—405, 406—409, 410—413, 414—416, 417—419; Chem. Zentr., 1927, ii, 105—106).—After administration of "thyreophorin" (0·3—1·0 g.) the blood-cholesterol and -calcium (usually) are increased, the residual nitrogen, potassium, and organic phosphorus decreased, and the sugar and organic phosphorus unchanged. In patients with marked exophthalmic goitre injection of tyramine tartrate (0·5 mg.) reduces the blood-sugar,

cholesterol, organic phosphorus and calcium, and increases the potassium and residual nitrogen, whereas with animals different results were obtained. Adrenaline raises the blood-sugar, calcium, and cholesterol, and diminishes the potassium and phosphorus. Atropine (with animals) increases the sugar and inorganic phosphorus and decreases the cholesterol and organic phosphorus. Choline causes a fall in sugar, cholesterol, and inorganic phosphorus, and a rise in organic phosphorus. A. A. ELDRIDGE.

Effect of thyroid substance, adrenaline, and insulin on the lactacidogen content of muscle and the phosphoric acid of organs. Y. TERADA (Folia endocrinol. japon., 1926, 2, 13—15, 302—331). —Injection of adrenaline or ingestion of thyroid substance reduces the lactacidogen content of the femoral quadriceps of the rabbit; insulin increases it. The total phosphorus of the blood, heart, and kidneys is increased, and that of the liver reduced, by adrenaline, thyroid, thyroidectomy, or insulin; muscle-phosphorus is increased by the last and diminished by the first three. CHEMICAL ABSTRACTS.

Effect of adrenaline on oxidation processes. A. BORNSTEIN (Arch. exp. Path. Pharm., 1927, **127**, 63—68).—Addition of adrenaline to oxygenated defibrinated goose-blood does not influence the oxygen consumption. Similarly, no increase in oxygen usage of a surviving leg of the dog perfused with dog-blood or calf-blood occurs when adrenaline is injected intravenously. Intraperitoneal injection of adrenaline causes a marked increase in the oxygen usage of normal dogs, but not in that of curarised dogs. This increased oxidation in the normal animal is not primary, but is attributed to the increased tension, excitability, and tremor of the muscles. A. WORMALL.

Influence of adrenaline on acetone excretion in disease. S. HIRSCHHORN and L. POLLAK (Z. klin. Med., 1927, **105**, 371—402; Chem. Zentr., 1927, ii, 102).—Acetonuria in normal metabolism is markedly increased by the subcutaneous injection of adrenaline (1 mg.); in diabetes the reaction is not constant. A. A. ELDRIDGE.

Insulin. III. Action of insulin on the formation of lactic acid in the liver. U. SAMMARTINO (Arch. Farm. sperim., 1927, **44**, 11—21).—In rabbits to which insulin is administered, the amount of lactic acid collecting in the liver amounts to 50·06 mg. per 100 g. of liver, which is similar to the quantity found in the same animals subjected to Bernard's puncture (A., 1924, i, 446). T. H. POPE.

Determination of dextrose insulin equivalents. K. L. E. LAMERS (XII Int. Cong. Physiol., 1926, 94; Chem. Zentr., 1927, ii, 103).—For the determination of the dextrose equivalent of insulin, the sugar must be administered subcutaneously. Part of the sugar actually undergoes combustion, and part may be converted into acid products. A. A. ELDRIDGE.

Decomposition of dextrose in toxic insulin action. F. FISCHLER (Münch. med. Woch., 1927, **74**, 680—682; Chem. Zentr., 1927, i, 3097).—In toxic insulin action there is an abnormal decomposition of dextrose with increased formation of methylglyoxal, to which the toxic effect is due. Traces of an iodoform-forming substance can be recovered from the blood and muscles of animals poisoned with insulin. A. A. ELDRIDGE.

Action of insulin. III. Action on the gaseous exchange of the tortoise. B. VON ISSEKUTZ and F. VÉGH (Biochem. Z., 1928, **192**, 383—389).—The gaseous exchange of the tortoise is greatly increased by insulin, but the R.Q. is unchanged (cf. A., 1927, 594). P. W. CLUTTERBUCK.

Influence of insulin and dextrose on the oxygen consumption of surviving frog's spinal cord. H. J. WOLF (Pflüger's Archiv, 1927, **216**, 322—336; Chem. Zentr., 1927, ii, 103).—Addition of insulin, not too long after the death of the animal, to the frog's spinal cord suspended in dextrose solution can effect a considerable increase in the oxygen consumption. Insulin alone scarcely affects the respiration of the spinal cord. Dextrose alone increases the oxygen consumption only when the cord is injured or the animal diseased. A. A. ELDRIDGE.

Effect of insulin on the morphological and chemical condition of the blood. A. SCHMIDT and R. SAATCIAN (Zhur. eksp. biol. med., 1926, 4, 353—379).—The blood solids are increased; the light petroleum extract, the inorganic phosphorus, and the serum-calcium are diminished. Convulsions cause an increase in serum-calcium and inorganic phosphorus. It is suggested that insulin promotes the formation of lactacidogen, which undergoes fission during convulsions; the phosphorus is swept into the blood. CHEMICAL ABSTRACTS.

Action of insulin on the lipins of the blood. I. OKU (Folia endocrinol. japon., 1926, **2**, 279—301).—The lipæmia caused by olive oil, lard, and cod-liver oil is attributable chiefly to the fatty acids. Alimentary lipæmia is suppressed by insulin. CHEMICAL ABSTRACTS.

Uric acid metabolism and insulin. L. KURTI and G. GYÖRGYI (Klin. Woch., 1927, **6**, 1426—1428; Chem. Zentr., 1927, ii, 1362).—Administration of insulin, in small doses, to persons with otherwise normal uric acid excretion produces delay in the excretion of exogenous uric acid. On long-continued administration of insulin a limitation of purine supply is indicated. A. A. ELDRIDGE.

Liver glycogen after partial pancreatectomy in the guinea-pig. B. SPLATT (Austral. J. Exp. Biol., 1927, **4**, 213—219).—The continued daily injections of pituitrin or of insulin into guinea-pigs effects a diminution of the glycogen content of the liver. In the latter case this effect is somewhat compensated by partial pancreatectomy. A diminution in the case of insulin, and a slight increase in the case of pituitrin, in the residual adrenaline of the suprarenals follows the injection of these substances into guinea-pigs in which a portion of the pancreas has been removed. E. A. LUNT.

Pituitrin and blood-lipins. G. BLIX and C. A. OHLIN (Skand. Arch. Physiol., 1927, **51**, 167—174; Chem. Zentr., 1927, ii, 1361).—Subcutaneous administration of pituitrin to rabbits and dogs does not affect

the blood-cholesterol; neutral fat is diminished, but the phosphatide-fatty acid fraction is considerably reduced (max. 3—9 hrs.). A. A. ELDRIDGE.

Relation of the parathyroid hormone to the calcium content of the blood and to blood coagulation. L. M. ZIMMERMANN (Klin. Woch., 1927, **6**, 726—730; Chem. Zentr., 1927, i, 3202).—The increased calcium content of the blood produced by Collip's parathyroid extract has no influence on the coagulation time. A. A. ELDRIDGE.

Placental hormone ("feminin"). E. GLIMM and F. WADEHN (Klin. Woch., 1927, 6, 999—1000; Chem. Zentr., 1927, ii, 273—274).—The crude extract of the placenta is treated with cold acetone in neutral and alkaline solution to separate it from phosphatides and part of the fatty acids; the residue after evaporation of the acetone is extracted with methyl alcohol, and the residue on evaporation is dissolved in ether and shaken with water. On evaporation of the ether there remains a brown oil which is poured into much light petroleum from which there falls a brownish precipitate containing 0·25—0·5 of the amount of hormone present. The solution of this substance in dilute ammonia solution is freed from resin by shaking with ether. A more active preparation can be obtained from the hormone remaining in the light petroleum. The hormone is attacked by atmospheric oxygen. A. A. ELDRIDGE.

Detection of thyroxine in hyperthyroidised mammals. B. ZAWADOWSKY and G. ASIMOV (Pflüger's Archiv, 1927, **216**, 65—81; Chem. Zentr., 1927, i, 2918).—Thyroxine was detected in hyperthyroidised guinea-pigs by the use of axolotls. The hormone accumulates in the liver; in the blood it appears chiefly in the serum. Hens destroy the hormone more slowly, and detection is easier. Acceleration of the metamorphosis of axolotls is a more convenient and certain test than the acceleration of metamorphosis and deceleration of growth of tadpoles. A. A. ELDRIDGE.

Vitamins of orange juice. S. G. WILLIMOTT (Biochem. J., 1928, **22**, 67—76).—The juice of the navel orange contains sufficient vitamin-*A* in 5 c.c. for growth and well-being of the rat; 10 c.c. of Valencia orange juice are adequate for the vitamin-*B* requirements of the rat. Vitamin-*D* is not present in the navel orange juice. Analyses of the juices are tabulated. S. S. ZILVA.

Vitamin-*A* deficiency and urolithiasis. E. C. VAN LEERSUM (J. Biol. Chem., 1928, **76**, 137—142).—The observation of Osborne and Mendel (J. Amer. Med. Ass., 1917, **69**, 32) regarding the frequency of occurrence of calcium phosphate calculi in rats on a diet deficient in vitamin-*A* is confirmed. It is suggested that the cause may be keratinisation of the epithelial cells of the renal tubules, analogous to the xerophthalmia known to be associated with deficiency of vitamin-*A*. C. R. HARINGTON.

Antineuritic yeast concentrates. III. Curative pigeon test: a critique. H. W. KINNERSLEY, R. A. PETERS, and V. READER (Biochem. J., 1928, **22**, 276—291).—The conditions necessary for obtaining good quantitative results with the curative test on pigeons are enumerated. A summary of the methods of feeding pigeons is given. S. S. ZILVA.

Vitamin-*B* required during lactation. H. M. EVANS and G. O. BARR (J. Biol. Chem., 1928, **76**, 263—272).—For satisfactory rearing of the young, the vitamin-*B* intake of the lactating rat must be increased to about 5 times the usual amount; the essential part of the extra requirement is the antineuritic fraction of vitamin-*B*. C. R. HARINGTON.

Effect of diastase on polyneuritis developed on diets rich in starch. L. RANDOIN and R. LECOQ (J. Pharm. Chim., 1927, [viii], **6**, 340—346).—The effect of the addition of diastase to diets rich in starch and free from vitamin-*B* has been found, in the pigeon, to accelerate slightly the rate of development of polyneuritis. This effect is attributed to the increased digestibility of the carbohydrate of the diet. Partial cooking of the diet is shown to have the same effect. The sources of starch used were separated rice and potato starch. Addition of diastase to a diet rich in barley flour appears to retard the development of the polyneuritis. E. A. LUNT.

Examination of yeast-fat for the presence of vitamins-*A* and -*D* before irradiation and of vitamin-*D* after irradiation. E. M. HUME, H. H. SMITH, and I. SMEDLEY-MACLEAN (Biochem. J., 1928, **22**, 27—33).—A sample of total fat derived from pressed brewer's yeast showed no activity for vitamin-*A* when administered in daily doses of 0·18 g. Daily doses of 0·14 g. of a sample of acetone-soluble fat prepared from yeast which had been incubated in a carbohydrate–phosphate solution were found to promote neither growth nor the formation of bone in rats on diet deficient in the fat-soluble vitamins (cf. Luce and Smedley-Maclean, A., 1925, i, 483). The same two kinds of yeast-fat together with a sample of fat prepared from yeast after a preliminary boiling with normal acid were irradiated with the mercury vapour quartz lamp and very small doses of these were fed to rats on a diet deficient in the fat-soluble vitamins. The best results were obtained with the fat derived from incubated yeast which promoted growth and bone formation in daily doses of 0·005 mg. S. S. ZILVA.

Determination of vitamin-*D*. H. JEPHCOTT and A. L. BACHARACH (Biochem. J., 1928, **22**, 60—62).—The lowering of the fæcal p_H of rats on a rachitic diet by the administration of vitamin-*D* is a function of the amount administered. S. S. ZILVA.

Determination of vitamin-*D*. E. POULSSON and H. LOVENSKIOLD (Biochem. J., 1928, **22**, 135—141).—The rats are kept on a Steenbock and Black or similar diet (A., 1925, i, 1020) and after a preparatory period of 25 days a skiagram of the left knee-joint is taken and the animals are weighed. The antirachitic substance to be tested is then given for 6 days, at the end of which time another skiagram is taken and the rats are again weighed. The minimum protective dose is taken as a unit and is expressed by the number of such units per g. of active substance. S. S. ZILVA.

Antirachitic substances. VII. Purified cholesterol. C. E. BILLS, E. M. HONEYWELL, and

W. A. MacNair (J. Biol. Chem., 1928, **76**, 251—262).—Provitamin-*D* is not entirely removed from cholesterol by bromination or treatment with charcoal but is reduced to about 3% of the original amount. A concentrated solution of cholesterol so treated shows the three characteristic absorption bands of ergosterol, together with two further bands at 315 and 304 $\mu\mu$; the latter bands may represent some substance other than ergosterol which can be activated by ultra-violet light. In addition to the previously recorded absorption bands of ergosterol, there has been observed a fourth band, common to it and to cholesterol, at 260 $\mu\mu$. C. R. Harington.

Sterols and antirachitic vitamin. A. Windaus and A. Hess (Nachr. Ges. Wiss. Gottingen, 1926, 175—184; Chem. Zentr., 1927, i, 2921—2922).—A discussion of the influence of irradiated foods on experimental rickets, of the properties of ergosterol, and of the differences between the provitamin and cholesterol. A. A. Eldridge.

Is the antirachitic vitamin of cod-liver oil an irradiated ergosterol? A. Adam (Klin. Woch., 1927, **6**, 1289; Chem. Zentr., 1927, ii, 1365).—Alcoholic extracts of cod-liver oil vitamin were prepared at various hydrogen-ion concentrations; with increasing p_H the extracts become darker, whereas at p_H 3—5 they are only faintly yellow. Fluorescence phenomena are different. The absorption spectra of the acid extracts closely correspond with those of irradiated ergosterol. The acid extracts have strong, and the alkaline extracts weak, antirachitic properties. Irradiation of the extract with the quartz lamp in presence of air affects the spectrum in the direction of greater permeability; hence the vitamin can be decomposed by irradiation. The whole of the substance precipitable by digitonin, including the vitamin, can be absorbed on animal charcoal. The spectrum of insulin is similar to that of an irradiated ergosterol. A. A. Eldridge.

Optical detection of a vitamin. R. Pohl (Naturwiss., 1927, **15**, 433—438; Chem. Zentr., 1927, ii, 711).—A lecture.

Influence of the cow's diet on the fat-soluble vitamins of winter milk. II. J. Golding and S. S. Zilva (Biochem. J., 1928, **22**, 173—182; cf. Golding and others, A., 1927, 79).—A winter ration for cows containing silage and hay is described which produced an antirachitic butter of moderate potency. The daily addition of 2 oz. of cod-liver oil to this ration did not significantly depress the percentage of milk-fat nor did it raise the vitamin-*D* of the butter to any appreciable extent. Higher doses of cod-liver oil depressed the percentage of milk-fat and raised the antirachitic potency of the butter. S. S. Zilva.

Relative food values of brown (from "entire" wheat grain) and white (from endosperm of grain) wheaten flour, and their comparative potency for prevention of xerophthalmia in guinea-pigs. E. J. Sheehy (Proc. Roy. Irish Acad., 1927, **37**, 415—425).—Guinea-pigs fed on mangels (20 g.), white flour *ad. lib.*, and 0·4 g. hydrogenated soya-bean oil decline in weight and contract xerophthalmia in 3—7 weeks. The xerophthalmia, but not the decline in weight, is cured when cod-liver oil is substituted for hydrogenated oil. When brown flour made from the entire wheat grain is substituted for white flour, xerophthalmia occurs much more rarely, although the animals decline in weight. If the diet is restricted, brown flour appears to be preferable as a food to white flour. W. O. Kermack.

Effect of irradiation and cod-liver oil on calcium balance in the human adult. M. C. Hart, D. Tourtellotte, and F. W. Heyl (J. Biol. Chem., 1928, **76**, 143—148).—Both irradiation and administration of cod-liver oil were without effect on the calcium balance of a human adult on a diet deficient in calcium. C. R. Harington.

Paralysis in sucklings of mothers deprived of vitamin-*E*. H. M. Evans and G. O. Burr (J. Biol. Chem., 1928, **76**, 273—297).—In the absence of a sufficiency of vitamin-*E* in the diet of the lactating rat, a large proportion of the young exhibit paralysis at the weaning period; this paralysis is specifically the result of deficiency of vitamin-*E*, since it occurs when all other vitamins and food constituents are administered in liberal amounts, and it is not associated with any deficiency in growth. C. R. Harington.

Rat technique for demonstrating interfering effect of cereals on bone calcification. H. N. Green and E. Mellanby (Biochem. J., 1928, **22**, 102—112).—A diet containing inactivated caseinogen, sodium chloride, "marmite," lemon juice, and dried cabbage was used. On such diet the rats grow. This and the ratio of ash of the bones to the difference between the weights of the fat-extracted dry bone and ash determined after a definite period (cf. Chick and others, A., 1927, 176) were used as criteria.

By this method the anti-calcifying action of cereals in rats was demonstrated (cf. Mellanby, Brit. Med. J., 1922, ii, 849; Med. Res. Counc. Report, series No. 93, 1925; J. Physiol., 1926, **61**, Proc., xxiv). The intensity of rickets was made worse by increasing the cereal intake whilst the other dietetic ingredients were kept constant. Oatmeal and wholemeal flour brought about the worst calcifications of the bones, whilst barley meal and white flour were associated with the best calcified bones. Germ of wheat and maize had a rachitic action. Cod-liver oil or cereal exposed to ultra-violet light neutralised the rickets-producing effect of these substances. The raising of the calcium carbonate or calcium phosphate content of the diet minimised the action of the cereals. The anti-calcifying action of cereals is destroyed by boiling with hydrochloric acid. S. S. Zilva.

[**Formation of oxygen from carbon dioxide by protein–chlorophyll solutions.**] M. Eisler and L. Portheim (Biochem. Z., 1928, **192**, 132—136).—The authors' original results (A., 1923, i, 424) are maintained in reply to the criticisms of Dolk and van Veen (A., 1927, 703). P. W. Clutterbuck.

Seasonal changes in conifer leaves, with reference to enzymes and starch formation. J. Doyle and P. Clinch (Proc. Roy. Irish Acad., 1927, **37**, 373—414).—The disappearance of starch from conifer leaves during the winter is associated with

various tissue changes and in particular with a decrease in the activity of certain carbohydrate-splitting enzymes. W. O. KERMACK.

Seasonal variations in the carbohydrate content of pine and fir stems. E. GAUMANN (Ber. deut. bot. Ges., 1927, **45**, 591—597).—Carbohydrate determinations by the Konig and Becker hexosan method were made on young and old pine and fir wood throughout the year. In young pine wood there were two periods of maximum carbohydrate content—in April and October—and a minimum period in February. Similar variations occurred in young fir wood. In both cases the spring maximum corresponded with a maximum in the water-soluble matter; but no autumn maximum in the water-soluble content was observed. In old wood variations in both carbohydrate and water-soluble matter contents were much smaller. Curves expressing the former were characterised by one minimum point occurring in March for the pine and in November for firs. The periodicity of the above values can be generally correlated with periods of maximum growth and assimilation. A. G. POLLARD.

Growth of grapes. II. Relationship between sugar and acid in the juice. III. Effect of environment on growth constants. P. R. v. D. R. COPEMAN (Trans. Roy. Soc. S. Africa, 1927, **14**, 389—393, 395—403; cf. A., 1927, 908).—II. The acid content of grapes decreases during ripening, whilst the sugar content increases. A mathematical expression of the relation is deduced and compared with the results of observation.

III. The constants occurring in the equations expressing the change in various factors during the growth of grapes are influenced by the locality in which the grapes are grown as well as by the variety of grape employed. W. O. KERMACK.

Effect of metallic salts on plant growth. M. CARETTE (J. Pharm. Chim., 1927, [viii], **6**, 151—156).—The effect of soaking seeds in potassium nitrate solution before planting has an excitatory rather than a nutritional value, and although it increases the rate of growth in the earlier stages it does not necessarily produce a high yield. E. A. LUNT.

Differential effect of the ions of three-salt solutions on growth of potato plants in sand culture. F. G. GREGORY (Proc. Roy. Soc., 1928, B, **102**, 311—327).—The work of Johnson (Maryland Agric. Exp. Stat. Bull., 1924, 270) is critically examined and discussed and the results are submitted to new statistical analysis. For a given relative ionic concentration, cations have a greater growth-producing effect than the anions examined. The effect of cations is in the order calcium (greatest), magnesium, potassium. Of the anions nitrate has a positive effect, sulphate is indifferent, and phosphate a negative effect. Based on these calculated values, it is shown that predicted yields for the solutions used by Johnson are more closely in agreement with the mean experimental results than are the results of duplicate experiments. A. G. POLLARD.

General presence of sodium in plants. G. BERTRAND and (MME.) M. ROSENBLATT (Compt. rend., 1928, **186**, 200—202).—The triple sodium magnesium uranyl acetate (cf. A., 1927, 1046) has been used in determining the sodium content of some 20 plants in which sodium has not hitherto been detected. The amounts of sodium found in the dry matter range from 0·0015% in wheat grain to 0·4112% in oat stems. The ratio K/Na ranges from 729 in potatoes to 2·05 in pea stems. B. W. ANDERSON.

Occurrence and significance of manganese in plants. D. H. WESTER (Festschr. A. Tschirch, 1926, 321—325; Chem. Zentr., 1927, i, 2914).—Fertiliser experiments show manganese to be of great importance in plant physiology. The active portions of *Lupinus luteus* are richest in manganese, which has a favourable influence on the content of active constituents of *Prunus laurocerasus*, *Brassica nigra*, and *Papaver somniferum*. A. A. ELDRIDGE.

Minimum toxicity of a mixture of two salts with respect to plants. L. MAUME and J. DULAC (Compt. rend., 1927, **184**, 1081—1083).—The root-growth of wheat in cultures containing standard dilute solutions of sodium or potassium chloride mixed in varying proportions with similar solutions of calcium or magnesium chloride has shown that the minimum toxic effect is produced when the two salts are present in such proportions that their ionisation coefficients are equal. B. W. ANDERSON.

Analysis of plant tissues. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1926, **1**, 397—402).—Recommendations by a committee of the American Society of Plant Technologists. CHEMICAL ABSTRACTS.

Physical structure of pine lignin. W. FUCHS (Biochem. Z., 1928, **192**, 165—166).—Willstatter's lignin is doubly refracting and in the polarising microscope shows indistinct crystalline aggregates (cf. A., 1927, 546, 650). P. W. CLUTTERBUCK.

Evidence for phosphatides in the external surface of plant protoplast. F. C. STEWARD (Biochem. J., 1928, **22**, 268—275).—Leaching experiments with various parenchymatous tissues produced no evidence that phosphatides are present in the surface layer of the protoplasm or that they diffuse from living tissues into distilled water. S. S. ZILVA.

***Curcuma magna* rhizome.** R. GUTTENBERG (Z. ges. exp. Med., 1927, **54**, 642—652; Chem. Zentr., 1927, ii, 599).—Extraction of the rhizome with alcohol and ether yields a terpene, *curcumene*, $C_{15}H_{24}$, b. p. 140—142°/12 mm., $d^{?}$ 0·90, α_D^{18} −10·5°; the compound is emetic, and has a slightly irritant action on the skin. It is partly excreted by the dog and rabbit conjugated with glycuronic acid. The extract also yields an irritant resin, and the alcohol extract a glucoside; the osazone of the sugar has m. p. 179—180°. A. A. ELDRIDGE.

Chemistry of kirondro fruit. I and II. Y. VOLMAR and B. SAMDAHL (J. Pharm. Chim., 1927, [viii], **6**, 295—299, 346—353).—A bitter principle, to which the name *kirondrin* has been given, has been isolated from the seeds of the kirondro (*Perriera Madagascariensis*). By crystallisation from a mixture of alcohol and ether it has been separated into two

fractions, *α-kirondrin* (m. p. 220—221°) and *β-kirondrin* (m. p. 237—240°) which are probably optical isomerides. To α-kirondrin the formula $C_{21}H_{27}O_{10}$ is assigned; it gives the general reactions for alkaloids, reduces silver nitrate and Fehling's solution in the cold, gives no phenylhydrazone even after hydrolysis, and exhibits an intense yellow fluorescence. It is thought to possess a lactonic structure, to be a derivative of anthracene, and to contain several aldehydo-groups, and no ethylenic linkings or phenolic groups. E. A. LUNT.

Seeds of *Nerium oleander*, L. H. MATTHES and P. SCHÜTZ (Festschr. A. Tschirch, 1926, 162—173; Chem. Zentr., 1927, i, 2753—2754).—The seed contains water 8·01, fat 17·43, nitrogen 2·8, crude protein 17·5, ash 3·76%. The seed oil has d^{15} 0·9355, n^{25} 1·4721, n_D^{40} 1·4669, acid value 2·5, saponification value 206·8, Reichert–Meissl value 16·30, Polenske value 0·40, iodine value (Hübl) 105·2 (2 hrs.), 108·6 (18 hrs.), acetyl value 12·5, Hehner value 92·09 (Hehner fatty acids n_D 1·4595), unsaponifiable matter 2·12%. The seta oil has d^{15} 0·9253, n_D^{70} 1·4550, saponification value 182·4, iodine value (Hübl) 91·4 (2 hrs.), unsaponifiable matter 8%. The solid fatty acids (iodine value 3·6) appeared to be a mixture of palmitic and stearic acids. The unsaponifiable matter contains a sitosterol, m. p. 137·5°. A. A. ELDRIDGE.

Occurrence of coumarin in indigenous plants. A. VON LINGELSHEIM (Festschr. A. Tschirch, 1926, 149—154; Chem. Zentr., 1927, i, 2914).—Coumarin is present in *Prunus avium*, *P. fructicosa*, and *P. fructicosa-Cerasus*. A. A. ELDRIDGE.

Non-alkaloidal constituents of ipecacuanha. O. KELLER (Festschr. A. Tschirch, 1926, 85—98; Chem. Zentr., 1927, i, 2916).—"Ipecacuanhic acid" is a glucotannoid or glucosidal tannin of weakly acid character. In addition to small quantities of fat and resin, an acid saponin, malic and citric acids are present. A. A. ELDRIDGE.

Extraction of asperuloside from *Galium verum*, L. Presence of the glucoside in *Rubiaceæ*. H. HERISSEY (Bull. Soc. Chim. biol., 1927, **9**, 953—956, and J. Pharm. Chim., 1927, [viii], **6**, 497—501).—See A., 1927, 1116.

Preparation of sinigrin. H. HÉRISSEY and R. BOIVIN (J. Pharm. Chim., 1927, [viii], **6**, 337—339). —See this vol., 207.

Chemical nature of the glucoside of *Alliaria officinalis*. H. HERISSEY and R. BOIVIN (J. Pharm. Chim., 1927, [viii], **6**, 385—387).—See this vol., 208.

Constituents of *Artemisia brevifolia*, Wallich. ANON. (Pharm. J., 1927, **119**, 688).—The following substances have been isolated from *A. brevifolia*: *l*-camphor, m. p. 177°, $[\alpha]_D$ −44° (monobromide, m. p. 76°); an essential oil (terpene), b. p. 110—180°, *d* 0·950, and a white, crystalline *substance*, m. p. 80°, present to the extent of 0·01%, for which the name *brevifolin* is suggested. This substance gives an intense blue colour with concentrated nitric acid, is optically inactive, and is unaffected by light. E. H. SHARPLES.

Separation of tannins and anthocyanidins occurring in the same organs of plants. Isolation of a new anthocyanidin from the red leaves of *Acer platanoides*. S. IONESCO (Compt. rend. Soc. Biol., 1927, **96**, 1020—1022, 1022—1023; Chem. Zentr., 1927, ii, 267).—Tannins may be separated from anthocyanidins by taking advantage of their solubility in ether. The anthocyanidin from the red leaves of *Acer platanoides* is named *aceridin* and is similar to pelargonidin except as regards solubility in water and acids. Substances can be extracted from organs by solvents in which the pure compounds are not soluble, owing to the existence of complexes or to adsorption phenomena. A. A. ELDRIDGE.

Red and blue colouring matters of flowers and fruits. A. E. TSAKALOTOS (Festschr. A. Tschirch, 1926, 291—298; Chem. Zentr., 1927, i, 2915).—The red and blue colouring matters of flowers are accompanied by chlorophyll and yellow colouring matters. A spectro-analytical examination of a solution of the anthocyanin zone indicates no sharp distinction of the anthocyans. The colouring matter of fresh, but not dried, whortleberries on capillarity separation yields a mixture of two components; a similar difference was observed with *Sambucus nigra*. Two distinct zones can also be observed with alkanet. A. A. ELDRIDGE.

Freezing as a method of preserving plant tissue for the determination of nitrogenous fractions. G. T. NIGHTINGALE, W. R. ROBBINS, and L. G. SCHERMERHORN (N.J. Agric. Exp. Sta. Bull., 1927, **448**, 1—16).—Methods for the determination of nitrogen fractions are described which give results unaffected by freezing. CHEMICAL ABSTRACTS.

Colloidal albumin content of living plant cells. T. BOKORNY (Kolloid-Z., 1928, **44**, 166—173).—An account of matter mainly already published on the aggregation of the cell contents of living plants. E. S. HEDGES.

Carbamide in fungi. N. N. IVANOV (Biochem. Z., 1928, **192**, 36—40).—Reply to the criticisms of Kiesel (Ergeb. Biol., 1927). P. W. CLUTTERBUCK.

Formation of diastase by *Aspergillus niger*. G. L. FUNKE (Rec. trav. bot. neerl., 1926, **23**, 200—244; Chem. Zentr., 1927, ii, 706).—Reducing sugars when sterilised in neutral solution become brown by the action of alkali from the glass, but in presence of acid phosphate there is no change. The brown material inhibits the growth of *Aspergillus* and retards the production of amylase; the production of amylase in lævulose solution, however, is increased Dextrose and starch promote, whereas lævulose, mannose, lactose, and inulin hinder amylase formation. Galactose as such does not reduce amylase formation, but the metabolic products of mannose do so. Glycerol has no effect. A. A. ELDRIDGE.

Rancidity of coconut oil produced by mould action. W. N. STOKOE (Biochem. J., 1928, **22**, 80—93).—*Penicillium palitans* was grown on a gelatin medium containing deodorised coconut oil. The melted medium and growths were then distilled in a current of nitrogen. The residue, the aqueous and

the oily distillates were examined. The odoriferous oily distillate was shown to contain methyl amyl, methyl heptyl, and methyl nonyl ketones. The methyl amyl ketone occurs in the greatest quantity and is responsible for the characteristic odour of the rancid oil. There were also present secondary alcohols corresponding with the ketones, ethyl alcohol, esters of the secondary alcohols and ethyl alcohol with caprylic acid and free fatty acids. The selective action of *P. palitans* and *Oidium lactis* was also studied on pure fatty acids, secondary alcohols, methyl ketones, keto-esters, and keto-esters in presence of beef-fat. The poisoning capacity of the fatty acids towards *Penicillium* increases with the mol. wt. up to *n*-octoic acid and then decreases. Only acids up to lauric acids are absorbed. The fatty acids with the exception of butyric acid and perhaps the lower acids are more poisonous to *O. lactis* than to *Penicillium*. *Oidium lactis* does not induce ketonic fission of the keto-acid. The fatty acids from coconut oil were oxidised with hydrogen peroxide by Dakin's method, but the formation of secondary alcohols as intermediate products could not be demonstrated. S. S. ZILVA.

Significance of the red crystals appearing, on treatment with cresol-blue, in the cells of certain algæ. G. MANGANOT (Compt. rend., 1928, **186**, 93—95).—Iodides react with cresol-blue to form red crystals of oxonium iodide. This reaction is sensitive enough to enable the distribution of iodides in the vacuoles of algæ to be accurately determined.

B. W. ANDERSON.

Ergot. A. DAMONTE (Giorn. Farm. Chim., 1927, **76**, 127—131; Chem. Zentr., 1927, ii, 150).—"Stabilisation" of ergot by means of alcohol under pressure is useless. Water extracts only part of the alkaloids, and the yield is scarcely increased when acidified water is used. A. A. ELDRIDGE.

[Non-]effect of X-rays on decomposition of starch. E. SCHNEIDER (Strahlentherapie, 1926, **23**, 326—335; Chem. Zentr., 1927, i, 3065).—Decomposition of starch was not observed.

A. A. ELDRIDGE.

Occurrence of barium and probably strontium in arable earths. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1928, **186**, 335—338).—The presence of barium in six samples of soils obtained from widely differing sources has been proved by spectroscopic examination of the alkali carbonate fusion products. In two cases the presence of strontium was observed. It is possible that all arable earths contain barium sulphate, and the occurrence of strontium is probably more common than has been shown. H. BURTON.

Automatic gas analysis for respiration experiments. M. KLEIBER and A. WIRTH (Biochem. Z., 1928, **192**, 241—249).—An apparatus for automatic gas analysis in respiration experiments is described in which the result is registered photographically as a difference of pressure, arising after absorption of one constituent, between measuring and compensating pipettes, the accuracy of the method being claimed to be practically as good as in the Haldane method.

P. W. CLUTTERBUCK.

Simple spectro-colorimeter. H. F. HOLDEN (Austral. J. Exp. Biol., 1927, **4**, 221—224).—This instrument is designed to obviate the use of the spectro-photometer in the determination of substances which themselves or in their derivatives show well-defined absorption bands in the visible spectrum, *e.g.*, for globin or for hæmoglobin. The apparatus consists of a colorimeter the illuminated cups of which provide a light source for a direct-vision spectroscope. The unknown and the standard solutions of the same substance are adjusted in the colorimeter until the intensities of their chief absorption band appear by means of the spectroscope to be equal.

E. A. LUNT.

Surface tension of physiological solutions. Difficulties of measurement and interpretation. J. M. JOHLIN (J. Gen. Physiol., 1928, **11**, 301—308).—Surface-tension values obtained by the ring method are not trustworthy when absolute values are required even with pure liquids, and with semi-colloids the changes in surface tension following the formation of a new interface are not consistently reproduced. The changes in the surface tension of gelatin solutions—a decrease sometimes followed by a rise as determined by the capillary rise method (cf. A., 1925, ii, 388)—show similar irregularities with the ring method, and the results indicate the impossibility of obtaining consistent results with solutions of this type. With solutions of semi-colloids, equilibrium values are not readily obtained and the rate of change of surface tension with time differs with similar solutions and occasionally with different samples of the same solution. A. WORMALL.

Nephelometric determination of chlorine and silver. T. VON HEIDLBERG (Biochem. Z., 1928, **192**, 238—240).—Nephelometric methods are described for the determination of silver and chlorine in small amounts. The limits of the method are about 0·005 mg. of silver nitrate when the error is about 3—5%. Above 0·1 mg., silver chloride precipitates.

P. W. CLUTTERBUCK.

Electrolytic determination of arsenic in biological material. A. E. OSTERBERG (J. Biol. Chem., 1928, **76**, 19—22).—A modification of the apparatus of Fink (A., 1927, 600) is described in which the whole sample may be placed in the cathode chamber, the reduction of the arsenic being thus facilitated.

C. R. HARINGTON.

Micro-colorimetry. I. Molybdic acid–stannous chloride reagent. Determination of phosphate and calcium in pus, blood-plasma, and cerebrospinal fluid. T. KUTTNER and H. R. COHEN (J. Biol. Chem., 1927, **75**, 517—531).—Substitution of stannous chloride for the quinol or other reducing agent employed by Briggs (A., 1922, ii, 718) and previous workers, yields a reagent which gives a more rapidly developing and intense colour with phosphates. With the aid of a micro-colorimeter the method allows of the determination of phosphates and of calcium (after incineration of the material and precipitation of calcium as tertiary phosphate) in 0·1—0·2 c.c. of the above biological materials.

C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

APRIL, 1928.

General, Physical, and Inorganic Chemistry.

Construction of wave-length scales for spectrograms. G. Barr (Trans. Opt. Soc., 1928, **29**, 22—27).—A method is described by which an approximate scale of wave-lengths may be projected geometrically on to a spectrogram from a uniformly divided scale when a number of easily recognisable lines have been identified. C. W. Gibby.

Use of single thermo-junctions and of echlette gratings in the far infra-red. R. M. Budger (J. Opt. Soc. Amer., 1927, **15**, 370—373).—Methods of focussing radiation of the order of 100 μ on to single thermo-junctions are described whereby the diffuse images due to aberrations in reflexion are avoided. The construction of a simple echlette grating from plane parallel glass strips is also described. R. W. Lunt.

Evolution of the theory of spectra. T. Negresco (J. Chim. phys., 1928, **25**, 142—153).—Historical. H. F. Gillbe.

Relativistic interpretation of the theory of fine structure of spectral lines of the hydrogen atom. S. Mohorovičić (Arh. Hemiju, 1928, **2**, 6—14).—The use of the special relativity theory is not permissible and the extended general theory is not capable of accurately defining the orbits of the electron around the proton. The introduction of the special theory into physics is regarded as wholly unnecessary. R. A. Morton.

Intensity distribution in Fraunhofer lines. M. Minnaest (Z. Physik, 1927, **45**, 610—619).—The distribution of intensity in the Fraunhofer lines H_a and Ca*K* has been determined. The results are discussed with reference to those of von Klüber (A., 1927, 909). R. W. Lunt.

Nebulium spectrum. J. C. McLennan and R. Ruedy (Nature, 1928, **121**, 319).—Following a discussion of observations on nebulæ, it is stated that the energy to excite the nebulium lines would be very small if the material (oxygen) were already ionised, and that the lines are essentially emission lines, having as yet no importance in absorption spectra. It is concluded that the oxygen which is responsible for the nebular lines is present as a molecule or molecular ion. A. A. Eldridge.

Origin of the nebulium spectrum. M. Saha (Nature, 1928, **121**, 418).—A discussion of the nature of the transitions, usually prohibited, from which the "nebulium" lines of ionised oxygen and nitrogen arise (Bowen, A., 1927, 997). A. A. Eldridge.

"Nebulium" spectrum in new stars. C. T. Elvey (Nature, 1928, **121**, 453).—The discrepancy between the conclusions of Pike (this vol., 210) and those of the author are ascribed to the inapplicability of the theory of thermal ionisation. A. A. Eldridge.

Nebulium and hydrogen in new stars. B. P. Gerasimovic (Nature, 1928, **121**, 422).—A modified method of calculation leads to a density of 6×10^{-16} as permitting the co-existence of hydrogen and ionised oxygen lines in the spectra of new stars. A. A. Eldridge.

Life of atomic states and the intensity of spectral lines. I. S. Bowen (Proc. Nat. Acad. Sci., 1928, **14**, 30—32; cf. A., 1927, 997).—From the previously published explanation of the strong nebular lines as due to electron jumps from metastable states in oxygen and nitrogen and the known highly rarefied state of the gases in nebulæ, it is concluded that metastable states are not absolutely metastable, but are states with mean lives of the order of a second or so. W. E. Downey.

Spark potentials in nitrogen. B. Frey (Ann. Physik, 1928, [iv], **85**, 381—424).—The influence of water vapour on the potential of the spark discharge in nitrogen has been studied. No change in the discharge potential is produced by the passage of a secondary spark when the gas is dried by liquid air. As the amount of moisture present increases, however, the sparking potential diminishes to a minimum and then increases. Since the same phenomenon is observed when hydrogen is introduced into the nitrogen, and since, also, the effect of moisture is nullified by the presence of a heated tungsten wire in the tube, it is concluded that the behaviour of water vapour is due to dissociation into its constituent gases. The potential lowering caused by very small quantities of hydrogen is probably due to the high activity of the proton in ionisation by collision. With increasing quantities of hydrogen larger ions are formed, ionisation diminishes, and the sparking potential increases. If sparking potental is plotted against the product of pressure and length of spark-gap, for different mixtures of nitrogen and hydrogen, the minimum sparking potential is lower than the minimum for the pure constituents. This appears to indicate that the hydrogen proton can ionise nitrogen better than the positive nitrogen ion, and can also ionise nitrogen better than it can ionise hydrogen. The influence of the electrode materials has been examined. In a state of moderate dryness the

sparking potential for magnesium electrodes is some volts lower than for silver, but the reverse is the case in well-dried gas. This behaviour is explained by the formation of a layer of magnesium nitride by the discharge in the dried gas. In the presence of a little moisture, however, this is destroyed.

M. S. BURR.

Regularities in the spectrum of ionised neon. P. K. KICHLU (Proc. Physical Soc., 1928, 40, 41—45).—Hund's theory is applied in tracing doublet terms and intercombinations between doublets and quadruplets. Almost all the lines between 2500 and 3800 Å. have been accounted for with few discrepancies. C. J. SMITHELLS.

Spark spectrum of neon. H. N. RUSSELL, K. T. COMPTON, and J. C. BOYCE (Nature, 1928, **121**, 357).—Fifteen new lines between 462·38 and 353·01 have been observed; 203 lines have now been classified in 59 multiplets. The ionisation potential of the neon ion is 40·9±0·05 volts. A. A. ELDRIDGE.

Spark spectrum of sodium. S. FRISH [with (FRL.) A. FERCHMIN] (Naturwiss., 1927, **15**, 507; Chem. Zentr., 1927, ii, 784).—Alkali halide is placed in the capillary of a silica Geissler tube, and the tube filled with hydrogen or helium under low pressure. The capillary is heated while a discharge is passed and the tube placed in a magnetic field; the intensity of the arc spectrum of the alkali metal is reduced, and new lines, belonging to the spark spectrum of the metal and the arc spectrum of the halogen, appear, the intensity increasing with that of the magnetic field. The effects are more marked with a Paschen concave cathode. A. A. ELDRIDGE.

Spectrum of ionised sodium. K. MAJUMDAR (Nature, 1928, **121**, 423).—A preliminary statement of the result of an analysis of the spectrum of ionised sodium. The lines $5L_2(M_1 \longrightarrow M_2)$ have been completely, and the lines $5L_2(M_2 \longrightarrow M_3)$ partly, identified. The ionisation potential is about 47 volts, and the radiation potential 32·8 volts. A. A. ELDRIDGE.

Polarisation of the sodium rumpf (core). H. BARTELS (Naturwiss., 1927, **15**, 487—488; Chem. Zentr., 1927, ii, 784).—The polarisability of the sodium rumpf remains unchanged up to the eleventh member of the first sodium subordinate series. Negative polarisability certainly does not occur up to the 17*d* term. A. A ELDRIDGE.

Intensity of the lines in the principal series of potassium. F. RASETTI (Atti R. Accad. Lincei, 1927, [vi], **6**, 503—505).—By means of the anomalous dispersion method described in a previous paper (A., 1927, 1118) the number of electrons per atom responsible for the dispersion (n) has been determined in the potassium series $4\text{-}S - m\text{-}P$ for the lines corresponding with $m=4, 5, 6, 7,$ and 8. The corresponding values of n are 1·0, $9{\cdot}0 \times 10^{-3}$, $7{\cdot}8 \times 10^{-4}$, 2×10^{-4}, and $1{\cdot}3 \times 10^{-4}$ within 5%. O. J. WALKER.

Structure of the cobalt I spectrum. II. M. A. CATALAN (Anal. Fís. Quím., 1927, **25**, 518—548, and Z. Physik, 1928, **47**, 89—113; cf. A., 1925, ii, 611).—The discovery of new terms has led to the classification of more than 700 lines, so that about 1200 lines in the arc spectrum have now been classified. The low terms result from two different outer electron configurations, viz., d^7s^2 and d^8s^1. They are in agreement with the theory of Hund. J. S. CARTER.

Spectra of krypton and xenon in the extreme ultra-violet. J. H. ABBINK and H. B. DORGELO (Z. Physik, 1928, **47**, 221—232).—Vacuum grating spectra of krypton and xenon under various conditions of excitation have been tabulated for the region 1500—500 Å. Certain lines ascribed by Taylor (A., 1927, 178) to krypton appear to belong to xenon. The following ionisation potentials are deduced: krypton 13·9, xenon 12·0 volts. R. A. MORTON.

Spark spectrum of silver. K. MAJUMDAR (Indian J. Phys., 1928, **2**, 257—266).—The known lines in the spark spectrum of silver have been analysed and classified with a view to a comparison with the spark spectra of copper and gold. New lines determined with the vacuum grating have also been given in the region from 3372·65 to 1932·76 Å.

M. S. BURR.

Intensity distribution in Wood's resonance spectrum of iodine. O. OLDENBERG (Z. Physik, 1927, **45**, 451—454).—By using plates sensitised with neocyanine the terms 27—37 (7687—8823 Å.) of the molecular spectrum of iodine, excited by the mercury green line, have been observed; the intensities of these newly-observed terms have been determined.

R. W. LUNT.

Recombination spectra of atomic ions and electrons. F. L. MOHLER (Physical Rev., 1928, [ii], **31**, 187—194).—With cæsium, continuous bands extending to the violet from the limit $2P_1$ of the subordinate series, from the limit of the F series, and faintly beyond the P series, were observed. Potassium shows a strong band beyond the subordinate series. Intensity measurements were made. Intensity distribution in the line spectrum indicates a relatively high probability of recombination into levels of high quantum number, and relatively improbable recombination into the normal level.

A. A. ELDRIDGE.

Influence of vapour pressure on the intensity and broadening of mercury resonance lines. W. ORTHMANN and P. PRINGSHEIM (Z. Physik, 1927, **46**, 160—167).—The diminution of intensity and the broadening of the resonance lines in mercury vapour have been determined in the mercury vapour pressure range 0·01—7·3 mm. The effect produced by the addition of a neon-helium mixture of 250 mm. partial pressure is the same as that due to the increase in mercury vapour pressure in the above range. The results are thought to afford evidence of abnormally large values of the effective radius of mercury atoms of the order of 10^{-7} cm. R. W. LUNT.

Hyperfine structure and polarisation of $1^1S_0 - 2^3P_1$ of mercury in resonance radiation. A. ELLETT and W. A. MACNAIR (Physical Rev., 1928, [ii], **31**, 180—186; cf. MacNair and Ellett, A., 1927, 911).—The incomplete polarisation is due to either or both of the outer hyperfine structure lines.

A. A. ELDRIDGE.

Density of a luminous gas and the emission of light by atoms in metastable states. B. VENKATESACHAR (Nature, 1928, **121**, 356).—The fact

that the intensity of the forbidden line 2270 Å. in the arc spectrum of mercury increases as the density of the vapour in a mercury arc is diminished is evidence in support of Bowen's view that the low density in nebulæ is favourable to the emission of light by atoms in metastable states (A., 1927, 997).

A. A. ELDRIDGE.

Sputtering of metals by disruptive discharge in a magnetic field. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 643—645).—Previous experiments on sputtering produced by passing a heavy current through metals in loose contact (cf. this vol., 97) were continued in a magnetic field of 30 kilogauss. The paths followed by the luminous particles ejected from different metals are described and photographed. Particles of titanium, chromium, and manganese follow straight paths until near the end of luminosity, when they fork, owing to separation into several parts. Aluminium particles follow curved paths at the end, when the luminous intensity becomes greatest. Tungsten and molybdenum follow straight paths and show sudden increases in luminosity. These effects are ascribed to the oxidation of the particles. The magnetic properties of the metals are not important, since the temperature is above that at which ferromagnetism ceases.

C. J. SMITHELLS.

Filtration of spark lines by disruptive discharge in magnetic field. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1927, **3**, 647—649).—The spectra of the disruptive discharge (preceding abstract) in the absence of a magnetic field show both arc and spark lines of the metal. When a magnetic field is applied the spark lines are confined mainly to the neighbourhood of the poles, and fade towards the middle, whilst the arc lines show little difference in intensity across the gap. Lines which show reversal in the absence of a magnetic field appear strongly marked when the field is applied.

C. J. SMITHELLS.

Discrepancies in Moseley's law. V. DOLEJSEK (Z. Physik, 1927, **46**, 132—141).—It is shown that for the homologous elements of atomic number 36, 54, and 86, the value of $\sqrt{\nu/R}$ is given by the empirical expression $a+bN+cN^2+dN^3$, where N is the atomic number and a, b, c, d are constants. The difference between the experimental value of $\sqrt{\nu/R}$ and that calculated from the above empirical expression is shown to be a periodic function of the atomic number.

R. W. LUNT.

γ-Ray spectrography by crystalline diffraction. FRILLEY (Compt. rend., 1928, **186**, 425—427). The wave-lengths and the corresponding quantum energies of the rays measured have been determined by the author's apparatus for γ-rays from various sources, the maximum error being 3%. The γ-radiation obeys the Einstein photo-electric law, the upper energy limit investigated being 617 kilovolts (for the ray 20×10^{-11} cm.). The K-rays of radium-C and radium-C' result from the disintegration of radium-B and radium-C, respectively.

J. GRANT.

Structure of the $K\alpha$-lines of the metals between calcium and copper. N. SELJAKOV, A. KRASNIKOV, and T. STEOOZKY (Z. Physik, 1927, **45**, 548—556).—An examination of the $K\alpha$-lines of the metals calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper by an improved form of Siegbahn spectrograph has revealed the existence of irregularities on one side of the maximum which are associated with the $K\beta$-line.

R. W. LUNT.

Polarisation of the iron $K\alpha$-radiation. H. HAAS (Ann. Physik, 1928, [iv], **85**, 470—482).—Within the limits of experimental error, in an apparatus described in detail, no polarisation of the iron $K\alpha$-lines has been found for a voltage interval of 7·4—12·6 kilovolts (excitation limit 7·1 kilovolts). This is not in accordance with the observation of Bishop on the molybdenum $K\alpha$-lines (A., 1926, 1187).

M. S. BURR.

Spectrographic researches in the intermediate region. J. THIBAUD and A. SOLTAN (J. Phys. Radium, 1927, [vi], 8, 484—494; cf. A., 1927, 1000).—The following new rays (in Å.) have been detected by the Thibaud vacuum spectrograph (A., 1927, 803), in which a ray of fluorescent oil covering the plates has been found unnecessary: K-rays of nitrogen 31·8, and of boron 68·0; N-rays of tantalum 58·3 and 61·4, of tungsten 56·0 and 59·1, of platinum 48·0 and 51·0, and of gold 46·8 and 49·4; O-rays of thorium 64·5 and 68·1. The N-rays of the heavy elements constitute a regular doublet due to the transition O—N IV—V, the most intense components having the longest wave-lengths. The quantum of the L II—III level of the light elements has been calculated from the energies measured for the K-rays and from the ionisation potentials, and a rise in Moseley's curve for this level, relative to these elements, is shown to exist. The deviations from the results of Dauvillier for the absolute wave-lengths of the K-rays of carbon and boron increase rapidly with the wave-length and are explained by the variation of the refractive index at the high wave-lengths. This variation, which follows the Drude–Lorentz rule, must be allowed for in the determination of high wave-lengths (above 20 Å.) from Bragg's formula.

J. GRANT.

Polarisation of spectral X-rays. E. WAGNER and P. OTT (Ann. Physik, 1928, [iv], **85**, 425—469).—The polarisation in a wave-length range of $\Delta\lambda=0{\cdot}055$ Å., at about 2 Å., has been examined by reflexion from a sodium chloride crystal at a glancing angle of 45°. The degree of polarisation is defined as the ratio of the reflexion intensity perpendicular to the cathode rays, to the reflexion intensity parallel to the cathode rays. The degree of polarisation increases with diminishing potential, the rate increasing as the minimum potential is approached. The degree of polarisation is not influenced to any great extent by the material of the anticathode. Lead, silver, copper, and iron, which were investigated, gave the same value, 1·4 0·2, for 10·88 kilovolts. A change in the degree of polarisation, due to the simultaneous appearance of approximately equally hard rays characteristic of the anticathode material, was not observed.

M. S. BURR.

Scattering of X-rays from gases. C. S. BARRETT (Proc. Nat. Acad. Sci., 1928, **14**, 20—23). Monochromatic radiation from an X-ray tube with a

molybdenum target was obtained by means of filters of strontium oxide and zirconium oxide. When such radiation was passed through carbon dioxide, the scattered rays showed interference; no interference, however, was shown by the rays scattered from hydrogen. W. E. DOWNEY.

Soft X-ray emission and absorption spectra with tangential grating. J. THIBAUD (Nature, 1928, **121**, 321—322).—By using an intense electronic current and elements of high at. wt. as anticathode, the author has demonstrated the emission of a continuous spectrum from solid bodies between 15 and 250 Å. The continuous background is divided by a succession of fine bands with abrupt edges on the short wave-length sides. A sensitive method for revealing minute quantities of gaseous matter is thus available. The wave-lengths of the -edges of carbon, nitrogen, and oxygen, respectively, are 43·5, 31·1, and 23·5 Å. A. A. ELDRIDGE.

Absorption of X-rays in various elements. E. JONSSON (Nature, 1928, **121**, 283).—A question of notation. A. A. ELDRIDGE.

Polarisation factor in X-ray reflexion. R. W. JAMES (Nature, 1928, **121**, 422—423).—James and Firth's determinations of the atomic scattering factor (this vol., 225) do not appear to be affected by errors arising from the degree of polarisation of the incident beam. A. A. ELDRIDGE.

Fine-structure and Zeeman effect for the mercury resonance line. M. SCHEIN (Ann. Physik, 1928, [iv], **85**, 257—312).—The intensity of the secondary resonance radiation of mercury vapour shows a sharp decrease in magnetic fields varying from 0 to 1300 gauss (corresponding with 0—5·8×10 Å.). The curve obtained by plotting intensity against magnetic fields over the range 0—13,000 gauss (0—5·8×10 - Å.) shows 5 maxima, corresponding with five equally spaced components approximately 0·01 Å. apart. A similar curve of the absorption of the resonance line shows minima in exactly the same positions as the maxima in emission. The resonance curve for absorption shows no further minima above 13,000 gauss, and it is concluded that the effective breadth of the resonance line under the given experimental conditions cannot exceed 0·076 Å. Each of the five components of the absorption line is resolved in a magnetic field into a triplet.

If the resonance line consists of five equidistant, equally intense, lines, the maxima in the resonance curve should be in the ratios 10 : 8 : 6 : 4 : 2, whereas the observed ratios are 10 : 6·5 : 5·4 : 3·6 : 2·3. Qualitatively, Wood's scheme of resolution is satisfactorily confirmed, but the minima of energy emission in the magnetic field show uniformly higher intensities than would be expected from Wood's scheme, assuming the Doppler effect as the sole line-broadening agency. The maximal absorption coefficient for a layer of vapour 1·1 cm. long at 0·0013 mm. pressure is 3·77. R. A. MORTON.

Nuclear moment and Zeeman effect for bismuth. E. BACK and S. GOUDSMIT (Z. Physik, 1928, **47**, 174—183).—A study of the Zeeman effect on bismuth lines with a strong field confirms the authors' view (A., 1927, 706) that the hyperfine structures are due to very narrow multiplet combinations brought about by a nuclear moment. The magnitude of the mechanical nuclear impulse moment is determined from the Zeeman effect to be 4·5 $h/2\pi$. For the first time, Landé's theory of fine structure in the Paschen–Back effect receives experimental confirmation. R. A. MORTON.

Zeeman effect in band spectra. R. DE L. KRONIG (Physical Rev., 1928, [ii], **31**, 195—198).—Anomalies observed by Kemble, Mulliken, and Crawford (A., 1927, 1119) in the intensities of the Zeeman components in the Ångstrom carbon monoxide bands are explained. A. A. ELDRIDGE.

Stark effect for the spectra of silver, copper, and gold. Y. FUJIOKA and S. NAKAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 263—276).—See this vol., 2.

Ionisation potential of helium according to Schrodinger's theory. H. G. GRIMM (Naturwiss., 1927, **15**, 561; Chem. Zentr., 1927, ii, 1123).—Schrodinger's theory gives term values 76·994, 77·316, 77·345, and 77·840, corresponding with values of 22·904, 23·226, 23·255, and 23·750 for the difference, in volts, between the energy value of the normal state (1*S*) and the ionisation potential of singly-ionised helium. The experimental term value is 78·564. A. A. ELDRIDGE.

Constitution of the solar atmosphere. S. B. NICHOLSON and N. G. PERRAKIS (Compt. rend., 1928, **186**, 492—495).—The solar atmosphere, so far as is known at present, contains neither the extremely stable nor the extremely unstable elements (*e.g.*, rare gases and radioactive elements, respectively). A comparison of the ionisation potentials of the elements from hydrogen to xenon with their atomic numbers shows that the absence of the elements concerned is reproduced periodically, and that they are grouped at the extremities of periods usually occupied by elements of high ionisation potentials. The exceptions (helium and boron) are apparent only, but the almost complete absence of heavy elements is difficult to explain. J. GRANT.

[Constitution of the solar atmosphere.] H. DESLANDRES (Compt. rend., 1928, **186**, 495; cf. preceding abstract).—The high ionisation potential and the exceptional nature of helium recorded by the authors are explainable by the ejection of radioactive substances from solar volcanoes, accompanied by doubly-ionised helium atoms in the form of α-particles. These combine with electrons with great force, with the emission of an intense spectrum. J. GRANT.

Photo-electric and thermionic work functions of outgassed platinum. L. A. DUBRIDGE (Physical Rev., 1928, [ii], **31**, 236—243).—With monochromatic light the final value of the photo-electric threshold is 1962 Å. (6·30 volts), and that of the thermionic work function 6·35 volts. A. A. ELDRIDGE.

Optical determination of the thickness of photo-electrically active rubidium films. H. E. IVES and A. L. JOHNSRUD (J. Opt. Soc. Amer., 1927, **15**, 374—381).—The thickness of photo-electrically active films of sodium and of rubidium deposited

on glass and on platinum surfaces has been determined from changes in the azimuth or phase of plane polarised light incident at 45° on the film. The results indicate that complete photo-electric emission is obtained from an approximately unimolecular film of rubidium.

R. W. LUNT.

Critical primary velocities in the secondary electron emission of tungsten. H. E. KREFFT (Physical Rev., 1928, [ii], **31**, 199—214).—The curve showing the number (n) of secondary electrons produced by one primary electron as a function of the primary velocity, obtained with tungsten at 1250—1450° Abs. and velocities of 10—700 volts, shows a maximum at 15·3 volts, a minimum at 20 volts, 18 breaks between 25 and 600 volts, and a maximum at 630 volts. The effect of adsorption of gas is investigated.

A. A. ELDRIDGE.

Restored electron theory of metals and thermionic formulæ. R. H. FOWLER (Proc. Roy. Soc., 1928, **A**, **117**, 549—552).—The electron theory of metallic conduction, as re-instated by Sommerfeld (Naturwiss., 1927, **15**, 825), is applied to the calculation of the density of evaporated electrons in equilibrium with the heated metal. A consideration of the equilibrium state of an assembly consisting of a heated metal and an atmosphere of free electrons shows that the vapour pressure has twice the value commonly accepted, owing to the fact that each electron has two orientations. This result is applied to the theory of thermionic emission, and gives values in good agreement with the best determinations for the metals tungsten, molybdenum, tantalum, and platinum in a very pure state.

L. L. BIRCUMSHAW.

Extraction of electrons from cold conductors in intense electric fields. O. W. RICHARDSON (Proc. Roy. Soc., 1928, **A**, **117**, 719—730).—The experimental results of Gossling and of Millikan and Eyring (cf. A., 1926, 448, 219) are discussed, and a theory is developed to account for the phenomenon of an electron current which is independent of the temperature of the emitting substance, but is a continuous function of the field intensity. The sharpness of the photo-electric effect at a metallic surface is explained, and, by treating the attraction of an electron by its mirror image in a conductor as a Schrödinger wave problem, a formula is derived for the field currents from cold conductors which agrees with the experimental data. The theory indicates that in the neighbourhood of a nucleus, electrons are discontinuously coming into space, and are generated at a rate proportional to $(\psi\bar{\psi})^{3/2}$. The experimental evidence does not support the view that the localisation of the discharge in restricted areas is due to these areas being sharp protuberances. It is considered that the localisation must be attributed to the possession by different parts of the surface of a different constitution.

L. L. BIRCUMSHAW.

Affinity of oxygen for electrons. M. A. DA SILVA (Compt. rend., 1928, **186**, 583—584).—The author's determinations of the ionisation of pure argon (A., 1927, 809) have been extended to the case of a thin layer of gas on the surface of a plate of the measuring condenser, the other plate, 5 cm. away, being connected to a quadrant electrometer. The current passing through the gas depends on the sense of the applied field, and the tension required to produce saturation is six times as great when it is carried by the positive as by the negative ions. A concentration of oxygen of 3×10^{-4}, or more, produced a deformation in the current–voltage curve in the latter, but not in the former case, indicating that oxygen molecules have a strong affinity for electrons, but not for the positive ions of argon. The latter may probably remove an electron from the neutral molecules of oxygen they meet. A comparison of the deformed curve with that obtained for positive ions indicates that the mean mobility of the negative ion is a function of the applied field. At low tensions they are similar, but as the tension increases the deformed curve approaches saturation more rapidly. The deformation decreases with the (atmospheric) pressure. These results are in agreement with J. J. Thomson's probability theory of ionisation.

J. GRANT.

Existence of sub-electronic charges. F. EHRENHAFT (Z. Physik, 1927, **45**, 577—560).—A review of recent work which indicates the existence of sub-electronic charges on small metallic particles and on oil droplets.

R. W. LUNT.

Errors in Ehrenhaft's technique for the detection of sub-electronic charges. E. WASSER (Z. Physik, 1927, **45**, 561—587).—The probable errors in Ehrenhaft's technique are analysed at length.

R. W. LUNT.

Magnetic moments of the cupric ion. (MLLE.) P. COLLET and F. BIRCH (Compt. rend., 1928, **186**, 499—501).—The work of Cabrera (A., 1926, 7) has shown that a study of the thermal variation of the coefficient of magnetisation is necessary for the determination of the Curie constant. The magnetic moments of the cupric ion in solids and in their solutions have thus been determined for temperature intervals for which the relation is linear. A dominant moment of 10 magnetons was found, and also values of 9 and 9·6 magnetons, but the last may be due to a mixture of carriers of moments of 9 and 10, produced, *e.g.*, by the formation of complex ions in solutions of cuprous chloride at various temperatures.

J. GRANT.

Activation of hydrogen by electric discharge. R. W. LUNT (Nature, 1928, **121**, 357).—A criticism of Glockler's hypothesis (this vol., 140) concerning Elliott's observations (A., 1927, 187).

A. A. ELDRIDGE.

Active nitrogen. E. J. B. WILLEY (Nature, 1928, **121**, 355).—In part, polemical against Lewis (this vol., 258). Between 1 mm. and 10 mm. pressure the process of decay of the after-glow is very complex, although bimolecular with respect to the active nitrogen. Probably the luminosity and the chemical activity are steps in an involved deactivation process, the first stage consisting of a ternary collision between two atoms and a molecule. Objection is raised to Lewis' theory of the formation of ammonia from atomic nitrogen and atomic hydrogen.

A. A. ELDRIDGE.

New effect in the electric discharge. I. R. MERTON (Proc. Roy. Soc., 1928, **A**, **117**, 542—549).—

A peculiar type of striated discharge has been observed in vacuum tubes containing helium. The discharge tubes were provided with tubes of 2 cm. bore, 20—40 cm. long, in place of the usual capillary. Carbon electrodes were used, and the phenomena were best observed at a pressure of 30—40 mm. A state is reached at which the helium tube, when excited by the uncondensed discharge from a high-tension transformer fed with alternating current at 50 cycles, shows an almost uniform green glow. By introducing a condenser and spark-gap into the circuit, it is possible to start a disturbance which gives rise to a new type of disc discharge, which is described in detail. The spectrum of the discs differs from that of the green glow in that the helium lines, which are feeble in the green glow, and the comet bands are very bright in the discs, whilst the Swan bands can be seen only in the green glow, being absent from the discs. On examination of the discs by means of a beam of sunlight it was found that the sunlight is strongly scattered in the neighbourhood of the discs. The scattering is probably due to very small particles of carbon, and the discs seem to be surrounded by an envelope of these scattering particles. An examination of the discharge made by two stroboscopic methods showed that, besides the stationary discs, there are rapidly moving striations throughout the tube (cf. Aston, *ibid.*, 1921, **A**, **98**, 50). The disc discharge is entirely unaffected by weak magnetic fields, unlike Langmuir's streamer discharge (Science, 1924, **60**, 392), which in some respects it resembles. Investigations with unidirectional discharges are described, and the mechanism of the disc discharge is discussed in the light of the results obtained. It is probably closely related to the migration of carbon compounds. A similar type of discharge has also been observed, although much less clearly, in a neon tube provided with carbon electrodes, but experiments with a large number of mixtures of gases gave negative results. It is suggested that the phenomenon of "ball lightning" may be an example of a single disc descending from a charged cloud to earth.

L. L. Bircumshaw.

High-frequency discharges in gases. S. P. McCallum (Nature, 1928, **121**, 353).

Electrical discharges in gases at low pressures. I. Langmuir (Z. Physik, 1927, **46**, 271—299).—An analysis is advanced of the motion of ions and electrons in gases at pressures such that the mean free path is of the order of 1 cm. with particular reference to discharges between a straight wire emitting electrons surrounded by a coaxial cylindrical anode. Methods of determining the velocity distribution of the ions and electrons are described, and it has been shown that in mercury vapour the Maxwellian distribution obtains. The "electron temperature" corresponding with the observed velocity distribution is not a function of the current, and it is therefore concluded that the ions and electrons are not in thermal equilibrium with the gas molecules, the temperature of which in such discharges is but little higher than that of the walls of the containing vessel. "Electron temperatures" up to 80,000° have been observed in discharges in mercury vapour; somewhat lower values are obtained in argon and in hydrogen.

R. W. Lunt.

Diffusion coefficients of flame gas ions in relation to temperature. H. Buckert (Ann. Physik, 1928, [iv], **85**, 63—80).—The diffusion coefficient D has been measured for positive and negative ions from hydrogen, coal gas, and carbon monoxide flames over the temperature range 20—120°, and in electrical fields ranging from 0 to 16 volts, and also for ions varying in age from 3 to 6·6 sec. For hydrogen D is almost constant at 0·00315 for the positive ion and 0·0037 for the negative ion from 20° to 50°; the values thereafter show a steady increase to 0·0068 and 0·0079, respectively, at or about 120°. Both carbon monoxide and coal gas exhibit similar curves, except that in the former the diffusion coefficients of positive and negative ions are almost identical. The mean value of D for coal gas at 100° is more than twice that for hydrogen and thrice that for carbon monoxide. Determinations of D in an electric field show that the values at 16 volts for both hydrogen and coal gas are about half those at zero voltage, the negative ions showing consistently higher values than the positive ions; in carbon monoxide the two ions behave alike and the effect of the field is less marked.

The ageing of ions from 3 to 6 sec. brings about reductions in D to 80, 60, and 40% of the original values for hydrogen, coal gas, and carbon monoxide, respectively. The values of D indicate large ion complexes and the discontinuity at 50° shows that they are then split up into smaller aggregates. The complex ions in carbon monoxide resist disruption, showing that since no water is formed in the combustion, carbon dioxide must be more strongly attached than water to ions. Lauster's data (Z. Physik, 1920, **3**, 396) are in agreement with these views.

R. A. Morton.

Scattering of canal rays in hydrogen. G. P. Thomson (Z. Physik, 1927, **46**, 93—105).—The scattering of hydrogen canal rays in hydrogen has been determined by a thermopile method; the results agree with those obtained by the photographic method, which is thus established.

R. W. Lunt.

Magnetic analysis of a luminous canal-ray beam in hydrogen. C. J. Brasefield (Physical Rev., 1928, [ii], **31**, 215—219).—A luminous canal-ray beam in hydrogen is separated by means of a transverse magnetic field into four component parts: neutral particles, and the charged ions H_2^+, H^+, and H_{2-1}^+ (ions which passed through the electric field as H_2^+, but dissociated into H^+ before reaching the magnetic field). Measurements of the variation of the intensity of the H_2^+ and H_{2-1}^+ beams with the pressure lead to a value for the free path for dissociation of a 1000-volt H_2^+ ion into H_{2-1}^+ of 0·37 cm. at 0·01 mm., about 0·25 of the value, calculated from the kinetic theory, for the neutral molecule.

A. A. Eldridge.

Theory of the Faraday effect in gases. R. de L. Kronig (Z. Physik, 1927, **45**, 508—511).—The author's theory of the Kerr effect in gases has been extended to an analysis of the Faraday effect.

R. W. Lunt.

Theory of the Kerr effect in gases. R. DE L. KRONIG (Z. Physik, 1927, **45**, 458—470).—Mathematical. R. W. LUNT.

Density, compressibility, and at. wt. of neon. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1928, **14**, 50—57; cf. A., 1927, 194).—Crude neon was subjected to exhaustive chemical purification followed by fractional adsorption. The normal density of neon is found to be 0·89990 and the at. wt. calculated therefrom 20·182. W. E. DOWNEY.

Density, compressibility, and at. wt. of argon. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1928, **14**, 57—63; cf. preceding abstract). —The normal density of argon is found to be 1·78364 and the at. wt. 39·943. The conventional method of calculating the deviation from Boyle's law makes the assumption that the value of PV for one atmosphere is correct. A more rational method is to find the best straight line to represent the observed values of some simple function of the density plotted against the pressure and then to extrapolate to zero pressure. This method of distributing the errors produces small differences between the calculated and observed values of the densities at different pressures. The effect on the calculated at. wt. is always less than 0·001 unit, although fortuitously the third decimal place is affected in the case of neon and argon. The values calculated by this method are: oxygen 16·000, nitrogen 14·008, neon 20·183, argon 39·944. The value of the limiting density of oxygen is 1·42764, which yields as the limiting value of molal volume 22·4146 litres (g=980·616). W. E. DOWNEY.

At. wt. of titanium. III. Analysis of titanium tetrabromide. G. P. BAXTER and A. Q. BUTLER (J. Amer. Chem. Soc., 1928, **50**, 408—415).—The above analysis gives 47·90 (Ag=107·88) as the at. wt. of titanium, in agreement with previous results (cf. A., 1927, 86). S. K. TWEEDY.

At. wt. of copper. R. RUER (Z. anorg. Chem., 1928, **169**, 251—256).—The amount of air taken up by copper under the conditions under which it was weighed in the determination of the at. wt. (A., 1926, 1075) has been found by the method previously described (A., 1927, 1134) to be 0·00102 g./100 g. Taking this into account, the at. wt. becomes 63·544±0·003. R. CUTHILL.

Rare earths. XXVI. Purification and at. wt. of erbium. A. E. BOSS with B. S. HOPKINS (J. Amer. Chem. Soc., 1928, **50**, 298—300).—The at. wt. of erbium as determined by the ratio of erbium chloride to silver (107·88) is 167·64 (cf. Hofmann, A., 1910, ii, 1073). Erbium material yielding a constant at. wt. for the element may be obtained from the erbium–yttrium material from gadolinite by fractionation by the nitrate fusion method or by fractional precipitation with sodium nitrite. S. K. TWEEDY.

The Bohr magneton and radioactivity. D. ENSKOG (Z. Physik, 1927, **45**, 852—868).—By adopting the view that magnetic forces are responsible for the attraction between an α-particle and the nucleus immediately previously to the emission of an α-particle, a theory is developed whereby values of the kinetic energy of the emitted α-particle may be calculated from the magnetic moments of the nucleus and of the α-particle and from the nuclear charge. Values calculated in this way are in fairly good quantitative agreement with experiment for a large number of radioactive changes. R. W. LUNT.

Protoactinium as a radioactive and chemical element. O. HAHN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 275—283).—New determinations of the period of protoactinium have been carried out by Walling by measuring the rate of growth of the element in uranium originally carefully freed from it (cf. von Grosse, this vol., 259). A quantitative examination of the amount formed has been made by using its isotope, uranium-Z, as a radioactive indicator. The period found is 20,000 years with a possible error of ±10%. The different views as to the origin and at. wt. of protoactinium are discussed. Protoactinium in a suitable quantity in a pure state would form a valuable source of actinium. It would also afford a means of studying the special chemical properties of the elements of atomic number 91 in relation to those of the lower members of the same group, niobium and tantalum, and of the neighbouring elements, uranium and thorium. Protoactinium is also interesting from the fact that elements of odd atomic number, especially in the last horizontal series of the periodic table, are comparatively rare. M. S. BURR.

Charge of α-particles emitted per sec. by 1 g. of radium. H. JEDRZEJOVSKI (Ann. Physique, 1928, [x], 9, 128—185).—A more detailed account of work already published (A., 1927, 710).

Recoil β-particles from thorium-B. K. DONAT and K. PHILIPP (Z. Physik, 1927, **45**, 512—521).—Using a modification of the technique of Barton, the recoil β-particles from thorium-B have been investigated. The results are in agreement with those of Barton on radium-B. R. W. LUNT.

Retardation of β-rays by matter. J. D'ESPINE (J. Phys. Radium, 1927, [vi], **8**, 502—507).—The values of the retardation of β-rays by aluminium, copper, silver, or gold, as determined with an accuracy of 10% from the magnetic spectra of some of the principal groups of β-rays from thorium-B and radium-B, have been compared with the results of other workers. Bohr's formula for the expression of this retardation gives a curve having the same shape as that derived from the experimental results, although the individual retardations are higher. Some previous results (A., 1926, 332) are revised. J. GRANT.

Study of atomic particles with the point-counter. W. BOTHE and H. FRANZ (Naturwiss., 1927, **15**, 445; Chem. Zentr., 1927, ii, 780).—By using a very pure polonium preparation as source of α-rays, atomic particles can be detected not only with the Geiger point-counter, but also by the absorption curve. Of the elements examined—boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, calcium, and copper—only boron, nitrogen, magnesium, and aluminium clearly gave particles, the range in air being >20, 16,

13, and 16 cm. in air at 15°, respectively. Paraffin gave hydrogen particles of range 15 cm.

A. A. ELDRIDGE.

Validity of Geiger's counter for β-particles and the β-particle emission from radium-*E* and radium-*D*. N. RIEHL (Z. Physik, 1928, **46**, 478—505).—The validity of Geiger's counter for β-particles has been examined and it has been shown that for particles of velocities 0·70—0·94*c* a counter chamber pressure of 2·5 atm. should be used for quantitative work; the true number of particles is not obtained at pressures less than 1150 mm. The absorption in argon, as with α-particles, is less than that in air at the same pressure. β-Particles from radium-*D*, 0·34—0·4*c*, are completely absorbed in air at 7 mm. The ratio of the number of β-particles emitted by radium-*E* to the number of atoms disintegrated has been shown to be not less than 1·2. Inconclusive results have been obtained with radium-*D*. R. W. LUNT.

Thermo-dissociation of atom-nuclei. S. SUZUKI (Proc. Imp. Acad. Tokyo, 1927, **3**, 650—654).—On the assumption that radium exists in thermal equilibrium with its disintegration products, the heat of reaction calculated from the kinetic energy of an α-particle being $-1{\cdot}1\times10^{11}$ g.-cal., $\log x^2/(1-x^2).p=2{\cdot}41\times10^{10}/T+2{\cdot}5\log T+0{\cdot}387$. The temperature T_c at which the maximum degree of dissociation should occur is given by $d(2{\cdot}4\times10^{10}/T+2{\cdot}5\log T)/dT=0$, whence T_c—10^{10} degrees. The amount of radium should therefore decrease up to 10^{10} degrees, but decompose into radon at higher temperatures. Unless $x^2/(1-x^2).p > 10^{27{\cdot}8}$ atm. no equilibrium can exist, and no observable change in the degree of dissociation would be expected at the b. p. of radium under a few thousand atmospheres pressure. Since the heat of reaction is of the same order for all the heavy elements, it is assumed that their disintegration into hydrogen, helium, and protons would take place at about 10^{10} degrees.

C. J. SMITHELLS.

Internuclear reactions. B. CABRERA (Compt. rend., 1928, **186**, 501—503).—The theory (this vol., 216) that the Aston packing fraction is a measure of the internal energy of the system and gives an indication of the evolution of atomic nuclei, is developed, and extended to internuclear reactions. The theory requires an emission of energy equivalent to $15{\cdot}2\times10^{-27}$ g. during the disintegration of nitrogen by bombardment with α-particles with the formation of a proton and an isotope of oxygen (O^{17}). This probably takes the form of a radiation hitherto unnoticed. The theory is also applied to the evolution of elements in the cosmos. J. GRANT.

Relative masses of a proton and an electron. J. C. GHOSH (Naturwiss., 1927, **15**, 445; Chem. Zentr., 1927, ii, 779).—The observed relations are derived on the supposition that if two light quanta of frequency ν impinge, a part *E* of the energy is converted into matter in the form of a proton and an electron, whilst the remainder is converted into heat-motion. Each photon is transformed into a hohlraum. A. A. ELDRIDGE.

Structure of the hydrogen atom. H. GHOSH (Naturwiss., 1927, **15**, 506—507; Chem. Zentr., 1927, ii, 1121).—The mass 1·008 of the hydrogen atom is regarded as that of the nucleus (1) plus that of 16 electrons (0·008), the latter mass being distributed in a spherical shell as radiation energy.

A. A. ELDRIDGE.

Scheme [for the prediction of the atomic masses] of isotopes. G. BECK (Z. Physik, 1928, **47**, 407—416).—Theoretical. Aston's results on isotopes are arranged in a tabular scheme and used to predict, by the regularities observed, other as yet unobserved isotopes. It is further concluded that there are arrest points in the building up of the various atomic nuclei. W. E. DOWNEY.

Quantum theory of the electron. P. A. M. DIRAC (Proc. Roy. Soc., 1928, **A**, **117**, 610—624).—The assignment to each electron of a spin and a magnetic moment, in order to make the quantum theory, when applied to the problem of the structure of the atom, agree with observation, is shown to be unnecessary. Agreement with experiment can be obtained without arbitrary assumptions by the correct relativistic application of quantum mechanics to the point-charge electron. The Hamiltonian function on which the present theory is based is linear in energy and momentum, and leads to an explanation of all duplexity phenomena without further assumption. The spinning electron model is, however, justifiable for many purposes, at least as a first approximation. Its most important failure seems to be that the magnitude of the resultant orbital angular momentum of an electron moving in an orbit in a central field of force is not a constant, as the model leads one to expect. L. L. BIRCUMSHAW.

Quantum theory of homopolar valencies. F. LONDON (Z. Physik, 1928, **46**, 455—477).—It is shown that homopolar valencies calculated from the symmetry characteristics of Schrodinger's characteristic function are in agreement with the periodic classification, and it is thought that they may be interpreted as quantum mechanical resonance effects.

R. W. LUNT.

Explanation of some properties of spectra from the quantum mechanics of the spinning electron. J. VON NEUMANN and E. WIGNER (Z. Physik, 1928, **47**, 203—220).—The kinematic properties of any system of spinning electrons (without further assumptions) have been deduced with the aid of the Dirac–Jordan transformation theory. R. A. MORTON.

Infra-red spectra of hydrogen halides according to Schrodinger's theory. M. CZERNY (Z. Physik, 1927, **45**, 476—483).—An analysis of the available data for the infra-red spectra of hydrogen halides by Schrodinger's theory leads to values of the molecular constant somewhat different from those derived from the quantum theory. R. W. LUNT.

Refraction quotient of the De Broglie waves of electrons. O. KLEMPERER (Z. Physik, 1928, **47**, 417—421).—It is shown that there is a limiting angle for the total reflexion of cathode rays on the theory of wave mechanics. W. E. DOWNEY.

Theory of collision processes in hydrogen. W. ELSASSER (Z. Physik, 1927, **45**, 522—538).—Mathematical. R. W. LUNT.

Theory of the collisions between atoms and slow electrons. (FRL.) L. MENSING (Z. Physik, 1927, **45**, 603—609).—The collision process between atoms or slow electrons has been analysed by wave mechanics; comparisons of the predictions of theory with experiment show that an atom cannot be regarded as a charged shell. R. W. LUNT.

Minimum proper time and its applications (1) to the number of the chemical elements, (2) to some uncertainty relations. H. T. FLINT and O. W. RICHARDSON (Proc. Roy. Soc., 1928, **A**, **117**, 637—649).—It has been shown that the proper time of a particle has a minimum value h/m_0c^2, where m is the rest mass. This conclusion is now reached by a method which is independent of the assumptions as to the metrics of space and time, made previously. An upper limit $[n/(n+1)]^{\frac{1}{2}}C$ is placed on the velocity of an electron in an atom in an orbit of total quantum number n. This involves an upper limit 97 for the atomic number of any chemical element, and also an upper limit for the quantum number of an intranuclear orbit. The limit is a function of the atomic number of the nucelus. L. L. BIRCUMSHAW.

[Use of Winther's gauze in] spectrophotometry. G. LANDSBERG (Z. Physik, 1927, **46**, 106—108).—The use of a blackened gauze as a constant extinction filter (Winther, A., 1923, ii, 519) has been examined in the visible region and up to 2026 Å. The extinction of such gauzes is constant within 1% in the range examined. R. W. LUNT.

Graphic representation of colours. S. ROSCH (Physikal. Z., 1928, **29**, 83—91).—Every colour can be defined by means of its "relative brightness," the relative width of its spectrum, and the mean wavelength. An apparatus is described whereby any colour may be compared by synthesis in terms of these three co-ordinates. W. E. DOWNEY.

Characteristic of the hydrogen molecule in the normal state. Y. SUGIURA (Z. Physik, 1927, **45**, 484—492).—Mathematical. R. W. LUNT.

Quantum levels and resulting constants of the hydrogen molecule. R. T. BIRGE (Proc. Nat. Acad, Sci., 1928, **14**, 12—19).—Theoretical. It is contended that the discrepancy between the observed value of the ionisation potential of hydrogen and the theoretical value as calculated from Richardson's analysis of the band spectrum (A., 1927, 916) is only apparent. W. E. DOWNEY.

Hydrogen molecule. O. W. RICHARDSON (Nature, 1928, **121**, 320).—A discussion (cf. Birge, this vol., 216). It now appears that the suspected coincidence of the author's 2^3P level with Dieke and Hopfield's C level is accidental; the case for the coincidence of the author's 2^1S level with their B level is much more convincing. An examination of Werner's plates shows that the 2^1S states are formed, and that they pass with difficulty into the 1^1S state; apparently the excitation energy is discharged by dissociation of the hydrogen molecules on collision. A. A. ELDRIDGE.

Residual effect in the actinic absorption of chlorine. W. TAYLOR and A. ELLIOTT (Proc. Durham Phil. Soc., 1926—1927, **7**, 172—181).—See A., 1927, 216.

Measurement of residual rays in the visible region of the spectrum. G. JOOS (Physikal. Z., 1928, **29**, 117—118).—The absorption spectra of potassium chromium selenate crystals, and of other chromium double salts of the alum type, disclose the existence of sequences of lines separated by about 43 cm.$^{-1}$ and containing as many as 11 terms. The frequency difference corresponds with 232 μ, a wavelength in the range of residual rays. R. A. MORTON.

Absorption spectra of potassium ferro- and ferri-cyanides. F. H. GETMAN (J. Physical Chem., 1928, **32**, 187—191; A., 1921, ii, 287).—A further, more refined, spectroscopic examination of 0·0005M-solutions of potassium ferro- and ferri-cyanides has been made. The absorption spectra differ markedly from each other. The molecular extinction coefficients of the compounds designated by Briggs (J.C.S., 1911, **99**, 1019) as the α- and β-ferrocyanides of potassium are identical, supporting the view of Bennett (A., 1917, i, 449) that these salts are not isomeric. The corresponding coefficients for the α- and β-ferricyanides are different from each other, however, confirming the previous finding of the author (*loc. cit.*) and the view of Locke and Edwards (A., 1899, i, 407). An apparatus for producing sparks under water between tungsten electrodes to detect narrow or weak absorption bands is described. L. S. THEOBALD.

Spectrochemical researches on some porphyrins and some compounds of hæmatoporphyrin with iron. E. BOIS (Can. Chem. Met., 1927, **11**, 261—264).—The absorption spectra are considered to provide a new basis for the explanation of molecular structure by spectra. The fluorescence spectrum is the most sensitive reaction for the detection of porphyrin and blood-spots. Synthetic hæmatin shows a stage in the transformation of foods into blood. CHEMICAL ABSTRACTS.

Spectrographic study of complex cyanogen compounds of iron. I, II. L. CAMBI and L. SZEGO (Gazzetta, 1928, **58**, 64—71, 71—76).—See A., 1927, 809, 916.

Optically excited iodine bands with alternate missing lines. R. W. WOOD and F. W. LOOMIS (Nature, 1928, **121**, 283).—A study of the fluorescence bands which develop around the "fundamental" doublets when iodine is excited, in presence of helium, by the green mercury line, shows that only those alternate lines occur in the spectrum of the fluorescence for which m' is even. Thus the rotational quantum number of the excited iodine molecules can change only by even numbers during these collisions of the second kind. The result, although incomprehensible on the classical Bohr–Lenz theory, affords direct evidence in support of the theories of Hund and Dennison. A. A. ELDRIDGE.

Band fluorescence of mercury vapour. P. PRINGSHEIM and A. TERENIN (Z. Physik, 1928, **47**, 330—343).—Mercury vapour fluoresces under the influence of an uncooled mercury lamp or of an aluminium spark. The intensity of the fluorescence

excited by a mercury lamp is not a quadratic function of the intensity of the incident light. It increases, at first, very strongly with increasing thickness of mercury vapour and then slowly. At small thicknesses the effect of indifferent gases is very marked. Hydrogen and oxygen weaken the effect. From the effect of hydrogen it is concluded that the duration of light emission has an upper limit of 10^{-3} sec. Parallel with the visible fluorescence there occurs an emission of the line at 2537 Å. W. E. DOWNEY.

Absorption of ultra-violet light by dextrose, lævulose, and lactose. L. KWIECINSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1927, **A**, 379—394).—Contrary to the statements of Purvis (J.C.S., 1923, **123**, 2515) and Niederhoff (A., 1927, 396), pure preparations of dextrose and lactose show no selective absorption in the ultra-violet. Even after several crystallisations *d*-lævulose shows a band at about 2800 Å. It is not certain, however, that all traces of impurity are removed by crystallisation and this particular result is not at present regarded as conclusive. J. S. CARTER.

Colour and colour equilibria of phenolphthalein and its derivatives. E. VOGT (Z. physikal. Chem., 1928, **132**, 101—130).—The quinone-phenoxide theory of Achree is regarded as the most satisfactory explanation of the colour changes experienced by phenolphthalein, the phthalein esters and sulphonephthaleins, and other triphenylmethane dyes.

Comparative measurements of the absorption of the various halogen derivatives of phenolphthalein indicate not a quinonoid ring, but the central carbon atom, as the chromophore. The extinction curves are substantially in agreement with Ostwald's theory of indicators, having regard to the dibasic nature of the phthaleins. The two dissociation constants of phenoltetrachlorophthalein are $7{\cdot}9\times10^{-9}$ and $3{\cdot}73\times10^{-9}$, respectively. For substances of which the two dissociation constants are widely different the simple theory applicable to monobasic acids is valid.

H. F. GILLBE.

Intensity ratio of the *D*-lines. W. LOCHTE-HOLTGREVEN (Z. Physik, 1928, **47**, 362—378).—The appearance of one *D*-line under fluorescence excitation by the other *D*-line has been quantitatively studied for both lines. In the presence of rare gases, the intensity ratio between the two lines is in accord with that required by theory. The extinction of secondary resonance by gases was established and a separation effected between collisions which force the atom back into the unexcited state without emission and those which transform it into the adjacent $2p$-state. Collisions between excited sodium atoms and sodium or potassium atoms are some two hundred times more effective for the second transition mentioned than are collisions with rare-gas atoms. W. E. DOWNEY.

Duration of fluorescence of solid uranyl salts and of their solutions. F. PERRIN and R. DELORME (Compt. rend., 1928, **186**, 428—430; cf. A., 1926, 223, 558).—The duration of emission of fluorescence of uranyl salts has been measured by means of the phosphorometer, an adaptation of Becquerel's phosphoroscope in which the rate of rotation of the vanes under the influence of the radiation is measured by means of an optical rotating-wheel device. For simple fluorescence the exponential decrease in luminescence after instantaneous illumination was confirmed. The mean lives (in 10^4 sec.) of crystalline uranyl sulphate and nitrate were 2·5 and 6·1, respectively. Solutions of the former in pure sulphuric acid gave times and fluorescing powers of the same order as the solid salt but slightly lower, and decreasing when the concentration or temperature was raised, or when water was added. J. GRANT.

Fluorescence of mercury–inert gas bands. O. OLDENBERG (Z. Physik, 1928, **47**, 184—202).—The question whether atoms can be excited by the joint action of collisions and irradiation, can be tested indirectly by considering the reverse process, viz., the distribution of energy of excitation between kinetic energy and emission. Investigation of the fluorescence spectrum of mercury vapour in the presence of helium or neon at atmospheric pressure discloses a range of continuous emission on both sides of the resonance line, extending from 2519 to 2570 Å. for helium. On the other hand, the spectra obtained with argon and krypton as the added gases exhibited banded structure, whilst with nitrogen the results resembled those obtained with helium and neon. Hydrogen and oxygen, as added gases, did not cause the appearance of either the continuous or banded spectrum. It appears that excited mercury atoms in the 2^3P_1 state can form " molecules " on colliding with an atom of argon or krypton, the attraction originating from a polarisation of the rare gas atom in the field of the excited mercury atom. The continuous spectra obtained with helium and neon may be unresolved band (molecular) spectra. If, however, they are not of this type, the continuous spectra must illustrate the joint action referred to. It is shown that the banded spectra also appear in absorption. R. A. MORTON.

Excitation of fluorescence by *X*-rays of different wave-lengths. R. GLOCKER, E. KAUPP, and H. WIDMANN (Ann. Physik, 1928, [iv], **85**, 313—332).—The relation between ionisation and fluorescent light intensity has been investigated for two zinc silicate screens of different thicknesses, using radiations ranging from 0·12 to 1·54 Å. At 0·19 Å. the brightness of the screen varies approximately with the thickness of fluorescent material, whereas at 0·71 Å. the linear relation no longer holds, because the absorption does not increase linearly with the thickness. From calculations of the fraction of incident *X*-ray energy which represents electron energy, it is shown that fluorescence largely originates from the electron energy, and not from the absorbed energy provided the screen consists of a very thin layer. An ionisation chamber responds much more readily to changes in wave-length than does the fluorescent screen. A method is given for evaluating losses in light intensity due to absorption and diffuse reflexion in the screen. The light emission from the zinc silicate screen consists of a broad band extending from 505 to 573 $\mu\mu$ (maximum 520—530 $\mu\mu$). The relative intensities of the short-wave and long-wave sides have been determined under different conditions of excitation, and no differences have been detected which could be

traced to changes in the wave-length of the exciting X-rays. R. A. MORTON.

Photoluminescence of solutions of æsculin at low temperatures. J. STARKIEWICZ (Bull. Acad. Polonaise, 1927, **A**, 459—471).—The fluorescence band of solutions of æsculin in glycerol moves gradually towards the violet as the temperature is depressed from $+20°$ to $-80°$. A faint green phosphorescence, more intense when a solution of sucrose is used as solvent, is observed at $-80°$. A more intense and more permanent phosphorescence is observed with glycerol solutions at $-180°$, the spectrum showing intensity maxima at the wave-lengths 480, 495, 515, 540, and 560 $m\mu$. Phosphorescence and fluorescence are not correlated phenomena. J. S. CARTER.

Light emission of gases excited by α-rays. H. GREINACHER (Z. Physik, 1928, **47**, 344—356).—The emission of light by air, carbon dioxide, oxygen, and hydrogen under the influence of α-particles has been studied. The intensity of the emitted light was examined photographically and was found to be independent of the recombination of the ions. The ratios of the light intensities for the gases examined were found to be different from those of Walter (Ann. Physik, 1906, [iv], **20**, 327). The light from hydrogen was found to be as strong as that from air, whereas Walter found it was only one tenth. This is explained as due to the use of a quartz filter by Walter which cut off the ultra-violet band spectrum. The energy and collision ratios are discussed in this light and are found to be in agreement.

W. E. DOWNEY.

Influence of temperature on the absorption bands of alkali halide phosphors. H. LORENZ (Z. Physik, 1927, **46**, 558—567).—The extinction coefficients of the following phosphors have been determined in the range 1800—3000 Å. and at temperatures from $-180°$ to $600°$: potassium chloride+thallium, potassium bromide+thallium, potassium chloride+lead. Reduction of the temperature diminishes the width of the bands; the long wave-length band shifts 30—40 Å. to the red and the short wave-length band 10—20 Å. in the temperature range investigated. R. W. LUNT.

Residual rays of mixed crystals. F. KRUGER, O. REINKOBER, and E. KOCH-HOLM (Ann. Physik, 1928, [iv], **85**, 110—128).—Residual ray spectra in the far infra-red have been obtained for mixed crystal series of sodium, rubidium, and thallium chlorides with potassium chloride. Wave-lengths characteristic of the components do not occur, but each mixed crystal shows a wave-length of its own, intermediate between those of the components. The frequency varies approximately linearly with the concentration change. The decomposition of a mixed crystal coincides with the disappearance of its own wave-length and the appearance of those of the components.

R. A. MORTON.

Refraction and absorption of electrical waves by electrolytes. I. K. ZAKRZEWSKI (Bull. Acad. Polonaise, 1927, **A**, 489—503).—The absorption indices κ at temperatures of the order of 19° of water and solutions of sodium chloride, the concentrations of which ranged up to 6%, have been determined for waves of wave-length 23 cm. Calculations based on the data of Pfannenberg (Z. Physik, 1926, **37**, 767) indicate values for the refractive indices n of the more concentrated salt solutions which are considerably smaller than the value for pure water. Even after making allowance for the absorptive effect of the solvent, the experimental numbers are not in agreement with the Maxwell relation $n\kappa=\sigma\tau$ (σ=conductivity). J. S CARTER.

Distribution of energy in molecules. L. S. KASSEL (Proc. Nat. Acad Sci., 1928, **14**, 23—30).—Theoretical. Given a number of oscillators and a value for the total energy of these oscillators, the chance that a specified one of the oscillators shall have energy in excess of some given value is calculated for a number of types of oscillators. W. E. DOWNEY.

Dielectric constant of liquid bromine. (MISS) A. I. ANDERSON (Proc. Physical Soc., 1928, **40**, 62—70).—The dielectric constant of liquid bromine was found to be 3·12 at 15°, and at a frequency of 187,000 per sec. The temperature coefficient referred to 0° is $-0·00191$. The value $0·40\times10^{-18}$ is deduced for the electric moment of the bromine molecule Br_2. The electrical conductivity was found to be $9·6\times10^{-10}$ ohm^{-1} cm.$^{-1}$ at 0°, and the temperature coefficient $-0·0188$ per degree. C. J. SMITHELLS.

Variation of dielectric constant of some gases with temperature at different pressures. (FRL.) M. FORRÓ (Z. Physik, 1928, **47**, 430—445).—The measurements were carried out in a similar apparatus to that of Herweg (Verh. Physikal. Ges., 1919, **21**, 572). The gases examined were hydrogen, nitrogen, air, carbon monoxide, and carbon dioxide between 0° and 300° and between 0 and 6 atm. For hydrogen, nitrogen, and air, the constants a and b in Debye's equation $(\epsilon-1)T/(\epsilon+2)d=aT+b$ are not found to vary with pressure; a is constant and b is zero. For carbon monoxide, the variation of b can be expressed either by a linear or by a quadratic relationship. For carbon dioxide, the variation of b follows a quadratic relationship with pressure.

W. E. DOWNEY.

Influence of electrostatic fields on dielectric constants. F. KAUTZSCH (Physikal. Z., 1928, **29**, 105—117).—The variation of the dielectric constant with varying electrostatic fields has been studied for ethyl ether, chloroform, and chlorobenzene. Saturation phenomena are found for ether and chloroform. Using the Debye kinetic theory of dielectrics, and extrapolating to zero voltage, the dipolar moments of ethyl ether, chloroform, and chlorobenzene are 12·02, 10·07, and $8·50\times10^{-19}$, respectively. Herweg's data (Z. Physik, 1921, **8**, 1) lead to values 12·07, 10·26, and $6·45\times10^{-19}$. The variation of the dielectric constant of carbon disulphide in different fields has been studied. R. A. MORTON.

Refractive indices of some molten salts. O. H. WAGNER (Z. physikal. Chem., 1928, **131**, 409—441).—Heck's method for the measurement of the refractive index of molten salts has been improved, and results are given at 800° for lithium, sodium, potassium, rubidium, cæsium, silver, and thallium nitrates, silver chloride, sodium chlorate, and sodium

tungstate. The refractive indices show a linear decrease as the temperature rises. The negative temperature coefficients of the first eight salts are approximately equal to the decrease of refractive index produced by the decrease of density, whilst those of the remaining two salts are much greater than the density effects. The absorption of the first group lies in the ultra-violet, and of the second group in the infra-red. Increase of temperature causes the absorption in both cases to shift towards the longer wave-length region, producing in one case a decrease, and in the other an increase, of the negative temperature coefficient. Sodium tungstate possesses an infra-red absorption band at $1\cdot777\ \mu$. Approximate values of the atomic refractions of the cations have been determined. H. F. GILLBE.

Refractive indices and rotatory power of sodium rubidium tartrate. S. KOZIK (Bull. Acad. Polonaise, 1927, A, 229—236).—The geometric properties of sodium rubidium tartrate (d^{16} 2·025) closely resemble those of other dialkali tartrates; $a:b:c=0\cdot8332:1:0\cdot4319$. Values of the refractive indices and of the angle of the optic axes at 9 wave-lengths between 670 and 405 $\mu\mu$ are tabulated (n_{α}^{17} 1·4909, n_{β}^{17} 1·4948, n^{17} 1·4975, V^{17} 50° 23′ [Na]). The crystals are feebly optically negative, with the optic axial plane b (010). Both the crystals and the solution are dextrorotatory. Values of the specific and molecular rotatory powers of the crystals and solution at 8 wave-lengths between 670 and 436 $\mu\mu$ are tabulated ($M[\alpha]_D$: crystals, 24,830°; solution, 6374°). The rotatory power of the crystals is the same along both optic axes. J. S CARTER.

Refraction in gases. J. TAUSZ and G. HORNUNG (Z. techn. Physik, 1927, 8, 338—355; Chem. Zentr., 1927, ii, 2040).—The constants of refraction for sulphur dioxide, methane, ethylene, acetylene, propylene, and carbon dioxide were measured for four wave-lengths (656·4, 587·6, 546·1, 435·8). From Nanton's equation, $a\Delta=[(3\pi e^2)/(e/m)]eM$, the number of dispersion electrons in the gases is computed to be 4·72, 4·46, 5·07, 4·56, 7·22, and 5·28, respectively. A. A. ELDRIDGE.

Visible and ultra-violet dispersion of organic substances. K. FEUSSNER (Z. Physik, 1927, 45, 689—716).—The refractive indices of acetophenone, aniline, benzaldehyde, quinoline, nitrobenzene, and carbon disulphide have been determined to six significant figures in the range 2500—6680 Å. The method of perpendicular incidence was used in the visible region and that of crossed prisms in the ultra-violet region. For benzaldehyde and carbon disulphide the optical constants have been calculated from the experimental curves. R. W. LUNT.

Anomalous dispersion of alkali halide phosphors. M. A. BREDIG (Z. Physik, 1927, 46, 73—79). —The variation of the refractive index of phosphors of potassium bromide containing 0·003—0·03% of lead has been determined by an interferometer method in the neighbourhood of the absorption maximum at 3020 Å. The density of electrons responsible for the observed dispersion has been calculated from Voigt's formula and is found to be approximately 1/600 of the calculated density of lead atoms. R. W. LUNT.

Ultra-violet dispersion of alkali halides. Z. GYULAI (Z. Physik, 1927, 46, 80—87).—The refractive indices of potassium chloride, bromide, and iodide, sodium bromide, rubidium chloride, and lithium fluoride have been determined in the range 1935—6150 Å. with an accuracy of 0·05%. The values for potassium chloride agree well with those of Martens for natural sylvine. Lithium fluoride is shown to be a suitable material for lenses and prisms in the ultra-violet. R. W. LUNT.

Paramagnetic rotation of the plane of polarisation. R. LADENBOURG (Z. Physik, 1927, 46, 168—176).—A review of recent experiments in the light of the author's theory. R. W. LUNT.

Optical and electrical properties of liquids. C. V. RAMAN and K. S. KRISHMAN (Proc. Roy. Soc., 1928, A, 117, 589—599; cf. A., 1927, 93, 397).—Theoretical. A review of the existing theories of the optical and electrical behaviour of liquids shows that they are inadequate to explain the changes of refractivity and dielectric behaviour with density and temperature. A new theory is developed, based on the assumption that the molecules of a liquid are optically and electrically anisotropic, and that the polarisation field acting on a molecule is a function of its orientation. The formulæ deduced are used to show why with increase of density the Lorentz refraction constant usually diminishes. The changes in refractivity and dielectric constant are closely related to a change in the effective optical or electrical anisotropy of the molecule produced by the influence of its neighbours. The anisotropic constants appearing in the formulæ can be evaluated with the aid of the theory of light-scattering in liquids previously developed (*loc. cit.*). L. L. BIRCUMSHAW.

Light-scattering in liquids at high temperatures. S. R. RAO (Indian J. Phys., 1928, 2, 179—193).—In continuation of previous work (A., 1927, 1127), the variations with temperature of the intensity and depolarisation factor of transversely scattered light have been investigated for the liquids octane, carbon tetrachloride, ethyl acetate, benzene, chlorobenzene, and toluene. The depolarisation factor diminishes with rise of temperature, at first slowly and later more rapidly, the fall again becoming less rapid as the critical temperature is approached. The molecular anisotropy at different temperatures has also been calculated for all the liquids. Graphs obtained by plotting anisotropy against temperature, when combined with the results of previous work (*loc. cit.*) and those of other investigators, have certain peculiarities. The curves for the paraffin hydrocarbons show a remarkable and progressive change in shape with increasing length of molecule. The curves for the esters are similar to one another in form, but the anisotropy of methyl acetate is greater at all temperatures than that of ethyl acetate, and, similarly, that of ethyl formate is greater than that of ethyl acetate. The toluene curve resembles that of benzene, but the chlorobenzene curve differs from both, and, whilst it has a higher anisotropy than toluene at the ordinary temperature, it has a lower one at 54°. In all cases the anisotropy of the liquid increases with

temperature and tends to attain the value for the vapour. M. S. BURR.

Valency. VIII. Extinction coefficients and molecular conductivities of Vernon's isomeric α- and β-dimethyltelluronium salts. Molecular structure of quadrivalent tellurium compounds. T. M. LOWRY, (MRS.) R. R. GOLDSTEIN, and F. L. GILBERT (J.C.S., 1928, 307—321; cf. A., 1924, i, 1212; 1905, ii, 298).—Precautions were taken during the measurement of the extinction coefficients of the α- and β-dihalides (between 2600 and 5000 Å.) to prevent hydrolysis. In spite of marked differences in colour and absorptive power between α- and β-dihalides there is a fundamental similarity of type in the absorption spectra of isomeric α- and β-compounds. The α- and β-di-iodides give twin maxima; this was also observed for iodoform and potassium tri-iodide. The two maxima given by the α-tetraiodide, $TeMe_2I_4$, agree well in wave-length and intensity with those predicted for a mixture of one molecule of α-di-iodide and one equivalent of tri-iodide ion. The molecular conductivities of the dihalides were determined to ascertain whether these compounds behave as binary or ternary electrolytes; the results show that the dihalides lose one halogen atom more or less completely by hydrolysis and the other atom forms a halogen ion, *e.g.*, $[TeMe_2Cl]Cl+H_2O \rightleftharpoons [TeMe_2OH]Cl+\overset{+}{H}\overset{-}{Cl}$. The hydroxy-halides produced are strong electrolytes which are not hydrolysed to any large extent even when the equivalent of acid shown in the equation is removed. The free bases are, however, weak electrolytes like ammonia. A discussion of the structural formulæ of these compounds is given, but the authors consider the evidence insufficient to decide between alternatives. H. INGLESON.

Symmetry of electrons [in atoms]. P. VINASSA (Atti R. Accad. Lincei, 1927, [vi], 6, 454—458).—The classification of the elements is discussed and presented in tabular form according to a system which differs from the Mendeleev or Moseley systems in being based, not on the positive nuclei of the atoms, but on the number of peripheral electrons. In this system the entity is not the atom but the atom plus or minus the number of electrons equal to its valency, according as the latter is negative or positive. An element may therefore appear more than once. This leads to certain conclusions regarding a symmetrical arrangement of the electrons in the atom and explains the almost exclusive occurrence of compounds with an even molecular number (*i.e.*, with the sum of the atomic numbers of the atoms in the molecule even). O. J. WALKER.

"Dative" chemical linking. A. W. C. MENZIES (Nature, 1928, **121**, 457).—The term "dative" is suggested to describe that linking involved when one atom contributes both of the shared electrons. A. A. ELDRIDGE.

Precision measurements in the *L*-series of the new element rhenium. (FRL.) I. WENNERLOF (Z. Physik, 1928, **47**, 422—425).—Three *L*-lines of rhenium have been measured with the following results: $L\alpha_1$ 1429·88, $L\beta_1$ 1236·04, and $L\beta_2$ 1204·1. W. E. DOWNEY.

Rare earths. XXV. Examination of certain rare-earth materials for element 72 [hafnium]. W. B. HOLTON and B. S. HOPKINS (J. Amer. Chem. Soc., 1928, **50**, 255—258).—*X*-Ray analysis of the most soluble (thorium and zirconium) fractions of two different crystallisation series from the yttrium group failed to indicate the presence of hafnium. Arc spectrum analysis showed that thorium is present and zirconium absent in Norwegian gadolinite, in the most soluble fractions from the cerium and yttrium groups, and in the accumulated soluble potassium sulphate residues from various yttrium group series. Hafnium was probably present in the latter. S. K. TWEEDY.

Radiograph of a crystal having the body-centred cubic lattice. M. MAJIMA and S. TOGINO (Sci. Pap. Inst. Phys. Chem. Res., 1927, 7, 259—261).—Fifty-five Laue photographs of the *X*-ray diffraction patterns produced by α-iron are reproduced. W. E. DOWNEY.

Determination of the crystal lattice of powdered micro-crystalline substances by means of radiograms. G. ALLARD (Compt. rend., 1928, **186**, 638—640).—Hull's method (A., 1922, ii, 624) may be made general for all crystalline systems by the application of Mauguin's conception of polar lattices (Bull. Soc. franç. Min., 1926, **49**, 5). Then the intervals between successive nodes of the same range of polar lattices are directly proportional to the sines of the angles of diffraction obtained directly from the radiograms. The planes of greatest reticular density give the most intense rays and the smallest angles of diffraction. The position and characteristics of all the rays of the radiogram can then be determined. The application of the method of least squares to the goniometric measurements increases the precision of the method. J. GRANT.

***X*-Ray examination of passivity.** F. KRÜGER and E. NÄHRING (Ann. Physik, 1927, [iv], **84**, 939—948).—By using the Debye–Scherrer method on finely-powdered specimens of iron, nickel, and chromium in the passive state evidence has been obtained in support of the view that passivity is associated with the formation of a layer of oxide on the metal. R. W. LUNT.

Crystal structure of graphite. H. OTT (Ann. Physik, 1928, [iv], **85**, 81—109).—The graphite lattice has been investigated by methods applied earlier to carborundum (A., 1926, 339, 562). Specimens of graphite embedded in calcite proved specially suitable. A lattice identical with that of Hassel and Mark (A., 1924, ii, 721) and Bernal (A., 1925, ii, 17) was deduced. The *X*-ray study indicates that the carbon atoms in graphite are tervalent and it is argued that Steiger's (A., 1920, ii, 355) calculations on the energy of linking likewise show tervalency to obtain in the aromatic linking. R. A. MORTON.

Crystal structure of carbonates. C. SCHAEFER, F. MATOSSI, and (FRL.) F. DANE (Z. Physik, 1927, **45**, 493—500).—The crystal structure of magnesite, siderite, dolomite, strontianite, and aragonite has been investigated from observations of the transmissibility of the crystal in the range 6·2—7·5 μ. The results

interpreted according to Brester's theory are in agreement with the view that the oxygen atoms are placed at three of the corners of a regular tetrahedron with the carbon atom at the centre. It is thought that the data of Schaefer and Schubert on nitrates (A., 1918, ii, 282) indicate that the nitrate group consists of a pyramidal structure in which the nitrogen atom is situated at one apex and the oxygen atoms are situated at the three basal corners.

R. W. Lunt.

Constitution of the silicates. W. Wahl (Z. Krist., 1927, **66**, 33—72).—Structural formulæ are derived for complex alkali aluminosilicates having an equal number of aluminium and alkali metal atoms on the assumption of a complex univalent anion of which the central aluminium atom is quadrivalent. More complex anions are formed by the union of SiO_3 or Si_2O_5 groups. In those compounds having a fewer number of aluminium than alkali atoms certain of the former are regarded as sexavalent, the complex anions being then tervalent. Similar types of formulæ are proposed for the alkaline-earth aluminosilicates. Compounds containing hydrogen are in many cases regarded as acid salts, and their formulæ are derived on this principle and on those given above.

H. F. Gillbe.

Constitution of the silicates. W. Wahl (Z. Krist, 1927, **66**, 173—190).—The structure of the additive compounds formed between aluminosilicates and inorganic salts is discussed. Natural non-aluminiferous silicates are regarded as salts of complex anions containing sexavalent silicon; more complex types of anions are produced by the linking of silicon dioxide groups by oxygen chains. Minerals of the pyroxene, amphibole, and mellilite groups are formulated on the hypothesis of bridge formation by SiO_3 groups and oxygen atoms. The structure and mode of polymerisation of the complex silicates are surveyed in the light of their infra-red absorption spectra.

H. F. Gillbe.

Constitution of aluminosilicates, conditions of their formation, and transformation in soil. W. Wahl (Finska Kemistsamfundets Medd., 1927, **36**, 22—61; Chem. Zentr., 1927, ii, 1682—1684; cf. preceding abstracts).—In those silicates which are formed at high temperatures, aluminium has a co-ordination number 4, whilst for those formed at low temperatures it tends to be 6. Formulæ with two aluminium atoms are improbable; in the crystalline state the aluminosilicates are highly polymerised. The reactions leading to the formation of minerals in the magma consist of (*a*) dehydration processes and (*b*) additive reactions; the effect of these processes is traced in the formation of hornblende and muscovite. The formation of biotite is summarised as follows:

$$\text{(i)}\ 6K[Al^{IV}O(SiO_2)]+12H_2O= K_6H_{12}[Al_6{}^{VI}O_6(OH)_{12}(SiO_3)_6],$$
$$\text{(ii)}\ 6Mg_2SiO_4+12H_2O=6MgSiO_2(OH)_2+6Mg(OH)_2,$$
$$\text{(iii)}\ K_6H_{12}[Al^{VI}O_6(OH)_{12}(SiO_3)_6]+6MgSiO_2(OH)_2= K_6H_{12}[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+12H_2O,$$
$$\text{(iv)}\ (K,H)_6H_{12}[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+6Mg(OH)_2= (K,H)_6Mg_6[Al_6{}^{VI}O_6(SiO_3)_6(MgSiO_4)_6]+12H_2O.$$

A. A. Eldridge.

Space-group of helvite. C. Gottfried (Z, Krist., 1927, **65**, 425—427; Chem. Zentr., 1927, ii, 1537).—The edge of the elementary cell of helvite. $(Mn,Fe)_3Be_3(SiO_4)_3,MnS$, is 8·52$_5$ Å.; space-group T_d^4. There are 2 molecules in the elementary cell.

A. A. Eldridge.

Structure of zinc hydroxide. C. Gottfried and H. Mark (Z. Krist., 1927, **65**, 416—424; Chem. Zentr., 1927, ii, 1537).—In the elementary cell of edges 6·73, 7·33, 8·47 Å. there are 8 molecules; the space-group is V_h^{16}.

A. A. Eldridge.

Crystal structure of the system cadmium–mercury. R. F. Mehl (J. Amer. Chem. Soc., 1928, **50**, 381—390).—The crystal structure of annealed cadmium amalgams was deduced from *X*-ray powder photographs. The spectra for all compositions in the mercury-rich ω-field are identical in type and dimensions and correspond with either a face-centred tetragonal lattice having $c:a=0·520$, or with a body-centred tetragonal lattice having $c:a=0·740$. The crystal structure of pure mercury at the m. p. is probably the same as that for ω-solid solutions. Solid solutions in the α-range (cadmium rich) have a triangular close-packed lattice with $c:a=1·89$. Both α- and ω-solid solutions contain hexagonal lattices of very similar dimensions, and in each case simple substitution occurs. There are no intermetallic compounds at the ordinary temperature.

S. K. Tweedy.

Structure of antimonite. C. Gottfried (Z. Krist, 1927, 65, 428—434; Chem. Zentr., 1927, ii, 1537).—The edges of the rhombic cell are 11·39, 11·48, 3·89 Å.; $a:b:c=0·992:1:0·338$. The cell contains 4 molecules of Sb_2S_3. The most probable space-group is V_h^1.

A. A. Eldridge.

Isomorphism of tervalent molybdenum and iron. G. Carobbi (Gazzetta, 1928, **58**, 35—45).—The isomorphism of compounds of the type R_2MoCl_5,H_2O and R_2FeCl_5,H_2O, where $R=NH_4$ or K, has been investigated. The ammonium compounds are rhombic and isomorphous, the crystallographic constants and molecular volumes of the two salts being practically equal. Isomorphous mixtures of the two salts have been obtained containing up to 10% of the molybdenum compound. The potassium salts are also rhombic and isomorphous and form mixed crystals containing up to 17% of the molybdenum salt. The *compound* $(NH_4)_4MoCl_7,H_2O$ has been prepared and a new case of anomalous mixed crystal formation is described, viz., that between ammonium chloride and molybdenum trichloride.

O. J. Walker.

Structure of tetraphenylsilicane, $SiPh_4$. H. Mark and H. Mehner (Z. Krist., 1927, **65**, 455—460; Chem. Zentr., 1927, ii, 1538).—The edges of the unit cell of tetragonal tetraphenylsilicane, which contains 2 molecules, are 11·50 and 6·97 Å. The space-group is V_d^4 or D_{4h}^9.

A. A. Eldridge.

Structure of some methane derivatives. H. Mark and W. Noethling (Z. Krist., 1927, 65, 435—454; Chem. Zentr., 1927, ii, 1537—1538).—The elementary cell of the cubic modification of tetranitromethane has an edge of 9·2 Å. and contains 4 molecules. The molecule has trigonal symmetry,

indicating the formula $(NO_2)_3C{\cdot}O{\cdot}NO$. The elementary cell of tetramethylmethane has an edge of 12·48 Å., and contains 8 molecules; this molecule also has trigonal symmetry. The molecular constitution cannot be determined crystallographically. For trigonal triphenylcarbinol the axes are *a* 17·9, *c* 12·5 Å.; edge of unit cell containing 3 mols., 11·1 Å. Corresponding values for triphenylbromomethane are 14·05, 22·0, 10·8 Å., respectively. The probable space-groups are discussed. A. A. ELDRIDGE.

Structure and dimensions of the ethane molecule. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 37—41).—Theoretical. A model of the ethane molecule is described. W. E. DOWNEY.

Lattice structure of ethane. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 40—45; cf. preceding abstract).—The *X*-ray diffraction effects as calculated from the model of the ethane molecule are in good agreement with those determined experimentally. W. E. DOWNEY.

Crystal structure of iodoform. J. F. WOOD (Proc. Durham Phil. Soc., 1927, **7**, 168—171).—Laue and rotation photographs show the iodoform molecule to be a tetrahedron in shape. The carbon atom is inside and the hydrogen and iodine atoms are at the corners. The line joining the hydrogen and carbon atoms is the trigonal axis of the molecule. The unit cell contains 2 molecules. W. E. DOWNEY.

Structure of pentaerythritol. H. MARK and K. WEISSENBERG (Z. Krist., 1927, **65**, 499—500; Chem. Zentr., 1927, ii, 1537).—The enantiomorphism demonstrated by Westenbrink and van Melle (*ibid.*, **64**, 548) is not at variance with the pyramidal configuration of the crystal molecule demonstrated by the authors. A. A. ELDRIDGE.

Pyro- and piezo-electricity in pentaerythritol. H. MARK and K. WEISSENBERG (Z. Physik, 1928, **47**, 301).—The fact that pyro-electricity has been detected in pentaerythritol is of importance in determining the crystal structure (cf. preceding abstract). R. A. MORTON.

Polarity and piezo-electric excitation. A. HETTICH and A. SCHEEDE (Z. Physik, 1927, **46**, 147—148).—Arguments are advanced claiming to invalidate the suggestion of Mark and Weissenberg (Z. Krist., 1927, **65**, 435) that the piezo-electric excitation of pentaerythritol affords evidence of polarity in the direction of the principal axis. R. W. LUNT.

Symmetry of crystals of pentaerythritol. H. SEIFERT (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 289—293).—As a result of crystallographic investigation pentaerythritol has been shown to belong to the symmetry class S_4. Only the old tetrahedral model of the pentaerythritol molecule can be reconciled with this class, and not Weissenberg's pyramidal model (A., 1926, 934). On the basis of the results of *X*-ray analysis the origin of the optical anomalies of pentaerythritol is discussed. This compound is apparently the first chemically pure substance with such anomalies which has been crystallographically described. M. S. BURR.

Crystal structure of *p*-nitrotoluene. B. N. SREENIVASAIAH (Indian J. Phys., 1928, **2**, 151—166).—The crystal structure of *p*-nitrotoluene has been examined by the Hull powder method and also by the Laue method. The unit cell appears to be made up of 8 asymmetric molecules and the edges of the cell have the following dimensions: a=10·1, b=11·18, and c=12·3 Å. The crystal structure is the simple orthorhombic lattice Γ_0 in the holohedral class and belongs to the space-group Q_h^1 $(2Di-1)$. Solid *p*-nitrotoluene has *d* 1·305. M. S. BURR.

Preparation of large single crystals. H. C. RAMSPERGER and E. H. MELVIN (J. Opt. Soc. Amer., 1927, **15**, 359—363).—The preparation of large single crystals of substances of m. p. up to 1500° is described. The essential conditions are: (1) a containing vessel sufficiently thin to yield under the strains produced by the cooling crystal (pure platinum foil 0·025 mm. thick is satisfactory); (2) the formation of an initial crystal at the base of the dish; (3) the temperature isotherms should be nearly horizontal to prevent convection currents; (4) the cooling must be sufficiently slow to remove all strains in the crystals. A furnace suitable for such operations is described together with a method of controlling the temperature. Single crystals of about 1 cm. edge of lithium fluoride, sodium chloride, sodium nitrate, and mercuric bromide have been produced in this way. The optical properties of these crystals are under examination. R. W. LUNT.

Magnetic properties of single crystals of zinc and cadmium. J. C. MCLENNAN, R. RUEDY, and (MISS) E. COHEN (Nature, 1928, **121**, 351).—Crystals of zinc and cadmium were obtained by Bridgman's method, and the magnetic susceptibility was determined for every 15° on rotation, correction being applied for the iron content. For zinc, the specific susceptibility in a direction parallel or perpendicular to the principal axis of the crystal is $-0{\cdot}183\times10^{-6}$ or $-0{\cdot}147\times10^{-6}$, respectively,; for cadmium, the corresponding values are $-0{\cdot}276\times10^{-6}$ and $-0{\cdot}169\times10^{-6}$. A. A. ELDRIDGE.

Relation of specific heat to ferromagnetism. J. R. ASHWORTH (Nature, 1928, **121**, 323).—The temperature coefficient of resistance and the thermoelectric power of ferromagnetic substances are abnormal below the critical temperature; the true specific heat rises to a high value (C_θ) at the critical temperature, and immediately above this temperature there is an abrupt change (ΔC) to a lower value. If m and n are the numbers of atoms of at. wt. A in the molecule below and above the critical temperature, respectively, $maC_\theta=5na\Delta C$. Further, $n\Delta CJ\rho=278R'I_0^2$, where I_0 is the maximum intensity of magnetisation, R' the reciprocal of Curie's constant, J Joule's equivalent, and ρ the density of the material. Heusler's alloy, like iron, cobalt, nickel, and magnetite, satisfies these and other energy relations. A. A. ELDRIDGE.

Grating theory of electrolytic conduction in crystals. A. SMEKAL (Z. Physik, 1927, **45**, 869—877).—Braunbek's theory of the mechanism of electrolytic conduction in crystals (A., 1927, 1016) is held to be unsound and the agreement with experiment in the case of potassium chloride consequently spurious. R. W. LUNT.

Temperature variation of the electrical conductivity of crystals. N. Ussataja and B. Hochberg (Z. Physik, 1927, **46**, 88—92).—The electrical conductivities of fluorspar, sodium nitrate, sodium chloride, and mica have been determined in the following temperature ranges, respectively: 200—500°, 20—306°, 200—740°, 100—500°. The conductivity, α, is related to the absolute temperature, T, according to the equation $\log \sigma$ for the first two substances, and for sodium chloride below 600°; in accordance with other work on heteropolar crystals A is approximately constant $(1\cdot1 \quad 0\cdot1)\times10^4$. The data obtained are discussed with reference to the phenomena of dielectric absorption. R. W. Lunt.

Constitution of solid electrolytes. II. Cuprous bromide. J. N. Frers [with F. Leopold] (Ber., 1928, **61**, [*B*], 377—392; cf. A., 1927, 521).—Cuprous bromide, tested as described for cuprous chloride (*loc. cit.*), is found to be a true, mixed conductor in which ionic and electronic conduction are due solely to the copper ion. A complete, continuous transition from exclusively electronic to exclusively ionic conduction is caused by rise of temperature within the range, about 200—330°. Increase in the electrolytic component of the conductivity is caused by surface action, prolongation of the duration of electrolysis, and, to a remarkable extent, by the discharge of silver or lead ions at the cuprous bromide. The observations are readily explained by the supposition of a functional differentiation of the ions in the lattice.
H. Wren.

Contact potential between the solid and liquid phases of bismuth. P. H. Dowling (Physical Rev., 1928, [ii], **31**, 244—250).—Solid bismuth has a contact potential with respect to the melted metal of $-0\cdot02$ volt. The effect of surface charges on melting conditions is discussed.
A. A. Eldridge.

Reflexion, dispersion, and absorption of calcite in the neighbourhood of 7 μ. F. Matossi and (Frl.) F. Dane (Z. Physik, 1927, **45**, 501—507).—The reflexion, dispersion, and absorption of calcite have been investigated for various orientations of the crystal to the incident radiation in the range 6·40—7·10 μ. R. W. Lunt.

Deformations and changes in optical properties of quartz under the influence of the electric field. N. T. Ze (J. Phys. Radium, 1928, [vi], 9, 13—37).—The piezo-electric deformations in a direction normal to the optical and electrical axes of a rectangular parallelepiped of quartz, placed in an electric field in the direction of its binary axis, follow Curie's rule up to 3000 volts and then tend towards a limit at about 160,000 volts. They are equal and opposite to those found in the direction of the optical axis. The dielectric deformations are made up of a contraction and an extension in the directions of, and normal to, the lines of force, respectively, and are proportional to the electrical energy per unit volume of the condenser. The variations in birefringence are linear. They change in sign with the sense of the electrical field and are therefore an electro-optical phenomenon, distinct from the Kerr effect.
J. Grant.

Internal strain in *X*-ray photographs. K. Becker (Z. Physik, 1928, **47**, 454—456).—Polemical against von Göler and Sachs (A., 1927, 1130).
W. E. Downey.

Change in structure and electrical resistance during cold working of metals. G. Tammann and M. Straumanis (Z. anorg. Chem., 1928, **169**, 365—380).—The fall in resistance of hard-drawn copper wire may be considerable even when very little recrystallisation has occurred, whereas the changes in tensile strength and extensibility run approximately parallel with the change in structure. Heating the wire at above 600° causes the resistance to increase again, apparently owing to a change in the structure of the matrix in which the crystallites are embedded. At 800°, the crystallites are so soft that their corners become rounded, with consequent formation of lacunæ, which cause a further increase in the resistance. In copper, there is a definite direction of slip, but this is not so marked in aluminium, which probably accounts for the fact that the resistance of pure aluminium is not affected by cold drawing. R. Cuthill.

Atom deformation in cold wrought tungsten. W. Geiss and J. A. M. van Liempt (Z. Physik, 1927, **45**, 631—634).—From measurements of the electrical conductivity of tungsten it has been shown that atom deformation exists in cold wrought specimens.
R. W. Lunt.

Effect of compression and tension on brass crystals. G. Sachs and H. Shoji (Z. Physik, 1927, **45**, 776—796).—The mechanical deformation of single crystals of brass in the form of rods has been examined for compressions and for tensions up to 200 kg./mm.². For forces of the order of 4 kg./mm.² such crystals exhibit mechanical hysteresis. R. W. Lunt.

Shrinkage in metals and alloys. F. Sauerwald, E. Nowak, and H. Juretzek (Z. Physik, 1927, **45**, 650—662).—Measurements have been made of the shrinkage on solidification of copper, lead, tin, aluminium, zinc, brass, copper–tin (30%), copper–tin (20%), and cast iron. From observations in an inert atmosphere of hydrogen or nitrogen reproducible values were obtained which were independent of the nature of the containing vessel. The values were in agreement with the accepted values for thermal expansivities. Except in the cases of cast iron and bronze no expansion was recorded at the commencement of solidification. R. W. Lunt.

Electrification produced by friction between gases and solid surfaces. I. M. A. Schirmann (Z. Physik, 1927, **46**, 209—236).—Two types of electrification by friction have been identified during the operation of mercury vapour diffusion pumps: the first, which takes place at low rates of vapour flow, is due to friction between mercury droplets and glass surfaces; the second takes place at flow rates of the order of 10^4 cm. sec. and is due to friction between the vapour and glass surfaces. Confirmatory experiments have been carried out by releasing compressed nitrogen from a highly insulated metal bomb in which the bomb attains a potential of several hundred volts. R. W. Lunt.

Relation between conductivity and thermo-electric power in magnetic fields. V. GIAMBALVO (Nuovo Cim., 1927, **4**, 176—189; Chem. Zentr., 1927, ii, 1444).—The thermo-electric power of antimony-copper alloys in a magnetic field decreases with increase of strength of the field; the changes were measured for weak fields. The results accord with theoretical predictions. A. A. ELDRIDGE.

Schtschukarev's magneto-chemical effect. S. GORBATSCHEV (Trans. Sci. Chem.-Pharm. Inst. [Moscow], 1925, **12**, 31—38; Chem. Zentr., 1927, iii, 1797).

Electrical conductivity of palladium in a vacuum and in different gases. A. PUODZIUKYNAS (Z. Physik, 1927, **46**, 253—270).—The conductivity of untreated palladium wire increases by about 15% when the gas contained in the metal is removed by ionic bombardment in a vacuum; the increase in conductivity was proportional to the amount of gas removed, and the total amount of gas evolved was approximately 300 times the volume of the wire. After treatment for 50 min. at bright red heat in pure hydrogen the conductivity fell by 50% and 1486 volumes of gas were absorbed. When the wire was maintained in hydrogen at 1 atm. its conductivity rose slowly, and more rapidly if the wire was in a vacuum until about 900 volumes of gas had been evolved; this indicates that after glowing in hydrogen the metal is supersaturated with hydrogen. When the gas is removed by heating in a vacuum the wire absorbs hydrogen slowly and nitrogen not at all; if, however, the gas is removed in the cold the wire becomes activated and absorbs approximately the same amount of nitrogen or hydrogen.
R. W. LUNT.

Variation of the resistivity of thin layers of platinum as a function of their thickness, and the influence of oxygenated substances. A. FERY (J. Phys. Radium, 1928, [vi], **9**, 38—48).—The optical density, D, measured by the Fabry microphotometer, is proportional to the thickness (a, in mμ) of a layer of platinum deposited on a sheet of mica by cathodic disintegration, and the relation $a=63{\cdot}4D$ may be used for the determination of the latter. By the elimination of water vapour, deposits 4·4—243 mμ thick, and having resistivities (ρ in ohms-cm.) stable for more than a year, were obtained, for which the relation $\log 10^5\rho=5{\cdot}7-0{\cdot}0156a$ was established. The adsorption of vapour of water or of its electrical analogues (sulphur dioxide, methyl alcohol) increased the resistance considerably, to extents which increased with the specific inductive capacities of the vapours at the temperature concerned. These deposits probably have an internal structure which differs from that of the compact but, as the nature of the results indicates, is homogeneous. J. GRANT.

Electrical conductivity of borax. S. OKA (J. Soc. Chem. Ind. Japan, 1927, **30**, 625—632).—The change of electrical conductivity of borax from the molten state to the vitreous state was investigated. The specific conductivity, of the molten borax was found to be much less than that of most of the other molten salts, *e.g.*, $\kappa\times10^3$ is 155 at 800°, 71 at 700°, 17·5 at 600°, and 1·76 at 500°. No break point was found in the conductance-temperature curve at the temperature that corresponds with the m. p. Borax at lower temperatures was in a vitreous state. In the diagram of $\log\kappa$ against $1/T$ a straight line of the type $\log\kappa=-A/T+B$ was found connecting the points found between 660° and 480° from the melted to the vitreous state; the points for the lower temperatures were on another similar straight line. The two intersected at about 480°, but the significance of this point is not known. N. KAMEYAMA.

Conductivity of, and electric absorption in, insulators (amber, sulphur, and paraffin wax), and the effect on them of X- and γ-rays. H. NEUMANN (Z. Physik, 1927, **45**, 717—748).—The following values of the resistivities of amber, sulphur, and paraffin wax have been assigned from elaborate measurements in a vacuum: 10^{20}—10^{18} ohms, 2×10^{18}—2×10^{19} ohms, and 3×10^{18} ohms, respectively. The dielectric absorption and subsequent slow release of charge have also been examined in these substances.
R. W. LUNT.

Relation of diamagnetic susceptibility in the liquid and vapour states. V. I. VAIDYANATHAN (Indian J. Phys., 1928, **2**, 135—150).—Measurements have been attempted of the magnetic susceptibilities of the vapours of the following liquids: carbon disulphide, benzene, *n*-pentane, *n*-hexane, carbon tetrachloride, methyl acetate, ethyl and methyl formate, ether, chloroform, acetone, and heptane. The method employed is based on the fact that a dia- or para-magnetic rod tends to orient itself across or along the field when suspended in a suitable heterogeneous field, and this orienting force is different when the rod is surrounded by different media (cf. Glaser, A., 1925, ii, 82; Hammar, A., 1926, 1197). The results are compared with those obtained by the author by a method described elsewhere. For carbon disulphide, benzene, pentane, and hexane vapours both methods yield a value 20—35% higher than for the corresponding liquids. This is larger than can be accounted for by the experimental errors. In the other cases the differences are smaller. The question of the influence of the proximity of neighbouring atoms or molecules on the diamagnetic properties of the atom is discussed. M. S. BURR.

Allotropic transition point of aluminium. W. GUERTLER and L. ANASTASIADIS (Z. physikal. Chem., 1928, **132**, 149—156).—Aluminium undergoes no transition at 560°; the observed thermal and electrical phenomena are due to the presence of silicon.
H. F. GILLBE.

Method of measuring the radiant heat emitted during gaseous explosions. C. H. JOHNSON (Phil. Mag., 1928, [vii], **5**, 301—322).—A method is described enabling discrimination to be made between the emission of radiant energy from the wave-front and that from the hot products of combustion from a gaseous explosion. The experiments were made in a long, narrow explosion vessel in which the rapid cooling of the burnt gases behind the explosion wave reduced to practically negligible proportions the amount of radiation from that source. A method of calibrating a linear thermopile, placed at some distance

from the bomb, is described which has allowed of a quantitative extension of the previous work of Garner and Johnson (A., 1927, 184). Water vapour and other catalysts have been shown to have a marked effect on the infra-red emission from the wave-front in explosions of carbon monoxide-oxygen mixtures. In a dry gas mixture 7% more of the total heat of combustion was radiated from the wave-front than in a mixture containing 1·9% of water vapour. The importance of this radiation factor in connexion with the effects of water vapour and other catalysts on the spreading of flame in explosions is stressed.

A. E. MITCHELL.

Thermal data of tin. J. N. BRÖNSTED (Z. physikal. Chem., 1928, **131**, 366—370).—Polemical.

H. F. GILLBE.

Molecular aggregation. Theory of liquefaction. Y. ROCARD (J. Phys. Radium, 1927, [vi], 8, 495—501).—The hypothesis of molecular aggregation independent of all molecular force, postulated by Duclaux and opposed by the author (A., 1925, ii, 1045), is shown mathematically to be incompatible with the variations with temperature of the viscosity of a gas. The assumption of intermolecular forces, with a dipole for each molecule, means that each double molecule has a double dipole. Such double molecules will thus tend to aggregate more readily than single molecules. A possible explanation of the mechanism of liquefaction is thus afforded, from which the vapour-pressure curve of a gas at low temperatures may be derived.

J. GRANT.

Conception of polarity derived from physical measurements and its relations to the electronic configuration of aromatic organic compounds. J. F. T. BERLINER (J. Physical Chem., 1928, **32**, 293—306; cf. A., 1927, 506).—Theoretical. The entropies of vaporisation of the nitroanilines and toluidines are greater than 13·8 g.-cal./degree, the value considered by Hildebrand (A., 1918, ii, 61) to be the normal for the conditions specified, and this is considered to indicate association of these liquids. The mononitrotoluenes similarly considered are practically non-associated. Using Crocker's conception of the electronic structure of benzene (A., 1922, i, 924), a relationship between electronic configuration and association derived from vapour-pressure measurements is shown to exist and is applied to interpret the variations in the entropies of vaporisation of the compounds in question.

L. S. THEOBALD.

Metal crystals. VI. Temperature variation of the thermal resistivity of normal metals. E. GRUNEISEN (Z. Physik, 1927, **46**, 151—159).—The author's earlier theory of the additivity of the "metallic" and "non-metallic" portions of thermal conductivity of crystalline metals (A., 1927, 1017) has been extended by showing that the temperature variation of each of these portions can be expressed in terms of the Debye atomic heat function for the metal concerned. The specific thermal conductivity, w, of a pure metal can on this basis be expressed in the form $w=(1+k\theta/T)f(\theta/T)/Z$, where k is the ratio of the "non-metallic" term w_i to the "metallic" term w_m ($w=w_i+w_m$), T is the temperature Abs., Z a universal constant, $2·2\times10^{-8}$ watts degrees^{-2}, and $f(\theta/T)$ the Debye atomic heat function. For pure annealed aluminium, copper, and gold the experimental values of w at 21·2°, 83·2°, 273°, and 373° Abs. are in close agreement with those calculated by the above expression. In impure samples of metals the thermal conductivity does not become zero at 0° Abs., but passes through a minimum in the neighbourhood of 30° Abs.; for such substances the thermal conductivity is given by $w'=w+\alpha/ZT$, where w refers to the pure metal and α is a parameter depending on the purity of the metal and its mechanical treatment.

R. W. LUNT.

Change of properties of substances on drying. H. B. BAKER (J. pr. Chem., 1928, [ii], **118**, 96).—A reply to Balarev (A., 1927, 613). The presence of phosphorus in Balarev's dried liquids is probably due to phosphorus trioxide in the pentoxide used.

C. HOLLINS.

Determination of vapour pressures of sodium and potassium chlorides. S. HORIBA and H. BABA (Bull. Chem. Soc. Japan, 1928, **3**, 11—17).—Measurements were made by a static method, using a quartz spring manometer sensitive down to a pressure of a few mm., on sodium and potassium chlorides over the ranges 800—1240° and 900—1250°, respectively. The heats of vaporisation, Q, calculated by the Clausius–Clapeyron equation were found to be 39·6 and 36·6 kg.-cal., respectively. Combining these data with those of other workers for the latent heat of fusion, M, and the heat of dissociation of the solid into gaseous ions, U, by means of the relationship $U=M+Q+D$, the heats of dissociation, D, of the gaseous chlorides into gaseous ions were found to be 18 and 42 kg.-cal., respectively. The dissociation constant of gaseous sodium chloride was calculated to be of the order of 10^{-39}.

S. J. GREGG.

Efflorescence of sodium sulphite. D. N. TARASSENKOV (Z. anorg. Chem., 1928, **169**, 407—412).—The vapour pressure of the system $Na_2SO_3,7H_2O \rightleftharpoons Na_2SO_3+7H_2O$ between 0° and 70° has been measured. At 15° the pressure is 9·3 mm.

R. CUTHILL.

Evaporation of tungsten under various pressures of argon. G. R. FONDA (Physical Rev., 1928, [ii], **31**, 260—266).—The rate of evaporation of tungsten filaments at 2870° Abs. in a mixture of argon (86%) and nitrogen (14%) varies from 2×10^{-9} to 230×10^{-9} g./cm.^{2} sec. as the pressure is reduced from 1650 to 0 mm. The author's view that the evaporating atoms diffuse through a surrounding film of stationary gas is supported by the fact that $m\propto P\log b/a$, where m is the rate of evaporation, P the pressure, and a and b are the diameters of the filament and gas film (calculated from Langmuir's equation for heat loss), respectively, is constant for gas pressures above 100 mm.

A. A. ELDRIDGE.

Vitreous state and dilatation of glasses. M. SAMSOEN (Ann. Physique, 1928, [x], **9**, 35—127).—The linear and cubic dilatations of a number of soda, silica, silicoborate, and industrial glasses have been determined by the Chevenard and ordinary industrial methods, respectively, at temperatures between −200° and 1500°. Boron and phosphorus enamels, resins, pitch, sucrose, "orca" (polymerised acraldehyde),

glycerol, and sodium thiosulphate were also examined. The anomalous linear dilatation (A., 1926, 567, 568, 570; B., 1926, 709) previously considered to be a property of silica dissolved in complex glasses is shown to be common to all the substances examined, when in the amorphous state. In the case of cubic dilatation, the anomaly takes the form of a change in the dilatation coefficient. Experiments on the influence of temperature on the rate of crystallisation of glycerol led to the conclusion that the molecules of a solid in the amorphous state are stationary with respect to one another, and that all crystallisation is impossible in the true amorphous state below the transformation temperature. This is in accord with the perfect isotropy of fluids and with the mechanical properties of solids. The transformation temperature, which exists for all amorphous substances, depends only on the viscosity. With thiosulphate and sodium silicates rich in sodium, glasses were obtained by rapid cooling of the substance below the transformation temperature. With boric anhydride and glycerol, the transformation temperatures were also determined from the change in specific heat accompanying them, but a value 25° lower than that given by the dilatation method was always obtained. This is unexplained. The curves expressing the variations of the transformation temperature as a function of chemical composition showed maxima at compositions corresponding with what are usually considered to be definite compounds, in particular with the compounds $2SiO_2,Na_2O$, $2B_2O_3,PbO$, and $2B_2O_3,Na_2O$. Grenet's law of additivity is not acceptable in its entirety, except perhaps in cases where the crystalline system does not correspond with a definite compound or a eutectic. The m. p. of glycerol was found to be 18·07°. J. GRANT.

Chemical affinity, cohesion, compressibility, and atomic volume. Effects of internal pressures. T. W. RICHARDS (J. Chim. phys., 1928, 25, 83—119).—A summary of numerous previous papers. H. F. GILLBE.

Reciprocal attraction and repulsion of gas molecules and their bearing on the theory of internal friction. L. SCHAMES (Physikal. Z., 1928, 29, 91—94).—Mathematical. It is shown that the potential energy, Φ, between two molecules when represented by the expression $-A/r^m+B/r^n$ for the attractive and repulsive forces, respectively, leads to the values $m=8$, $n=8$ for helium. W. E. DOWNEY.

Surface tensions and parachors of fused organic substances. S. S. BHATNAGAR and B. SINGH (J. Chim. phys., 1928, 25, 21—27).—The surface tensions of fused naphthalene, α-nitronaphthalene, phenanthrene, phenol, *o*- and *p*-nitrophenol, and *p*-nitrotoluene have been determined by the use of a modified form of Bircumshaw's apparatus (A., 1926, 895). The parachors of the nuclei of naphthalene and phenanthrene and of the hydroxyl group have been calculated and used in the determination of the theoretical parachors of the above substances, which agree well with those observed. L. F. GILBERT.

Deviation of gaseous mixtures from Dalton's law of partial pressures due to chemical causes. III. Hydrogen chloride and methyl alcohol. J. SHIDEI (Bull. Chem. Soc. Japan, 1928, 3, 25—42; see this vol., 229).—The apparatus was arranged so that the gases came in contact only with mercury and glass, special care being taken to remove all traces of adventitious air. The gaseous pressure of methyl alcohol at several different concentrations was measured at a number of temperatures between 70° and 130°, and the relationship between the pressure and the density of the gas was found to be rectilinear. The pressures of gaseous hydrogen chloride over the range 50—130° show good agreement with van der Waals' equation if the temperature variation of the constants *a* and *b* be corrected for by van Laar's equations. Measurements on the mixture show a diminution in pressure on mixing the gases, which is discussed in the light of the reactions $MeOH+HCl \rightleftharpoons MeOH,HCl$; $MeOH,HCl \rightleftharpoons MeCl+H_2O$. The observed diminutions are too small, however, to permit the accurate determination of the extent of the reactions. S. J. GREGG.

Dielectric constants of binary mixtures. Electric moments of certain nitro-derivatives of benzene and toluene. J. W. WILLIAMS and C. H. SCHWINGEL (J. Amer. Chem. Soc., 1928, 50, 362—368).—Dielectric constant and density data for 25° are recorded for benzene solutions of nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzene, *s*-trinitrobenzene, and *o*-, *m*-, and *p*-nitrotoluene. The changes produced in the electric moments of the solute molecules by substituent nitro-groups are closely parallel to the effects produced by hydroxy- and chloro-groups (Smyth and Morgan, A., 1927, 611). The results, which are critically discussed, are in agreement with previously published work. S. K. TWEEDY.

Internal friction of solutions and mixtures. W. HERZ and G. SCHELIGA (Z. anorg. Chem., 1928, 169, 161—172).—The viscosity at 20°, 40°, and 60° of solutions of iodine, phenanthrene, and naphthalene in benzene, toluene, carbon tetrachloride, carbon disulphide, and acetone increases with increasing concentration, the effect becoming less pronounced, however, with rise in temperature, and being usually greatest with phenanthrene, and least with iodine. With solutions containing both naphthalene and phenanthrene, the viscosity usually differs only slightly from the value calculated additively from the viscosities of the corresponding solutions with only one solute. The viscosity of mixtures of carbon disulphide with benzene or toluene exhibits negative deviations from the mixture rule. Equal amounts of maleic and succinic acids increase the viscosity of alcohol by nearly the same amount, but fumaric acid has a greater effect. The viscosities of aqueous solutions of *d*-tartaric acid and racemic acid of the same concentration are usually unequal, but the difference varies both in sense and magnitude with change in the temperature and concentration. With *l*-malic acid and *dl*-malic acid, however, the difference is always negligible. The viscosity at 20° of aqueous solutions of sodium chloride can be represented fairly satisfactorily by an equation of the type $1/x=ky^n$, where y is the viscosity, x is the concentration in g.-mol. of water/g.-mol. of salt, and k and n are

constants. With solutions of magnesium chloride, however, no such equation can be employed, and the viscosities are considerably greater than those of sodium chloride solutions of equivalent concentrations.

R. CUTHILL.

Volume changes attendant on mixing pairs of liquids. J. B. PEEL, W. M. MADGIN, and H. V. A. BRISCOE (J. Physical Chem., 1928, **32**, 285—292; cf. A., 1927, 521; this vol., 21).—For 28 pairs of non-aqueous liquids the volume changes have been calculated from the densities at 25±0·1° of the pure liquids and of various mixtures. The absence of any relation between the volume and temperature changes accords with the values obtained for the heat of mixing and the external work associated with the change in volume, the latter being only an insignificant fraction of the energy change involved. The thermal effect must be attributed to changes in the internal work, and in many cases is due to chemical change.

L. S. THEOBALD.

New kinds of mixed crystals. II. Formation of mixed crystals by barium sulphate and potassium permanganate. H. G. GRIMM and G. WAGNER (Z. physikal. Chem., 1928, **132**, 131—148; cf. A., 1927, 721).—Barium sulphate and potassium permanganate form a series of mixed crystals which at 50° can be studied up to a molar percentage of 60% of potassium permanganate. The content of potassium permanganate in the crystals is approximately proportional to the concentration in the solution with which the crystals are in contact. Mixed crystals containing more than 40% of potassium permanganate are metastable, and are rapidly decomposed by acetone. Crystals stable to acetone are partly broken up by water; the residue, which contains about 8% of potassium permanganate, is very stable towards reducing agents. Barium selenate and chromate, strontium selenate and sulphate, and potassium fluoborate also form mixed crystals with potassium permanganate.

H. F. GILLBE.

New kinds of mixed crystals. VIII. D. BALAREV (Z. anorg. Chem., 1928, **169**, 257—263; cf. this vol., 223).—If barium sulphate is precipitated by the free diffusion of barium chloride and potassium sulphate into a potassium chloride solution, the amounts of water and potassium sulphate included in the precipitate pass through a minimum with increase in the potassium chloride concentration, but are never zero. When the anisotropic crystals of $BaSO_4(K_2SO_4,H_2O)$ are rendered isotropic by warming, they are much more rapidly penetrated by a potassium permanganate solution, probably owing to the capillaries of the small regular crystals constituting the larger crystals becoming connected up in a more regular manner. Similarly, a pure solution of barium chloride diffuses very slowly through a semi-permeable membrane of barium sulphate, but in presence of sugar or potassium permanganate the rate is much increased, because these substances make the barium sulphate crystals isotropic, and so increase their capillaries. The amount of a foreign salt included in precipitated barium sulphate does not appear to depend in any fundamental manner on structural considerations. When a barium sulphate crystal starts to grow in a solution containing a foreign salt, such as permanganate, the thickness of the layer of permanganate solution adsorbed on the surface increases as the crystal grows, and thus the layer becomes less and less readily penetrated by the barium sulphate molecules. When, however, the crystal has reached a certain size, any further increase occurs in the form of deformed growths on its surface, some of the adsorbed layer and a little mother-liquor thereby being mechanically included. With increase in the concentration of foreign salt, the maximum possible size of regular sulphate crystal diminishes.

R. CUTHILL.

Diffusion of thorium through tungsten. P. CLAUSING (Physica, 1927, **7**, 193—198).—Experiments with thoriated tungsten wires, coated with a layer of tungsten, show that at 2150—2800° Abs. thorium moves outwards along the tungsten crystal interfaces, whilst diffusion through the intact tungsten lattice takes place to a negligible extent.

CHEMICAL ABSTRACTS.

Heterogeneity of iron–manganese alloys. C. R. WOHRMAN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1927, No. 14, 32 pp.).—Photomicrographic study of iron–manganese alloys containing 30, 8, and 3% Mn leads to the view that the Widmanstattian and martensitic patterns structures result from the breaking up of a solid phase into two. The latter structure is finer, less well defined, and less regular than the former. On thorough annealing there is formed an aggregate consisting of a ferritic constituent, probably a solid solution of a little manganese in α-iron, and a cementitic constituent, an intermetallic compound rich in manganese. A eutectoid of the two (6% Mn) is also believed to exist, at first martensitic and then pearlitic. The valuable properties of steels are considered to be vested in the solid solutions which iron tends to form, the influence of carbon having been over-emphasised.

CHEMICAL ABSTRACTS.

Incomplete miscibility phenomena in aqueous solutions of ammonia and an inorganic salt. E. JANECKE (Z. Elektrochem., 1927, **33**, 518—526).—When concentrated aqueous solutions of potassium carbonate and ammonia are mixed, two liquid layers are formed, the upper being richer in ammonia and the lower in potassium carbonate (cf. Newth, J.C.S., 1900, **77**, 775). Raising the temperature leads to the disappearance of one of the layers and for a system of given composition there is a definite "clearing temperature." For a fixed temperature there is a critical ratio of ammonia to potassium carbonate such that on dilution with water the compositions of the two layers eventually become identical: with a higher ratio, dilution leads to homogeneity through disappearance of the lower layer; with a lower ratio, through disappearance of the upper layer. Similar phenomena are exhibited by using tripotassium phosphate, rubidium carbonate, or potassium vanadate instead of potassium carbonate. Equilibria in the systems K_2CO_3–NH_3–H_2O and K_3PO_4–NH_3–H_2O have been investigated in detail and the results exhibited by curves. The conditions for the separation of the solid phases $K_2CO_3,2H_2O$ and $K_3PO_4,8H_2O$ are also indicated. A four-dimensional

equilibrium diagram of the system $K_2O-CO_2-NH_3-H_2O$ is given in perspective, together with a projection of this on the triangular base representing the co-ordinates of K_2O, CO_2, and NH_3 (cf. A., 1927, 731).

H. J. T. ELLINGHAM.

Miscibility-gap in molten iron–copper alloys. A. MÜLLER (Z. anorg. Chem., 1928, **169**, 272).—Polemical against Ruer (A., 1927, 928). R. CUTHILL.

Determination of vapour pressure of saturated aqueous solutions. F. POHLE (Mitt. Kali-Forschungs-Anst., 1927, 33—43; Chem. Zentr., 1927, ii, 2047).—Determinations were made of the saturation pressure of saturated solutions of magnesium, sodium, and potassium chlorides and sulphates, and of various mixtures of the salts. The b. p. were also determined. A. A. ELDRIDGE.

Relation between water and salts in crystalline hydrates and in solutions. J. N. RAKSHIT (Z. Elektrochem., 1927, **33**, 578—581; cf. A., 1926, 788). —The molecular contraction observed when a salt forms a crystalline hydrate or a solution with water has been determined for various salts. The values obtained for solutions are generally greater than those for the crystalline hydrates and increase notably with dilution, but for concentrated (including supersaturated) solutions of sodium acetate the molecular contraction is less than for the trihydrate, and for manganous sulphate solutions it is almost negligible compared with the values for the crystalline hydrates. For solutions of sodium sulphate and of sodium carbonate at various concentrations, the molecular contraction has been measured at various temperatures between 15° and 90°, but no indication of transition points corresponding with dissociation of definite hydrates is obtained. It is inferred that the relation between the salt and water in solutions is different from that in the crystalline hydrate.

H. J. T. ELLINGHAM.

Solubility equilibria. F. FLÖTTMANN (Z. anal. Chem., 1928, **73**, 1—39).—The solubility in water and the values of d and n_D for saturated and for 1% solutions of 22 common salts have been determined at 15°, 20°, and 25°, and the results are compared with those obtained by previous investigators.

A. R. POWELL.

Adsorption of strong electrolytes by pure carbon free from ash. I. M. KOLTHOFF (Z. Elektrochem., 1927, **33**, 497—501).—Purified sucrose was carbonised and the finely-powdered product activated by heating for 24 hrs. at 900—960°. The amounts of various inorganic acids adsorbed from $0{\cdot}1N$-solutions by this charcoal decrease in the sequence thiocyanic, hydriodic, nitric, iodic, hydrochloric, hydrobromic, sulphuric, phosphoric; the value for sulphuric acid is very low and that for phosphoric acid is zero. This sequence corresponds with that for the activity of the acids in lowering the surface tension of water. Not only do neutral salts of a strong acid increase the adsorption of that acid by charcoal, but addition of a second inorganic acid has a similar effect. Whereas phenol or amyl alcohol practically prevents the adsorption of the strong acids, the strong acids will partly displace acetic acid from a charcoal surface. It is inferred that the strong acids are adsorbed in the undissociated form. Zero or negative adsorption in the case of strong inorganic bases is confirmed, but a small positive adsorption was obtained with ammonia. Aliphatic primary amines are relatively well adsorbed and the secondary amines much more so: aromatic primary amines are strongly adsorbed. Notable adsorption is found with the strong aromatic and heterocyclic bases, but, whereas alkaloids of low mol. wt. are slightly adsorbed, zero or perhaps negative adsorption is exhibited by alkaloids of high mol. wt., although these substances have a very marked lowering effect on the surface tension of water. Salts of inorganic acids and bases are only adsorbed "hydrolytically" by pure charcoal, the acid being adsorbed and the base remaining in solution. For salts of a given base, the sequence for the extent of this hydrolytic adsorption is the same as that for the adsorption of the corresponding acids. The salts of surface-active organic acids with inorganic bases or of surface-active organic bases with inorganic acids are adsorbed partly hydrolytically but mainly molecularly. Salts of surface-active organic acids and bases are almost entirely adsorbed molecularly. The results obtained for salts of various types are discussed. The polar character of surface-active organic acids and bases is regarded as the essential factor in giving rise to molecular adsorption.

H. J. T. ELLINGHAM.

Comparative adsorption by active charcoal. II. Isoelectric point of charcoal. O. SPENGLER and E. LANDT (Z. ver. deut. Zucker-Ind., 1928, 81—98).—The charcoal is added to a series of buffer solutions at various p_H values, and the isoelectric point of the charcoal is taken to be the p_H value of the buffer solution which is not changed by the addition of the charcoal. The isoelectric points so obtained fell between p_H 5·7 and 8·7.

W. O. KERMACK.

Adsorption of ferric chloride by crystalline barium sulphate. (MLLE.) L. DE BROUCKERE (Bull. Acad. roy. Belg., 1927, [v], **13**, 827—836).—The adsorption of ferric chloride by crystalline barium sulphate at 25°, and the influence of varying concentration of hydrochloric acid ($0{\cdot}1$—$0{\cdot}001N$) on the adsorption, have been investigated. In acid-free solutions a larger value for the quantity of iron adsorbed is found when the washed barium sulphate is fused with crystalline sodium carbonate than when it is digested with pure water; it thus appears that a portion of the electrolyte is irreversibly adsorbed, the digestion method removing only the active portion of the micelle. Moreover, the amount of adsorbed iron, as determined by the former method, is much more than equivalent to the adsorbed chlorine ($\frac{1}{3}$Fe : Cl varies from 4 to 10) and hence adsorption of the micelle, which has the composition $[Fe_2(OH)_6]_m,Fe_2Cl_6$, is also postulated. This is also the case with low concentrations of added hydrochloric acid, but the ratio $\frac{1}{3}$Fe : Cl decreases towards a minimum value of 0·6 (corresponding with $H_4Fe_2Cl_{10}$) as the concentration of the acid is increased. It is assumed that the addition of acid breaks down the micelle, adsorption of which is the main factor. Other conditions being the same, the adsorption of iron is 20—100 times as great as that of uni- and bi-valent cations. J. W. BAKER.

Adsorption at crystal faces. I. Growth and dissolution of single copper sulphate crystals in presence of gelatin and dyes. T. S. ECKERT and W. G. FRANCE (J. Amer. Ceram. Soc., 1927, **10**, 579—591).—Kinematographic observations, at a magnification of 1000, on the growth of crystals from saturated copper sulphate solutions are recorded. Gelatin is very effective in retarding the rate of crystal growth. It is probable that the gelatin is adsorbed to different degrees at different crystal faces, thus changing the crystal habit. The ash of gelatin, *per se*, is without effect in modifying the crystal habit. Quinoline-yellow, Bismarck-brown, and methylene-blue greatly change the crystal habit and decrease the rate of growth of copper sulphate crystals, but naphthol-yellow, ponceau-2R, and methyl-violet do not show such effects. The theory of adsorption in relation to the influence of gelatin and dyes is discussed. It is shown that specific adsorption is largely responsible for changes in crystal form. Viscosity and convection currents affect the rate of dissolution. A. T. GREEN.

Molecule ion absorption. S. GORBATSCHEV (Trans. Sci. Chem.-Farm. Inst. [Moscow], 1925, **12**, 7—30; Chem. Zentr., 1927, ii, 1801).—" Sorption " of ions by neutral molecules is postulated; such sorption accompanies dissociation in electrolytes. If the solution contains foreign neutral molecules, one of the ions is " sorbed," and the degree of dissociation and conductivity of the solution are increased. A. A. ELDRIDGE.

Adsorption and chemical nature of some organic compounds. N. A. SCHILOV and B. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 103—112).—See A., 1927, 1135.

Retrograde adsorption of colloidal ferric hydroxide. W. STOLLENWERK and M. VON WRANGELL (Z. Elektrochem., 1927, **33**, 501—503).—Ferric hydroxide " gels " prepared either (*a*) from ferric chloride solution as a dark brown precipitate or (*b*) by oxidation of ferrous hydroxide with hydrogen peroxide, giving a yellow product, were shaken with solutions of mono-, di-, or tri-sodium phosphate of various concentrations, and the amounts of the phosphate radical adsorbed were measured at intervals over a period of 4 days. In the more concentrated solutions of the disodium phosphate, the preparation (*a*) adsorbs rapidly increasing amounts of phosphate, but after about 12 hrs. a maximum is reached and part of the adsorbed phosphate is gradually given up again, whereas the preparation (*b*) adsorbs smaller but continuously increasing amounts, so that eventually the amounts adsorbed by the two preparations tend to approach one another. In more dilute solutions the amounts of phosphate adsorbed in the first 12 hrs. by the two gels are less divergent, and the subsequent retrograde adsorption by the gel (*a*) is less marked. The retrograde adsorption is strongly marked with the gel (*a*) in concentrated solutions of trisodium phosphate and is exhibited to a slight extent by the preparation (*b*) in such solutions, but it is not shown by either preparation in solutions of monosodium phosphate. The interpretation of these results is discussed. H. J. T. ELLINGHAM.

Molecular orientation at surfaces of solids. I. Measurement of contact angle and the work of adhesion of organic substances for water. A. H. NIETZ (J. Physical Chem., 1928, **32**, 255—269). —The contact angle for water, the effect on the surface tension of water, the spreading, and the work of adhesion of 70 organic solids have been investigated with results which are in accord with the work of Harkins (A., 1921, ii, 242) and of Langmuir (A., 1917, ii, 525). The Ablett cylinder method and the plate method for measuring the contact angle have been compared in favour of the latter, the former giving inconsistent results which are as yet unexplained. Substances which spread considerably do not always greatly affect surface tension. The effect of humidity during crystallisation or solidification of the solid is marked, increased humidity causing a large increase in the work of adhesion. L. S. THEOBALD.

Comparison of thickness of oxide films determined by interference colours and by weighing. G. TAMMANN and K. BOCHOV (Z. anorg. Chem., 1928, **169**, 42—50).—Calculation of the thickness of an oxide film on the surface of nickel from its colour gives a value about 98 $\mu\mu$ less than that determined by direct weighing. This must be ascribed to the presence on the surface both of the bright and the oxidised metal of a film, which, from its loss in weight on reduction, appears to consist of hydrated nickel oxide and absorbed air and water vapour. On iron, the film has a thickness of 85 $\mu\mu$, and on copper 91 $\mu\mu$ (cf. Vernon, A., 1926, 1108). R. CUTHILL.

Surface tension of solutions. W. HERZ and E. KNAEBEL (Z. physikal. Chem., 1928, **131**, 389—404).—The surface tension of an ammonium hydrogen sulphate solution is identical with that of a mixture of equimolar solutions of sulphuric acid and ammonium sulphate of the same equivalent concentration. The formation of an acid salt is indicated in general by an increase of the surface tension of the mixed solution over the arithmetic mean of the surface tensions of the separate solutions. The influence of the alkali and alkaline-earth chlorides and nitrates on the surface tension of water is the same at 20° as at 40°; for each group of cations the increase of surface tension decreases with rise of atomic weight. The surface tension of acetone–water mixtures is lowered by sodium, potassium, and barium salts to an extent which is independent of the salt concentration; this effect is probably due to the insolubility of the salts in acetone, since the solution will then have a lower active water content, *i.e.*, the acetone percentage will increase and the surface tension of the water will thereby be lowered. The chlorides and nitrates of the other alkali and alkaline-earth metals produce at first an increase of the surface tension, and then, at higher concentrations, a decrease. At low concentrations, complexes are formed between the salt and acetone, and the concentration of the latter is lowered; as the salt concentration increases the active water content diminishes, and the reverse effect is observed. A number of measurements have been made of the surface tension of solutions of iodine, naphthalene, and phenanthrene in various organic solvents. In all cases iodine produces a decrease,

and the other substances an increase of the surface tension of the solvent. H. F. GILLBE.

Permeability of thin dry collodion membranes. J. H. NORTHROP (J. Gen. Physiol., 1928, **11**, 233—237).—Dry thin collodion membranes, having a thickness of 2—3 μ and having permeabilities similar to those of the membrane of the sea-urchin egg, have been prepared. The membrane is permeable to water, ammonia, weak acids of low mol. wt., gaseous hydrogen chloride, oxygen, carbon dioxide, and hydrogen sulphide, but impermeable to strong electrolytes and substances of high mol. wt. The rate of effusion of gases through the membrane shows no connexion with the density of the gas and thus the membrane cannot be regarded as a sieve. The results as a whole indicate that the rate of passage of a substance through the membrane is determined by the solubility of the substance in collodion and its diffusion coefficient in collodion, the former probably being the more important factor. A. WORMALL.

Function of carbon membranes in osmosis. F. E. BARTELL and H. J. OSTERHOF (Fourth Colloid Symposium Monogr., 1926, 234—245).—Experiments with silica or carbon membranes show that the flow is from water to organic liquid with the former, and eventually the reverse with the latter. Two liquids were separated by a silica or carbon membrane, and the pressure resulting from the osmotic flow was measured. The results indicate that in a strictly semi-permeable membrane one component is adsorbed to the practical exclusion of the other. When the membrane has greater permeability the initial osmotic force and direction of flow are mainly determined by the relative adsorption of the liquids; the membrane may or may not play an active part.

CHEMICAL ABSTRACTS.

Hydrolysis of sugars by membranes in presence of electrolytes. J. LOISELEUR (Compt. rend. Soc. Biol., 1927, **96**, 1273—1275; Chem. Zentr., 1927, ii, 678).—Fall in p_H of an electrolyte solution in presence of a colloid is observed when sucrose or other hydrolysable sugar is hydrolysed.

A. A. ELDRIDGE.

Chemical method of preparing carbon hydrosol. E. CHIRNOAGA (J.C.S., 1928, 298—301).—By stirring small amounts of carbon in aqueous solutions of sodium hypochlorite a very stable sol is obtained which may be evaporated without suffering irreversible coagulation. The size of the particles is estimated at 60 $\mu\mu$. The negative charge carried by the sol is ascribed to the adsorption of chlorine or hydroxyl ions. A theory of the process is advanced and mention is made of the possible industrial application of the sol as a resistant carbon ink.

H. INGLESON.

Preparation of silver hydrosols free from protective colloids and with particles of a uniform size. II. J. VOIGT and J. HEUMANN (Z. anorg. Chem., 1928, **169**, 140—150; cf. A., 1927, 932).

If silver hydrosols with particles of a uniform size are employed as nuclei in the reduction of a silver oxide solution with hydrazine sulphate and sodium carbonate, the silver submicrons grow in an irregular manner, and there is no relation between the number of particles resulting and the number of nuclei. This is due to the formation of colloidal particles by the sodium carbonate itself, these acting as false nuclei. If, however, the presence of sodium carbonate is avoided by using hydrazine hydrate for the reduction, sols are obtained having particles the size of which is uniform and determined by the number of nuclei. Gold nuclei prepared with the aid of phosphorus also yield satisfactory results, and sols have also been prepared with saturated solutions of silver oxide.

R. CUTHILL.

Colloid syntheses with the aid of titanium trichloride. VI. Colloidal palladium. A. GUTBIER and H. WEITHASE (Z. anorg. Chem., 1928, **169**, 264—266; cf. A., 1927, 933).—If a solution of titanium trichloride is nearly neutralised with sodium acetate, then boiled, and after cooling added to a 1% solution of palladium dichloride, colloidal palladium is formed by the reaction $Pd^{\cdot\cdot}+2Ti^{\cdot\cdot\cdot}=2Ti^{\cdot\cdot\cdot\cdot}+Pd$. The product is relatively insensitive towards acids, owing to the presence of titanium dioxide as protective colloid, and on dialysis passes into a gel, which can be peptised with water only after being treated with concentrated hydrochloric acid. Undialysed preparations of palladium titanium purple are thixotropic.

R. CUTHILL.

Preparation and stabilisation of colloidal mercury. A. CHISTONI (Boll. soc. biol. sperim., 1926, **1**, 408—410; Chem. Zentr., 1927, ii, 905).—Mercuric chloride (0·5 g.), sodium hydroxide (2 g.), and fresh egg-albumin (100 g.) form a gel which when warmed with water is converted into a black sol, stable towards boiling and towards heating at 110° in an autoclave. It is coagulated by an equal volume of 10% barium chloride, but not by sodium chloride solution. The electric charge is negative. The sol is not precipitated by hydrogen sulphide or ammonium sulphide; drying at the ordinary temperature and pulverising yields a substance which is again soluble. The disperse phase consists of a sulphide of mercury, produced by hydrogen sulphide from the albumin.

A. A. ELDRIDGE.

Presence of arsenious oxide in arsenic trisulphide hydrosol. V. GAZZI (Zymologica, 1927, **2**, 1—10; Chem. Zentr., 1927, ii, 26—27).—The quantity of arsenious oxide, even in a highly purified sol, is always much greater than that which can be obtained by complete hydrolysis of soluble arsenic trisulphide. The solubility of precipitated arsenic trisulphide is $2{\cdot}10\times10^{-6}$ mol./litre, yielding 0·4135 mg. per litre of the trioxide, whereas 1·5—3·0 mg. are found. The value is not connected so much with the solubility of the trioxide as with the loss of hydrogen sulphide. It is impossible to separate the ultramicellar liquid by ultrafiltration without changing its composition. A. A. ELDRIDGE.

Interpretation of the analysis of arsenic trisulphide hydrosol. V. GAZZI (Zymologica, 1927, **2**, 10—12; Chem. Zentr., 1927, ii, 27).—The results obtained by Murphy and Mathews (A., 1923, ii, 156) are considered to be due to the presence of a mixture of arsenious oxide and sulphide. A. A. ELDRIDGE.

[Catalysts for hydrogenation in the cold.] M. BOURGUEL (Bull. Soc. chim., 1928, [iv], **43**, 231;

cf. this vol., 28).—A printer's omission is corrected and the directions given in the paper for the preparation of colloidal palladium are amplified. H. INGLESON.

Aluminium hydroxide gels. D. G. R. BONNELL (Z. anorg. Chem., 1928, **169**, 345—355; cf. A., 1927, 1025).—Aluminium hydroxides *B* and *C* form lakes with gold hydrosols, the colour with the *C* gel depending on the relative amounts of gold and alumina. With hydrochloric acid, gels *B* and *C* are not peptised, but pass into crystalloidal solution. Gel *A* is attacked only slightly with hydrochloric acid if an excess of acid is used, but if heated with a small amount of concentrated acid and then diluted it readily yields hydrosols, with particles which are the smaller the greater the quantity of acid used. These sols can be concentrated considerably without the occurrence of gelatinisation, and when evaporated in a vacuum or subjected to ultrafiltration leave a residue again which passes into colloidal solution in water. R. CUTHILL.

Theory of the preparation of silica gel by means of water-soluble metal salts. P. N. GRIGORJEV (J. pr. Chem., 1928, [ii], **118**, 91—95).—Silica gels are obtainable from water-glass ($Na_2O,3SiO_2$) by the action, not only of heavy metal salts (Holmes and Anderson, A., 1925, ii, 518), but also of alkali and light metal salts. Salts of calcium, magnesium, strontium, and barium give silica gels of low activity. The gel formation depends on the hydrolysis of the metal silicates formed by double decomposition. Ferric salts behave exceptionally (cf. Jordis, A., 1907, ii, 876; 1908, ii, 291; 1910, ii, 416). C. HOLLINS.

Size-distribution of colloidal particles. N. RASHEVSKY (Physical Rev., 1928, [ii], **31**, 115—118). —Theoretical. A. A. ELDRIDGE.

State of polarisation of the Tyndall beam of colloids. B. LANGE (Z. physikal. Chem., 1928, **132**, 1—26).—Gans' formula for the depolarisation coefficient θ_0 of individual colloidal particles has been verified by measurements with arsenious sulphide, ferric and aluminium hydroxide, cerium dioxide, and vanadium pentoxide sols. For small spherical particles θ_0 becomes zero, *i.e.*, the Tyndall beam is completely polarised; these conditions hold for caoutchouc, mastic, arsenious sulphide, and cerium dioxide sols. Colloidal particles of ferric and aluminium hydroxides and of vanadium pentoxide deviate considerably from the spherical form, and in the case of the latter the deviation increases on ageing. Thixotropic gelatinisation of a cerium dioxide sol results in a reversible increase of θ_0, indicative of aggregation of the particles. H. F. GILLBE.

Depolarisation and light absorption of solutions of colloidal gold. B. LANGE (Z. physikal. Chem., 1928, **132**, 27—46).—A series of gold sols having particle sizes from 6 to 150 $\mu\mu$ have been prepared and the absorption coefficients measured. The latter are in close agreement with Mie's theoretical values when calculated on the assumption of spherical particles. The mean particle size calculated thus from the absorption differs widely from the values obtained by ultramicroscopical measurements; this is attributed to the relatively large influence exerted by a small proportion of very small particles. Values obtained from the rate of sedimentation agree closely with those calculated from the absorption. Mie's theory requires the absorption coefficient to be independent of the particle size, but this is shown experimentally not to be the case. The depolarisation coefficient θ_0 for small gold particles deviates from zero, since a certain fraction of the particles is non-spherical. The colour change which accompanies coagulation is associated also with a decrease of θ_0, and is therefore not due to a greater deviation of the particles from the spherical form, but to an increase of size. The sols contain chiefly metallic gold, with but little aurous hydroxide; the percentage of the latter in one case was 1·26. H. F. GILLBE.

Stability of colloidal solutions towards electrolytes. A. BOUTARIC (Bull. Soc. chim., 1928, [iv], **43**, 146—155).—Measurements are described in which a spectrophotometer is employed to determine the time *t* required by a colloidal solution to reach its maximum opacity in the presence of an electrolyte of concentration *c*. By successively reducing the concentration of electrolyte the equation $t=f(c)$ can be evaluated and the highest value of *c* at which no coagulation occurs can be calculated, thus providing a measure of the stability. When electrolytes with multivalent ions are employed, *e.g.*, ferric chloride, the curve $t=f(c)$ with certain sols reveals the existence of two zones of flocculation. Gelatin, albumin, and gum, when added to colloidal solutions of arsenic sulphide, ferric hydroxide, or gamboge in small amounts up to a certain limit, reduce the resistance of the colloid to coagulation by an electrolyte, but subsequent additions exert a protective action. When a sol is treated with an amount of electrolyte insufficient to coagulate it, the sol is able to withstand the action of an amount of electrolyte which would have been sufficient to precipitate the untreated sol. Contrary to many published statements, the nature of the visible light by which a sol is illuminated has no effect on the time required for coagulation, illumination by intense red and intense blue light giving the same values as those found in the dark. H. INGLESON.

Protection of colloidal solutions. A. BOUTARIC (J. Chim. phys., 1928, **25**, 120—141).—An experimental investigation of the influences exerted on colloidal solutions by small quantities of added substances. H. F. GILLBE.

Kinetics of coagulation of colloids. K. JABŁCZYNSKI and M. SOROCZYNSKI (Bull. Soc. chim., 1928, [iv], **43**, 159—163; see A., 1925, ii, 34, 35, 665, 666; 1926, 1203).—The equation previously established (using a spectrophotometer), $(\log\tan\alpha-\log\tan\alpha_0)/t=K$, is shown to be a particular case of the more general equation $\log[(\log\tan\quad-\log\tan\alpha_0)/(\log\tan\alpha_\infty-\log\tan\alpha)]=K_1t$, where α_0, α, and α_∞ are the angles of rotation of the Nicol at zero time, time *t*, and infinite time respectively. The general equation expresses the fact that the rate of increase of opacity at a given time is proportional to the difference of the opacity in the final state and at the given time. Values of K_1 obtained experimentally with ferric hydroxide sols are in good agreement. H. INGLESON.

Coagulation of colloids by electrolytes. II. Conductometric study of the coagulation of arsenic trisulphide sols. A. J. RABINOVITSCH and W. A. DORFMANN (Z. physikal. Chem., 1928, **131**, 313—337).—Addition of a solution of an electrolyte to an arsenious sulphide sol causes at first a rapid increase of conductivity, which gradually slows down and finally becomes linear. The initial rapid increase is ascribed to the displacement of the rapidly moving hydrogen ions by the cations of the electrolyte, a process which ceases as the conductivity curve becomes linear. The degree of acidity calculated from the form of the conductivity curve is not in agreement with the value obtained from potentiometric measurements with the quinhydrone electrode. When salts of ter- and quadri-valent ions are employed the degree of acidity cannot be calculated on account of hydrolysis. The point at which the linear portion of the conductivity curve sets in varies directly with the concentration of the sol and inversely as the concentration of the electrolyte, whilst the difference between the coagulative powers of cations of different valencies diminishes with increasing sol concentration. The Hardy–Schulze law is applicable only to the coagulation and not to the completion of the displacement of the hydrogen ions by the adsorbed cations; the two processes are essentially different. In order to produce coagulation a cation must either partly or completely displace the hydrogen ions which are attached to the colloidal particles; a certain excess of the cation is also necessary, which is the greater the lower the valency of the ion. The adsorption of cations of different valencies by the colloidal particles reaches a maximum at approximately the same equivalent concentration, but the quantities adsorbed vary. The influence of the dilution of the sol on the coagulative power of various cations forms an argument against the theory that coagulation is due to the solubility product of the added and stabilising ions being exceeded. H. F. GILLBE.

Coagulation of colloids with electrolytes. A. RABINOVITSCH and R. BURSTEIN (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 35—53; Chem. Zentr., 1927, ii, 1007).—An investigation of mastic emulsions, prepared (*a*) by addition of water to an alcoholic mastic solution and filtering, (*b*) by pouring alcoholic mastic solution into water and filtering; in this case the residue is greater. Conductometric titration of the latter sols is impossible for lack of a minimum; that of the former gives definite results. Both sols are feebly acidic. The particles of the (*b*) sols are greater than those of the (*a*) sols. On coagulation of the sols with neutral salts, no development of acidity takes place, as with arsenious sulphide sols; a corresponding amount of the coagulating cation is retained in the precipitate. A. A. ELDRIDGE.

Influence of temperature on rate of coagulation of colloids. K. JABŁCZYNSKI and M. KNASTER (Bull. Soc. chim., 1928, [iv], **43**, 156—159).—From spectrophotometric measurements of the rate of coagulation of a ferric hydroxide sol by potassium chloride solution at intervals of 10° between 0° and 45° the average temperature coefficient of the rate was found to be 2·19 per 10°. The conclusion is reached that the rate of coagulation cannot be determined simply by the rate of diffusion of the particles, since a rise in temperature of 10° increases the rate of diffusion by only 30% in this range of temperature. H. INGLESON.

Kinetics of coagulation. B. N. DESAI (Trans. Faraday Soc., 1928, **24**, 181—195).—The coagulation of thorium oxide sols by electrolytes has been studied by an accurate optical method, which eliminates those sources of error which probably have prevented other workers from observing the period of slow coagulation. The rates of coagulation agree with Smoluchowski's theory (A., 1917, ii, 129) only up to a certain concentration of coagulator. Evidence for the autocatalytic nature of the coagulation process is adduced. A formula for the velocity coefficient of the process has been derived. Freundlich's theory of coagulation is supported and extended. L. F. GILBERT.

Action of ultra-violet light on some colloidal dispersions of gold. J. J. BEAVER and R. H. MULLER (J. Amer. Chem. Soc., 1928, **50**, 304—321).—The photochemical properties of gold sols depend on the nature and conditions of preparation. Sols prepared with hydrazine, phosphorus, formaldehyde, and acetylene as reducing agents, and also Bredig's gold sol, are quite stable towards ultra-violet light; other sols turn blue after 2 days' exposure and are finally peptised to stable red sols. The change is accompanied by an increase and a subsequent decrease in refractive index, and also in conductivity. The colour, rate of formation, and photochemical properties of chemical gold sols vary continuously with the hydrogen-ion concentration of the reducing solution. The absorption spectra of some gold sols are recorded. The photosensitive sols absorb radiation below 2150 Å.; the radiant energy from this region decreases rapidly with ageing of the lamp. The results are explained on the basis of Wilson's theory of the structure of colloidal gold particles (A., 1916, ii, 604), it being assumed that radiation influences the already unequal distribution of ions between the particle surface and the bulk of the solution. The rate of precipitation of Bredig sols is not affected by radiation. S. K. TWEEDY.

Coagulation of colloidal clay. R. BRADFIELD (J. Physical Chem., 1928, **32**, 202—208; cf. Oakley, this vol., 16).—The coagulation of a colloidal clay, separated from a silt loam by centrifuging, by potassium and calcium hydroxides and chlorides has been investigated by the method previously used (A., 1923, ii, 470). A portion of the clay was freed from exchangeable bases and electrolytes by electrodialysis, and its behaviour compared with the natural clay. The coagulation values for calcium hydroxide in both cases were linear functions of the concentration of the clay, but the much greater values obtained with the electrodialysed material showed that base exchange must play an important role in coagulation phenomena. With potassium hydroxide as coagulant the effect of electrodialysis is even more pronounced, and with the chlorides of potassium and calcium as coagulants the concentration of clay is without effect

on the coagulation value. Coagulation values are very sensitive to hydrogen-ion concentration, and this is very pronounced with the electrodialysed clay. L. S. THEOBALD.

Colloid researches on discharge phenomena and adsorption with quartz suspensions. E. RAMANN and collaborators (Kolloidchem. Beih., 1927, **25**, 279—427).—**Coagulation experiments and microscopical observations on quartz suspensions.** [With J. A. HANLEY.]—Methods are given for the preparation and preservation of quartz suspensions containing particles of nearly uniform size, graded according to the rate of fall under gravity. In the sedimentation of suspensions containing the finer particles the production of layers was observed. The layers are very sensitive to light and heat, strong sunshine soon destroying them. The bounding surfaces are usually concave, showing that the walls of the vessel hinder the fall of the particles. Experiments were made both macroscopically and under the microscope on the flocculation of quartz suspensions on addition of lime-water. Microscopical observation showed the coagulation to take place in a series of steps, and the first clustering of the particles did not coincide with the threshold concentration of electrolyte necessary to produce macroscopic coagulation, but the agreement was better the smaller were the particles.

Preparation of chemically indifferent quartz of definite particle size and surface. [With G. KRAUSS.]—A detailed account is given of the purification of finely-ground quartz both from the products with which it is naturally contaminated and from those which are picked up in the grinding process. Directions are given for the preparation and sterilisation of suspensions of the quartz powder. The suspensions were separated into fractions of uniform particle size by means of elutriation. The size of the particles was determined by taking numerous photomicrographs of the suspensions. The difficulty inherent in the pronounced irregularity of the particles was overcome by constructing on the photomicrograph a circle equal in area to the particle, and taking the diameter of the circle as the mean diameter of the particle. A method is deduced from theoretical considerations for estimating the surface of the particles.

Slipping phenomena in sedimentation on inclined surfaces. [With G. KRAUSS and R. RÜGER.]—When non-spherical particles of quartz of uniform size settle from a suspension in distilled water on to a glass surface inclined at an angle to the horizontal, the particles readily slide down the plane and accumulate at the bottom of the vessel. On the other hand, when an electrolyte is present in the suspension, either the slipping does not occur or the angle which the surface makes with the horizontal has to be increased. It is shown that there is a quite definite "sliding-angle," which increases rapidly with increasing concentration of the electrolyte, and that this angle is a measure of the discharging effect. Particles of diameter 0·01—0·02 mm. were most favourable for the experiments, and the electrolytes used were hydrochloric acid, potassium chloride, calcium chloride, calcium hydrogen carbonate, aluminium chloride, and the hydroxides of calcium, potassium, and ammonium. In these cases, Schulze's valency law was found to be valid for the discharging effect of the electrolytes.

Influence of dilute solutions of electrolytes on the movement of suspended quartz particles in a filter of quartz sand. [With M. STORZ.]—A filtering apparatus was constructed by filling a lamp glass, the bottom of which was closed by a mesh, with quartz sand, and experiments were carried out on the efficiency of such a filter towards increasing volumes of a fine suspension of quartz. It was found that the weight of retained quartz particles increases with increasing volume of the suspension, at first linearly, and later tends to a constant value, showing that the filter has a saturation capacity. In presence of increasing amounts of electrolyte (hydrochloric acid), however, the curve approaches more and more to a straight line, and with 0·0015N-hydrochloric acid in the suspension the quartz sand acts as a nearly perfect filter. Experiments of a similar kind were conducted on the amount of quartz suspension appearing in the filtrate in presence of various quantities of hydrochloric acid, in some cases finely-divided silica being distributed in the filter before the experiment. Experiments in which the filter was divided into vertical sections, each of which could be weighed separately so as to ascertain the amount of quartz retained, showed that the weight of quartz retained diminishes with the depth of the filter, the gradient being greater in presence of increasing concentrations of hydrochloric acid. The capillary rise of quartz suspensions into this type of filter was also investigated. The amount of quartz passing up into the filter increases with the concentration of the suspension, but decreases rapidly with increasing concentration of added hydrochloric acid. The amount of quartz thus transported in presence of N-hydrochloric acid is practically nil. A study of the sedimentation of quartz suspensions in presence of electrolytes has led to the construction of a filter of glass balls by means of which the electrolyte in the region of its critical concentration produces rapidly a visible effect on a suspension.

Effect of small concentrations of electrolytes on sedimentation of quartz suspensions. [With H. SALLINGER.]—Evidence is adduced to show that concentrations of electrolytes smaller than the critical value required to produce complete flocculation have some effect on suspensions. The effect of various concentrations of the following electrolytes on a quartz suspension was investigated: the chlorides of aluminium, calcium, potassium, and sodium, and calcium hydroxide, sodium carbonate, and hydrochloric acid. It is shown that the curve connecting the velocity of sedimentation with the concentration of electrolyte consists of three parts. For low concentrations of electrolytes the sedimentation velocity is slightly accelerated, then at a certain critical concentration the velocity rises very greatly, and is followed by a third region in which increase of concentration of electrolyte causes only a small increase in sedimentation velocity. It appears that the critical concentration of the electrolyte rises with

increasing concentration of the suspension in the case of strongly adsorbable ions such as aluminium and calcium, and the reverse is the case with weakly adsorbable ions.

Adsorption measurements on quartz. [With H. SALLINGER.]—Suspensions of quartz were left in contact with solutions of the hydroxides of calcium, strontium, barium, lithium, sodium, potassium, and ammonium, and the carbonates of lithium, sodium, and potassium, respectively. The amount of the electrolyte adsorbed by the quartz was measured directly by titration with hydrochloric acid. Measurements were also made of the total surface of the quartz, and the results point to the formation of a unimolecular adsorption layer. The quartz was never left in the alkali solution for more than an hour, for if left for a longer interval, chemical interaction takes place. The exponent n of the adsorption isotherm for the hydroxides of calcium, strontium, and barium is proportional to the reciprocal squares of the radii of the respective unhydrated cations.

Cause of formation of layers in suspensions. [With G. KRAUSS.]—The production of layers in suspensions of quartz is considered to be due to the operation of a uniform velocity of fall of the particles. This will operate when the diameter of the particles is below a certain value (the velocity of fall increases with the third power of the diameter), and when the mean distance between the particles is such that a mutual attraction can be exerted. The presence of electrolytes, by partly discharging the particles, should also exert an effect. It is shown that these deductions are in agreement with experiment. Actually, layers were observed only when the diameter of the particles was less than 1 μ, and when the suspension fell between certain limiting concentrations. Layers are not produced in presence of electrolytes.

Theoretical conclusions from measurement of "sliding-angle." [With H. SALLINGER.]—A mathematical treatment of the sliding of charged particles of quartz down an inclined plane during sedimentation (see p. 362). From the measurements, an expression is derived for the absolute value of potential at the quartz–water interface, and, taken in conjunction with adsorption measurements, the thickness of the electrical double layer.

Theory of adsorption in dilute solutions. [With H. SALLINGER.]—The values obtained in experiments on the adsorption of alkali and alkaline-earth hydroxides on quartz (see above) are compared with some adsorption equations, and conclusions are reached concerning the hydration of the cations.

Dependence of the amount of adsorbed material on the amount of the adsorbent. [With H. SALLINGER.]—The expression $x{-}Km \cdot \log d/d_0$ is deduced, where x is the amount of adsorbed material, the amount of adsorbent, K a constant, and d_0 the thickness of the adsorption layer. The value of d is given by $v/m \cdot O_1$, where v is the volume of solution, and O_1 the surface of 1 g. of adsorbent. Since d_0 has been determined, it is possible to calculate the specific surface O_1 of the adsorbent from the formula $O_1=v/m \cdot d_0 \cdot 10^{x/Km}$.

Calculation of the hydrolysis constant of dissolved sodium carbonate from adsorption measurements of sodium carbonate and sodium hydroxide on quartz. [With H. SALLINGER.]—Since the adsorption of neutral salts by quartz is scarcely measurable, the adsorption of sodium carbonate is due chiefly to the sodium hydroxide produced by hydrolysis. Therefore, in the adsorption equilibrium, an amount x of adsorbed sodium hydroxide must indicate a definite amount c' of dissolved sodium hydroxide. The hydrolysis constant K_h is given by the expression $K_h=2c'(c+x) \cdot 10^{-2}/(c-x-2c')$, where c is the total alkali titre of the solution after the adsorption. The values of c and x are obtained from adsorption measurements of sodium carbonate on quartz, and c' can be determined, knowing x, from the adsorption isotherm for sodium hydroxide on quartz. The value $3{\cdot}4\times10^{-4}$ is given for the hydrolysis constant of sodium carbonate.

Calculation of the electrolytic dissociation constant of ammonia from adsorption data (quartz/ammonia and quartz/potassium hydroxide). [With H. SALLINGER.]—The formula $k=(c')^2/v(c-c')$ is derived, where k is the dissociation constant, v the volume of solution, c the total amount of ammonia after the adsorption, and c' the effective amount of ammonium hydroxide. Evaluating the expression from adsorption data, the values k— $1{\cdot}65\times10^{-5}$ and $2{\cdot}5\times10^{-5}$ are obtained for two different concentrations of ammonia. Comparison of c and c' shows that in $0{\cdot}00238M$-ammonia only 8%, and in $0{\cdot}00442M$-ammonia only 7·2% of the total ammonia is present in the form of ammonium hydroxide.

E. S. HEDGES.

Ferric acetates. A. KRAUSE (Rocz. Chem., 1927, 7, 402—435, Bull. Acad. Polonaise, 1927, **A**, 237—272, and Z. anorg. Chem., 1928, **169**, 273—292).—The action of acetic acid on ferric hydroxide hydrogel is a typical Zsigmondy's inhibited chemical reaction. As the concentration of acetic acid in the sol rises, three types of sorption take place, *i.e.*, chemisorption, adsorption, and absorption, then peptisation, and finally chemical reaction. The sorption has a periodic character, the minimum value lying at $0{\cdot}069N$-acetic acid (p_H 3·05). Peptisation coincides with absorption, being strongest in 0·035—$0{\cdot}153N$-acetic acid (p_H 3·2—2·8), and is complete in $0{\cdot}79N$-acid, above which value and up to $1{\cdot}58N$-acid there supervenes the ionising effect of the addition of acetic acid, as is shown by coagulation, change of colour, and augmentation of surface tension of the sol. An examination of the dry residue from the above sols indicated a minimum acetic acid content from sols the acid concentration of which was $0{\cdot}069N$; above this, the ratio [AcO]/[Fe] of the residues increases with concentration of acid. Thus with $1{\cdot}58N$-acetic acid the monoacetate is formed, with $11{\cdot}56N$-acid the diacetate, and with $14{\cdot}45N$-acid the triacetate. The monoacetate is probably the only chemical compound present in the system ferric hydroxide hydrogel–acetic acid. The above ferric acetates, obtained as dry residues, are unstable, losing acetic acid on exposure to the atmosphere, with the exception of that originating from the sol of 3·05, *i.e.*, at the isoelectric point of ferric acetate, the dissociation constant of which is estimated to be 10^{-13}.

R. TRUSZKOWSKI.

Action of neutral salts on the artificial caking of collagen. J. NAGEOTTE (Compt. rend. Soc. Biol., 1927, **96**, 828—830; Chem. Zentr., 1927, ii, 29).—The recoagulation of collagen is affected by the process, the acidity, and the quantity and nature of the electrolytes. A. A. ELDRIDGE.

Colloid-chemical model of the double-ring phenomenon. R. DOERR and E. BERGER (Klin. Woch., 1927, **6**, 1562—1563; Chem. Zentr., 1927, ii, 1717).—A double ring of precipitate, such as is obtained when 0·1 c.c. of normal horse serum is covered with 1 c.c. of 0·1% thorium sulphate solution, is also obtained when the serum is replaced by 1 c.c. of a 2% solution of sodium carbonate in 5 c.c. of sodium chloride solution. A. A. ELDRIDGE.

Cataphoretic protein mobility. H. A. ABRAMSON (J. Amer. Chem. Soc., 1928, **50**, 390—393).—Quartz particles suspended in dilute protein solutions under certain conditions move cataphoretically as if the surfaces of the particles were pure protein. Using the previously described apparatus based on this principle (Freundlich and Abramson, A., 1927, 931), the migration data for egg-albumin at various hydrogen-ion concentrations recorded by Svedberg and Tiselius (A., 1926, 1104) are confirmed. S. K. TWEEDY.

Viscosity and cataphoretic potential of casein sols. B. J. HOLWERDA (Rec. trav. chim., 1928, **47**, 248—263).—Viscosity measurements and kinetic potential determinations on alkaline casein sols were made to elucidate the condition of hydration of casein in various circumstances. The method of preparing the casein is detailed. The protein content of casein being known, sols of a known casein content could be prepared. Measurements of the relative viscosity of alkaline sodium caseinate and calcium caseinate sols at 25° showed agreement with Poiseuille's law. The casein sols are liable to alteration of viscosity with time and temperature of storage, and with exposure to carbon dioxide. From observations on the influence of hydroxyl ions on the viscosity of sodium and calcium caseinate sols it was found that the viscosity (25°) reaches a maximum at p_H 11·6 and 11·4, respectively. In the case of calcium caseinate, the p_H of the maximum is independent of the concentration of casein in the sols. The influence of neutral salts in small concentrations on the maximum viscosity of sodium and calcium caseinate sols was measured, using equivalent concentrations of the chlorides of sodium and calcium, and of hexamminecobaltic chloride. In all cases, viscosity and p_H value decrease with increasing concentration of the added neutral salt.

A study of the cataphoretic potential showed that the maximum of the viscosity does not correspond with the maximum of the electrokinetic potential. The results suggest a variation in the hydration of the sol particles with a variation of p_H. R. A. PRATT.

Geometrical molecular specificity. R. FERRIER (Compt. rend., 1928, **186**, 577—578).—The adsorption phenomena of certain colloidal substances (*e.g.*, proteins) which precipitate one another from solution in a specific fashion may be explained by the assumption that the molecules of the different substances are oriented in polygons, and that substances which precipitate one another contain geometrically equal polygons oriented in an inverse sense. J. GRANT.

Binding of acids and bases by proteins. J. WEBER (Z. physiol. Chem., 1928, **172**, 1—37).—When fibrin is allowed to swell in 0·1*N*-hydrochloric acid, the binding of chlorine ions corresponds with that of hydrogen ions and thus no electrolytic decomposition of the protein hydrochloride occurs. The binding of hydrogen ions by fibrin reaches a well-defined maximum and further addition of acid causes no increase. The acid-binding curve for fibrin is not an adsorption curve, and the titration curves of fibrin with hydrochloric acid, sulphuric acid, oxalic acid, and phosphoric acid and with sodium hydroxide are similar to those for soluble proteins. Washed fibrin, heated fibrin, and dried fibrin usually bind different amounts of hydrogen ions, but in some cases washing and drying of the fibrin has no influence on the binding capacity. The isoelectric point of fibrin is p_H 4·7—4·8. During the digestion of fibrin (or other protein) by pepsin, the increase in acid-binding power shows no connexion with the dissolution or digestion of the fibrin, or with changes in optical activity, viscosity (gelatin), surface tension (egg-albumin), or electrical conductivity (egg-albumin, caseinogen, or fibrin). In addition, no relationship exists between the increase in free amino-groups as digestion proceeds and the increase in bound acid, but the latter appears to run parallel with the increase in free carboxyl groups. The results support the view that chemical union occurs between acids and proteins and that acid-binding constituents other than the amino-groups are present. A. WORMALL.

Physico-chemical changes in egg-albumin hydrosols caused by latex. I—III. S. VISCO (Arch. sci. biol., 1926, **9**, 41—73, 74—77; Chem. Zentr., 1927, ii, 906).—On addition of papain from *Carica* latex the viscosity and gelatinising power of gelatin are reduced. In regard to gelatinising power, the optimal temperature is 70°, and the longer the time of reaction the greater is the effect; the action is independent of p_H. For viscosity, the optimal temperature is 70°, and the effect is more noticeably remote from the isoelectric point. The latex of *Ficus carica* is very effective; its action on the p_H is more marked than that of papain. The density of gelatin solutions is increased by the latex. The results are considered theoretically. A. A. ELDRIDGE.

Swelling of rubber. P. STAMBERGER (Rec. trav. chim., 1928, **47**, 316—320).—The swelling of raw rubber, of over-rolled rubber, and of over-rolled rubber containing varying amounts of carbon black has been studied. Determinations were carried out in a liquid medium and in its vapour, the lowering of vapour pressure being followed. At the point of maximum swelling in benzene vapour, over-rolled rubber gave a viscous liquid, whilst raw rubber under similar conditions appeared to be stable. With increasing quantities of carbon black, the hardness of these jellies was found to increase. Observations were also made with benzene containing 10% of triolein. The

variations in the amount of swelling of raw and of over-rolled rubber, whether swollen in vapour or in liquid, were very marked, being 1880% by volume and 120% by volume, respectively. The results could not be brought into line with any known interpretation of swelling phenomena. R. A. PRATT.

New form of Raoult's laws. I. N. LONGINESCU (J. Chim. phys., 1928, **95**, 70—82).—Raoult's f.-p. and b.-p. formulæ are given a form in which the "constants" are much less variable than is usually the case. A modified form of Raoult's equation for the lowering of vapour pressure, which is frequently met, viz., $(P_0-P)/P_0=x/d$, where d is the density of the solvent, is incompatible with Clapeyron's equation. L. F. GILBERT.

Theory of the Soret effect. E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 283—291).—The equations (cf. A., 1926, 797) for the equilibrium states resulting from reversible Soret effects are transformed into $s_A-dF_A/dT=-S_A$, where s_A is a Soret coefficient, F_A the free energy change, and S_A the entropy change, of the surroundings when one mole of constituent A is transferred. The coefficient s_A is proportional to the ordinary coefficient, $d\log_e N_A/dT$, when the solution is sufficiently dilute. The heats of transfer which determine reversible Soret effects in electrolyte solutions are due to changes in the outer of three spheres surrounding the moving ions; the two inner spheres (the "ion-cavity" and the strongly attracted and oriented molecules) move with the ion, whilst the outer changes with the environment of the ion. Values of s are calculated for some electrolytes in water on the basis of this hypothesis; the results agree fairly well with the direct determinations, but are higher than those of Chipman (A., 1926, 1206). Indirect determinations are probably capable of greater accuracy than the direct. The theory requires that the Soret coefficients are additive, individual values being assignable to all ions at infinite dilution (cf. A., 1927, 419). In infinitely dilute solution s is zero for the solvent but not for the solute; the theory indicates a maximum value of s at higher electrolyte concentrations, with the possibility of a minimum as well. Strong electrolytes in dilute aqueous solutions have negative coefficients. In series of chemically similar ions the Soret effects are of the same order. The Soret coefficient in non-electrolyte solutions, and the irreversible Soret effect in all liquid solutions, are small. S. K. TWEEDY.

Theory of hydrates. E. N. GAPON (J. Chim. phys., 1928, **25**, 154—156).—The relationship $T\sqrt{m}/d\sqrt{n}-c_1$, in which T is the m. p. in degrees Abs., m the number of ions composing the molecule, d the density, n the number of atoms in the molecule, and c_1 a constant, approximately 58, has been verified for a number of hydrated salts. If MX_n be a salt which forms a hydrate, MX_n,mH_2O, of density d, the molecular volume has the value given by $V_m=MX_n/d+mH_2O/d$; writing this as $V_m=A+B$, the quantity $AB/(A+B)$ has for a large number of salts an approximately constant value of about 0·45. H. F. GILLBE.

Hydrogen-ion concentration of aqueous iodine solutions. H. M. DAWSON (J.C.S., 1928, 259—263).—The practical difficulties of making direct measurements of the concentration are referred to and an indirect method of calculation depending on a knowledge of the equilibria: $I_2+H_2O=\overset{+}{H}+\overset{-}{I}+HIO$; $H_2O=H+OH$; $I_2+I=I_3$, is described. The values obtained are applicable only to the freshly prepared solutions. The results indicate that for a fixed concentration of iodine, the hydrogen-ion concentrations fall with increase in the amount of iodide, whilst for solutions with a fixed ratio $[KI]/[I_2]$ they increase with the dilution. H. INGLESON.

Equilibrium between methoxyl and hydroxyl ions in mixtures of methyl alcohol and water. II. Electrometric hydrogen-ion measurements. A. UNMACK (Z. physikal. Chem., 1928, **131**, 371—388).—The hydrogen-ion activity in alkaline mixtures of water and methyl alcohol has been determined at 18° by electrometric measurements, and the partition coefficients of basic ions between water and water-methyl alcohol mixtures have been calculated. The partition exponent at infinite dilution between water and methyl alcohol is about 1·8. On the assumption that the partition coefficient of the hydroxyl ion is equal to that of the hydrated hydrogen ion, the equilibrium constant of the reaction $OH'+MeOH \rightleftharpoons OMe'+H_2O$, calculated on the basis of the Bjerrum–Larsson theory, is about 0·47. H. F. GILLBE.

Micelles and the activity coefficient in alkali silicate solutions. M. RANDALL and (MISS) J. Y. CANN (J. Amer. Chem. Soc., 1928, **50**, 347—358).—If the negative ion of a uni-univalent strong electrolyte, AB, is replaced by an ionic micelle of the form $(B_n)^{n-}$, then, neglecting hydrolysis, the mean molality is m_+ When n is infinite the whole of the solute may be regarded as a single particle possessing the entire negative charge of the solution, and surrounded by univalent positive ions. As n increases the micelle becomes progressively a weaker electrolyte, and in the limit probably behaves as a non-electrolyte. The activity coefficients of various sodium silicate solutions are calculated from f.-p., b.-p., dew-point, and vapour-pressure observations. Metasilicate solutions behave as typical uni-bivalent electrolytes; the value of ν in the Lewis and Randall f.-p. equation is taken as 3 instead of 4. The acid silicates have very low activity coefficients, which are explained by the formation of ionic micelles, and are not largely hydrolysed; the formula $NaHSiO_3$ is preferred and $\nu=2$. The fraction of silicate existing as micelles, and the number and size of the micelles, increase with the ratio of silica to sodium oxide. The influence of the micelles on the activity coefficient of the sodium ion is discussed. S. K. TWEEDY.

Production of glycerol by fermentation. IV. Dissociation of acetaldehyde–sodium hydrogen sulphite complex in alkaline solution. Y. TOMODA (J. Soc. Chem. Ind. Japan, 1927, **30**, 747—759).—The dissociation equilibrium is represented by $\alpha/(1-\alpha)=K+(K_1/K)[H^{\cdot}]+KK_2/[H^{\cdot}]$, where α is the degree of dissociation, K the dissociation constant of the complex$=2{\cdot}84\times10^{-6}$, K_1 and K_2 the constants for the first and second stage dissociation of the acid.

The above equation for α shows that at p_H 6—8 the dissociation of the complex is not appreciable, but reaches 50% at p_H 10·5. The variation of p_H value during the titration of the complex by alkali was examined, and the p_H of the solution, containing equimolecular alkali and the complex, found to be 12—13, which suggests that the sulphite-aldehyde complex is almost completely dissociated. In the production of glycerol, the p_H value of the fermenting medium scarcely exceeds 8·3, so that the dissociation of the complex must be relatively small (less than 5%). The relation between the degree of dissociation of the complex and the value of the medium was confirmed by measuring the distribution of the free aldehyde between water and benzene at various p_H values. When a solution of acetaldehyde containing an excess of sodium hydrogen sulphite was titrated with 0·1*N*-iodine solution at about p_H 8, the total sulphite was titrated, whereas when the titration was conducted at p_H 1—2, the free sulphite was titrated. The difference represents the amount of the combined sulphite and therefore the acetaldehyde. When a solution of sodium hydrogen carbonate and the complex was distilled, the whole of the acetaldehyde was evolved. S. OKA.

Graphical representation of the law of mass action. K. I. SKARBLOM (Tekn. Tidskr., Kemi, 1927, **57**, 87—90; Chem. Zentr., 1927, ii, 2033).—A triangular diagram is employed; a curve is obtained whereby the composition of a mixture can be read. A. A. ELDRIDGE.

Combination and space. N. S. KURNAKOV (Z. anorg. Chem., 1928, **169**, 113—139).—The relation of the physico-chemical changes of matter to the geometrical transformations of space is considered, and topology applied to the development of an analogy between a property-composition surface and a contour map. R. CUTHILL.

Graphical methods and empirical formulæ for the study of electrolytic dissociation. E. DENINA (Notiz. chim.-ind., 1927, **2**, 491—497).—A graphical method of representing the ideal dissociation formula is developed, and diagrams showing variations in the dissociation coefficient are discussed. CHEMICAL ABSTRACTS.

Influence of buffering capacity on the solubility of uric acid. A. JUNG and F. LEUTHARDT (Deutsch. Med. Woch., 1926, **52**, 1985—1988; Chem. Zentr., 1927, i, 3053).—For two different buffer mixtures the solubility of uric acid fell from 0·67 to 0·14 on dilution from 1 : 15 to 1 : 1920, with a corresponding increase of acidity. A. A. ELDRIDGE.

Lead-tin system of alloys re-examined by an electrical resistance method. F. H. JEFFERY (Trans. Faraday Soc., 1928, **24**, 209—211).—The continuous method of recording change of electrical resistance as a function of temperature previously described (A., 1927, 1030) has been applied to the lead-tin system. The equilibrium diagram has been determined down to 75° and is of the Roozeboom type 5, without any complication. The line of eutectic points is at 183°, the phases forming the eutectic mixture containing 16·5 and 97% of tin, respectively. The composition of the eutectic mixture is 66% Sn. L. F. GILBERT.

Transformation of austenite into martensite by liquid air. K. SCHROETER (Z. anorg. Chem., 1928, **169**, 157—160).—The conversion of austenite into martensite by liquid air is shown by the action of the steel on a magnet to occur during the cooling, and not during the subsequent restoration to the ordinary temperature. Measurement of the magnetic saturation before and after cooling indicates a greater relative transformation in a steel hardened in oil than in the same steel hardened in water, the strain due to the increase in volume accompanying the γ—α change being less in the former steel than in the latter owing to its lower austenite content. R. CUTHILL.

Equilibrium pressure over co-existing salt hydrates at temperatures below 0°. J. B. AUSTIN (J. Amer. Chem. Soc., 1928, **50**, 333—386).—The aqueous vapour pressure over a pair of co-existing salt hydrates is less than that over ice or water, and it follows that the heat of hydration of salts per mol. of water is always less than the molar heat of fusion of ice, thus affording a criterion of the accuracy of data on salt hydration. The data for the ten salts which apparently do not obey this rule are open to suspicion. S. K. TWEEDY.

Dissociation of sodium sulphate decahydrate. E. P. PERMAN and W. D. URRY (Trans. Faraday Soc., advance proof, Feb., 1928).—The dissociation pressure of sodium sulphate decahydrate has been measured, using the method of Downes and Perman (A., 1927, 194). The results have been applied in the calculation of (i) the free energy change associated with the hydration of anhydrous sodium sulphate to decahydrate by ice, and (ii) the heat of hydration of sodium sulphate by liquid water. The heat of hydration of sodium sulphate has been measured at four temperatures between 20° and 30°, employing the method of Harrison and Perman (A., 1927, 207). The results are in good agreement with the heats calculated from the free energy changes by means of Nernst's heat theorem. The chemical constant of water is calculated, giving a mean value of 3·63. W. A. RICHARDSON.

Thermodynamic studies on zinc iodide and mercurous iodide. F. ISHIKAWA and E. SHIBATA (Sci. Rep. Tohoku, 1928, **17**, 99—109).—See A., 1926, 1103.

Binary system manganous orthosilicate-calcium orthosilicate. L. TOKODY (Z. anorg. Chem., 1928, **169**, 51—56).—The results of Kallenberg's investigation of the above system (A., 1915, ii, 348) have been confirmed. R. CUTHILL.

M.-p. curves of the nitrobenzaldehydes in the presence of acetic anhydride. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 309—315).—The m.-p. curves were determined in presence of phosphorous or sulphuric acid as catalyst. Two modifications of *o*-nitrobenzylidene diacetate were found, of m. p. 56° and 75°, respectively, but they could not be isolated in the pure state. The yield of diacetate was greater when using sulphuric acid as catalyst and the product showed no discrepancy in m. p. The

m.-p. curve of the *o*-compound showed only the 1 : 1 compound (m. p. 73°) to exist. This was confirmed by adding a drop of sulphuric acid to pure diacetate and setting aside in a sealed tube. With sulphuric acid as catalyst, equilibrium is established from either side after 7 days. For *m*-nitrobenzylidene diacetate, phosphorous acid is a better catalyst. Here again equilibrium between the substance and its components is reached in 7 days. Only the 1 : 1 compound (m. p. 57°) was found to exist, its existence being confirmed by catalysing the pure diacetate with phosphorous acid. The m.-p. curve of *p*-nitrobenzaldehyde–acetic anhydride also shows only the 1 : 1 compound (m. p. 126·8°) to exist, phosphorous acid being used as catalyst. R. A. PRATT.

Conductometric and cryoscopic study of the dimethylpyrone compounds of acetic and the chloroacetic acids in benzene. M. RABINOVITSCH (Z. physikal. Chem., 1928, **132**, 83—100).—The occurrence of salt formation by the action of dimethylpyrone on acetic, mono-, di-, and tri-chloroacetic acids in benzene solution has been studied conductometrically, and the cryoscopic relationships of the dimethylpyrone acetate solutions have been investigated. The maxima in the conductivity curves correspond in each case with the formation of the diacid salt. The conductivities of benzene solutions of the four acids are less than those of the pure substances. The order of the conductivities of the three chloroacetic acids in benzene solution is the same as that of their degrees of association; in presence of dimethylpyrone the order of both is reversed. As regards ionisation the role of dimethylpyrone in benzene is similar to that of water in aqueous solution.
H. F. GILLBE.

Eutectic f.-p. depression in binary mixtures. IV. Effect of pressure on eutectic equations. E. KORDES (Z. anorg. Chem., 1928, **169**, 246—250; cf. this vol., 117).—Taking Hasselblatt's data for the effect of pressure on the m.-p. diagram of mixtures of the tetrahydrates of cadmium and calcium nitrates (A., 1922, ii, 61), and assuming that the hydrates are completely dissociated according to the equations $Cd(NO_3)_2,4H_2O=Cd(NO_3)_2,H_2O+3H_2O$, and $Ca(NO_3)_2,4H_2O=Ca(NO_3)_2,2H_2O+2H_2O$, the relation $(T_b-T_e)/T_b:(T_a-T_e)/T_e=a:b$, where T_e is the eutectic temperature, and a and b are the molecular concentrations of the two components, with m. p. T_a and T_b, respectively, in the eutectic, is true over the whole range of pressure. The equation $\{(T_b-T_e)/(T_a-T_e)\}^k=T_b/T_a$, where k is a constant (A., 1927, 1132) is also apparently independent of the pressure. R. CUTHILL.

Equilibria at high temperatures in the system iron–oxygen–carbon. R. E. GARRAN (Trans. Faraday Soc., 1928, **24**, 201—207).—The equilibria in the systems iron–ferrous oxide–carbon dioxide, carbon monoxide, and ferrous oxide–ferrosoferric oxide–carbon dioxide, carbon monoxide have been studied over the approximate range 600—1300°. The results would seem to be concordant with those for the temperature range covered by Bone, Reeve, and Saunders (cf. B, 1927, 484). L. F. GILBERT.

System calcium oxide–alumina–ferric oxide. W. C. HANSEN, L. T. BROWNMILLER, and R. H. BOGUE (J. Amer. Chem. Soc., 1928, **50**, 396—406).—The above system exhibits one ternary compound, viz., $4CaO,Al_2O_3,Fe_2O_3$, *d* 3·77, which melts congruently at 1415°, and forms with $2CaO,Fe_2O_3$ a complete series of solid solutions having a melting range of about 10°. The compounds CaO,Al_2O_3 and CaO,Fe_2O_3 form limited solid solutions. A diagram is given showing the fields in which CaO, $4CaO,Al_2O_3,Fe_2O_3$, $3CaO,Al_2O_3$, $5CaO,3Al_2O_3$, and solid solutions of $4CaO,Al_2O_3,Fe_2O_3$ with $2CaO,Fe_2O_3$ separate as primary phases. Two quadruple and four quintuple points have been established, and extensive optical data are recorded. S. K. TWEEDY.

Systems uranyl nitrate, alkali nitrate, water, at 25°. A. COLANI (Bull. Soc. chim., 1928, [iv], **43**, 194—199).—See this vol., 131.

Double salt formation. I. Formation of copper sodium sulphate. II. Formation of manganese potassium and ammonium sulphates. R. M. CAVEN and W. JOHNSTON (J. Roy. Tech. Coll. Glasgow, 1927, [4], 32—41).—See A., 1927, 1142.

Equilibria in systems containing water and chlorides of iron, cobalt, and nickel. Y. OSAKA and T. YAGINUMA (Bull. Chem. Soc. Japan, 1928, **3**, 4—10).—The systems $FeCl_3$–$CoCl_2$–H_2O and $FeCl_3$–$NiCl_2$–H_2O form neither double salts nor solid solutions. In the system $CoCl_2$–$NiCl_2$–H_2O, the hexahydrated chlorides form a complete series of solid solutions. The system $FeCl_3$–$CoCl_2$–$NiCl_2$–H_2O has also been examined. S. J. GREGG.

System potassium nitrate–calcium nitrate–sodium nitrate–water. F. FROWEIN (Z. anorg. Chem., 1928, **169**, 336—344; cf. A., 1927, 22).—Determination of the solubility isotherms for the systems sodium nitrate–calcium nitrate–water and potassium nitrate–calcium nitrate–water at 0° and 20° shows that in the latter system each salt increases the solubility of the other, the effect being greater at 0° than at 20°, whereas calcium nitrate depresses the solubility of sodium nitrate, and its own solubility is not affected by sodium nitrate. The three-salt points for the system potassium nitrate–calcium nitrate–sodium nitrate–water at 0° and 20° have also been determined. R. CUTHILL.

Plane representation of multicomponent systems. W. N. LODOČNIKOV (Z. anorg. Chem., 1928, **169**, 177—245).—The application of the method of graphical representation previously described (A., 1926, 358) to systems of four or more components is explained in detail. R. CUTHILL.

Specific heat of electrolytes. K. BENNEWITZ (Z. Elektrochem., 1927, **33**, 540—542).—Theoretical.
H. J. T. ELLINGHAM.

Heats of dilution of strong electrolytes and limits of Debye and Hückel's theory. E. LANGE and G. MESSNER (Naturwiss., 1927, **15**, 521—522; Chem. Zentr., 1927, ii, 790).—The heats of dilution of 0·01*M*-potassium, sodium, and lithium chlorides, lithium bromide, and potassium nitrate, 0·001*M*-calcium nitrate, 0·002*M*-sodium and magnesium sulphates, and 0·00236*M*-calcium sulphate solutions

have been accurately measured by means of an adiabatic differential calorimeter. The results are all positive. For original concentrations below $0{\cdot}01M$ for the uni-univalent halides, or $0{\cdot}002M$ for the uni-bivalent electrolytes the experimental values are slightly below the theoretical. Potassium nitrate, however, in $0{\cdot}01M$-solution, exhibits a large negative deviation from the theoretical value. With bi-bivalent electrolytes the heats of dilution for original concentrations of $0{\cdot}002M$ vary, and are greater than the theoretical values. A. A. ELDRIDGE.

Heat of dilution of moderately concentrated solutions. S. M. NAUDE (Z. Elektrochem., 1927, **33**, 532—534).—The theory put forward recently by Nernst (this vol., 127) is further developed and heats of dilution of solutions of sodium chloride, potassium chloride, sodium nitrate, and potassium nitrate are shown to be represented by $W=-U(1-$ αc, where α is the true degree of dissociation of the electrolyte, U the heat of dissociation, and B is the Debye–Hückel coefficient which is now shown to increase linearly with temperature. Data are given for concentrations, c, ranging from 0·004 to 0·333 g.-mol./litre. With increasing concentration W increases to a maximum and then decreases again, becoming negative at high concentrations. These variations are represented very closely by the above formula. H. J. T. ELLINGHAM.

Vapour pressure and heat of dilution. V. Activity. E. P. PERMAN (Trans. Faraday Soc., advance proof, Jan., 1928).—At 80°, solutions of sucrose up to 500 g. per litre behave as perfect solutions. The lower the temperature, the lower is the concentration up to which the solution remains perfect. For dilute solutions of carbamide at 80° and 60° the activity is slightly higher than unity, and this is attributed to the formation of traces of ammonia by hydrolysis at these temperatures. Allowing for this error carbamide solutions remain perfect at these temperatures up to a concentration $n/N-0{\cdot}8$.

To calculate the activity of potassium chloride, it was assumed that $a_2/N_2=1$ at a dilution of $N_1/N_2=$ 10,000. The activity of the solute reaches a high value in concentrated solution, and is greater at 60° than at 80°. The activity coefficient γ for a molal solution is 0·52 at 80° and 0·60 at 60°. The activities have been calculated in a similar manner for calcium chloride solutions, and are shown to reach enormously high values at high concentrations. W. A. RICHARDSON.

Heat of vaporisation and number of molecules [in unit volume]. W. HERZ (Z. anorg. Chem., 1928, **169**, 173—176).—For non-associated liquids, and many associated liquids, the value of $Z/\sqrt{L}$, where Z is the number of molecules in unit volume at a particular temperature (calculated from the molecular volume and Avogadro's number), and L the latent heat of vaporisation at that temperature, is approximately constant over a wide range of temperature although a very flat minimum is usually present. The value for liquefied gases falls slowly but continuously with rise in temperature, but data are available over only a small range of temperature. For hydrocarbons and esters, but not for associated compounds such as alcohols and fatty acids, $\sqrt{Z/L}$ for the normal b. p. has a value about $8{\cdot}5\times10^8$. R. CUTHILL.

Reversible mixing of substances in the condensed state at the absolute zero of temperature. R. D. KLEEMAN (Science, 1927, **61**, 216—217).—The internal heat of mixing a number of substances is zero at 0° Abs. if the substances and resultant mixture are under the pressures of their vapours. Near 0° Abs. the internal heat of mixing is proportional to the cube of the absolute temperature. A. A. ELDRIDGE.

Errors in the determination of heat of combustion. E. BERNER (Tidskr. Kemi Bergv., 1927, **7**, 31—34; Chem. Zentr., 1927, i, 3211).—A discussion of the precision of the temperature measurement and of the computation of the heat exchange with the surroundings. A. A. ELDRIDGE.

Determination of heat of combustion with Fery's calorimeter. F. KARAS (Chem. Obzor, 1926, **1**, 121—125; Chem. Zentr., 1927, ii, 1373).—The maximum deviation of results obtained with Fery's and the Berthelot–Mahler–Kroeker calorimeters is 1·21%; Fery's method occupies half the time of the latter method. Errors may arise from the radiation from incandescence lamps; day- and night-values may differ by 2%. A. A. ELDRIDGE.

Heat of combustion of some secondary and tertiary amides. A. PARTS (Z. physikal. Chem., 1928, **131**, 405—408).—The following heats of combustion, in kg.-cal./mol., have been determined: diacetamide 518·9, dipropionamide 809·2, acetylbenzamide 1065·1, dibenzamide 1634·8, tribenzamide 2425·5. H. F. GILLBE.

Methods in use at the International Bureau of Physico-Chemical Standards. II. Calorimetric precision measurements. L. MARICQ and M. BECKERS (Bull. Soc. chim. Belg., 1928, **37**, 1—32).—A detailed description is given of a calorimetric method for the determination of heats of combustion. The experimental error does not exceed 1 part in 4000 and might be further reduced by using a more sensitive thermometer, *e.g.*, a resistance thermometer instead of a mercury thermometer. The applicability of Regnault's correction is discussed. The heat of combustion of pure benzoic acid prepared by Poulenc was found to be identical with that of the benzoic acid standard supplied by the U.S. Bureau of Standards (cf. Dickinson, Bull. Bur. Standards, 1915, **11**, 192—203). M. S. BURR.

Electrochemistry of the system benzamide–bromine–nitrobenzene. W. FINKELSTEIN and O. KUDRA (Z. physikal. Chem., 1928, **131**, 338—346).—The specific conductance of the additive compound bromobenzamide, NH_2Bz,Br_2, in nitrobenzene solution increases with increase of concentration up to 52%. The curves at 25° and 35° are parallel, the temperature coefficient being negative. The molecular conductivity–dilution curves at 35° have a maximum at about 900 c.c. dilution. The relationship between the conductivity and the ratio benzamide : bromine confirms the existence of the complex as a true electrolyte; on electrolysis bromine is liberated quantitatively at the anode. The decom-

position potential cannot be measured on account of the thermal decomposition products.

H. F. GILLBE.

Electrical conductivity of solid sulphide mixtures. P. FISCHER (Z. Elektrochem., 1927, **33**, 571—577).—Following work on mixtures of salts and of oxides (A., 1926, 478; 1927, 23), the electrical conductivity of compressed mixtures of powdered sulphides has been determined for direct and for alternating current at various temperatures. For mixtures of two sulphides the conductivity does not vary in a simple manner with the percentage composition of the mixture. With silver sulphide and lead sulphide the conductivity increases with increasing proportion of lead sulphide, but eventually reaches a maximum at about 90% PbS. Although the conductivity of silver sulphide is essentially electrolytic and that of lead sulphide electronic, migration experiments on a 50% mixture indicate that only about 1% of the conductivity is electrolytic. For mixtures of silver sulphide with ferrous sulphide, which is practically a non-conductor, the conductivity–composition curve exhibits a minimum and a maximum. Mixtures of ferrous sulphide and lead sulphide are practically non-conducting up to 50% PbS, but with higher proportions the conductivity increases rapidly. Mixtures containing sulphides of copper, zinc, cadmium, and barium were also examined. It appears that the type of conductivity exhibited by a solid substance may be modified by certain conditions. The observed phenomena are attributed to distortion of the crystal lattices and electron orbits as a result of compression.

H. J. T. ELLINGHAM.

Conductivity cells with electrodes of "brominated silver" instead of platinum. W. A. ROTH (Z. Elektrochem., 1927, **33**, 508—511).—Pure silver covered with a very thin film of silver bromide by exposure to bromine vapour or by dipping in a solution of bromine in hydrobromic acid, is recommended as a cheap substitute for platinum in the construction of electrodes for conductivity cells. Such electrodes give, in conductivity measurements, a balance point about as definite as is obtained with smooth platinum electrodes, whilst, if covered with a thin deposit of platinum-black, the minimum is as sharp as with platinised platinum electrodes. For dilute solutions of silver salts or of formic acid, brominated silver electrodes give better results than platinised platinum. A number of demonstration experiments using a conductivity apparatus fitted with an amplifier and a loud speaker are described. These illustrate the relative solubility of sparingly soluble salts, the relative adsorption of sodium and potassium chlorides by soils, and of potassium chloride and nitrate by precipitated barium sulphate, and the principle of conductometric titration. For the last-mentioned purpose a simple type of apparatus with vertical electrodes of brominated silver is described. Reference is made to the conductometric determination of chlorides, bromides, or iodides of heavy metals by titration with thallium hydroxide solution in the presence of alcohol; of metals with insoluble fluorides with silver fluoride solution; of potassium with lead fluosilicate or barium perchlorate solutions in the presence of alcohol; and of sulphates of heavy metals, including double ammonium sulphates, with barium hydroxide solution.

H. J. T. ELLINGHAM.

Conductivities and p_H values of mixtures of acids in solution. J. A. CRANSTON and J. DUNCAN (J. Roy. Tech. Coll. Glasgow, 1927, **4**, 41—47).—The hydrogen-ion concentration (measured by a hydrogen electrode) and the conductivity of hydrochloric acid solutions containing varying amounts of acetic, oxalic, citric, tartaric, and orthophosphoric acids have been determined. Replacement of water in 0·5N-hydrochloric acid by solutions of acetic, citric, or tartaric acid results in an increase of the hydrogen-ion concentration as determined by the *E.M.F.* method, whereas the conductivity falls. When phosphoric acid solution is substituted, the p_H value increases, whilst the conductivity rises to a maximum and falls. It is suggested that some of the hydrogen ions supplied by the added acid are sufficiently free to contribute to the potential of a contiguous hydrogen electrode, but are insufficiently free to contribute to the conductivity of the solution. When hydrochloric acid solutions of greater than N-concentration are used, substitution of water by solutions of varying oxalic acid concentration has no effect on the conductivity; when solutions of phosphoric acid are substituted, the conductivity of the hydrochloric acid solution is diminished. It is suggested that the hydrogen ions from the hydrochloric acid may not only prevent the dissociation of the phosphoric or oxalic acid into ions, but in the case of the former acid, may also attach themselves transiently to undissociated phosphoric acid molecules, since in phosphoric acid there is an oxygen atom possessing a "lone" pair of electrons, which may be shared by the hydrogen nucleus.

L. M. CLARK.

Potential of the saturated calomel electrode between 0° and 40°. E. VELLINGER (Arch. phys. biol., 1927, **5**, 119—122; Chem. Zentr., 1927, ii, 674).—The relation $E=0·2622-0·00066t$ holds.

A. A. ELDRIDGE.

Potentials and activities of the metals in zinc amalgam cells. J. N. PEARCE and J. F. EVERSOLE (J. Physical Chem., 1928, **32**, 209—220).—*E.M.F.* measurements of zinc amalgam concentration cells have been made at 18°, 25°, and 30°, with amalgam concentrations ranging from a mol. fraction of zinc equal to 0·0003024 up to saturation. The changes in free energy, heat content, and entropy on dilution, and the activities of the zinc and the mercury in the amalgams have been calculated. The deviation between the observed and ideal potentials increases continuously with an increase in concentration of the zinc and approaches zero at infinite dilution. Hildebrand's equation (A., 1913, ii, 470) expressing the *E.M.F.* of a zinc amalgam concentration cell applies throughout a large portion of the range studied. The present results decide in favour of the work of Richards and Forbes (A., 1907, ii, 424) and against that of Crenshaw (A., 1910, ii, 258).

L. S. THEOBALD.

Palladium diffusion electrodes. C. DRUCKER (Z. Elektrochem., 1927, **33**, 504—507).—Two solutions, A and B, are separated by a thin plate of

palladium which is charged with hydrogen by cathodic polarisation, using as anode a platinum wire in solution *A*. By means of standard electrodes arranged with their tips close to the two sides of the plate respectively, the *P.D.* on both sides can be measured, and hence, if the hydrogen-ion concentration of *A* is known, that of *B* can be determined. By using a rotating commutator the polarisation circuit is broken when the potentiometer circuits are made, and *vice versa*. With a polarisation current of 0·07—0·10 milliamp. at a plate with surface area 20—80 sq. mm. and thickness 0·004 mm., reproducible values were obtained, although the effective pressure of hydrogen in the palladium was only about 0·01 atm. Preliminary experiments in which *A* and *B* were both 0·1*N*-hydrochloric acid showed that under these conditions the effective hydrogen pressures on both sides of the plate become equal after about 20 min. and direct measurements are then possible. In any case determinations can be made by making a measurement with solutions *A* and *B*, and then making a further measurement when a solution *B'* of known hydrogen-ion concentration has been substituted for *B*. The method has the great advantage of being applicable to the determination of the hydrogen-ion concentration of solutions which change in composition if a stream of hydrogen gas is passed through them, and of solutions which are mild reducing agents. Measurements on solutions of sodium hydrogen carbonate and of sodium hydrogen sulphite are recorded. The second dissociation constant of sulphurous acid is thus estimated to be about 5×10^{-7}. Again, a blood-serum was found by the diffusion electrode to have a hydrogen-ion concentration of $1{\cdot}4\times10^{-7}$, whereas the value obtained by means of the ordinary hydrogen electrode was $3{\cdot}3\times10^{-9}$. H. J. T. ELLINGHAM.

Solution tension of silver in non-aqueous solvents. F. K. V. KOCH (J.C.S., 1928, 269—280).—The solution tension of silver has been measured in solutions of silver nitrate in pyridine, aniline, methyl and ethyl alcohols, acetone, and various nitriles with the view of correlating the results with the dielectric constants of the solvents and also to ascertain whether the solution tension in different solvents runs parallel with the solubility of the salt in these liquids. There appears to be no kind of regularity in the series of corresponding values of dielectric constant, solution tension, and solubility, but the general result of the investigation shows that in solvents of ammoniacal or nitrile character the metal has a higher solution tension than in those containing hydroxyl or ketonic groups. H. INGLESON.

Silver nitrate concentration cells in acetonitrile and benzonitrile. F. K. V. KOCH (J.C.S., 1928, 524—527; cf. A., 1927, 420, and preceding abstract).—Previous work on the validity of the Nernst formula applied to concentration cells containing non-aqueous solutions is reviewed. Experimental results on the measurements at 0° and 25° of *E.M.F.* of concentration cells of silver nitrate in acetonitrile and in benzonitrile are recorded and compared with the values calculated from the formula $E=2(1-n_c)RT/F\ \log_e \kappa_1/\kappa_2$, where n_c is the transport number of the silver ion, and κ_1 and κ_2 are the specific conductivities of the two electrode solutions. Very good agreement was shown. The results for such concentration cells support the Nernst formula, and also show that the solution laws are obeyed in these solvents at least as nearly as in water. R. A. PRATT.

Modifications of the Sand auxiliary electrode. T. B. SMITH (Trans. Faraday Soc., 1928, **24**, 216—225; cf. J.C.S., 1911, **91**, 373).—By the use of a porous diaphragm instead of the special "conducting" tap of the Sand electrode, and by other modifications, the working resistance of the auxiliary electrode can be reduced to about one tenth of the former value. This enables the potentiometer voltmeter to function also as a null-point detector without causing any appreciable error on account of concentration polarisation of the half-cell. A second modification is described in which the use of either special taps or diaphragm in the electrical circuit is avoided. It has about the same resistance as the first pattern, but permits the use of connecting liquids of high conductivity. The null-point detection is thus brought within the range of a voltmeter of relatively low sensitivity. This modification is to be preferred for most purposes, but the diaphragm pattern has the advantage that it may be used for a considerable time without refilling with electrolyte. The second modification can be employed conveniently as a quinhydrone electrode. Use is made in the electrical circuit of the better class of radio apparatus, the compact design of which facilitates the enclosure of parts most easily attacked by acid fumes. L. F. GILBERT.

***E.M.F.* of electrolytic thermocouples and thermocells and the entropy of transfer and absolute entropy of ions.** E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 292—297).—Electrolytic thermocouples of the type: electrode(T)/soln.I(T)/soln.II($T+dT$)/soln.I(T)/electrode(T) are discussed, the solutions containing uni-univalent electrolytes with a common anion, and the equations previously given for thermocells are modified by considering the entropy of transfer of the ions. Utilising previously published data and the principles of the preceding paper (this vol., 365), the entropy of transfer of some ions in a 0·02*N*-solution at 25° is calculated, as well as the partial molal entropy of the chloride ion. S. K. TWEEDY.

Haber's glass cell. W. S. HUGHES (J.C.S., 1928, 491—506; cf. A., 1909, ii, 785; 1925, i, 1201).—The influence of the composition of the glass used for a Haber cell on the reproducibility of results was studied. The best results were obtained with a glass of small alumina content but of high sodium content. The manufacture of a modified Haber cell is described. Such a cell showed no evidence of the "mixed electrode function" in acid solution described by some workers. An explanation is put forward of the means whereby the hydrogen-ion concentration in the glass phase is maintained relatively constant when that of the solution changes. It is considered that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action

of the sodium silicate in the glass. If, however, in a cell Hg|HgCl|KCl(satd.)|NaOH|glass|*N*-HCl|HgCl|Hg the concentration of the sodium hydroxide is increased to 0·1*N*, the buffer action breaks down. At p_H 9, the buffer action becomes less effective, and this p_H value corresponds with the p_H of a sodium acid silicate buffer mixture half neutralised with respect to the first hydrogen ion of silicic acid (dissociation constant 10^{-9}). Beyond p_H 13, the glass surface is rapidly attacked owing to neutralisation of the second hydrogen ion of silicic acid (dissociation constant 10^{-13}), and the *E.M.F.* falls rapidly. It is shown that the glass is partly acting as a hydrogen electrode in alkaline solution. The extent to which the glass cell *E.M.F.* departs from the value it would have if the glass had a perfect hydrogen electrode function was also studied.

Since the glass cell can be used to measure hydrogen-ion concentration under conditions which render the hydrogen electrode useless, by measuring the p_H of half-neutralised buffer mixtures, the following dissociation constants were determined: the second-stage constants of arsenic and chromic acids ($8·3\times10^{-8}$ and $1·0\times10^{-7}$ respectively), the first-stage constant of arsenious acid (6×10^{-10}), and the constants of azoimide ($2·56\times10^{-5}$) and hydrazine hydrate ($1·4\times10^{-6}$).

The hydrogen-ion activity of copper sulphate solutions was measured, 0·05*M*-solutions having a p_H of 4·24. It was shown that hydrolysis of the sulphate is a slow reaction at the ordinary temperature. The basic copper sulphate formed by addition of alkali has the composition $3CuO,CuSO_4,xH_2O$.

The p_H of an iodide–iodate mixture was found to be about 6·9 after two thirds of the iodate had been decomposed by the addition of hydrochloric acid.

R. A. PRATT.

Reducing power of dextrose. S. A. SCHOU and R. WURMSER (Compt. rend., 1928, **186**, 367—369).—The production of the stable potential gradually set up when a platinum or gold electrode is placed in a solution of dextrose protected from the air (A., 1927, 1218) may be followed by means of the ultra-violet absorption spectrum of the solution, the constant maximum potential corresponding with a maximum absorption band at 2650 Å. The nature of the reducing substance responsible for this is discussed. It is not methylglyoxal, but may be the result of an enolic transformation. J. GRANT.

[Influence of gelatin on the potential and discharge potential of zinc in zinc sulphate solution.] E. RABALD (Z. Elektrochem., 1927, **33**, 532).—A reply to Isgarischev and Titov (A., 1927, 833). H. J. T. ELLINGHAM.

Decomposition potential of zinc sulphate and ferrous sulphate. B. KAMIENSKI (Przemysl Chem., 1927, **11**, 374—381; Chem. Zentr., 1927, ii, 547).—The decomposition potential of zinc sulphate for a sulphide anode is 1·8 volts and 2·62 volts with a lead dioxide anode; when powdered zinc blende on a carbon rod is employed as anode zinc is deposited at 2 volts. A. A. ELDRIDGE.

Overpotential at metallic cathodes. Silver in neutral and alkaline solutions. J. GRANT (Trans. Faraday Soc., 1928, **24**, 225—233; cf. A., 1927, 317).—Polarisation data for silver cathodes in solutions of neutral and alkaline electrolytes have been determined. A fixed value for the overvoltage is attained for a particular current density after a certain time peculiar to each electrolyte. This time decreases as the electrolytes approach the neutral point. The phenomenon is independent of the current density except with regard to the final constant value attained. The overvoltages as measured by both the "commutator" and the "direct" method increase rapidly with the current density when this is low. With the former method a constant value is finally attained, but with the latter method the overvoltage increases at a lesser rate after a critical higher value. This value is close to the constant overvoltages obtained by the commutator method. The decay of polarisation was investigated by varying the interval of the commutator. The decay curves of polarisation sink to values which remain nearly constant over a considerable time, and usually approximate to the constant overvoltages otherwise attained. The voltage between a saturated calomel electrode and a hydrogen electrode placed in the solution varies approximately linearly with the overvoltage. The deviations may be due to secondary influences. The conditions of the formation of a black deposit on the silver and the effect of this on the overvoltages have been investigated. In general, the results are analogous to those already obtained for an antimony cathode. L. F. GILBERT.

"Anode effect." H. VON WARTENBERG (Z. Elektrochem., 1927, **33**, 526—527).—The author maintains his theory as to the origin of the "anode effect" in the electrolysis of fused salts (A., 1926, 912) against the views of Arndt (B., 1927, 659).

H. J. T. ELLINGHAM.

Maxima on current–voltage curves. Electrolysis of nickel salt solutions with the mercury dropping cathode. N. V. EMELIANOVNA and J. HEYROVSKY (Trans. Faraday Soc., advance proof, Feb., 1928).—The prominent maxima sometimes shown on polarisation curves of electro-reductions obtained with the mercury dropping cathode have been studied in electro-deposition from nickel salt solutions. The effect of oxygen is to inhibit the appearance of maxima, which become developed only after long bubbling of hydrogen through the solutions. This influence of oxygen appears to operate by the formation of mercurous ions, as the addition of mercurous ions decreased the maximal currents by amounts which were direct functions of their concentrations. That the stability of maxima is greatest in the presence of iodides, less in chlorides, and least in sulphates, when the concentration of mercurous ions can be the greatest, is thus explained. The suppressive effect of other substances was studied. Cations suppress maxima by degrees which run in the same order as the coagulating powers on negative sols. The influence of anions was not specially examined, as it seemed to matter little. Fuchsin hydrochloride and dextrose solutions are also very effective in suppressing maxima. The phenomena

of the formation of the maximum and its suppression are considered to be due to adsorption of the reducible matter at the mercury-solution interface and to the replacement of the reducible ions by other adsorbable matter, respectively. The sudden fall of current after the maximum is explained by concentration polarisation, which starts when the velocity of deposition of ions becomes greater than the velocity of adsorption in the surface film at the mercury dropping cathode. L. F. Gilbert.

Maxima on current-voltage curves. II. Maxima on the polarisation curves of uranyl salt solutions. P. Herasymenko (Trans. Faraday Soc., advance proof, Feb., 1928; cf. preceding abstract).—The current-voltage curves of the first reduction stage of uranyl ions in aqueous solution at the mercury dropping cathode have been investigated with special reference to the maxima developed. The maximal currents in pure uranyl salt solutions are nearly proportional to the concentrations of uranyl ions. Added salts reduce the maximal current by amounts depending only on the total number of electric charges in solution, so that equivalent quantities of ions of different valencies produce the same effect. Some non-electrolytes also give an appreciable effect. This difference as compared with the behaviour of added ions on the maxima for nickel salts may be ascribed to the presence of products of reduction of uranyl salts, *i.e.*, of quinquevalent uranium ions (see following abstract), which accumulate in the interfacial layer and are preferentially adsorbed. With increase of the polarisation voltage the current falls, after the maximum, to a constant value which is almost independent of the concentration of other electrolytes in solution, and is proportional to the concentration of uranyl ions. From measurements of the interfacial tension between cathodically polarised mercury and solutions of uranyl salts in presence of different concentrations of potassium chloride it is deduced that the cathode potential varies only slightly with the polarising voltage, but the decrease of current after a maximum is accompanied by a sharp increase in the polarisation of the cathode. L. F. Gilbert.

Electro-reduction of uranyl salts by means of the mercury dropping cathode. P. Herasymenko (Trans. Faraday Soc., advance proof, Feb., 1928; cf. preceding abstract).—The reduction of uranyl salts at the dropping mercury cathode proceeds in three stages, in which quinquevalent, quadrivalent, and tervalent ions are formed successively. At still greater potentials hydrogen ions deposit. The first reduction potential depends only on the concentration of uranyl ions, being uninfluenced by the concentration of hydrogen ions. Quinquevalent but not quadrivalent uranium ions readily form complexes with neutral salts. L. F. Gilbert.

Simultaneous reactions of the type A → C. F. E. C. Scheffer and (Miss) A. E. Korvezee (Rec. trav. chim., 1928, **47**, 235—247).—Theoretical. If the relative concentrations of the substances A, B, and C taking part in a reaction of the type A B C are designated by x, $1-x-y$, and y, the composition of the mixture can be expressed by an equation $f(y,x)=0$. The form of this equation and the direction of the corresponding reaction curves are discussed. By choosing the initial concentrations suitably, the reaction can give rise to the maximum and minimum concentrations of all the reactants. By solving the equations, $dy/dt=f(y,x)$ and $dx/dt=f(y,x)$, the time taken to reach these maxima and minima can be found. R. A. Pratt.

Homogeneous gas reactions. I. L. S. Kassel (J. Physical Chem., 1928, **32**, 225—242).—Lewis' definition of energy of activation as the minimum internal energy which must be possessed by molecules in order to react (A., 1925, ii, 799) is considered to be preferable to the definition given by Tolman (A., 1925, ii, 799). Further, it is shown that the activation by collision theory as treated by Hinshelwood (A., 1927, 26, 212), and further developed by Rice and Ramsperger (A., 1927, 833), in which all activated molecules have the same specific reaction rate regardless of their energy content, whilst agreeing with experimental data for propaldehyde, disagrees with such data in the decompositions of diethyl ether, dimethyl ether, and azomethane. An expression is now developed showing the variation of the specific reaction rate of activated molecules with their energy content, and from this is derived an equation which gives this rate for a unimolecular reaction at any pressure. This equation agrees with Ramsperger's experimental results for the decomposition of azomethane (A., 1927, 737). The differences between the present theory and that of Rice and Ramsperger (*loc. cit.*) are considered (cf. also Fowler and Rideal, A., 1927, 114). L. S. Theobald.

Pressures developed in gaseous explosions. W. T. David and B. H. Thorp (Nature, 1928, **121**, 420).—The non-variation of the specific heat of steam over a wide range of maximum temperatures (Maxwell and Wheeler, this vol., 248) is doubted; the apparent value, calculated from explosions of air with excess of hydrogen, is practically constant, but this result is ascribed to incomplete combustion. Minimal values of the percentage of incomplete combustion for various mixtures of hydrogen, nitrogen, and oxygen are tabulated. It is believed that combustion is far from complete even when excess of hydrogen is present. A. A. Eldridge.

Effect of anti-knock materials on the condenser-discharge-spark energy required to ignite a mixture of air with the vapour of ethyl ether. Y. Nagai (Proc. Imp. Acad. Tokyo, 1927, **3**, 670—671).—Values are given for the energy required to ignite a mixture of 4·25% of ethyl ether and 95·75% of air by means of a spark, when various amounts up to 1·5 mol.-% of diethyl selenide, tin tetramethyl, and lead tetramethyl are present. The energy is increased by about 50% for 1 mol.-% in each case. C. J. Smithells.

Effect of anti-knock materials on the limits of inflammability of ethyl ether and hydrocarbons. Y. Nagai (Proc. Imp. Acad. Tokyo, 1927, **3**, 664—669).—The effect of lead tetramethyl and tin tetramethyl on the limits of inflammability of mixtures of air and ethyl ether or hydrocarbons

was determined. A straight-line relation was found between the molecular percentage of the tetramethyl compounds and the upper and lower limits of composition of the mixtures. A similar explanation is given to that previously advanced (cf. A., 1926, 1106). The theoretical flame propagation temperatures of the lead and tin compounds are both 1680°, that of diethyl selenide is 1750°, and that of ethyl ether and hydrocarbons 1450°. This value is raised to that of the anti-knock material when a small percentage is present. C. J. SMITHELLS.

Chemically induced "chain reactions" in mixtures of a halogen with hydrogen or methane. S. VON BOGDANDY and M. PÓLANYI (Z. Elektrochem., 1927, **33**, 554—559).—Previous work (Beutler and Polanyi, Naturwiss., 1925, **13**, 711) has indicated that the vapour of the alkali metals reacts with a halogen according to the equation $Na+Cl_2=NaCl+Cl$. Experiments have now been made to determine the reactivity of free halogen atoms liberated in this way. Hydrogen at 5—10 mm. pressure was passed over molten sodium at 150—250°, whereby it took up sodium vapour at $0{\cdot}5-5\times10^{-4}$ mm. pressure. On meeting a stream of chlorine at 0·2—0·3 mm. pressure, sodium chloride is deposited, but hydrochloric acid is produced in enormously greater amounts. It is considered that this is due to a reaction chain of the type postulated by Nernst for the photochemical formation of hydrochloric acid, viz., $Cl+H_2=HCl+H$; $H+Cl_2=HCl+Cl$; etc. In the present case the number of reactions in a chain is estimated to vary from 700 to 10,000, according to conditions. Increase of the pressure of the sodium vapour decreases the length of the chain. But even under given conditions the length of the chain may vary greatly, probably owing to impurities or the condition of the wall of the reaction vessel. Thus, if the pressure of sodium vapour is increased and then decreased again to its initial value, the length of the reaction chain may be much greater than it was originally: the sodium chloride deposited may prevent combination of chlorine atoms on the wall of the vessel. With potassium instead of sodium the results were similar but the reaction chains shorter. With methane instead of hydrogen, the essential product was methyl chloride, but the number of reactions in a chain was only 100—300. With hydrogen, bromine, and sodium vapour very little action occurs and even when the sodium was heated to 385° only very short reaction chains were obtained. The influence of bromine vapour mixed with chlorine in inhibiting the reaction of the latter with hydrogen in the presence of sodium vapour was also investigated. From probability considerations it is concluded that if α is the ratio of the partial pressure of bromine to that of chlorine and W the ratio of the velocity coefficients for the combination of hydrogen with bromine and chlorine, respectively, the number of reactions in a chain will be $2(\alpha W+1)/\alpha W(\alpha+1)$. The experimental results are in reasonable agreement with this relation, if W is put equal to 0·13. The fact that hydrochloric acid does not inhibit the reaction between chlorine and electrolytic gas has been quoted as an objection to the Nernst reaction chain theory. In a discussion of the subject it is shown that this objection may be invalid. H. J. T. ELLINGHAM.

Explosion temperature and sensitivity to shock of liquid and solid explosives. G. TAMMANN and C. KROGER (Z. anorg. Chem., 1928, **169**, 1—32).—Experiments with a variety of liquid and solid explosives have shown that the temperature at which explosion occurs on heating usually increases in a linear manner with the rate of heating, and decreases with increase in the amount of explosive. For substances exploding below their m. p., the lines representing the effect of rate of heating on the explosion temperature for different quantities of explosive are parallel, but with explosives which melt and are appreciably volatile below their m. p. and explode above it the lines tend to converge at high rates of heating. With explosives of the former group, such as lead azide and mercury fulminate, the explosion limit, *i.e.*, the minimum amount which will explode with any particular rate of heating, is considerably depressed by heating in an inert atmosphere, oxidation thus being avoided, and increase in the coarseness of grain has the same effect. The explosion limits of the more volatile explosives, on the other hand, may be lowered by increasing the pressure. By varying the factors determining the rate at which the heat of reaction is lost, *e.g.*, by compressing a powder into a tablet, the effect of rate of heating and amount of explosive on the explosion temperature may be partly annulled. With small amounts of lead azide, the relation between explosion temperature and rate of heating is abnormal, apparently owing to the formation of an explosive basic azide. The explosion temperature of silver azide does not vary in any regular manner with the rate of heating and amount of explosive. From heating curves, 2 : 4 : 6-trinitrotoluene is found to begin to decompose at 150°, and 2 : 4 : 6-trinitro-*m*-cresol at 180°. If the former is heated at a steady temperature for some time, there are formed decomposition products, which raise the explosion temperature. A liquid explosive can be caused to explode by the uniform propagation through it of a shock. A shock applied to a solid explosive by actual contact with a solid is more effective than an equal shock applied indirectly through hydrostatic pressure over all its surface. Under certain conditions, crystalline explosives may explode when flowing through an orifice. R. CUTHILL.

Velocity of ionic reactions. II. R. N. J. SAAL (Rec. trav. chim., 1928, **47**, 264—285; cf. this vol., 248).—The reaction constant of the reaction $CO_2+OH'\longrightarrow HCO_3'$ was found to be $3{\cdot}7\times10^3$ at 13·7° from conductivity measurements, the hydroxyl-ion concentration being so chosen that the amount of hydrogen carbonate in the solution was negligible. The total concentration of the solution was found to have no influence on the reaction constant, thus agreeing with Bronsted's theory (cf. A., 1922, ii, 699; 1925, ii, 681). Determinations were made of both the conductivity and the hydrogen potential of the equilibrium $H_2CO_3 \rightleftharpoons H^{\cdot}+HCO_3'$ and of the reaction $H_2CO_3\longrightarrow CO_2+H_2O$; but it was not possible to decide whether the carbon dioxide

originates from carbonic acid or whether it is the result of interaction of hydrogen and hydrogen carbonate ions. The reaction constant of the reaction $H^{\cdot}+HCO_3' \rightleftharpoons H_2CO_3 \longrightarrow CO_2+H_2O$ is 8 at 13·5°. The equilibrium constant of the reaction $H_2CO_3 \rightleftharpoons CO_2+H_2O$ is $1{\cdot}1\times10^3$ at 13·7°. It was possible to follow the behaviour of the p_H during acidimetric titrations with alkali containing carbon dioxide.

The reaction dichromate $\longrightarrow$ chromate was also studied; the equilibrium $Cr_2O_7''+H_2O \rightleftharpoons 2HCrO_4'$ exists with an equilibrium constant of $0{\cdot}019\pm0{\cdot}001$. The decomposition of dichromate to chromate may take place in three ways: (i) In the alkaline region, $Cr_2O_7''+OH' \longrightarrow CrO_4''+HCrO_4'$. (ii) In the acid and neutral region, $Cr_2O_7''+H_2O \longrightarrow 2HCrO_4'$. (iii) On large dilution with acid and water, $Cr_2O_7''+H^{\cdot}+H_2O(\rightleftharpoons HCr_2O_7'+H_2O) \longrightarrow 2HCrO_4'+H^{\cdot}$.
R. A. Pratt.

Primary salt effect in a zero type reaction. M. Kilpatrick, jun. (J. Amer. Chem. Soc., 1928, **50**, 358—362).—The reaction $6H_2O+Cr[CO(NH_2)_2]_6^{\cdots} \longrightarrow Cr(H_2O)_6^{\cdots}+6CO(NH_2)_2$ is investigated, the rate of disappearance of the first-named ion being measured by precipitation with potassium cobalticyanide. The reaction serves as a critical test of theories of reaction rate; the results are in agreement with Bronsted's theory. S. K. Tweedy.

Activation of chemical reactions by neutral salts. II. Activation of the dissolution [in acids] of marble by neutral salts. N. Isgarischev and S. Schapiro (Z. physikal. Chem., 1928, **131**, 442—445; cf. A., 1927, 945).—The velocity of dissolution of marble in hydrogen chloride solutions in presence of chlorides and in acetic acid solutions in presence of acetates has been determined by measurement of the rate of evolution of carbon dioxide. In the former case the velocity is in general increased, but there is no relationship between the velocity and the p_H of the solution. In the acetate solutions the velocity is proportional to the p_H. The results are in agreement with the Debye–Hückel theory.
H. F. Gillbe.

Kinetics of the decomposition of nitrous acid. I and II. E. Abel and H. Schmid (Z. physikal. Chem., 1928, **132**, 55—77).—The mode of decomposition of nitrous acid has been studied, regarding as the essential factor the reaction between nitrogen tetroxide and water. If supersaturation of the solution with nitric oxide is not prevented the rate of disappearance of nitrous acid is not a measure of the progress of the reaction $3HNO_2 \longrightarrow H^{\cdot}+NO_3'+2NO+H_2O$. H. F. Gillbe.

Reactivity of dextrose in hydrochloric acid. E. A. Moelwyn-Hughes (Trans. Faraday Soc., advance proof, Feb., 1928).—The change of rotation of solutions of dextrose (10—50 g. per 100 c.c.) in *N*-hydrochloric acid at 60° and 70° has been investigated. The observed increase in positive rotation, which is distinct from the ordinary mutarotation, is complete in about 200 hrs. Following Harrison (A., 1914, i, 498), the change in rotation is ascribed to a condensation product "diglucose." The relative hydrogen-ion activities in *N*-hydrochloric acid solutions containing 10—50 g. of dextrose in 100 c.c. are given, and it is shown that the value of k calculated from the equation for unimolecular reactions, divided by the relative hydrogen-ion activity, is constant for all the solutions. The van 't Hoff method also indicates that the reaction is of the first order. The critical increment of the reaction is 33,500 g.-cal. The order of the reaction is explained by assuming the condensation of dextrose under these conditions to be a pseudo-unimolecular change, in which the concentration of one of the reactants (normal dextrose) far exceeds that of the other (active dextrose). The nature of this active form is discussed. W. A. Richardson.

Kinetics of the hydrolysis of glucosides (salicin, arbutin, and phloridzin). E. A. Moelwyn-Hughes (Trans. Faraday Soc., advance proof, Feb., 1928).—The rates of hydrolysis at 60° and 70° of salicin, arbutin, and phloridzin by *N*-hydrochloric acid have been determined polarimetrically. By using dilute solutions (about 5%) the production of "diglucose" (cf. preceding abstract) is negligible under these conditions. The critical increment of the hydrolysis of disaccharides and glucosides is a more significant quantity than the velocity itself, as it lends itself more readily to comparative treatment. The mean critical increment for three fructosides (sucrose, raffinose, and melezitose) is 25,700 g.-cal. ($\pm1\%$), for three glucosides (maltose, salicin, and arbutin) it is 31,600 g.-cal. ($\pm1\%$), and for the galactoside lactose it is 27,100 g.-cal., whilst the velocity coefficients show no simple relationships. The experimental value of the critical increment appears to depend on the nature (whether fructosidic or glucosidic) of the linking ruptured, and to be independent of the stereochemical (α or β) character of the linking. The critical increment for phloridzin, 23,100 g.-cal., is abnormally low.
W. A. Richardson.

Mutarotation. IV. Consecutive reactions in the mutarotation of dextrose and galactose. F. P. Worley and J. C. Andrews (J. Physical Chem., 1928, 32, 307—315; cf. A., 1927, 631, 736; this vol., 25).—The mutarotation of α- and β-glucose and of α- and β-galactose in aqueous solution has been studied polarimetrically at 0° in order to examine the initial stages of the action. In each case, an initial divergence from the subsequent unimolecular nature of the change has been observed. With α-galactose an initial retardation is observed followed by an acceleration. In the case of β-galactose mutarotation is arrested for 30 min. With α-glucose there is an initial retardation, and with β-glucose an acceleration. None of these changes can be ascribed wholly to a temperature effect. These divergences are said to show that mutarotation is not a simple unimolecular reaction, but involves two stages, *e.g.*, α-sugar $\rightleftharpoons$ X $\rightleftharpoons$ β-sugar, with the formation of an intermediate substance, X, the varying nature of the divergence being determined by the magnitude of the rotation of X, and the relative values of the velocity coefficients. For a rise of 10°, the velocity of mutarotation is increased 2·8 and 2·9 times for dextrose and galactose, respectively. L. S. Theobald.

Sulphite addition to unsaturated compounds. II. E. HAGGLUND and A. RINGBOM (Z. anorg. Chem., 1928, **169**, 96—98; cf. A., 1926, 363).—The velocity coefficients at 80° of the reactions between sulphite and methylpropiolic and phenylpropiolic acids are considerably less than those of the reactions between sulphite and the corresponding ethylenic acids. With phenylpropiolic acid, the velocity coefficient falls continuously during the course of the reaction, apparently owing to decomposition.

R. CUTHILL.

Kinetics of chemical reactions between one solid and one gaseous component which result in the formation of complex compounds. A. PREDVODITELEV and A. WITT (Z. physikal. Chem., 1928, **132**, 47—54).—A micro-balance has been constructed by the aid of which the kinetics of the reaction between anhydrous cupric sulphate and gaseous ammonia at the ordinary temperature and at various pressures have been studied. The reaction follows the equation $dc/dt=qp(B-C)(C_0-C)$, where C is the concentration of the cuprammonium sulphate, the pressure, and q, B, and C_0 are constants.

H. F. GILLBE.

Decomposition of water and aqueous chloride solutions by powdered iron. S. MICEWICZ (Przemysl Chem., 1927, **11**, 501—511; Chem. Zentr., 1927, ii, 1551).—The speed of reaction with powdered iron in aqueous solution increases in the series: sodium, potassium, calcium, magnesium chloride. Nitrobenzene is readily reduced to aniline by iron powder and magnesium chloride solution; the compound $2NH_2Ph,MgCl_2,6H_2O$ appears to be formed intermediately.

A. A. ELDRIDGE.

Action of acids on metals under pressure. G. TAMMANN and K. BOCHOV (Z. anorg. Chem., 1928, **169**, 33—41).—When dilute sulphuric or hydrochloric acid acts on metals such as iron and zinc in a closed vessel, the reaction comes to an end some time before all the metal has been attacked. Measurements of the resistance afford no indication of the existence of a protective film of hydrogen, but *E.M.F.* determinations show that the potential of the metal becomes more electronegative, owing to the dissolution of hydrogen in the metal. The potential of the hydrogen also becomes more electronegative, but to a smaller extent, so that under favourable conditions the reaction ceases. In the action of sulphuric acid on magnesium, a coating of basic salts appears to be formed.

R. CUTHILL.

Corrosion. J. CZOCHRALSKI and E. SCHMID.—See B., 1928, 160.

Passivity and protective oxide films. U. R. EVANS (Nature, 1928, **121**, 351—352).—A discussion of the conditions influencing the thickness of protective oxide films. The X-ray method of examination, employed by Kruger and Nahring, is unsuitable. Air-passivity appears to be a property of the pure metal.

A. A. ELDRIDGE.

Passivity limit in mixed crystals. G. TAMMANN (Z. anorg. Chem., 1928, **169**, 151—156).—If it is assumed that in mixed crystals of iron and chromium each atom of the latter is able to impart its power of becoming passive when brought into contact with dilute solutions of electrolytes to one atom of iron, a consideration of the crystal structure leads to a value for the minimum amount of chromium necessary to produce passivity which is considerably greater than that actually found. It therefore appears that other factors, such as the presence of foreign substances, are also involved. Van Liempt appears to have been under a misapprehension as to the true nature of resistance limits, and the values given by him for mixed crystals of molybdenum and tungsten (A., 1927, 196) are therefore to be rejected.

R. CUTHILL.

Effect of catalysts on the speed of flame, infrared emission, and ionisation during the combustion of carbon monoxide and oxygen. W. E. GARNER and C. H. JOHNSON (J.C.S., 1928, 280—298; cf. A., 1927, 184; Johnson, this vol., 353).—Measurements were made of the rate of emission of radiation, the duration and magnitude of ionisation, and the speed of flame for mixtures of carbon monoxide and oxygen to which various catalysts were added. It being already known that the loss of radiant energy increases with the introduction of water-vapour into such mixtures, the effect of introducing other substances containing hydrogen into the reaction mixture was observed. A new experimental arrangement was devised whereby the emission of radiation, the ionisation, and the speed of flame could be measured simultaneously. The standard mixture was 2 vols. of carbon monoxide with 1 vol. of oxygen, dried for 2 hrs. over commercial phosphorus pentoxide. Its mean radiation on explosion was $6{\cdot}00\times10^6$ g.-cal., and its mean speed of flame 100 cm. per sec. Addition of 1·95% of water vapour reduced the radiation to $1{\cdot}63\times10^6$ g.-cal., but increased the flame speed more than tenfold. Similar results were observed with the addition of ethyl nitrate, ethyl iodide, ethyl bromide, and chloroform. Carbon tetrachloride acted as a negative catalyst, the radiation being increased and the flame speed decreased. Nitrogen peroxide was an anomalous case, behaving as a feebly positive catalyst in a dried mixture, but as a negative catalyst in an imperfectly dried mixture.

Analysis of the total radiation records showed that, except for small residues, radiation ceases abruptly at times dependent on the nature of the catalyst present. Evidence is adduced pointing to a possible connexion between this residual radiation and the persistence of ions in the gases after explosion.

The duration of steady radiation was correlated with the duration of flame within the bomb. The bulk of the radiant energy has its origin in the wave-front where chemical change is proceeding, and not in the hot products of reaction.

In the dry gases, two waves of ionisation accompany the explosion wave. The first wave corresponds with the explosion wave itself, but the second is associated with processes occurring some distance behind the wave-front. The persistence of the ionisation associated with the second maximum increases as the flame passes along the bomb. It is suggested that the secondary emission of radiation in explosions of carbon monoxide and oxygen discovered by Ellis and Wheeler is caused by the recombination of ions produced behind the wave-front. These phenomena disappear

in the presence of hydrogen. Substances containing hydrogen increase the rate of attainment of thermal equilibrium both in, and behind, the explosion wave.
R. A. PRATT.

Catalysis of hydrolytic reactions by acids and bases. H. VON EULER and A. OLANDER (Z. Elektrochem., 1927, **33**, 527—532).—A detailed reply to Skrabal's criticisms (A., 1927, 942) of the theoretical principles put forward by Euler (cf. A., 1921, ii, 498; 1926, 580).
H. J. T. ELLINGHAM.

Complex homogeneous catalysis of hydrogen peroxide by sodium molybdate. E. SPITALSKI and A. FUNK (J. Russ. Phys. Chem. Soc., 1928, **60**, 47—74).—See A., 1927, 426.

Catalytic decomposition of sodium hypochlorite solutions. I. Mechanism. J. R. LEWIS (J. Physical Chem., 1928, **32**, 243—254; cf. Howell, A., 1923, ii, 634; Chirnoaga, A., 1926, 916).—The mechanism of the decomposition of sodium hypochlorite solutions using the oxides of cobalt, copper, and iron as catalysts has been studied by two methods, one at 35° and the other at 30°, the first being that used by Walton (A., 1904, ii, 319). The values obtained by this method for $k=x/t$, where x is the volume of oxygen evolved, remain constant at first and then decrease after 20—30% of the reaction has been completed; those for the usual unimolecular coefficient increase as the reaction proceeds, whilst the greatest constancy is given when k is of the form of the Freundlich equation given by Chirnoaga (*loc. cit.*). The second method, in which a fresh supply of hypochlorite solution is passed over a fixed amount of catalyst, gives constant values for $k=x/t$ over a wide range of concentration (46·5—34·2 g./litre), after which k diminishes with decreasing concentrations of the hypochlorite. The rate of reaction is proportional to the concentration of the catalyst, and the values of k_{15}/k_{35} by the first method and k_{40}/k_{30} by the second are 2·02 and 2·0, respectively. The decomposition of the hypochlorite is considered to be due to the formation of a catalyst–hypochlorite complex with subsequent decomposition, and the rate of decomposition remains constant so long as the catalyst surface is completely covered by the reactant.
L. S. THEOBALD.

Experiments on the theory of heterogeneous reactions. G. ADHIKARI and J. FELMAN (Z. physikal. Chem., 1928, **131**, 347—362).—Iodine reacts but slowly with the surface of pure mercury, although considerable adsorption takes place. The production of mercuric iodide is autocatalytic, combination taking place with appreciable velocity only at the interface between the three phases.
H. F. GILLBE.

Decomposition of carbon monoxide in presence of reduced nickel. S. HORIBA and T. RI (Bull. Chem. Soc. Japan, 1928, **3**, 18—25).—An improved apparatus is described whereby reaction velocities as well as equilibrium quantities can be measured. The rapid pressure measurements necessary were made possible by a special quartz spring manometer, and precautions were taken to avoid contamination by grease from stopcocks. At 230° the reaction became unimolecular after 15 min., whilst the rapid initial fall in pressure is explained by the adsorption of carbon monoxide on the reduced nickel.
S. J. GREGG.

Hydrocarbon synthesis from carbon monoxide and hydrogen. O. C. ELVINS.—See B., 1928, 178.

Catalytic activity of metallised silica gels. IV. Oxidation of methane. L. H. REYERSON and L. E. SWEARINGEN (J. Physical Chem., 1928, **32**, 192—201; cf. Berl and Fischer, A., 1923, i, 641; Tropsch and Roelen, A., 1924, i, 253; this vol., 252).—Oxidation of methane by oxygen in the presence of metallised silica gels, prepared as previously described, has been studied over the temperature range 200—400°. The copper, platinum, and palladium gels, but not the silver gel, act catalytically, promoting complete oxidation of methane to carbon dioxide and water. No partly oxidised products were found. Both the silver and copper catalysts remove oxygen from the gas stream in the initial stages of the reaction without oxidation of the methane, and then the copper or copper oxide acts as a catalyst initiating the reaction at 200°. The platinised gel which is the most active catalyst for this reaction acts at 240°, the palladised gel at 330°, and the efficiency of these two catalysts depends on the oxygen content of the gas mixture. An optimum concentration ratio of methane to oxygen apparently exists.
L. S. THEOBALD.

Behaviour of methyl alcohol over aluminium and zinc oxides. H. ADKINS and P. D. PERKINS (J. Physical Chem., 1928, **32**, 221—224).—The dehydration of methyl alcohol over the temperature range 240—440° has been investigated by the methods and with the catalysts previously described (A., 1925, i, 626). With the alumina catalyst, an almost quantitative conversion of the methyl alcohol into dimethyl ether results up to 350°. This is followed by a slight decomposition of the ether between 350° and 380°, after which decomposition is rapid. With the zinc oxide catalyst, ether formation is negligible and decomposition becomes marked above 325°. The optimum concentration of water vapour for maximum hydration of the dimethyl ether varies, at a constant rate of flow, with the amount of catalyst present.
L. S. THEOBALD.

Corrosion phenomena. XII. Apparent contradiction between the catalytic influence of silver on the dissolution of zinc in acids and its position in the overvoltage series. A. THIEL and J. ECKELL (Z. physikal. Chem., 1928, **132**, 78—82).—The anomaly is ascribed to poisoning of the silver by zinc salts.
H. F. GILLBE.

Activation of the dissolution of marble by neutral salts. N. ISGARISCHEV and F. S. SCHAPIRO (J. Russ. Phys. Chem. Soc., 1928, **60**, 127—137).—See A., 1927, 945.

Acitivty of a nickel catalyst. E. J. LUSH.—See B., 1928, 182.

Electrolytic preparation of magnesium from fused fluorides containing magnesium oxide. G. GRUBE [with J. JAISLE] (Z. Elektrochem., 1927, **33**, 481—487).—The f. p. of mixtures of the fluorides of sodium, barium, and magnesium in various pro-

portions have been determined and the results are expressed on a triangular diagram. The compound NaF,MgF_2 has m. p. about 1030° and the existence of a compound, BaF_2,MgF_2, is also indicated. Three ternary eutectics are recognised: MgF_2–BaF_2,MgF_2–NaF,MgF_2 (850°); BaF_2,MgF_2–BaF_2–NaF,MgF_2 (800°); and BaF_2–NaF–NaF,MgF_2 (750°). Fused mixtures of various compositions containing excess of magnesium oxide were electrolysed using an iron cathode and a graphite anode. The mixture corresponding with the 750° eutectic dissolves most magnesium oxide, but only sodium is obtained on electrolysis. The 800° eutectic mixture gives sodium and magnesium, the current efficiency for the deposition of the latter being 22—25%. Electrolysis of the 850° eutectic mixture yields only magnesium at 900°; the current efficiency is about 50%, the loss being attributed to volatilisation and formation of "anode fog." Absence of sodium deposition in this case is regarded as due to the compound NaF,MgF_2 dissociating into $Mg^{\cdot\cdot}$ and NaF_3'' ions in the presence of free magnesium fluoride. H. J. T. ELLINGHAM.

Preparation of a catalyst by the electrolytic corrosion of nickel. S. IKI (J. Soc. Chem. Ind. Japan, 1928, **31**, 1—9).—An active nickel catalyst is prepared by the electrolytic corrosion of nickel in alkali hydroxide or carbonate solution (0·05—0·1*N*) containing a small amount of alcohol. When only an alkali salt is used the current efficiency of corrosion is very low and the product is oxidised from the nickelous to the nickelic state. By addition of 3—5 c.c. of alcohol to 1 litre of the solution the current efficiency increases remarkably and the product is nickelous hydroxide. Acetaldehyde acts in the same way as alcohol. When the hydroxide is used the nickelous hydroxide produced tends to adhere to the surface of the nickel anode, increasing the resistance; this tendency is small when the carbonate is used. A current density of 0·01—0·05 amp./cm.^{2} at 3—5 volts is used. The current efficiency of corrosion decreases with increase of current density. Alternating current alone has but slight effect on the anode. The nickelous hydroxide produced is easily separated from the alkali. The efficiency of corrosion is 78%. K. KASHIMA.

Electrodeposition of indium with dropping-mercury cathode. S. TAKAGI (J.C.S., 1928, 301—306; cf. A., 1923, ii, 119; 1924, ii, 598; 1925, ii, 673, 678).—The behaviour of acidified indium trichloride solutions when electrolysed with a dropping-mercury cathode was investigated, the results being applied to the determination of indium in the presence of zinc and gallium. The electrodeposition from solutions of indium trichloride in 0·1*M*-hydrochloric acid proceeded reversibly in conformity with the Nernst logarithmic equation. The normal deposition potential of the indium ion in this concentration of acid is −0·500 volt, with reference to the normal calomel electrode. This value depends on the concentration of the hydrochloric acid, being more negative the higher the concentration. The sulphate ion in presence of an insufficient concentration of hydrogen ions appears to remove indium ions, probably in the form of a basic salt. For the detection and determination of indium in metallic gallium and zinc, the metals were dissolved in hydrochloric acid, the free acid concentration being 0·1*M*, when as little as 10^{-5} mol. of indium chloride per litre could be detected and determined. The deposition potential of gallium could not be determined in acid solution. R. A. PRATT.

Electrolytic oxidation of formic acid. E. MULLER [with G. HINDEMITH] (Z. Elektrochem., 1927, **33**, 561—568; cf. A., 1923, i, 743).—Further investigation has been made of the relations between anode potential and current density in the electrolysis of a *M*-formic acid–*M*-sulphuric acid solution, using as anode material (*a*) rhodium, (*b*) platinised platinum, (*c*) platinum coated with finely-divided rhodium, or (*d*) palladium coated with finely-divided palladium. At anodes (*a*) and (*b*) the current–potential curves exhibit two distinct branches, one (*A*) lying at potentials about 1 volt less positive than the other (*B*). The transition from *A* to *B* occurs by a sudden jump. With electrode (*d*) there is evidence of three branches of the current–potential curve, and with (*c*) and (*d*) the *A* branch is broken by pulsations between normal values of the potential and values as much as 0·4 volt less positive. In all cases, however, curves obtained by decreasing the current follow the *B* branch until the current is practically zero. In order to explain these complex relations, a theory is developed based on the supposed reactions of formic acid and formate ions adsorbed in a polar manner on the electrode surface. The transition from the *A* to the *B* branch is regarded as due to superficial oxidation of the anode material. Rise of temperature, or addition of sodium formate instead of sulphuric acid, causes the *A* branches of the curves to extend to higher current densities. In special experiments with 10*M*-formic acid–*M*-sodium formate solution at 0·015 amp./cm.^{2} at anode (*c*), the anode potential fluctuated periodically between −0·11 and +0·33 volt (against the *N*-calomel electrode), whereas with a 2*M*-formic acid–*M*-sodium formate solution at 0·21 amp./cm.^{2} the anode potential of +1·290 volts remained steady when once established. In both cases, however, the products of electrolysis were hydrogen and carbon dioxide in amounts corresponding exactly with the equation $H\cdot CO_2H + 2$ faradays $= H_2 + CO_2$. H. J. T. ELLINGHAM.

Anodic oxidation of free propionic acid. F. MULLER [with H. SCHWAB] (Z. Elektrochem., 1927, **33**, 568—571).—Contrary to statements in the literature, free propionic acid can readily be oxidised electrolytically. Using solutions of the acid in 2*N*-sulphuric acid in a diaphragm cell fitted with smooth platinum electrodes, the current efficiency of oxidation is found to increase with the current density and the concentration of propionic acid, and reaches about 98% in a 10*M*-solution at 0·09 amp./cm.^{2} The main products of oxidation are carbon dioxide and ethyl propionate, but small amounts of ethylene, carbon monoxide, and pyruvic acid are also formed. Two main processes appear to occur. In the more important, complete oxidation to carbon dioxide and water is believed to occur by way of lactic acid and pyruvic acid. In the other, ethyl propionate is

produced either by direct oxidation or through the intermediate formation of ethyl alcohol. It is shown that oxidation of lactic acid or pyruvic acid in $2N$-sulphuric acid occurs at a lower oxidising potential at smooth platinum electrodes than is required for the oxidation of propionic acid, so that the former acids do not accumulate in the solution during the electrolysis of the latter. H. J. T. Ellingham.

Photochemical yields with complex light. V. M. Padoa and N. Vita (Gazzetta, 1928, **58**, 3—6; cf. A., 1926, 1014).—From a further survey of their own experiments and of those of Berthoud and Beraneck (A., 1927, 528) the authors consider their view justified, that the sum of the photochemical effects produced by the component radiations is different from and in general greater than that of the resulting complex light, not only owing to variations in the intensity of the light, but also, and in some cases solely, on account of specific effects due to variations in the frequency of the light. The reactions discussed are the bromination of cinnamic acid, the oxidation of hydriodic acid, and the decomposition of ferric oxalate. O. J. Walker.

Photochemistry of the halogens. Action of bromine on ethyl alcohol. A. Berthoud and J. Beraneck (J. Chim. phys., 1928, **25**, 28—39; cf. Bugarszki, Z. physikal. Chem., 1910, **71**, 705).—The rate of reaction of ethyl alcohol and bromine in the presence of potassium bromide has been studied in the dark and under various intensities of blue and violet light. Bugarszki's results for the influence of the concentrations of alcohol and bromine are confirmed, but the retarding influence of potassium bromide is less than stated by him. Potassium bromide retards also in light. It is considered that the effect of light is to dissociate bromine molecules, and that, probably, an intermediate compound, EtO, is formed. The reaction is too complex to be analysed thoroughly from the data obtained.

L. F. Gilbert.

Photochemistry of the halogens. Action of bromine on α-phenylcinnamonitrile. A. Berthoud and G. Nicolet (J. Chim. phys., 1928, **25**, 40—64; cf. preceding abstract).—This reaction has been studied in the dark and in light; it is reversible. In the dark, however, the inverse reactions are slower than found by Bauer and Moser (A., 1907, i, 307), whose reaction vessels (of brown glass) did not exclude light completely. The photochemical results disagree entirely with those of Plotnikov ("Lehrbuch der Photochemie," 1920, 250). Expressions are derived which describe the rate and equilibrium of the reaction under different conditions.

L. F. Gilbert.

Photochemical union of hydrogen and chlorine. L. Harris (Proc. Nat. Acad. Sci., 1928, **14**, 110—112).—Hydrogen and chlorine were carefully freed from oxygen. Chlorine together with an excess of hydrogen was exposed to blue light and the quantum efficiency of the union measured. A minimum yield of 6×10^5 molecules of hydrogen chloride per quantum was obtained. W. E. Downey.

Photochemical decomposition of hydrogen iodide; mode of optical dissociation. B. Lewis (J. Physical Chem., 1928, **32**, 270—284; cf. A., 1927, 428; this vol., 31).—Details are given of the results previously announced on the photochemical dissociation of hydrogen iodide at pressures low enough for the collision frequency to be comparable with the mean life of the excited state. Under these conditions the quantum efficiency is still about two, which is the same as that found by Warburg for higher pressures. Hence, hydrogen iodide is considered to dissociate in an elementary act as a result of the absorption of radiation without the necessity of a collision (cf. Stern and Volmer, A., 1920, ii, 461). Further, the continuous spectrum shows dissociation to take place into a normal hydrogen atom and an excited atom of iodine in the metastable $2P_1$ state, any excess energy being dissipated as kinetic energy. The time which elapses between absorption and dissociation is less than 2×10^{-10} sec. The decomposition of hydrogen iodide is discussed on the basis of results already published. L. S. Theobald.

Measurements of velocity, reaction per quantum, and effect of intensity of radiation in reactions between chromic acid and organic acids. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1928, **169**, 381—393).—The orders of the reactions between chromic acid and the following acids in sunlight and in the dark, respectively, are: citric acid, 2, 2·5; tartaric acid, 2, 3; lactic acid, 3, 3. Manganous sulphate accelerates most of the reactions, and, except with the reaction with tartaric acid in light, reduces the order. With decrease in the order of the reaction, the temperature coefficient of the velocity coefficient usually rises. The temperature coefficient for the reaction in the light is always greater than unity, and less than that of the corresponding reaction in the dark. In all the reactions, numerous molecules react for each quantum of light absorbed, the number increasing with increase in concentration and also with rise in temperature. It is therefore concluded that Einstein's law of photochemical equivalence is not valid for exothermic photochemical reactions. The rate of reaction in either presence or absence of manganous sulphate is directly proportional to the intensity of the incident radiation, except in the reactions with citric acid and tartaric acid in absence of manganous sulphate, the rates of which are proportional to the square root of the intensity of radiation. R. Cuthill.

Luminescence of mercurous chloride of standard purity. J. Krepelka (Nature, 1928, **121**, 457).—Pure, dry mercurous chloride exhibits a greenish-white luminescence when stirred with a glass rod; the effect lasts for about 5 sec., and cannot be again produced unless the rod is first cleaned. Luminescence is also produced if the soiled rod is lightly rubbed with a dry cloth.

A. A. Eldridge.

Tentative hypothesis of the latent image. II. A. P. H. Trivelli.—See B., 1928, 212.

Action of sulphuric acid on copper. J. G. F. Druce (Chem. News, 1928, **136**, 81—83).—The main reaction which occurs when copper is heated at 130—170° with twice its weight of concentrated sulphuric

acid is represented by the equation $6Cu + 6H_2SO_4 = 4CuSO_4 + Cu_2S + SO_2 + 6H_2O$. With excess of acid at 270°, the reaction is $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$. R. CUTHILL.

Reduction of magnesium pyrophosphate by carbon. K. D. JACOB and D. S. REYNOLDS (J. Assoc. Off. Agric. Chem., 1928, **11**, 128—132).—Mixtures of equal weights of pure finely-powdered magnesium pyrophosphate and carbon were heated in a current of nitrogen at the desired temperatures for definite periods. The residues, after burning off the carbon below 800°, were analysed for magnesium oxide and phosphorus pentoxide, and the percentage of phosphorus lost by volatilisation was calculated from the change of the ratio $P_2O_5 : MgO$ of the residues, as compared with that found for the pyrophosphate used. The loss of phosphorus was negligible below 975°. Heating for 1 hr. at 1000° resulted in a loss of 2·5%, at 1050° of 12·5%, and at 1100° of 32% of the total phosphorus originally present.

F. R. ENNOS.

Composition of bleaching powder. C. T. KINGZETT (J.C.S., 1928, 528).—Calcium hypochlorite prepared from bleaching powder and rapidly dried between sheets of filter-paper has the composition $Ca(ClO)_2,4H_2O$, being mechanically associated with some water. This formula does not represent its constitution as a hydrate of calcium hypochlorite (cf. O'Connor, B., 1928, 88). R. A. PRATT.

Bleaching powder. VII. Decomposition of calcium hypochlorite by heat in presence of calcium chloride. S. URANO (J. Soc. Chem. Ind. Japan, 1928, **31**, 46—52).—The decomposition of calcium hypochlorite in presence of large amount of calcium chloride, occurs chiefly according to the equation: $Ca(OCl)_2 + CaCl_2 = 2CaO + 2Cl_2$ (i) and partly according to the equations $Ca(OCl)_2 = CaCl_2 + O_2$ (ii) and $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$ (iii). The evolution of chlorine is caused by the mutual reaction between hypochlorite and chloride, but not by expulsion of chlorine monoxide; reaction (i) is reversible. The phenomena attending the decomposition of bleaching powder result from these three reactions. K. KASHIMA.

Production of carbon by the decomposition of carbon monoxide. VON WANGENHEIM.—See B., 1928, 146.

Production of pure carbon at low temperatures. F. FISCHER and P. DILTHEY.—See B., 1928, 146.

Graphitic acid and the varieties of carbon obtained by its decomposition. U. HOFMANN (Ber., 1928, **61**, [B], 435—441).—Graphitic acids, prepared by treatment of very finely-divided Ceylon graphite with a mixture of nitric and sulphuric acids and potassium chlorate (cf. Kohlschütter, A., 1919, ii, 151), is crystalline and yields a characteristic, well-defined Röntgen spectrum somewhat similar to that of graphite. When heated cautiously to about 200° it decomposes explosively with formation of voluminous "carbon I," which is incipiently crystalline but differs from graphite in the extreme smallness of its crystallites and the distinctly closer proximity of the interference lines (002) and (111). When strongly compressed it becomes denser and more suitable for Röntgen investigation without changing the position of the lines (cf. Lowry and Morgan, A., 1925, ii, 1053; Ruff and others, A., 1927, 1138). When graphitic acid is heated at 200° under pressure, the "carbon II" thus produced is more distinctly crystalline and its Röntgen spectrum closely approximates to that of lustre carbon prepared at 900° except that the interference lines (002) and (111) are closer. When the graphitic acid is decomposed under sulphuric acid at 150°, a more highly crystalline "carbon III" is obtained in which the arrangement is similar to that in retort graphite. All the types of carbon derived from graphitic acid differ from lustre carbon and retort graphite in the remarkable sharpness of their interferences. H. WREN.

Gaseous silicon monoxide. K. F. BONHOEFFER (Z. physikal. Chem., 1928, **131**, 363—365).—Ultraviolet absorption spectra indicate the formation of considerable quantities of gaseous silicon monoxide during the reduction of the dioxide by carbon at 1500°. H. F. GILLBE.

Compounds of hydrated silica and ammonia. W. BILTZ (Z. Elektrochem., 1927, **33**, 491—497).—Preparations of hydrated silica prepared by methods described by Schwarz (A., 1924, ii, 753; 1925, ii, 222) were treated with liquid ammonia in a special extraction apparatus, until no more water could be extracted. The composition and vapour pressure of the products were examined at various temperatures. From metasilicic acid the product had the composition $6SiO_2,2H_2O,4NH_3$ at −78·5°, but with rise of temperature it loses ammonia in stages of one molecule, and finally yields the compound $6SiO_2,2H_2O,NH_3$ which is stable at the ordinary temperature. This result supports the view that the minimum molecular formula for metasilicic acid is $6SiO_2,6H_2O$. Partly dehydrated metasilicic acid preparations gave on treatment with ammonia the same compounds as the original substance yielded. Treatment of disilicic acid with ammonia yielded the additive product $2SiO_2,H_2O,NH_3$. Since this loses ammonia in a continuous and not a step-wise manner when examined in the tensimeter, there is no evidence that the molecular formula of disilicic acid is more complex than $2SiO_2,H_2O$. From similar experiments with the so-called "granitic acid," $3SiO_2,2H_2O$, and with a preparation having the composition of "trisilicic acid," $3SiO_2,H_2O$, it is concluded that these are not definite compounds but mixtures of meta- and di-silicic acids and of disilicic acid and silica, respectively (cf. Schwarz, A., 1926, 1112). *X*-Ray examination supports these conclusions. A few experiments on the extraction of silica gels with ammonia did not lead to the isolation of any definite compounds. Hence only two definite silicic acids appear to exist. To prepare these substances the corresponding sodium salts must be used as the starting material, since subsequent conversion of one acid into the other has not been observed to occur. The wider application of the ammonia extraction process to the study of the constitution of hydrates is referred to. H. J. T. ELLINGHAM.

Preparation and properties of some germanous salts. J. BARDET and A. TCHAKIRIAN (Compt. rend., 1928, **186**, 637—638).—Brown germanous oxide is produced with small quantities of germanous hydride, by the reduction of germanic salts with zinc and 25% sulphuric acid. It is stable when dry and almost insoluble in hydrochloric or sulphuric acid, and may be used for the detection of 0·1 mg. of germanium by means of titration with a solution of potassium permanganate. By reduction with hypophosphorous and hydrochloric acids at 100° for 2 hrs., followed by neutralisation in the cold with ammonia, the orange-yellow hydroxide is produced. It is very soluble in alkalis and in hydrochloric or hydrobromic acid, but not in hydrofluoric acid, whilst sulphuric acid dehydrates it and forms the soluble brown oxide. Hydriodic acid and oxidising agents convert it into a red, insoluble iodide, and into the dioxide, respectively. The hydrochloric acid solution yields the chloride ($GeCl_2$), which is hydrolysed by water to a white oxychloride, and is a strong reducing agent. The bromide behaves similarly, but the fluoride is stable towards water. Hydrogen sulphide precipitates the orange-red sulphide (GeS) from solutions of the above salts. J. GRANT.

Oxidation of hydrazine. VIII. Mono-de-electronators and di-de-electronators. R. E. KIRK and A. W. BROWNE (J. Amer. Chem. Soc., 1928, **50**, 337—347; cf. A., 1916, ii, 245).—Oxidation is regarded as a process of de-electronation, and the similarity in behaviour of various oxidising agents towards hydrazine is explained on the ground that mono-de-electronators—*i.e.*, oxidising agents which accept one electron only per active unit—yield ammonia as the only by-product, whereas di-de-electronators yield both ammonia and azoimide. Many examples are considered in detail from this point of view. S. K. TWEEDY.

Sodium pyrophosphates. J. R. PARTINGTON and H. E. WALLSOM (Chem. News, 1928, **136**, 97—100).—Repetition of the work of Salzer (A., 1895, ii, 14) and Giran (A., 1902, ii, 549) confirms the existence of the salts $Na_3HP_2O_7$, $Na_3HP_2O_7,H_2O$, $Na_3HP_2O_7,4H_2O$, and $NaH_3P_2O_7$ and establishes the existence of the *salt* $Na_3HP_2O_7,5H_2O$. The salt formed on heating trisodium pyrophosphate has the composition $Na_6P_4O_{13}$ and is possibly a polymerised metaphosphate. For analysis, pyrophosphates are boiled with a large excess of dilute hydrochloric acid for 2 hrs., and for a further 10 min. with magnesia mixture. J. S. CARTER.

Sodium thiopyrophosphates. H. E. WALLSOM (Chem. News, 1928, **136**, 113—115).—*Sodium thiopyrophosphates*, $Na_2H_2P_2S_7$, $Na_3HP_2S_7$, $Na_4P_2S_7$, $Na_6P_4S_{13}$, and Na_2HPS_4, have been prepared by the action of sodium sulphide or hydrosulphide on phosphorus pentasulphide. They are easily decomposed by water with the production of hydrogen sulphide and generally also of sulphur. C. W. GIBBY.

Vanado-vanadates. G. CANNERI (Gazzetta, 1928, **58**, 6—25).—A study was made of the compounds containing quinquevalent and quadrivalent vanadium obtained by fusing in the required proportions vanadic anhydride with salts of the alkali metals, and especially of the evolution of oxygen which accompanies the cooling of such molten systems (cf. Prandtl, A., 1905, ii, 170). This evolution occurs appreciably only when salts of the alkali metals or of thallium are used, and is independent of the anion with which the metal is combined. The systems V_2O_5–Na_2O, V_2O_5–K_2O, V_2O_5–Li_2O, and V_2O_5–Tl_2O have been investigated thermally and diagrams of state constructed. These show that vanadic anhydride forms with the oxides of the alkali metals and of thallium three definite compounds corresponding with the meta-, pyro-, and ortho-vanadates. The evolution of oxygen is accompanied by the formation of compounds of vanadic anhydride with its reduction product V_2O_4 of the type xV_2O_5,yV_2O_4,zM_2O, where M=Na or K (vanado-vanadates). By fusing vanadic anhydride with the alkali carbonates, the *compounds* having the following values of x, y, and z, respectively, have been obtained for sodium and potassium: 5, 1, 1; 4, 1, 1; 4, 1, 2; 1, 1, 1, and in addition for sodium the compound 5, 1, 3. O. J. WALKER.

Antimonic acid. A. LOTTERMOSER (Z. Elektrochem., 1927, **33**, 514—518).—So-called "soluble antimonic acid" was prepared by gradual addition of antimony pentachloride to water at 0°, and solutions of the filtered and washed product were made. During dissolution to a clear liquid, the electrical conductivity increases; afterwards, it decreases rapidly and then more slowly, approaching a limiting value, whilst the solution gradually becomes opalescent. Rise of temperature raises the limiting value somewhat and greatly increases the rate at which it is approached, but varying the initial concentration of the solution has practically no effect on the limiting value, unless the concentration is below about 0·1%. It is concluded that the more concentrated solutions become saturated with a mixture of complex hydrated acids, whereas more dilute solutions remain unsaturated with respect to this mixture. Determinations of the p_H value of the solutions by means of indicators gave similar results, and ultramicroscopical examination showed that, whereas in the more concentrated solution ageing led to a notable increase in the number of colloidal particles, no such increase was observed in the more dilute solutions. Conductometric titrations of concentrated fresh solutions with lithium, sodium, or potassium hydroxides (MOH) gave breaks in the titration curves when the ratio M : Sb was 1 : 3 and 1 : 2. With the corresponding aged solutions, however, the breaks occurred at different points with different alkalis and these points did not in general correspond with simple ratios of M : Sb. With very dilute solutions the titration curves are unchanged by ageing and exhibit only one break, the position of which is independent of the nature of the alkali used, but does not represent a simple ratio of M : Sb. Conductometric titrations of potassium pyroantimonate solutions with hydrochloric acid are also recorded. H. J. T. ELLINGHAM.

Change in composition of compressed air after long storage in a steel cylinder. A. F. SEREQUE (J. Amer. Chem. Soc., 1928, **50**, 419).—The percent-

ages of oxygen and of carbon dioxide in compressed air decreased by 0·6 and 0·01, respectively, after 17 years' storage in a steel cylinder. S. K. TWEEDY.

Higher polythionic acids. I. Hexathionic acid. E. WEITZ and F. ACHTERBERG (Ber., 1928, **61**, [*B*], 399—408).—*Potassium hexathionate* is prepared by the addition of a solution of potassium nitrite (1 mol.) and potassium thiosulphate (about 3 mols.) to well-cooled hydrochloric acid. The mixture is vigorously shaken until the colour passes through brown and green to yellow, after which the nitrous fumes are removed in a current of air, leaving a solution having an odour of sulphur dioxide; it is preserved in a freezing mixture until it becomes almost colourless. Precipitated potassium chloride is removed and the filtrate concentrated under diminished pressure, whereby potassium hexathionate, mixed with potassium chloride, separates. The chloride is removed by water and the residue washed with alcohol and ether. The mother-liquors from the hexathionate contain considerable quantities of potassium tetrathionate. The production of the latter compound is readily explained either by the intermediate formation of nitrosylthiosulphuric acid or as a simple oxidation of the thiosulphate, but the mode of formation of the hexathionate is obscure. The smallest proportion of nitrite required to prevent precipitation of sulphur when the solution is acidified depends on the presence or absence of air and on the concentration of nitrite and thiosulphate in the solution. Potassium hexathionate is stable when dry, but readily decomposes in aqueous solution with formation of sulphur or a higher polythionate. Addition of acid stabilises the solutions. It crystallises with difficulty from aqueous or feebly acidic solutions, most readily from such as contain considerable amounts of mineral acid; from these solutions it can be salted out. Like the pentathionates, it deposits sulphur when treated with alkali, gives yellow and yellowish-white precipitates with mercurous nitrate and mercuric chloride, no reaction with copper sulphate, and a brown coloration passing into a black precipitate with ammoniacal silver solution. It is more rapidly decomposed than pentathionates by dilute ammonia, tetrathionate being the first isolable product; sodium carbonate solution behaves similarly. Alkali sulphite rapidly converts hexathionate into trithionate. Potassium hexathionate gives crystalline *precipitates* with hexammine-cobaltic and -chromic chlorides and nitrates and with *trans*-dichlorodiethylenediaminecobaltic chloride; this behaviour is also shown by the lower polythionates towards the last-mentioned reagent. The anhydrous *benzidine* salts of hexa-, penta-, tetra-, and tri-thionic acids are described. Preliminary examination of Wackenroder's solution discloses the absence of hexathionic acid and presence of acids containing a larger proportion of sulphur. H. WREN.

Reactions in liquid hydrogen sulphide. III. Thiohydrolysis of chlorides. A. W. RALSTON and J. A. WILKINSON (J. Amer. Chem. Soc., 1928, **50**, 258—264; cf. Quam and Wilkinson, A., 1925, ii, 542).—Metallic chlorides are mostly insoluble in liquid hydrogen sulphide, except those of zinc, bivalent mercury, aluminium, and tervalent iron, the last-named forming a white precipitate of ferrous chloride. Mercuric chloride is thiohydrolysed to the black sulphide which later turns red; the iodide crystallises out in the yellow form, which becomes red. Insoluble mercurous chloride reacts to give mercurous hydrogen sulphide as a brown, gelatinous mass; cuprous chloride and silver chloride are also thiohydrolysed. Boron trichloride yields white *crystals* of $BCl_3,12H_2S$. Chlorides of non-metallic elements which are readily hydrolysed by water are either soluble in liquid hydrogen sulphide in all proportions without change (*e.g.*, carbon tetrachloride; silicon tetrachloride, which, however, produces a little silicon disulphide when kept for several weeks at the ordinary temperature; and tin tetrachloride, which slowly produces stannic sulphide at the ordinary temperature) or else form thiohydrates, additive products, or sulphides (*e.g.*, titanium tetrachloride, which forms the *compound* $2TiCl_4,H_2S$; cf. Biltz and Keunecke, A., 1925, ii, 986), possibly together with a thiohydrate; phosphorus trichloride, which produces trisulphide at the ordinary temperature; phosphorus and antimony pentachlorides, which form the respective thiochlorides, $PSCl_3$ $SbSCl_3$; bismuth trichloride, which yields an orange-red *solid*, $BiSCl,BiCl_3$). The conductivities of some saturated solutions of metal chlorides in liquid hydrogen sulphide are recorded; the specific conductivity of the pure solvent is 1×10^{-11} ohm^{-1} at about $-80°$. S. K. TWEEDY.

Molybdates of lanthanum and sodium. G. CAROBBI (Gazzetta, 1928, **58**, 53—56; cf. Carobbi and Tancredi, following abstract).—At 25° the following two *compounds* are formed:

$$La_2(MoO_4)_3,Na_2MoO_4,2H_2O \text{ and } La_2(MoO_4)_3,2Na_2MoO_4,3H_2O.$$

O. J. WALKER.

Tungstates of cerium and sodium. G. CAROBBI and G. TANCREDI (Gazzetta, 1928, **58**, 45—52; cf. A., 1926, 810).—The system $Ce_2(WO_4)_3$–Na_2WO_4–H_2O has been studied at 25°. The three *compounds* $Ce_2(WO_4)_3,Na_2WO_4,11H_2O$; $Ce_2(WO_4)_3,3Na_2WO_4,16H_2O$, and $Ce_2(WO_4)_3,5Na_2WO_4,23H_2O$ are shown to exist. They are crystalline and stable in air. The dehydration of these salts by means of calcium chloride or sulphuric acid is not effected at a constant velocity; this fact points to the possible existence of other hydrates. O. J. WALKER.

Tungsten carbides and their applications. F. SKAUPY (Z. Elektrochem., 1927, **33**, 487—491).—The products obtained by heating tungsten powder with lamp-black in hydrogen or in a vacuum at 1400° or 2000° by means of a carbon-tube furnace or a tungsten-wire furnace have been examined by chemical analysis and by *X*-ray methods. The carbides W_2C and WC are recognised. These compounds are also produced by heating a tungsten wire electrically in an indifferent gas (hydrogen or a mixture of hydrogen and nitrogen) containing a small proportion of methane. Wires carburised in this way have their carbon content removed again if the methane concentration falls below a certain critical value dependent on the temperature and the composition of the indifferent

gas. The graph of the critical concentration of methane in hydrogen against temperature exhibits three branches, of which two correspond with WC and W_2C, respectively, whilst the third, which lies above 2400°, may correspond with the carbide W_3C found by Ruff. The development of the alloy "Widiametall" (tungsten, cobalt, carbon) now produced by Fried. Krupp A.-G. is referred to.

H. J. T. ELLINGHAM.

Oxidations with fluorine. F. FICHTER (Z. Elektrochem., 1927, **33**, 513—514).—Mainly a review of published work. W. Bladergroen has shown that fluorine reacts with phosphoric acid or phosphate solutions giving perphosphates. E. Brunner finds that in the oxidation of chromic, thallous, or manganous salts with fluorine, the reaction proceeds smoothly only when the sulphates are used; this is regarded as due to the intermediate formation of sulphur tetroxide. It is concluded that all oxidations with fluorine are almost completely paralleled by electrolytic oxidations at platinum anodes.

H. J. T. ELLINGHAM.

Black nickel oxide. G. LUNDE (Z. anorg. Chem., 1928, **169**, 405—406).—A reply to Le Blanc and Sachse (this vol., 142). R. CUTHILL.

Oxidation states of ruthenium in its halide compounds. W. R. CROWELL and D. M. YOST (J. Amer. Chem. Soc., 1928, **50**, 374—381).—Ruthenium compounds in hydrochloric acid solution are reduced by potassium iodide to the tervalent state, in agreement with the conclusions of Ruff and Vidic (A., 1925, ii, 480). Ruthenium hydroxide prepared by the method of Krauss and Kükenthal (A., 1924, ii, 196) contains both tervalent and quadrivalent ruthenium. If the hydrochloric acid solution of the hydroxide is chlorinated, all the ruthenium is converted into the quadrivalent state, and electrometric titration of the solution with titanous sulphate, both before and after chlorination, shows an end-point when all the ruthenium is reduced to the tervalent and not the bivalent state (cf. Zintl and Zaimis, A., 1927, 533). The dark blue compounds formed when the titanous sulphate is in slight excess are compounds of bivalent ruthenium. If ruthenium chloride is digested with bromine and hydrobromic acid, and evaporated with potassium bromide, a black *salt* containing quadrivalent ruthenium is obtained, probably K_2RuBr_5OH. S. K. TWEEDY.

Iridium fluorides. O. RUFF and J. FISCHER (Z. Elektrochem., 1927, **33**, 560—561).—For the preparation of iridium hexafluoride and pentafluoride by the passage of pure gaseous fluorine over heated finely-powdered iridium, the metal was contained in a boat of calcined fluorspar supported in a tube of the same material and heated electrically. Vessels of fluorspar calcined at 1280° are resistant to fluorine at high temperatures and are readily worked mechanically by means of an emery wheel. For analysis of the hexafluoride, reaction with sodium carbonate in a platinum crucible was carried out at the temperature of liquid air. Subsequent heating to redness yielded insoluble iridium oxide, which was reduced to the metal and weighed. The atomic ratio of iridium to fluorine obtained in this way was 1:6·08. Some properties of iridium hexafluoride and pentafluoride are described.

H. J. T. ELLINGHAM.

Magnitude of observation errors in chemical analysis. B. D. HARTONG (Chem. Weekblad, 1928, **25**, 105—106; cf. Goudriaan, this vol., 262).—A criticism of the calculations in the earlier paper. The employment of approximated atomic weights does not necessarily lead to errors as serious as appears; the error introduced by using 107·9 for the atomic weight of silver, for example, is only 0·02 and not 0·1. The method of calculating the cumulative effect of errors is also criticised.

S. I. LEVY.

Drop reactions. F. FEIGL (Mikrochem., 1928, **6**, 50—62).—A claim for priority. Many of the drop reactions recently described by Tananaev and his co-workers (A., 1925, ii, 324; 1927, 223, 1159) had been described by Feigl and his co-workers several years previously. A. R. POWELL.

Determination of dissolved gases in water. H. RICHTER.—See B., 1928, 214.

Measurement of gases dissolved in water. L. DUNOYER (J. Phys. Radium, 1928, [vi], **9**, 1—12).—A more detailed account of work already published (A., 1927, 845).

Determination of hydrogen-ion concentration in very small volumes of liquid. S. GIRGOLOV and J. SCHUKOV (Z. ges. exp. Med., 1927, **56**, 710—713; Chem. Zentr., 1927, ii, 1869).—An iridium electrode, made by depositing an iridium mirror on a fine glass capillary, is employed in place of a platinised platinum wire. A. A. ELDRIDGE.

Applicability of the quinhydrone electrode in electrometric titration. A. RABINOVITSCH and V. KARGIN (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 3—33; Chem. Zentr., 1927, ii, 1054).—Strong acids can be titrated with the quinhydrone electrode in all concentrations; with dilute weak acids the quinhydrone electrode shows at >6 smaller p_H values than does the hydrogen electrode. The inflexion point of the titration curve is reached with greater quantities of alkali than when the hydrogen electrode is employed. Presumably the hydrogen-ion concentration of the solution is increased by dissociation of the quinol, atmospheric oxidation of the quinol in alkaline solution tending to reduce it. The deviation is maximal at p_H 10, and is smaller in the presence of buffers.

A. A. ELDRIDGE.

[Theory of end-point in electrometric titration.] Correction. E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 418).—An algebraical error in the previous paper (A., 1925, ii, 594) is corrected. The result obtained by Roller (this vol., 262) concerning the limiting strength of acid necessary for an inflexion point to appear during titration with a strong base is confirmed. S. K. TWEEDY.

Simple continuous-reading method of electrometric titration with bimetallic electrodes. N. H. FURMAN and E. B. WILSON, jun. (J. Amer. Chem. Soc., 1928, **50**, 277—283).—Platinum and tungsten wires are dipped into (*e.g.*) the reducing

solution, and connected in series through a variable high resistance and a galvanometer. The oxidising agent is added a drop at a time; the graph of the galvanometer readings (ordinate) against volume of reagent added is exactly analogous to the graphs obtained potentiometrically, there being a sudden permanent change in *P.D.* at the end-point. This "galvanometer method" is as accurate as the potentiometric method. S. K. TWEEDY.

Simple bimetallic electrode systems for potentiometric titrations. I. Application of platinum-gold amalgam system to certain oxidation-reduction titrations. II. Notes on the use of the platinum-gold electrode system. N. H. FURMAN (J. Amer. Chem. Soc., 1928, **50**, 268—273, 273—277).—I. Amalgamated gold electrodes behave like calomel electrodes in solutions containing chloride and like mercurous sulphate electrodes in solutions containing sulphate. The construction of small amalgamated gold electrodes is described; they are suitable for use as reference electrodes in oxidation-reduction titrations (ferrous iron with potassium permanganate and dichromate, and with vanadic acid) in solutions as dilute as $0{\cdot}05N$; they also serve as indicator electrodes for certain precipitation reactions, and for following the neutralisation of hydrochloric and sulphuric acids.

II. A sharp change in *E.M.F.* occurs at the end-point of some oxidation-reduction reactions (*e.g.*, potassium permanganate and ferrous sulphate) in 0·1 or $0{\cdot}05N$-solutions. The chief disadvantage of the amalgamated gold electrode system is the variable nature of the readings for the same type of titration. S. K. TWEEDY.

Determination of combined water in natural sulphates. O. ŠEBELÍK (Chem. Obzor, 1927, **2**, 46—49; Chem. Zentr., 1927, ii, 962).—Minerals containing alunite, a colloidal mixture of silica and alumina, quartz crystals, and water lose water at 350° upwards, complete elimination being effected only at white heat. Sources of error are discussed; the methods of Kurizianov and of Dittrich give good results. A. A. ELDRIDGE.

Bromometric determination of chlorates. K. PETERS and E. DEUTSCHLANDER (Apoth.-Ztg., 1926, **41**, 594—595; Chem. Zentr., 1927, ii, 1055).—The chlorate (0·05 g. ClO_3) is dissolved in $0{\cdot}1N$-arsenious oxide solution (25 c.c.) and dilute hydrochloric acid (10 c.c.) and gently boiled for 10 min. after addition of potassium bromide (0·05—0·1 g.); the solution is then diluted to about 100 c.c. and titrated hot (using methyl-orange) with $0{\cdot}1N$-potassium bromate solution until colourless. A. A. ELDRIDGE.

Direct oxidimetric determination of perchlorate in presence of large amounts of chlorate and chloride. E. SPITALSKI and S. JOFA (Z. anorg. Chem., 1928, **169**, 309—318, and J. Russ. Phys. Chem. Soc., 1928, **60**, 75—84).—By treatment of a solution containing perchlorate and a large amount of chlorate with sulphur dioxide, the chlorate is completely reduced to chloride, and after removing the excess of sulphur dioxide by passing a current of air or carbon dioxide through the solution near its b. p., the perchlorate may be determined by boiling with an excess of titanous chloride and titrating back with permanganate (Rothmund, A., 1909, ii, 434). Provided that the solution is not too concentrated, this titration is not affected by the presence of chlorides, and the addition of manganous sulphate is actually disadvantageous. Small amounts of chromate do not interfere with the determination. R. CUTHILL.

Electro-analytical methods. III. Potentiometric titration. J. GILLIS (Natuurwetens. Tijds., 1927, **9**, 129—148; cf. *ibid.*, **8**, 37, 115).—The changes of value in the silver-ion concentration and the potential of a silver electrode immersed in the solution are calculated for the titration of chlorides, iodides, and cyanides, by means of silver nitrate, and shown to agree with the values determined by measurement during actual titrations. S. I. LEVY.

Analysis of bromine. KUBIERSCHKY.—See B., 1928, 190.

Determination of iodide in mixtures of halides. H. BAINES.—See B., 1928, 190.

Determination of hydrogen sulphide in sea-water. G. DRUCKER (Internat. Rev. Hydrobiol. Hydrogr., 1926, **16**, 130—133; Chem. Zentr., 1927, ii, 1189).—The sea-water is run directly into 15 c.c. of $0{\cdot}01N$-iodine solution acidified with 1—2 c.c. of concentrated hydrochloric acid. A. A. ELDRIDGE.

Determination of sulphate in chromic acid. W. H. D. (Chemist-Analyst, 1927, **16**, No. 2, 8).—The sample (10 g. in 200 c.c. of water) is treated with hydrochloric (10 c.c.) and acetic acids (15 c.c.) before precipitation with barium chloride (10% solution, 5 c.c.), and the barium sulphate washed at least 5 times with 1% hydrochloric acid. CHEMICAL ABSTRACTS.

Iodometric determination of selenium. R. BERG and M. TEITELBAUM (Chem.-Ztg., 1928, **52**, 142).—The reduction of selenious acid by hydriodic acid to give the equivalent amount of iodine may be carried out quantitatively when the reaction takes place in the presence of carbon disulphide. The iodine is then completely dissolved by the organic solvent and is not partly adsorbed on the precipitated selenium as in the method of Muthmann and Schafer (A., 1893, ii, 318). It is determined in the usual way by titration with sodium thiosulphate solution. L. M. CLARK.

Detection of selenium in decolorised bottle glasses. E. J. C. BOWMAKER and J. D. CAUWOOD. —See B., 1928, 192.

[Micro-]determination of nitrogen. R. EHRENBERG (Z. ges. exp. Med., 1927, **56**, 466—469).—The Kjeldahl-ammonia is distilled in a silica vessel into a 10 c.c. flask containing 5 c.c. of $0{\cdot}001N$-lead nitrate solution; the mixture, diluted to 10 c.c., is centrifuged, and 1 c.c. of the solution is treated with 0·5 c.c. of a radioactive (thorium-*B*) $0{\cdot}001N$-lead nitrate solution and 0·5 c.c. of $0{\cdot}001N$-potassium chromate solution. After removal of lead chromate by the centrifuge, 1 c.c. of the solution is evaporated, and its activity after 9 hrs. is determined with the electrometer. The activity of the solution is inversely proportional to the ammonia content. A. A. ELDRIDGE.

Determination of small quantities of phosphorus by Deniges' method. V. V. Ciurea (Bul. Soc. Chim. Romania, 1927, **9**, 86—89).—Small quantities of phosphorus may be accurately determined by a volumetric method involving the oxidation of the blue compound obtained in the usual Deniges colorimetric method with chlorine water, the quantity of the latter required for decolorisation being directly proportional to the phosphorus present. The phosphorus solution (5 c.c.) is shaken with 4 drops of the sulphomolybdic reagent, 4 drops of a freshly-prepared stannous chloride solution are added, and the solution is left for 10 min. for the colour to reach a maximum. The solution is then diluted with 10—15 c.c. of water and chlorine water added from a microburette until the colour is just destroyed. The operations are repeated on a solution of known phosphorus content and the volume of chlorine water used in each case is directly proportional to the phosphorus present. In no case did the error exceed 4·1%, a value much smaller than the errors in the colorimetric or nephelometric methods. J. W. Baker.

Influence of sulphates on the volumetric method for the determination of phosphorus. C. M. Bible (J. Assoc. Off. Agric. Chem., 1928, **11**, 126—128).—The A.O.A.C. volumetric method for the determination of phosphorus is unsatisfactory in presence of sulphates, which may be derived either from the original material or from the extraction solvent. Accurate results may be obtained without removal of the sulphate by careful control of the temperature when precipitating the ammonium phosphomolybdate. F. R. Ennos.

Iodometric determination of phosphorous acid and the use of sodium hydrogen carbonate in iodometry. P. Carré (Compt. rend., 1928, **186**, 436—438).—The production of iodate is shown to be the cause of errors obtained in the determination of phosphorous acid by oxidation with 0·1*N*-iodine solution in the presence of sodium hydrogen carbonate (5—15 mols. per mol. of acid), the excess of iodine being titrated after 1·5 hrs. with sodium thiosulphate. If, however, the solution is acidified with hydrochloric acid before the final titration, the iodate is reduced and the iodine regenerated; otherwise the thiosulphate is oxidised to sulphate. A large excess of hydrogen carbonate should be avoided in such cases, and loss of iodine in the carbon dioxide spray is prevented by the use of a closed vessel. Phosphorous acid may be determined in the presence of phosphorous esters, $P(OH)_2 \cdot OR$, by this method. J. Grant.

Comparison of two methods used in determination of phosphorus pentoxide as magnesium ammonium phosphate. W. M. McNabb (J. Amer. Chem. Soc., 1928, **50**, 300—304).—The ammonium acetate method (Schmitz, A., 1925, ii, 67) is compared with the method in which this substance is not used (Treadwell and Hall, "Analytical Chemistry," 1924, 2, p. 380). In each case a final washing of the precipitate with a saturated ammoniacal solution of ammonium nitrate previously to ignition is recommended in order completely to oxidise any organic material which may be present. The two methods give average errors of +0·02%, −0·02%, respectively (ignition over a Meker burner); in presence of molybdate ions the average error ranges from 0·1 to 0·3%, although if the ignition is carried out in an electric muffle at 1000° the error is −0·05%. In the absence of molybdate ions the acetate method more easily produces a crystalline precipitate. S. K. Tweedy.

Reinsch's test. H. Leffmann and M. Trumper (Bull. Wagner Free Inst. Sci., 1927, **2**, 89—92).—The closed tube containing the copper strip should be heated for a short time only with a spirit-lamp. Chemical Abstracts.

Gutzeit method for the determination of arsenic. H. Heidenhain (J. Assoc. Off. Agric. Chem., 1928, **11**, 107—112).—In the A.O.A.C. method as modified by the U.S. Bureau of Chemistry, the length of the arsenic stain is shown to be affected by changes of temperature both of the generating and of the absorption apparatus. Lower temperatures of the former produce shorter and more intense stains than higher temperatures, the opposite effect being observed on varying the temperature of the latter. By immersing the whole apparatus in a water-bath at constant temperature, *e.g.*, 30°, the stains obtained with definite quantities of arsenic are uniform both in length and intensity, thus rendering the use of permanent standards possible. A modified Gutzeit method including in addition several minor changes in the preparation of the solution is suggested. F. R. Ennos.

Separation of arsenic from antimony. L. W. McCay (J. Amer. Chem. Soc., 1928, **50**, 368—373).—If excess of silver nitrate solution is added to a hydrofluoric acid solution of arsenic and antimonic acids which has been made slightly alkaline with ammonia, the arsenic is quantitatively precipitated as silver arsenate, free from antimony. The arsenic is determined by dissolving the precipitate in nitric acid and determining the silver by Volhard's method. If the filtrate from the silver arsenate is treated with the minimum amount of hydrochloric acid for precipitation of silver, mixed with concentrated sulphuric acid, evaporated to fuming point, and then boiled with a piece of sulphur, the antimony may be determined by titrating the resulting solution with potassium permanganate or bromate (cf. Petriccioli and Reuter, A., 1902, ii, 177; Gyory, A., 1893, ii, 554). S. K. Tweedy.

Volumetric determination of antimony in presence of lead, tin, and copper. A. Vassiljev and W. Kargin (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 143—156; Chem. Zentr., 1927, ii, 1055—1056).—The reaction (Gyory): $KBrO_3 + 3SbCl_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O$, using as indicator methyl-orange, which is decolorised by excess of bromate, is employed. When the liquid contains lead sulphate, low (1—3%) values are obtained; the solution is therefore siphoned off, the lead sulphate dissolved in concentrated hydrochloric acid, and the diluted solution titrated with bromate. The presence of tin does not affect the results. Low (0·3—1·7%) values are obtained in presence of copper. In presence of lead and copper 96—97% of the antimony is found; treatment of the precipitate (as

above) indicates a further 2% of antimony. With the pure metals, but not with technical alloys, tartaric acid is not oxidised by the bromate.

A. A. ELDRIDGE.

Determination of sodium borate. M. FRANÇOIS and (MLLE.) L. SEGUIN.—See B., 1928, 156.

Volumetric determination of sodium. A. NAU (Bull. Soc. Pharm. Bordeaux, 1927, **65**, 67—76; Chem. Zentr., 1927, ii, 467).—Blanchetière's method is modified in that the uranyl compound is reduced with zinc and sulphuric acid, and then titrated with permanganate.

A. A. ELDRIDGE.

Determination of small quantities of sodium. WEILAND (Mitt. Kali-Forsch.-Anst., 1927, 21—28; Chem. Zentr., 1927, ii, 1871).—Manipulative details are given for the method preferred, viz., the precipitation of sodium ions by a concentrated uranyl magnesium acetate solution, with the production of the compound $3(UO_2)(C_2H_3O_2)_2,Mg(C_2H_3O_2)_2,NaC_2H_3O_2,9H_2O$, which is practically insoluble in alcohol.

A. A. ELDRIDGE.

Uranyl acetate as a reagent in microscopic qualitative analysis. E. M. CHAMOT and H. A. BEDIENT (Mikrochem., 1928, **6**, 13—21).—In applying the uranyl acetate test for sodium the best procedure consists in evaporating the solution to be tested on a microscope slide until a dry film is formed, placing a drop of the reagent close to the edge of the film, and drawing a platinum wire through the drop, thence across the film. The formation of isotropic tetrahedra indicates the presence of sodium; fine clusters of hair-like crystals the presence of the alkaline earths or of lead; tetragonal prisms potassium, rubidium, cæsium, silver, thallium, or ammonium; square plates barium, and orthorhombic plates or prisms manganese, magnesium, zinc, cadmium, iron (ferrous), nickel, cobalt, or copper. The presence of sodium together with a member of the last-named group results in the separation of monoclinic triple acetates in the form of polysynthetic twins of somewhat indefinite chemical composition. In the absence of metals other than alkalis the formation of sodium zinc uranyl acetate is probably the most sensitive test for the presence of sodium; so sensitive is this reaction that silica object slides should be used to avoid possible contamination from sodium of the ordinary glass slide.

A. R. POWELL.

Potash charge removal from platinum crucibles [in alkali determinations]. T. C. GREEN (Chemist-Analyst, 1927, **16**, No. 2, 16).—In the Lawrence Smith method of determining alkali in silicates the crucible is charged through a cork-borer, the space between this and the walls of the crucible being filled with calcium carbonate.

CHEMICAL ABSTRACTS.

Capillary analysis. R. DUBRISAY (Mon. Prod. chim., 1927, **9**, No. 90, 4—7; Chem. Zentr., 1927, ii, 1180).—The volume of 40 drops of $1/600N$-sodium hydroxide solution (free from carbonate), dropped from a constricted tube into "vaseline" oil containing 1% of oleic acid, was 1·20 c.c., whilst if to the solution an equal volume of 1/800 or $1/80N$-sodium chloride solution was added, the volume of 40 drops was 0·98 or 0·20 c.c. The method should be applicable to the determination of alkali halide in $0{\cdot}0002M$-solution.

A. A. ELDRIDGE.

Influence of impurities arising from glass vessels on the titre of alkali hydroxides. K. SEILER (Schweiz. Apoth.-Ztg., 1927, **65**, 229—233; Chem. Zentr., 1927, ii, 852).—A study of "fixanal" sodium hydroxide ampoules; silica, boric acid, and calcium were detected, but not antimony, arsenic, or iron.

A. A. ELDRIDGE.

Alkaline-earth metals in "saccharate" solutions and their use in alkalimetry. A. C. SHEAD (J. Amer. Chem. Soc., 1928, **50**, 415—416).—Metallic calcium of known purity may be weighed out directly in air and dissolved in sucrose solution in order to prepare a carbonate-free standard alkali solution with a single weighing. Warm calcium does not tarnish readily, and in any case the film formed is too thin to affect the accuracy of the method. The chief impurity is magnesium, which, together with its oxide, is almost insoluble in 30% sucrose solution.

S. K. TWEEDY.

Qualitative separation of calcium, barium, and strontium. O. MACCHIA (Notiz. chim.-ind., 1927, **2**, 311—312; Chem. Zentr., 1927, ii, 853).—The mixed carbonates are dissolved in a little dilute hydrochloric acid, and the solution is evaporated to 5—8 c.c. One portion is neutralised with ammonia, and 4—5 vols. of saturated potassium ferrocyanide solution are added; the precipitate of the compound $K_2Ca[Fe(CN)_6],3H_2O$ is collected, the barium in the diluted filtrate being precipitated as chromate, and (after filtration) the strontium as carbonate. The other portion is slightly warmed and stirred with malonic acid (0·5 g.) and a slight excess of concentrated aqueous ammonia solution; the filtrate after removal of precipitated barium malonate is warmed with 4—5 vols. of methyl alcohol to precipitate strontium and some calcium, calcium being precipitated from the filtrate as carbimide.

A. A. ELDRIDGE.

Rapid determination of calcium and magnesium. C. J. SCHOLLENBERGER (Chemist-Analyst, 1927, **16**, No. 2, 6—7).—Calcium and magnesium are precipitated together as oxalate and ammonium arsenate, respectively; the precipitate is dissolved in dilute sulphuric acid, the oxalate determined volumetrically with permanganate, and the arsenate determined iodometrically.

CHEMICAL ABSTRACTS.

Detection and determination of small quantities of beryllium by means of 1:2:5:8-tetrahydroxyanthraquinone. H. FISCHER (Z. anal. Chem., 1928, **73**, 54—64; cf. A., 1927, 36).—Further details of the method previously described are given and the method is extended to the rapid determination of beryllium in alloys and minerals. Copper and nickel alloys (0·1 g.) are dissolved in hydrochloric acid and "perhydrol," the solution is evaporated to dryness on the water-bath, and the residue dissolved in a little warm water. The solution is treated with sufficient potassium cyanide to convert the copper and nickel into soluble double cyanides, then with sodium hydroxide until the alkalinity is at least $0{\cdot}25N$. An

aliquot part of the clear solution is used for the volumetric determination with a 0·05% solution of quinalizarin in 0·25*N*-sodium hydroxide. For the determination of beryllium in beryl, 0·2 g. of mineral is fused with sodium carbonate and the silica removed by evaporation with hydrochloric acid and filtration. The filtrate is treated with sodium hydroxide to 0·25*N* and the determination finished as usual. The use of tartaric acid to retain aluminium and other metals in solution in the alkali leads to high results, as under these conditions aluminium reacts similarly to beryllium. A. R. POWELL.

Detection of traces, and colorimetric determination, of beryllium. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1928, **50**, 393—395).—One drop of a 0·01% solution of curcumin in alcohol, 0·5 c.c. of 4*N*-ammonium chloride, and 6 drops of 4*N*-ammonia solution are added to the solution. A red or an orange-red flocculent precipitate is obtained, the sensitivity of this reaction extending to 0·05 mg. of beryllium per litre. By comparison with a standard which has been kept for the same length of time after precipitation a good quantitative determination may be made. Magnesium decreases the sensitivity somewhat; aluminium and ferric iron must be first precipitated by addition of sodium fluoride. It is suggested that curcumin may be useful for detecting amounts of magnesium between 1 and 10 mg. per litre in strongly alkaline solution. The indicator 1 : 2 : 5 : 8-tetrahydroxyanthraquinone was unsuitable for the colorimetric determination of beryllium. S. K. TWEEDY.

Pyrophosphate method for the determination of magnesium and [of] phosphoric anhydride. (MISS) A. W. EPPERSON (J. Amer. Chem. Soc., 1928, **50**, 321—333).—A critical examination of the published directions for carrying out the above analyses leads to the formulation of standard procedures, which are detailed in the original. A second precipitation under specified conditions is essential. In the first case, when excess of potassium chloride is present a third precipitation is necessary. S. K. TWEEDY.

[Detection of zinc and calcium.] R. W. HUFFERD (Proc. Indiana Acad. Sci., 1926, **36**, 183—184).—(*a*) Zinc is precipitated as sulphide with sulphur after addition of potassium dichromate, and the hot hydrochloric acid extract of the precipitate is tested with potassium ferrocyanide or hydrogen sulphide.

(*b*) After removal of barium as chromate, the filtrate is evaporated to 15 c.c., and diluted with 45 c.c. of hot water; to half, one drop of saturated calcium sulphate solution is added. Ammonium oxalate solution (5 drops) is added to each, and a precipitate smaller in quantity than that produced in the control is ignored. CHEMICAL ABSTRACTS.

Determination of the free acidity of solutions of heavy metal salts. E. MULLER and F. MULLER (Z. anal. Chem., 1928, **73**, 47—51).—Potentiometric titration with sodium hydroxide of the free acidity of solutions containing the sulphates of zinc, copper, manganese, cadmium, or nickel yields accurate results using a hydrogen or quinhydrone indicator electrode, the end-point being marked by a very pronounced change of potential. If a hydrogen electrode is used a further sharp change of potential occurs when the metal is entirely precipitated as hydroxide, but the results obtained are accurate only to 1—2% owing to adsorption. The use of methyl-orange as indicator for the determination of the acidity of solutions containing the above-named sulphates gives results which agree with those obtained potentiometrically. A. R. POWELL.

Sensitive microchemical reactions of cadmium salts. A. MARTINI (Mikrochem., 1928, **6**, 1—4).—Solutions of cadmium salts yield characteristic white, microcrystalline precipitates with sodium bromide and brucine acetate and with sodium bromide and a concentrated acetic acid solution of quinine sulphate. These reactions serve for the microchemical detection of cadmium, a distinct precipitate being obtained with 1 drop of a solution containing 0·3 mg./c.c. A. R. POWELL.

Precipitation of copper with sodium thiosulphate. M. G. ROEDER (Tidskr. Kemi Berg., 1927, **7**, 94—95; Chem. Zentr., 1927, ii, 1740).—Precipitation of copper with sodium thiosulphate is complete in the presence of nitric, hydrochloric, or sulphuric acid. The cuprous sulphide is washed with cold sulphurous acid solution. A. A. ELDRIDGE.

Gravimetric separation of copper and mercury. G. SPACU (Bul. Soc. Stiinte Cluj, 1927, **3**, 171—174; Chem. Zentr., 1927, ii, 2087).—The neutral or slightly acid solution containing copper and mercury is heated to boiling, excess of pyridine is added with production of an intense blue colour, and then, with vigorous shaking, solid ammonium thiocyanate. After 1 hr. the precipitate is collected, washed with a cold solution containing ammonium thiocyanate (0·5%) and pyridine (5 c.c. per litre), dried at 140—150°, heated slowly, and finally ignited to cupric oxide. After acidification of the filtrate with hydrochloric acid, the mercury is precipitated as sulphide. Solutions containing much nitric acid are first evaporated to dryness, the residue is dissolved in hot water, and the solution mixed with much pyridine. If too little pyridine is employed, the copper is precipitated, and must be redissolved by addition of a few drops of nitric acid. A. A. ELDRIDGE.

Micro-determination of mercury in organic compounds and the determination of carbon and hydrogen in such compounds. A. VERDINO (Mikrochem., 1928, **6**, 5—12).—The destruction of the organic matter by heating with concentrated sulphuric and nitric acids leads to a small loss of mercury, but good results are obtained by heating for 2 hrs. at 250—270° with fuming nitric acid in a sealed tube. The mercury may be recovered from the solution by electrolysis with 2·5—3·2 volts, using a gold-plated platinum gauze cathode. A. R. POWELL.

Potentiometric determination of cerium. K. SOMEYA (Sci. Rep. Tohoku, 1928, **17**, 93—97).—See this vol., 146.

Quantitative microscopic analysis of commercial felspar. H. INSLEY.—See B., 1928, 193.

Action of hexamethylenetetramine on solutions of salts of metals of the third group, and

quantitative separation of iron from manganese, zinc, nickel, and cobalt. P. RAY and A. K. CHATTOPADHYA (Z. anorg. Chem., 1928, **169**, 99—112).—Iron, aluminium, chromium, and titanium are precipitated as hydroxides from boiling solutions of their salts containing ammonium salts by hexamethylenetetramine. Under the same conditions, manganese, zinc, cobalt, and nickel are not precipitated, because the hydrogen-ion concentration resulting from the hydrolysis of their salts is not great enough to furnish by hydrolysis of the precipitant a hydroxyl-ion concentration sufficient for precipitation. In order to separate iron from manganese, cobalt, nickel, or zinc, ammonium chloride is added to the solution, which is then almost neutralised with ammonium carbonate, and the iron is precipitated at the b. p. with a 10% solution of the reagent. It is not possible to separate chromium from zinc, cobalt, and nickel in this way. Kollo's method of separating iron and manganese with hexamethylenetetramine (A., 1921, ii, 218) does not seem to give satisfactory results, and his explanation of the mechanism of the process is apparently incorrect. R. CUTHILL.

Determination of cobalt as Co_3O_4. R. CERNATESCO and (MME.) VASCAUTANU (Ann. Sci. Univ. Jassy, 1928, **15**, 69—70).—The hydroxide is precipitated from boiling solution by potassium hypobromite, filtered, dried, and ignited with the filter-paper in a Rose crucible in a current of oxygen. The temperature is raised as soon as the carbon is burnt, and the conversion into Co_3O_4 is complete. Any remaining alkali can be washed out, and the ignition repeated. C. W. GIBBY.

Microchemical reactions [with hexamethylenetetramine sulphate and with piperazine]. A. MARTINI (Mikrochem., 1928, **6**, 28—33).—Addition of hexamethylenetetramine sulphate and ammonium thiocyanate solutions to a solution of cobalt chloride yields glistening, blue, triclinic prisms of a complex, non-ionised compound. Under similar conditions copper chloride yields light yellow, triclinic tables, zinc chloride a mass of thin, white needles, ferrous chloride light red crystals, vanadyl chloride light red hexagons, indium chloride reddish-white, tetragonal prisms, and ammonium molybdate red, hexagonal crystals or yellow prisms. A mixture of antimonious chloride and sodium iodide yields with an acetone solution of piperazine microscopic, monoclinic, yellow tablets and prisms. Under similar conditions bismuth chloride gives intense red crystals isomorphous with the antimony compound. Auric chloride, sodium bromide, and piperazine produce orange-yellow to red microscopic prisms. A. R. POWELL.

Analysis of chrome iron ore. E. DITTLER.—See B., 1928, 195.

Metal complexes with pyrocatechol and their use in microchemical analysis. A. MARTINI (Mikrochem., 1928, **6**, 63—66).—Addition of 1 drop of a saturated solution of pyrocatechol acetate followed by 1 drop of aniline or of a saturated solution of piperazine to solutions of sodium molybdate, tungstate, or vanadate produces characteristic precipitates of the type $[OM(OH)(O{\cdot}C_6H_4O)_2],AcOB$, where M is quinquevalent molybdenum, tungsten, or vanadium, and B is aniline or piperazine. The respective colours of the precipitates are red, yellow, and black; those containing aniline crystallise in triclinic prisms and plates, whilst those with piperazine separate out in tufted clusters of needles. A. R. POWELL.

Separation of tungsten from silicon and tin. J. CIOCHINA (Z. anal. Chem., 1927, **72**, 429—434).—Tungstic acid may be separated from a freshly-precipitated mixture of tungstic and metastannic acids or from a mixture of tungstic acid and silica dehydrated at 130° by treating the mass with a warm, concentrated solution of sodium tungstate, in which it dissolves with the formation of metatungstate. Prolonged digestion of the mixture may cause dissolution of part of the silica to form silicotungstate, but a good separation is obtained by treating the mixed acids on the filter-paper with a warm 20—30% solution of sodium tungstate and washing the residual silica or metastannic acid with hot water, hydrochloric acid, and hot water successively. For the determination of silica in ferrotungsten the finely-divided metal is heated for 3—4 hrs. with bromine at 50°, the solution evaporated to dryness, the residue heated at 130°, cooled, and extracted with 10% hydrochloric acid, and the insoluble tungstic acid–silica mixture is collected, washed, and treated as described above. For the alkalimetric determination of tungstic acid it is recommended to wash the precipitated acid with a saturated solution of sodium chloride until the wash water ceases to react acid, transfer the filter and precipitate to a beaker containing an excess of $0{\cdot}1N$-sodium hydroxide, and titrate the excess of alkali with $0{\cdot}1N$-sulphuric acid using phenolphthalein as indicator. A. R. POWELL.

Precipitation of earth-acids by sodium compounds and quantitative separation of tungsten from tantalum and niobium. W. R. SCHOELLER and K. JAHN (Z. anorg. Chem., 1928, **169**, 321—335).—See A., 1927, 32, 1047.

Titration of tin with "chloramine." E. RUPP (Z. anal. Chem., 1928, **73**, 51—53).—Chloramine (the sodium salt of *p*-toluenesulphonylchloroamide) may be used instead of iodine in the titration of stannous chloride provided that the acidity of the solution does not exceed 3—5%; a small crystal of potassium iodide is added to the tin solution together with the usual starch indicator. Solutions containing stannic salts are reduced by means of zinc filings and the spongy tin is dissolved in warm concentrated hydrochloric acid, the excess of which is neutralised by the addition of a solution of sodium hydroxide and carbonate just prior to titration. A. R. POWELL.

Use of liquid amalgams in volumetric analysis. X. Determination of vanadium, chromium, and nitro-compounds. K. SOMEYA (Z. anorg. Chem., 1928, **169**, 293—300; cf. A., 1927, 746).—Ammonium vanadate may be determined by reducing in concentrated hydrochloric acid solution with lead amalgam, then titrating after removal of the amalgam with a $0{\cdot}1M$-solution of cupric sulphate, the acid concentration being maintained at 10—12N. Safranine or neutral-violet is used as indicator, 10 c.c. of a 0·1% solution being added to the vanadate when it

has been reduced to the vanadous state, and reduced to the leuco-compound by further treatment with amalgam. The completion of the re-oxidation in the subsequent titration is then indicated by the reappearance of the original colour of the indicator. If zinc amalgam is substituted for lead amalgam, iodine may be used instead of copper sulphate for the titration, and the method is then a convenient one for the determination of vanadium in ferrovanadium, as ferric salts do not interfere. Chromic salts may be determined by reduction to the chromous state with zinc amalgam (cf. *ibid.*, 333) followed by titration with iodine, iodate, or bromate, the indicator for the first two of these being starch, and for the third starch and potassium iodide. A solution of chromous chloride prepared in this way may also be employed to reduce *p*-nitroaniline or *p*-nitrophenol, which is then titrated with ferric alum, with ammonium thiocyanate as indicator. The results obtained in the determination of picric acid by this method are, however, about 1% too low. R. CUTHILL.

Determination of bismuth as oxyiodide. R. STREBINGER and W. ZINS (Z. anal. Chem., 1927, 72, 417—429; cf. this vol., 39).—The microchemical method previously described has been modified for the determination of larger quantities of bismuth as follows: The solution of the nitrate is evaporated to dryness on the water-bath, the residue dissolved in 1 c.c. of 1 : 1 nitric acid and 10—15 c.c. of water, and the solution treated with crystals of potassium iodide until the liquid above the black precipitate is pale golden in colour; a further 50 c.c. of water are added and the solution is heated on the water-bath until the black precipitate changes to copper-coloured scales of the oxyiodide. Hot water is added until the liquid becomes almost colourless, followed by a solution of sodium acetate (25 g./litre) until the colour entirely disappears. The precipitate is collected in a glass filtering crucible, washed with hot water, dried at 105°, and weighed as BiOI. Small amounts of lead do not interfere, but in the presence of much lead a preliminary separation of the bismuth must be made; the boiling slightly acid solution of the metals is treated with a few drops of methyl-orange followed by 2*N*-sodium formate solution until the liquid becomes yellow. The precipitate of basic bismuth formate, containing only traces of lead, is collected on a glass filtering crucible, washed with hot water, and dissolved in nitric acid for the iodide precipitation. A. R. POWELL.

Potentiometric determination of gold. E. MÜLLER and F. WEISBROD (Z. anorg. Chem., 1928, **169**, 394—398).—In determining gold by the method previously described (A., 1926, 1117), the concentration of free hydrochloric acid in the solution should be small, as otherwise the auric ion combines to a large extent to form chloroauric acid, and the change in potential corresponding with the completion of the reaction $Au^{\cdot\cdot\cdot}+3Fe^{\cdot\cdot} \longrightarrow Au+3Fe^{\cdot\cdot\cdot}$ is therefore indistinct. Nitric acid has an even more marked effect, but this may in a large measure be overcome by adding to the solution potassium sulphate before the titration commences, and alcohol when the reduction of the chlorine is complete. Copper, mercury, and lead, even at high concentrations, and solid silver chloride do not affect the determination, but appreciable amounts of palladium or platinum make the titration impossible, although the effect of palladium may be partly overcome by addition of alcohol and potassium sulphate. When gold is titrated with titanous chloride after being oxidised with potassium bromate in hydrochloric acid solution, according to Zintl and Rauch's method (A., 1925, ii, 1005), any excess of bromate may give rise to errors by causing the solution to attack the platinum electrode. R. CUTHILL.

Osmium. II. Determination. E. FRITZMANN (Z. anorg. Chem., 1928, **169**, 356—364; cf. A., 1927, 742).—Sufficient of the material for analysis to give about 0·1 g. of metallic osmium is heated with a mixture of 5 c.c. of concentrated sulphuric acid, 10 c.c. of water, and 5 c.c. of a 10% solution of chromium trioxide, a further 5 c.c. of this solution being added 10 min. after boiling commences, and again after 20 min., and after 30 min. 5 c.c. of water are added. Osmium tetroxide distils over, and is condensed into a solution of sodium hydroxide. Sodium sulphide is then added to the distillate, and the mixture acidified at 90° with hydrochloric acid, ammonium chloride being added to cause the precipitated sulphide to coagulate satisfactorily. The precipitate is ignited in a current of hydrogen, and weighed as the metal. This method cannot be used for the determination of osmium in osmiridium, or in presence of ruthenium. R. CUTHILL.

Mercury spectrum tube. E. RUMPF (Z. physikal. chem. Unterr., 1927, 40, 205—206; Chem. Zentr., 1927, ii, 1869).

Ultra-violet refractometry. L. C. MARTIN (Trans. Opt. Soc., 1927—1928, 29, 1—21).—A critical-angle method is described for determining the refractive indices of small quantities of liquid for ultra-violet light. Two quartz hemispheres, between which is a thin film of the liquid, are rotated in a beam of approximately parallel radiation, and the critical angles for various wave-lengths are measured by means of a quartz spectrograph. A detailed procedure is described and discussed. C. W. GIBBY.

Simple form of photo-electric photometer. J. H. J. POOLE (Nature, 1928, **121**, 281—282).—The phenomenon of the intermittent discharge through a neon lamp is applied to the measurement of small illuminations with a vacuum photo-electric cell. The cell and the neon lamp are connected in series with a high-tension battery, and the lamp is shunted with a condenser; the frequency of the intermittent flashes increases with the illumination. A. A. ELDRIDGE.

Adiabatic microcalorimeter for radiological researches. W. SWIENTOSLAWSKI and (MLLE.) A. DORABIALSKA (Rocz. Chem., 1927, 7, 559—566).—See A., 1927, 1163.

Micro-determination of mol. wt. H. JORG (Mikrochem., 1928, 6, 34—49).—An apparatus is described and illustrated diagrammatically for the micro-determination of the mol. wt. of organic substances by the depression of f.-p. method. It consists essentially of two thermostats containing tubes hold-

ing the liquid used as solvent and provided with copper–constantan thermocouples either of which may be connected through a resistance to a sensitive galvanometer by means of a throw-over switch. One of the vessels serves for standardising the galvanometer, which is adjusted to zero at the f. p. of the solvent, and the other vessel is used for determining the f. p. of the solution. When both solution and solvent are just melting the difference between the galvanometer readings corresponds with the depression of the f. p. Several examples are given of the results obtained and the method of calculation is explained. A. R. POWELL.

Resistance wire for use in the laboratory. J. PICCARD (J. Amer. Chem. Soc., 1928, **50**, 406—408).—"White gold," an alloy of nickel and gold, is a suitable non-corrosive material for the measuring wires of Wheatstone bridges. The alloy is hard and ductile, and has a tensile strength greater than that of steel. The resistance, temperature coefficient of resistance, and thermoelectric force against copper are recorded for two commercial specimens of "white gold," and for platinum and constantan. S. K. TWEEDY.

Pipette for micro-analyses. A. T. SHOHL (J. Amer. Chem. Soc., 1928, **50**, 417).—Van Slyke and Neill's modified Ostwald pipette is fitted with a hypodermic needle (made of platinum if necessary). Drops of the order 0·00015 c.c. can be removed from such a tip. S. K. TWEEDY.

Modified weighing pipette. G. EDGAR (Ind. Eng. Chem., 1928, **20**, 158).—A Lunge weighing pipette contains three bulbs of definite volume with graduation marks between them. It enables triplicate weighings of nearly the same quantity of material to be conveniently made. C. IRWIN.

Apparatus for micro-filtration. A. T. SHOHL (J. Amer. Chem. Soc., 1928, **50**, 417—418).—The liquid is filtered by suction through a thin layer of asbestos packed over a glass bead in a filter funnel. The precipitate can be washed five or ten times with 1 c.c. of solution. S. K. TWEEDY.

Suction flask for quantitative analysis. G. W. KÜHL (Chem.-Ztg., 1928, **52**, 131).—The suction funnel is carried in a stopper which fits into a tubulure on the top of a spherical container. The tubulure carries a side tube connected through a 3-way cock either to the vacuum pump or to the atmosphere. Another tube provided with a stopcock is connected to the lower end of the spherical container.

S. I. LEVY.

Laboratory cooling device using liquid sulphur dioxide. A. F. GILL (Ind. Eng. Chem., 1928, **20**, 212).—The "cold test" of castor oil for use in aircraft engines requires the maintenance of a temperature of −10° for 10 days. This is conveniently obtained by placing the test-tube containing the oil in a small Dewar flask charged with slowly-boiling liquid sulphur dioxide (b. p. −10°). The only attention required was addition of 100 c.c. of sulphur dioxide every second day. C. IRWIN.

Electrical solution-mixing device. K. HICKMAN and D. HYNDMAN (Ind. Eng. Chem., 1928, **20**, 213—216).—The automatic control of the proportions in which two solutions are being mixed is effected by carrying forward in a current of air a gas which is either a participant in the reaction or is added as an indicator, into a conductivity cell. Ammonia may be used either in the neutralisation of sulphuric acid with ammonia, or in the neutralisation of this acid with sodium hydroxide, a trace of ammonia being added in the last case. Other indicators are sulphur dioxide and chlorine. The resistance of the cell used with tap water was 2000 ohms. This is coupled to a 110-volt A.C. supply and the variable current produced actuates a solenoid which is capable of rotating a hollow drum pivoted axially through a few degrees. In the sides of the drum are two outlets for the liquor under regulation, one a feed and the other a by-pass. In effect, a frictionless valve controls the feed actuated by the conductivity of the indicator cell. C. IRWIN.

Extraction apparatus for liquids. J. FRIEDRICHS (Chem Fabr., 1928, 91).—A new apparatus is described in which the usual glass spiral is replaced by a porous filter plate. C. W. GIBBY.

Metallographic etching. M. SCHNEIDER (Z. physikal. chem. Unterr., 1927, **40**, 175—176; Chem. Zentr., 1927, ii, 1001).—A lecture demonstration.

A. A. ELDRIDGE.

Geochemistry.

[Variation of] the layer of ozone in the upper atmosphere during the night. D. CHALONGE (Compt. rend., 1928, **186**, 446—448).—The thickness of the layer of ozone encircling the upper atmosphere of the earth (Dobson and Harrison, A., 1926, 493) was determined for a few days and nights from the spectral intensities of the radiations (up to 3050 Å.) from the sun and moon, respectively. It remained constant during a particular night (about 3 mm.) but was less during the day (about 2·2 mm.). A longer series of measurements is required to confirm this.

J. GRANT.

Nitrate in the sea. II. H. W. HARVEY (J. Marine Biol. Assoc., 1928, [ii], **15**, 183—189).—The nitrates in the sea-water south-west of Plymouth are used up by the phytoplankton during the summer but reappear during the autumn as their synthesis during this period is more rapid than their decomposition. Nitrates from land drainage cannot be detected more than a few miles from the land.

W. O. KERMACK.

Seasonal variations in the phosphate and silicate content of sea-water during 1926 and 1927 in relation to the phytoplankton crop. W. R. G. ATKINS (J. Marine Biol. Assoc., 1928, [ii], **15**, 191—205).—The silicate and phosphate contents of sea-water undergo rapid reduction during the late spring and early summer as a result of the rapid

proliferation of diatoms. The silicates may show a rise in late summer which is not exhibited by the phosphate, and comparing various seasons a high phosphate minimum may accompany a low silicate minimum and *vice versa*. The date of the fall of the phosphates in spring varies from season to season and is correlated chiefly with the amount of sunlight.

W. O. KERMACK.

Photosynthesis of diatom cultures in the sea. S. M. MARSHALL and A. P. ORR (J. Marine Biol. Assoc., 1928, [ii], **15**, 321—360).—With increasing depth photosynthesis by diatoms, as determined by the oxygen production (Winkler's method), reaches a maximum and then decreases. This maximum occurs very near the surface in winter or in the absence of direct sunlight, and occurs at a depth of 20—30 metres in the summer, but under similar conditions is nearer the surface in the more turbid waters nearer the coast than in the open sea. W. O. KERMACK.

p_H of the Black Sea compared with that of the salt lake Tekir-Ghiol. N. L. COSMOVICI (Ann. Sci. Univ. Jassy, 1928, **15**, 131—132).— values have been determined colorimetrically in July in the Black Sea and in the adjacent salt lake Tékir-Ghiol. For the former, values between 8·3 and 8·5 were found in all cases, independent of temperature, wind, and the nature of the sea bed. The presence of algæ increased the p_H. The p_H of the lake Tekir-Ghiol was 8·6 under all observed conditions.

C. W. GIBBY.

Comparison of the absorptive powers of Russian and other clay. A. MONOSSON (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 169—173; Chem. Zentr., 1927, ii, 1009).—The absorptive power of clays for ozokerite in kerosene is increased by heating the material at 350—400°, but not at 105° or 700°. Treatment with acid, and pulverisation, also often increase the absorptive power. A. A. ELDRIDGE.

Kaolin content of clays. H. BOEGE (Chem. Erde, 1927, **3**, 341—369).—Chemical analyses are given of eight clays from German localities. By digesting the material in hydrochloric acid (*d* 1·1) for 2 hrs. from 6·00 to 14·08% $Al_2O_3+Fe_2O_3$ passed into solution, this representing the colloidal portion of the aluminium silicate. After ignition of the material at 700° hydrochloric acid extracted more (up to 36·82%) alumina, the additional amount representing the broken-down kaolin. From these results the amount of kaolin in the clay can be calculated. The amount of kaolin present in each of these clays was also determined by the dehydration method of Calsow (A., 1927, 38). L. J. SPENCER.

Mineralogical constitution of clays. G. LINCK (Chem. Erde, 1927, **3**, 370—374).—Remarks on the paper by Boege (preceding abstract).

L. J. SPENCER.

Kaliophylite. O. MÜGGE (Z. Krist., 1927, **65**, 380—390; Chem. Zentr., 1927, ii, 1140).—Kaliophylite from Mt. Somma contained SiO_2 39·04, Al_2O_3 31·96, Fe_2O_3 0·98, CaO 0·33, MgO 0·15, K_2O 22·84, Na_2O 3·89, H_2O (>105°) 0·60%, but no carbon dioxide, chlorine, or sulphur; ω 1531_6, ε 1527_3, *d* 2·61.

A. A. ELDRIDGE.

Mineral phosphates in the province of Lecce. G. TARULLI and A. MARCUCCI (Annali Chim. Appl., 1928, **18**, 40—46).—The whole of the subsoil of the heel of Italy appears to contain higher or lower proportions of phosphates at varying depths, in some cases capable of economic utilisation. T. H. POPE.

Chemical and provincial relations of the younger eruptive rocks of Germany and northern Bohemia. H. JUNG (Chem. Erde, 1927, **3**, 137—340).—A large number of chemical analyses of Tertiary igneous rocks from Germany and northern Bohemia, collected from the literature, are tabulated and plotted on diagrams. Variation curves are given for each of the constituent oxides. The rocks of the "Oligocene province" are all alkali-rocks of the "Atlantic type," whilst in the "Miocene province" there are also lime-alkali-rocks of the "Pacific type."

L. J. SPENCER.

Mineralogy of Western Australia. I. E. S. SIMPSON (J. Roy. Soc. W. Australia, 1927, **12**, 57—66).—Lithiophilite (from near Wodgina) contained: P_2O_5 45·99, MnO 30·80, FeO 10·44, CaO 2·78, MgO 0·94, Li_2O 7·87, Na_2O 0·34, K_2O —, H_2O (<110°) 1·11, total 100·27%; *d* 3·39, hardness 5. Leucite (from Fitzroy valley) contained: SiO_2 52·45, Al_2O_3 8·64, Fe_2O_3 5·48, FeO 0·94, MnO 0·13, MgO 6·42, CaO 2·01, Na_2O 0·38, K_2O 10·42, H_2O (<110°) 1·99, H_2O (>110°) 2·89, TiO_2 5·85, P_2O_5 1·58, BaO 1·19, total 100·37%; *d* 2·6. Ferrimolybdite (Mulgine) contained: Fe_2O_3 17·87, MoO_3 62·90, H_2O (over calcium chloride) 10·20, H_2O (250°) 9·95, total, 100·92%; *d* 2·99. The formula $(Fe_2O_3,4MoO_3,5H_2O),5H_2O$ is proposed. Kyanite and staurolite are described. CHEMICAL ABSTRACTS.

Crystals of cornetite, and their refractive indices. A. SCHOEP (Natuurwetens. Tijds., 1927, **9**, 125—128).—Very well formed crystals, distributed in a layer of chrysocolla covering a brown sandstone, probably from the Star of the Congo mine at Katanga, are found to have the angles and axial ratios already measured by Cesaro and by Hutchinson and Macgregor (A., 1921, ii, 701); besides the forms *m* (100) and *v* (221), a new form *a* (100) is recorded. Measurement of the refractive indices by the immersion method, using the powdered mineral, gives $\alpha=1{\cdot}765\pm0{\cdot}003$, $\beta=1{\cdot}79-1{\cdot}80$, $\gamma=1{\cdot}83-1{\cdot}84$. S. I. LEVY.

Structure of millerite. H. W. V. WILLEMS (Physica, 1927, **7**, 203—207).—Millerite, NiS, is ditrigonal-bipyramidal, space-group C_{3v}, the co-ordinates being Ni $(u,0,0)$ $(0,u,0)$ $(0,0,u)$, S (x,x,z) (z,x,x) (x,z,x), where $u=0{\cdot}265$, $x=0{\cdot}75$, $z=0{\cdot}41$; hence one sulphur atom is surrounded by three nickel atoms distant 2·24 Å., two nickel atoms at 2·43 Å., and one nickel atom at 3·45 Å. The elementary rhombohedron has α 116° 35′, *r* 5·65 Å., and contains 3 mols., $d_{calc.}$ 5·25. CHEMICAL ABSTRACTS.

Association of water with serpentine. P. G. NUTTING (J. Washington Acad. Sci., 1928, **18**, 81—89).—An attempt is made to distinguish between dissolved, adsorbed, and chemically combined water. The material used for the experiments consisted of clear homogeneous yellowish-green grains of serpentine sieved to 0·15—0·05 mm., and gave on analysis

SiO_2 35·56, Al_2O_3 2·46, Fe_2O_3 4·62, MgO 39·88, FeO 2·02, NiO 0·22, CaO 0·10, H_2O (at 110°) 0·88, H_2O (over 110°) 15·04, corresponding with the ratios $SiO_2 : R^{III}{}_2O_3 : R^{II}O : H_2O = 1·73 : 0·16 : 3·00 : 2·59$ [differing appreciably from the formula $3MgO,2SiO_2,2H_2O$]. The weights of this material at temperatures of 26°, 36°, and 46° are plotted against the humidities of the atmosphere; the curves show greater variations in the more arid and more humid regions. The dehydration (weight–temperature) curve shows no break, but the logarithmic curve shows breaks at 368° (corresponding with $2H_2O$) and at 620° (corresponding with $1·25H_2O$).

L. J. SPENCER.

Bolivianite and Silesite. F. AHLFELD (Zentr. Min. Geol., 1927, **A**, 320—321; Chem. Zentr., 1927, ii, 1807—1808).—Polemical against Pauly (Zentr. Min. Geol., 1926, **A**, 43). A. A. ELDRIDGE.

Blue rock-salt. K. PRZIBRAM (Kali, 1927, **21**, 253—255; Chem. Zentr., 1927, ii, 1807).—Radioactivity develops a blue colour in rock-salt similar to that in the natural substance, especially under pressure (400 kg./cm.^{2}). Under a pressure of 100 kg./cm.^{2} a yellow colour develops. Potassium may be the origin of radioactivity. A. A. ELDRIDGE.

Mud from lake Tekir-Ghiol [Romania]. A. BURADA (Ann. Sci. Univ. Jassy, 1928, **15**, 129—130).—A detailed analysis of wet mud from this salt lake shows 63·36% of solids, of which 4·43% consists of soluble salts (mainly sodium chloride and sulphate).

L. J. SPENCER.

Granite of Cicurova [Romania]. D. M. CADERE (Ann. Sci. Univ. Jassy, 1928, **15**, 81—88).—A petrographical description and a chemical analysis are given of this hornblende-granite, and the analytical results are plotted on diagrams of various kinds. It is an alkali-granite bordering on syenite.

L. J. SPENCER.

Chemical constitution of natural hydrated iron oxide. N. S. KURNAKOV and E. J. RODE (Z. anorg. Chem., 1928, **169**, 57—80).—See this vol., 41.

Meteoric irons from Bolivia, W. Arkansas, and Michigan. G. P. MERRILL (Proc. U.S. Nat. Mus., 1927, **72**, Art. 4, 1—4).—The Bolivian specimen (21·25 kg.) contained Fe 94·212, Ni 5·626, Co 0·320, Cu 0·0004, S 0·014, P 0·261, Pt trace, insol. 0·042, total 100·475%. The Arkansas specimens (1·75 kg.) contained Fe 94·858, Ni 5·121, Co 0·353, Cu 0·013, P 0·020, S 0·009, insol. 0·013, Mn trace, total 100·387%. The Michigan specimen (11·5 kg.) contained Fe 87·77, Ni 11·41, Co 0·26, Cu 0·01, S 0·05, P 0·15, total 99·65%. CHEMICAL ABSTRACTS.

Oxidation of meteoric irons. New examples of magnetic iron oxides from terrestrial sources. E. V. SHANNON (Proc. U.S. Nat. Mus., 1927, **72**, Art. 21, 1—15).—In the oxidation of meteoric iron, magnetite is formed in relatively small quantities as a transitory and unstable stage; the magnetite and the iron are rapidly converted into limonite. The formation of ferromagnetic trevorite, NiO,Fe_2O_3, and of analogous cobalt and copper compounds, seems established. Chlorides promote the formation of amorphous hydrated ferric oxide. Terrestrial ferromagnetic iron oxide is not analogous to the oxidation product of meteorites. CHEMICAL ABSTRACTS.

Connexion between commercial oil deposits and major structural features with special reference to Asiatic fields. L. D. STAMP (J. Inst. Petrol. Tech., 1928, **14**, 28—63).—A critical examination of the occurrence of oilfields shows their frequent association with geosynclinal areas of deposition and occurrence round the margins where the deposits are of a deep-water type, or in the centre in the case of shallow-water deposits. No genetic connexion between oil and belts of folding or between oil and vulcanicity can be traced. H. S. GARLICK.

Telegdite, a fossilised resin. L. ZECHMEISTER and V. VRABÉLY (Z. Min. Geol. Palaont., 1927, **A**, 287—290; Chem. Zentr., 1927, ii, 1461).—The resin, formerly regarded as succinite, and now named *telegdite*, was found at Szaszcsór; it has *d* 1·09, hardness 2½, n_D^{22} 1·5416, and contains C 76·93, H 10·17, S 1·71, O 11·17%; acid value 0, saponification and ester value 180. Decomposition with alkali yields a crystalline acid. A. A. ELDRIDGE.

Proportion of barium in arable soil. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1928, **186**, 477—480; cf. this vol., 336).—Barium in soil (20 g.) is determined after destruction of organic matter by heat, by fusion for 30 min. with 60 g. of an equimolecular mixture of sodium and potassium carbonates. The washed, water-insoluble residue is reheated and extracted with hydrochloric acid, the remaining residue re-fused and again extracted, and the combined acid filtrates (125 c.c.) are precipitated with 10 drops of 10% sulphuric acid. The barium sulphate is stirred frequently, and filtered after 2 days. A number of soils from various parts of France were found to contain 0·082—0·829 g. (in an exceptional case, that of Langlade, Gard, 1·717 g.) of barium per kg. If it is assumed that all the barium is present in the soil as sulphate, these values account for 10—38% (80·5% in the exceptional case) of the total sulphur available for nutritive purposes. J. GRANT.

"Fossil" soils and tropical weathering. P. W. E. VAGELER (Z. Pflanz. Dung., 1928, **10A**, 193—205).—A formal statement of the author's views in which a plea is entered against the too loose use of the term "fossil" soils. Laterite soils can be formed only under certain well-defined climatic conditions. They can become "fossilised" by two processes only; (*a*) by becoming covered with a humus layer, and (*b*) by becoming covered by a hard crust formed by the precipitation of material brought to the surface by capillary action. Fossil loess soils also undoubtedly exist. H. J. G. HINES.

Organic Chemistry.

Röntgen rays and organic chemistry. A. Karssen (Chem. Weekblad, 1928, **25**, 114—127).—An account of the results achieved in the elucidation of structure of organic compounds by *X*-ray analysis.
S. I. Levy.

Theory of the meso-structure of organic compounds. I. I. Kotjukov (Bull. Siberian Inst. Tech., 1927, **48**, 1—35).—The basis of the arguments developed in this theoretical paper is the great, often dominant, importance of hydrogen in structural organic chemistry. The more stable are the carbon–carbon linkings, the less stable is the carbon–hydrogen linking and hence the greater the residual affinity of the carbon, this being termed meso-valency and being identical with Werner's secondary valency. With halogens the reverse is the case, this explaining the formation of linkings between halogens and hydrogen and also the specificity of the linking of halogen with carbon. Linkings formed as a result of the reciprocal saturation of meso-valencies are termed meso-linkings.

Benzene has no central linkings, its carbon linkings representing a peculiar whole, in consequence of which the hydrogen atoms exhibit marked meso-valency. In the benzene hexachlorides the chlorine is united, not with carbon, but with hydrogen. Substitution reactions proceed so that the meso-linkings formed in the initial product of combination remain undisturbed in the final product. Every substituent entering the benzene nucleus combines, not only with the carbon of the nucleus, but also with the neighbouring *ortho*-hydrogen atoms with formation of meso-linkings, unless the entering radical possesses unsaturated atoms. Introduction of a substituent is accompanied by redistribution of the affinity, which in one case causes loosening of the *ortho–para*, and in another that of the *meta*-hydrogen atom; initiation of meso-linkings enhances this phenomenon. Radicals possessing unsaturated atoms connected directly to the nucleus are *ortho–para*-dirigents, whilst *meta*-dirigents are those with unsaturated atoms not combined with the nucleus; the cause of the directing influence lies in the unequal distribution of the affinity. These views furnish explanations for a number of problems, such as the velocity of reaction of substitution, the varying stability of radicals in the nucleus, etc. A meso-formula is suggested for naphthalene.

The phenomenon of steric hindrance is founded, not on the magnitude of the radical, but on the appearance of meso-linkings between the radical and the neighbouring *ortho*-hydrogen atoms and on uneven distribution of the affinity. Physical isomerism is structural isomerism and is encountered only when more than one meso-linking is possible; in the great majority of cases the number of isomerides known corresponds with the possible number. The isomerism of benzophenone, β-dinaphthyl ketone, benzil, and phenylmethylpicramide is discussed from this point of view, meso-formulæ being suggested for these compounds.

The isomerism of ethylene compounds rests, not on the presence of double linkings as such and on their rigidity, but on the presence of hydrogen atoms with meso-valency and of atoms having affinity towards them. Isomerism arises only when the possibility of forming meso-valencies exists. Ethylenic isomerism is never observed when the radicals at the double linkings are aliphatic and saturated, hydrogen atoms with meso-valencies being absent from such radicals. This isomerism is annulled by replacement of the hydrogen atoms with meso-valency by other radicals, even if these contain double linkings and different radicals. The isomerism of fumaric and maleic acids, stilbene, nitrobenzylidenedeoxybenzoin, cinnamic acid, and hydroxylepidine is considered, and meso-formulæ are given. The isomerism of β-butene and allylpropenyl is doubtful.

The isomerism of the oximes is conditioned by the setting-up of meso-linkings between the oxygen of the oximino-group and the hydrogen of the radical situate at the carbon atom. If this radical has an unsaturated atom, the hydrogen and the oximino-groups take part in the isomerisation. The isomerism is completely annulled by replacement of the hydrogen atom with meso-valency or of the hydroxyl of the oximino-group by any inert radical. Here, too, the number of known isomerides is in accord with the meso-theory and not with the requirements of the classical theory. Both isomerides of acetylacrylic acid are regarded as *anti*-compounds. The isomerism of the diazo-compounds is also explainable by the author's theory.
T. H. Pope.

Slow combustion of hydrocarbons. S. Landa (Compt. rend., 1928, **186**, 589—591).—Slow combustion of paraffin, m. p. 51°, at 280—300° yields the following identified products: methyl and ethyl alcohols, acetone, methyl ethyl ketone, acetaldehyde, propaldehyde, hexaldehyde, heptaldehyde, octaldehyde, nonaldehyde, and undecaldehyde. The identification of the alcohols amongst the products of combustion is important in relation to the hydroxylation theory of Bone (J.C.S., 1902, **81**, 535).
G. A. C. Gough.

[Preparation of] Δ^{β}-pentene. J. F. Norris (Org. Syntheses, 1927, **7**, 76—77).

Decomposition of methyl chloride at high temperatures. K. Wiesler (Chem.-Ztg., 1928, **52**, 182—183).—Methyl chloride decomposes at high temperatures, giving an equivalent quantity of hydrogen chloride. Decomposition is appreciable at 500° and nearly complete at 900°. The presence of methane has no effect on the equilibrium, but the decomposition is slightly increased by water vapour and to a much greater extent by carbon dioxide.
C. J. Smithells.

Catalytic oxidations in aqueous solutions. II. Oxidation of primary alcohols. N. A. Milas (J. Amer. Chem. Soc., 1928, **50**, 493—499; cf. A., 1927, 973).—Addition of a solution of sodium chlorate (73 g.) in aqueous 2·5% sulphuric acid (130 c.c.) to methyl alcohol (64 g.), water (50 c.c.), and vanadium pentoxide (0·3 g.), at 75—80°, with stirring, with subsequent heating for 10 hrs., addition of 6*N*-sul-

phuric acid (36 c.c.), and continued heating for 36 hrs. affords methyl formate, formic acid, a trace of chloroform, and an unidentified product. Similar oxidation of ethyl alcohol affords ethyl acetate in 60—61% yield, together with acetaldehyde and acetic acid. Acetal (100 g.) yields similarly ethyl acetate (45 g.), acetic acid (36 g.), and ethyl alcohol, whilst an equimolecular mixture of paracetaldehyde and ethyl alcohol (total 102·3 g.) yields ethyl acetate (54 g.) and acetic acid (21·3 g.). Acetaldehyde alone yields paracetaldehyde, which then remains unattacked. *n*-Propyl alcohol yields similarly propyl propionate (48—51%), together with propionic acid and small proportions of propaldehyde and a chlorinated ester; *n*-butyl alcohol yields *n*-butyl butyrate (47—49%); *iso*butyl alcohol yields *iso*butyl *iso*butyrate (46—48%), together with carbon dioxide, acetone, *iso*butaldehyde, and chlorinated products, whilst *iso*amyl alcohol affords *iso*amyl *iso*valerate (45—48%), *iso*valeraldehyde, chlorinated products, acetone, and carbon dioxide. It is concluded that aldehydes are the primary oxidation products, these then condensing with unchanged alcohols to form semi-acetals, the secondary alcoholic groups of which are then oxidised with formation of esters; any free acid present in the product is derived from the latter by hydrolysis. F. G. WILLSON.

Catalytic dehydration of *iso*propyl alcohol. W. J. ALLARDYCE (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 315—321).—The catalytic dehydration of *iso*propyl alcohol at 360° has been studied in presence of tertiary, secondary, and primary calcium phosphates, tertiary and secondary magnesium phosphates, and aluminium phosphate and sulphate. In all cases the reaction was almost entirely represented by the equation $CHMe_2{\cdot}OH \longrightarrow CHMe{:}CH_2+H_2O$. The catalyst improved with use at first, but ultimately attained constant values which were much closer to one another than the initial values. Treatment of the aluminium sulphate with ammonia gas, or with hydrogen chloride, decreased its efficiency by about 2%. In the former case the reactivity of the catalyst could be restored by treatment with carbon dioxide. Treatment of fresh samples of aluminium sulphate or primary calcium phosphate with carbon dioxide gave initial yields 2—3% higher than those given by the untreated samples, but had no effect on the yields after the constant value was reached. The yield of propylene was varied over a range of 3% by changing the rate at which the alcohol was passed over aluminium sulphate. The catalyst darkens with time and the darkening is not confined to the surface. Its extent varies with the catalyst. M. S. BURR.

Preparation of sodium formaldehydesulphoxylate. N. BACH-NIKOLAJEVA (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 92—100; Chem. Zentr., 1927, ii, 1014).—The reduction according to G.P. 276,984 is complete in 2—3 hrs.; long boiling decomposes the product. A. A. ELDRIDGE.

Electrolytic oxidation of formic acid. E. MULLER.—See this vol., 377.

Decomposition of acid anhydrides. Preparation of anhydrides by direct dehydration of acids. J. CAMPARDOU and M. SEON (Compt. rend., 1928, 186, 591—593).—Acid anhydrides are converted into ketones by passage over heated thoria more easily than the corresponding acids; thus at 300° acetic acid yields acetone, and a mixture of acetic and benzoic anhydrides yields acetophenone. At 400° acetic anhydride yields some mesityl oxide. In the synthesis from acids it is suggested that it is more probable that the ketones arise from the intermediate formation of the acid anhydrides than through the formation and decomposition of a thorium salt. This view is supported by the preparation of acetic anhydride from acetic acid by passage over titanic oxide at 300°. G. A. C. GOUGH.

Action of acetic anhydride on carboxylic acids. A. W. VAN DER HAAR (Rec. trav. chim., 1928, 47, 321—328).—The action of acetic anhydride on simple monocarboxylic acids yields only the simple acid anhydride (which often crystallises with 1 mol. of acetic anhydride of crystallisation) and not a mixed anhydride as stated by Autenrieth (A., 1888, 230) and by Askenasy and Meyer (A., 1895, i, 506). Mol. wt. determinations of the products were made, since the empirical formula of the simple anhydride containing 1 mol. of acetic anhydride of crystallisation is the same as that of the mixed anhydride. Thus when benzoic acid is heated with acetic anhydride for 0·75 hr. and the resulting solution concentrated over potassium hydroxide in a vacuum, the crystalline product has the composition $Bz_2O,C_4H_6O_3$, m. p. 100—105°. The crystals effloresce with loss of acetic anhydride, and by warming with 5% sodium carbonate solution the whole of the acetic anhydride is removed, leaving benzoic anhydride, m. p. 40—42°. By similar treatment *p*-dimethylaminobenzoic acid yields its anhydride with 1 mol. $C_4H_6O_3$, m. p. 109°, to which the structure $(NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot})_2O{:}OAc_2$ is assigned, but by heating above its m. p. acetic anhydride is expelled, and the anhydride has m. p. 218°. Thus with increasing mol. wt. of the acid the acetic anhydride of crystallisation is more firmly held, confirming the composition previously assigned to the compounds obtained similarly from the sugar saponins (this vol., 68). When aldehydo- or keto-acids are heated with acetic anhydride the acid is converted into the enol lactone form and the resulting hydroxyl group is acetylated, $R{<}{}^{CH(OAc)}_{CO}{>}O$ Thus opianic acid yields acetyl-ψ-opianic acid, m. p. 125°, which can be crystallised from water without loss of its acetyl group (cf. Liebermann and Klerman, A., 1887, 47). J. W. BAKER.

Aromatic properties of some aliphatic compounds. Local anæsthetics derived from aliphatic carboxylic acids. H. GILMAN, L. C. HECKERT, and R. MCCRACKEN (J. Amer. Chem. Soc., 1928, 50, 437—439).—The following compounds were prepared by treating diethylaminoethyl alcohol with the appropriate acid chlorides in benzene or ether: *diethylaminoethyl acrylate hydrochloride*, m. p. 93°; *diethylaminoethyl* ββ-*dimethylacrylate hydrochloride*, m. p. 128·5—130°; *diethylaminoethyl trichloroacetate hydrochloride*, m. p. 144—145°, and *diethylaminoethyl acetate hydrochloride*, m. p. 116—117°. Taking the

relative pharmacological activities of cocaine, apothesin (diethylaminopropyl cinnamate), diethylaminoethyl thiophen-2-carboxylate, and diethylaminoethyl furan-2-carboxylate as 10, 8, 1, and <1, respectively, those of the above compounds, in that order, are 1, 1, <1, and 0, from which it is deduced that pharmacological activity ascribed to aromatic groupings can be approached by suitable unsaturated aliphatic structures (cf. Gilman and Pickens, A., 1925, i, 333). β-*Chloroethyl* αβ-*dibromopropionate*, b. p. 153°/20 mm., n^{30} 1·9080, d_4^{20} 1·5241, is described. F. G. WILLSON.

Anodic oxidation of free propionic acid. F. MULLER.—See this vol., 377.

Allyl hexoate and octoate. V. DEULOFEU (J.C.S., 1928, 528).—Allyl iodide reacts with silver hexoate and silver octoate, yielding, respectively, *allyl hexoate*, b. p. 186—188°, and *allyl octoate*, b. p. 225—230°. M. CLARK.

Oxidation of unsaturated acids by chlorates in presence of osmium tetroxide. I. Oleic and elaidic acids. S. MEDVEDEV and E. ALEXÉEVA (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 128—142; Chem. Zentr., 1927, ii, 1012).—The oxidation was effected with aqueous sodium chlorate and osmium tetroxide in presence or absence of sodium carbonate or hydrogen carbonate. Crotonic acid (10 hrs. at 80°) afforded oxalic acid (13% of crotonic acid) and dihydroxybutyric acid. Cinnamic acid (15 hrs. at 80°) gave phenylglyceric acid (50%), benzaldehyde (20%), and a liquid of styrene-like odour. Oleic acid yielded dihydroxystearic acid, m. p. 132°, and elaidic acid ; elaidic acid gave dihydroxystearic acid, m. p. 95°, and oleic acid. It is curious that only one dihydroxystearic acid is produced in each case, although both acids are present; experiments show, however, that one acid does not inhibit the oxidation of the other.
A. A. ELDRIDGE.

Chemical constitution of selacholeic acid. M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1927, **30**, 868—873).—Selacholeic acid, $C_{21}H_{46}O_2$, m. p. 42·5—43°, was first found from *Alizame* liver oil (cf. B., 1926, 712). A mixture of equal parts of hydrogenated selacholeic acid, m. p. 83·5°, and synthetically prepared *n*-tetracosoic acid, m. p. 84°, melts at 83·8°, so the former has the straight carbon-chain structure. The normal ozonide, $C_{21}H_{46}O_5$, gave *n*-nonoic acid and tridecane-αν-dicarboxylic acid, m. p. 113°. Selacholeic acid, $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{13}\cdot CO_2H$, is identical with nervonic acid (cf. Klenk, A., 1927, 691).
K. KASHIMA.

Esters of orthoacetic acid. P. P. T. SAH (J. Amer. Chem. Soc., 1928, **50**, 516—518).—Triethyl orthoacetate, b. p. 144—146°, d_4^{25} 0·8847, n_D^{25} 1·39485, is obtained by keeping acetimidoethyl ether hydrochloride in absolute alcohol for 2 weeks, with occasional shaking, and fractionating the filtrate from the precipitated ammonium chloride under reduced pressure. The following orthoacetates were prepared by condensation of alcohols as above with appropriate acetimidoalkyl ether hydrochlorides: *trimethyl*, b. p. 107—109°, d_4^{25} 0·94375, n_D^{25} 1·38585; *dimethyl ethyl*, b. p. 123—126°, d_4^{25} 0·91915, n_D^{25} 1·38885; *methyl diethyl*, b. p. 135—136°, d_4^{25} 0·90085, n_D^{25} 1·39185; *ethyl di*-n-*propyl*, b. p. 190—194°, d_4^{25} 0·87129, n_D^{25} 1·40635; and *ethyl di*-n-*butyl orthoacetate*, b. p. 220—225°, d_4^{25} 0·86461, n_D^{25} 1·41485. When the alkyl radicals of the imido-ether and the alcohol are not the same, the mixed orthoacetate is always accompanied by the simple orthoacetate derived by replacement of the lower alkyl radical by the higher (cf. Pinner, A., 1883, 1089). F. G. WILLSON.

Configurational relationships of β-hydroxyvaleric and lactic acids, and of methylethyl- and ethyl-*n*-propyl-carbinols. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1928, **76**, 415—422; cf. A., 1927, 643, 1053).—*d*-*n*-Butane-αβ-diol gave *l*-α-bromobutan-β-ol, $[\alpha]^{22}$ −10·2°, which yielded d-α-*cyanobutan*-β-*ol*, b. p. 110—112°/12 mm., $[\alpha]_D^{21}$ +13·1° in alcohol; this gave *l*-β-hydroxyvaleric acid, $[\alpha]_D^{23}$ −15·2° (*sodium* salt, $[\alpha]^{23}$ −9·3°). *d*-Δ^ε-Hexen-γ-ol, $[\alpha]^{22}$ +0·3°, gave, on reduction, d-*hexan*-γ-*ol*, b. p. 132—134°, $[\alpha]_D^{25}$ +1·35°; by means of ozone this was oxidised to *d*-β-hydroxyvaleric acid, $[\alpha]_D^{25}$ +2·3° (*barium* salt, $[\alpha]^{22}$ +1·25°). From these and earlier results it follows that *l*-butan-β-ol and *d*-hexan-γ-ol are configurationally related, which is in disagreement with the conclusions of Pickard and Kenyon (J.C.S., 1914, **105**, 830).
C. R. HARINGTON.

[Preparation of] β-hydroxypropionic acid. R. R. READ (Org. Syntheses, 1927, **7**, 54—56).

[Preparation of] ethyl *n*-butylacetoacetate. C. S. MARVEL and F. D. HAGER (Org. Syntheses, 1927, **7**, 36—38).

[Preparation of] ethyl bromomalonate. C. S. PALMER and P. W. MCWHERTER (Org. Syntheses, 1927, **7**, 34—35).—The interaction of bromine and ethyl malonate is effected in carbon tetrachloride solution. A. A. ELDRIDGE.

Oxidation of maleic and fumaric acids by potassium permanganate. T. SABALITSCHKA and H. TIETZ (Continent. Met. Chem. Eng., 1927, **2**, 232). —Maleic or fumaric acid can be accurately determined by adding excess of permanganate to a hot, acidified solution, decolorising with oxalate, and titrating to the end-point with permanganate. The reaction is: $5C_4H_4O_4+12MnO_4'+36H^{\cdot} \longrightarrow 20CO_2+12Mn^{\cdot\cdot}+28H_2O$ (cf. Lange and Kline, A., 1923, ii, 180). CHEMICAL ABSTRACTS.

Synthesis of αβγ-trimethylglutaric acid. F. E. RAY (J. Amer. Chem. Soc., 1928, **50**, 558—563).—Treatment of ethyl ethylidenedimalonate with methyl iodide and alcoholic sodium ethoxide affords *ethyl* γ-*methyl*-n-*pentane*-ββδδ-*tetracarboxylate*, b. p. 190—195°/2—3 mm., from which the corresponding *acid*, m. p. 190°, is obtained on hydrolysis with boiling aqueous hydrochloric acid. When heated at 190—200°, the latter loses approximately the expected amount of carbon dioxide, but the residue is a mixture. Condensation of ethyl tiglate with ethyl cyanoacetate affords *ethyl* α-*cyano*-βγ-*dimethylglutarate*, b. p. 150—170°/30 mm., from which *ethyl* α-*cyano*-αβγ-*trimethylglutarate*, b. p. 140—150°/1—2 mm., is obtained on methylation. The latter yields α-*carboxy*-αβγ-*trimethylglutaric acid*, m. p. 144—145°

(decomp.), on hydrolysis with boiling concentrated aqueous potassium hydroxide, and this, when heated at 150—160°, affords *αβγ-trimethylglutaric acid*, m. p. 134°. Condensation of ethyl malonate with ethyl tiglate affords analogously *ethyl γ-methyl-n-pentane-βδδ-tricarboxylate*, b. p. 121°/25 mm., from which the trimethylglutaric acid is obtained by hydrolysis and decomposition of the resulting acid. The "αββ-trimethylglutaric acid" obtained by Noyes and Skinner (A., 1918, i, 65) from *iso*aminocamphonanic acid is shown to be identical with Perkin and Thorpe's ααβ-trimethylglutaric acid (J.C.S., 1899, **75**, 65). F. G. WILLSON.

α-*iso*Propylglutaconic acid. K. V. HARIHARAN, K. N. MENON, and J. L. SIMONSEN (J.C.S., 1928, 431—438).—Ethyl sodiodicarboxyglutaconate condenses with *iso*propyl iodide at 140—160°, yielding ethyl trimesate. Ethyl *iso*propylcyanoacetate condenses with ethyl β-iodopropionate in presence of sodium ethoxide, yielding *ethyl α-cyano-α-*iso*propylglutarate*, b. p. 195°/32 mm., which is hydrolysed by 50% sulphuric acid, giving α-*iso*propylglutaric acid. Bromination of α-*iso*propylglutaryl chloride yields, as main product, α-bromo-α-*iso*propylglutaryl chloride (cf. A., 1925, i, 358), since esterification of the bromination product yields an acid ester, converted by treatment with alkali into the lactone of γ-hydroxy-β-methylpentane-γε-dicarboxylic acid. Treatment of ethyl potassioacetonedicarboxylate with *iso*propyl iodide in alcoholic solution gives *ethyl α-*iso*propylacetonedicarboxylate*, b. p. 142—143°/9 mm., converted by prolonged reduction with a large excess of sodium amalgam into *ethyl β-hydroxy-α-*iso*propylglutarate*, b. p. 145—146°/10 mm. The hydroxy-ester reacts with phosphorus pentachloride, giving *ethyl β-chloro-α-*iso*propylglutarate*, which is converted by treatment with diethylaniline at 180—190° into *ethyl α-*iso*propylglutaconate*, b. p. 148—150°/15 mm. Hydrolysis yields the acid, separated by treatment with acetyl chloride into cis-α-*iso*propylglutaconic acid, m. p. 101° (*calcium*, *barium*, and *copper* salts; *potassium* salt of *hydroxy-anhydride*), and trans-α-*iso*propylglutaconic acid, m. p. 132° (*barium* salt). Neither acid is identical with the acid obtained from d-Δ^3-carene by oxidation with potassium permanganate in acetone solution (J.C.S., 1923, **123**, 553). Reduction of the monomethyl ester of caronic acid with sodium and alcohol yields the *lactone* of *δ-hydroxy-ββ-dimethylvaleric acid*, b. p. 137°/43 mm., 232—235°/685 mm., converted by treatment with potassium cyanide at 275°, followed by hydrolysis of the resulting nitrile, into ββ-dimethyladipic acid. M. CLARK.

Salts of mesotartaric acid. I. F. HECKELE (Österr. Chem.-Ztg., 1928, **31**, 28—32).—The following salts of mesotartaric acid are described: disodium salt; additive *compound*, $C_4H_5O_6Na,C_4H_6O_6$ (unaltered by crystallisation from water); dipotassium salt ($2H_2O$); potassium hydrogen salt (this salt forms many soluble additive compounds with metallic hydroxides); sodium potassium salt (H_2O); diammonium salt; ammonium hydrogen salt; potassium ammonium salt (H_2O); dilithium salt; lithium hydrogen salt (H_2O); potassium lithium salt (H_2O); calcium salt ($3H_2O$); barium salt (H_2O); strontium salt; magnesium salt ($2H_2O$); zinc salt ($2H_2O$); lead salt, $PbC_4H_4O_6,2PbO$; cadmium salt ($2H_2O$); normal aluminium salt (from which the aluminium is not precipitated by ammonia); normal manganese salt ($3H_2O$). The copper, nickel, and iron salts could not be obtained in a state of purity. The solubilities of many of the salts are recorded.

G. A. C. GOUGH.

Inhibition of the precipitation of calcium tartrate by salts. M. E. STAS (Pharm. Weekblad, 1928, **65**, 107—108).—The commoner sodium, ammonium, and magnesium salts inhibit the precipitation, especially in warm solutions; 0·1 g. of sodium chloride in 4 c.c. completely prevents precipitation if not more than 10 mg. of tartaric acid is present. For small quantities, therefore, the acid should be extracted by means of ether before applying the test.

S. I. LEVY.

Composition of a series of bismuth sodium tartrates. W. F. VON OETTINGEN and Y. ISHIKAWA (J. Amer. Pharm. Assoc., 1928, **17**, 124—134).—The preparation of bismuth tartrate by the addition of sodium tartrate solution to an acetic acid solution of bismuth nitrate and of soluble sodium bismuth tartrate has been examined. Both preparations pass through different compounds. The following *compounds* were isolated: $C_4H_1O_6Bi{\cdot}OAc$, $C_4H_5O_6Bi$, $C_4H_2O_6NaBi$, $C_4H_2O_8NaBi_2$, $O(C_4H_2O_7NaBi)_2$, $C_4H_2O_7ClNaBi_2$, $C_4H_2O_7Bi_2$, $C_4H_2O_9NaBi_3$, $C_4H_3O_9Bi_3$.

E. H. SHARPLES.

Optically active copper compounds. W. WAHL (Soc. Sci. Fennica Comm. Phys. Math., 1927, **4**, (14), 1—5).—Diethylenediaminediaquocupric tartrate has been prepared from barium tartrate and the complex sulphate which is obtained when aqueous solutions of cupric sulphate and ethylenediamine are mixed and evaporated to dryness. After filtration from barium sulphate the copper complex salt is precipitated by the addition of alcohol to the solution. The salt has $[M]$ +28·3°. After two extractions with alcohol the residual compound has $[M]$ −59·4°. When obtained by vacuum evaporation of the aqueous solution, the salt has $[M]$ −38·3°, and of the residue after alcoholic extraction −134°. The *l*-diaquodiethylenediaminecupric ion must have $[M]$ at least 190°. A series of optically active iodides has been prepared from the tartrates. Nickel yields corresponding tartrates of varying activity, the highest observed value being about +420°.

H. F. GILLBE.

Preparation and properties of *l*-mannono- and *d*-glucono-lactones. F. W. UPSON, L. SANDS, and C. H. WHITNAH (J. Amer. Chem. Soc., 1928, **50**, 519—525).—Crystalline *l*-gluconolactone, m. p. 134—135°, $[\alpha]_D$ −68·7°, to −13·7° in 15 days, subsequently increasing (cf. Hedenburg, A., 1915, i, 76), has now been obtained from *l*-arabinose by Fischer's method (cf. A., 1890, 1389), through the *brucine* salt, m. p. 181—182°, $[\alpha]^{20}$ −25·43°. l-*Gluconophenylhydrazide*, m. p. 200°, $[\alpha]_D^{20}$ −11·7°, is described. l-*Mannono-γ-lactone*, m. p. 150·5—151°, $[\alpha]_D^{20}$ −51·8°, obtained from *l*-mannonolactone by Nef's method (A., 1914, i, 490) was converted by methyl iodide and silver oxide into *methyl tetramethyl*-l-*mannonate*, from which, on hydrolysis, *tetramethyl*-l-*mannono-γ-lactone*, m. p.

109°, $[\alpha]_D^{20}$ −65·51°, to −47·4° in 18 days, was obtained. The slow change in rotation, together with the slow titration with alkali at the ordinary temperature, supports the δ-lactonic structure. *Tetramethyl*-d-*mannono*-γ-*lactone*, m. p. 151°, $[\alpha]_D^{20}$ +66·6°, was obtained analogously. Treatment of calcium *l*-mannonate with oxalic acid affords an l-*mannonolactone*, m. p. 160—162°, $[\alpha]_D^{20}$ −113·6°, to −30·9° in 32·5 hrs., subsequently increasing, to which, as well as to the corresponding *d*-mannonolactone of Hedenburg (*loc. cit.*), the δ-lactonic structure is ascribed, from theoretical evidence presented. Oxidation of tetramethyl-*d*-mannose with bromine affords a *tetramethyl*-d-*mannonolactone*, liquid, $[\alpha]_D^{19}$ +132·3°, to +59·5° in 6 days, subsequently increasing, which also appears to be a δ-lactone. F. G. WILLSON.

Semiacetal formation and the refractive indices and densities of mixtures of certain alcohols and aldehydes. H. ADKINS and A. E. BRODERICK (J. Amer. Chem. Soc., 1928, 50, 499—503).—The refractive indices and densities of certain alcohol–aldehyde mixtures, taken over the range from pure alcohol to pure aldehyde, indicate that condensation takes place in all cases, presumably with formation of semiacetals. In the cases of acetaldehyde–ethyl alcohol, heptaldehyde–ethyl alcohol, and acetaldehyde–*iso*propyl alcohol, semiacetal formation appears to be almost quantitative. F. G. WILLSON.

Action of chloroacetaldehyde on the mixed dimagnesium derivative of acetylene. Acetylenic glycol and erythritol. R. LESPIEAU (Bull. Soc. chim., 1928, [iv], 43, 199—210).—When chloroacetal is treated with oxalic and sulphuric acids there is produced, in addition to polymerised chloroacetaldehyde, some βδ-dichlorocrotonaldehyde, b. p. 80°/15 mm., d^{20} 1·361, n^{20} 1·512, which with ethyl orthoformate, alcohol, and a trace of hydrochloric acid yields βδ-*dichlorocrotonaldehyde diethyl acetal*, b. p. 101—102°/15 mm., d^{23} 1·128, n^{23} 1·4601, R 51·73. This compound yields with sodium ethoxide β-*chloro*-δ-*ethoxycrotonaldehyde diethyl acetal*, b. p. 117°/13 mm., d^{-1} 1·033, n^{21} 1·446. The action of chloroacetaldehyde on the product of reaction of acetylene and magnesium ethyl bromide is to give α-*chloro*-β-*hydroxy*-Δγ-*butinene*, b. p. 157°/760 mm., 62—63°/14 mm., d^{21} 1·171, n^{21} 1·475, and αζ-dichloro-Δγ-hexinene-βε-diol (not isolated) [*dibromide*, m. p. 141—142·5° (crystallographic data given)]. The former compound when treated with dry potassium hydroxide in ether yields *ethinylethylene oxide*, b. p. 86—87°/760 mm., d^{23} 0·945, n^{23} 1·427, hydrolysed to Δγ-*butinene*-αβ-*diol*, m. p. 39·5—40·5° (*diphenylcarbamate*, m. p. 134—134·5°; *dibromide*, m. p. 47—48°), whilst the latter furnishes the *dioxide*,

$\underset{H_2C}{\overset{O}{|}}\!\!>CH\cdot C{:}C\cdot CH\!<\!\underset{CH_2}{\overset{O}{|}}$, b. p. 87·5—88·5°/10 mm., 98—99°/20 mm., d^{23} 1·1189, n^{23} 1·4871 (cis- and trans-*dibromides*, m. p. 57—58° and 101—102·5°). Ethyl αβ-dichloroethyl ether furnishes two stereoisomeric αζ-*dichloro*-βε-*diethoxy*-Δγ-*hexinenes*, having b. p. 136—137°/11—12 mm., m. p. 12—14°, d^{21} 1·110, n^{21} 1·4705 (*dibromide*, m. p. 107—108°), and b. p. 138—139°/13 mm., m. p. 21°, d^{21} 1·112, n^{21} 1·471 [*dibromide*, m. p. 71—72° (crystallographic data given)], respectively, when regenerated from the dibromides. When the form of m. p. 12—14° is treated with acetic acid and acetic anhydride at 150°, there is produced a *diacetate*, b. p. 160—162°/11 mm., d^{21} 1·144, n^{21} 1·4669, hydrolysed by cold alcoholic sodium hydroxide to βε-*diethoxy*-Δγ-*hexinene*-αζ-*diol*, b. p. 125—128°/3·5 mm., d^{18} 1·026, n^{18} 1·4503. The form of m. p. 21° is unaffected by similar treatment. The above dioxide is acted on by methyl alcohol and a small amount of sulphuric acid, forming αζ-*dimethoxy*-Δγ-*hexinene*-βε-*diol*, b. p. 143—143·5°/3·5 mm., d^{23} 1·122, n^{23} 1·477 (*dibromide*, m. p. 150—151·5°), and by water, yielding Δγ-*hexinene*-αβεζ-*tetraol*, m. p. 113—114·5° (*dibromide*, m. p. 184—185°). H. BURTON.

Condensing action of mixed magnesium alkyloxides. V. GRIGNARD and M. FLUCHAIRE (Ann. Chim., 1928, [x], 9, 5—54; cf. Grignard and Dubien, A., 1923, i, 896).—Magnesium alkyloxyhalides, RO·MgHal, for use as condensing agents (cf. Meerwein and Schmidt, A., 1925, i, 1239) are prepared by treating magnesium alkyloxides with etherated magnesium halides (Menschutkin, A., 1906, i, 131, 552). The etherated halides themselves are inactive as condensing agents, whilst the alkyloxides have a smaller reactivity than the mixed derivatives. During condensations of aldehydes two reactions usually proceed simultaneously, (*a*) aldol formation, (*b*) ester formation, $2R\cdot CHO \longrightarrow R\cdot CO_2CH_2R$, whilst with ketones only aldol condensation takes place.

Acetaldehyde and magnesium butoxyiodide react in presence of ether to form ethyl acetate, aldol, and butyl acetate, this being obtained from the interaction of ethyl acetate and the magnesium derivative. *n*-Butaldehyde and magnesium butoxyhalides give *n*-butyl butyrate, γ-hydroxy-β-ethyl-*n*-hexaldehyde, and αγ-*dihydroxy*-β-*ethyl*-n-*hexyl butyrate*, b. p. 255°, 148—149°/15 mm., d_4^{15} 0·9473, n_D^{15} 1·4452, R 60·72. β-*Ethyl*-n-*hexane*-αγ-*diol* has b. p. 116°/5 mm., 133—134°/15 mm., d_4^{15} 0·9367, n_D^{15} 1·4535. Benzaldehyde reacts slowly, forming benzyl benzoate and benzyl oxide, whilst furfuraldehyde affords furfuryl alcohol, b. p. 75—76°/15 mm., d_4^{16} 1·1359, n_D^{16} 1·4940, R 25·12, together with α-furfurylidenebutaldehyde, b. p. 234—235°, 114—115°/15 mm., d_4^{12} 1·061, 1·5668.

Benzaldehyde and acetone condense in presence of magnesium butoxybromide to form benzylidene- and dibenzylidene-acetones.

Condensation of methyl alkyl ketones proceeds $2R\cdot COMe \longrightarrow R\cdot CO\cdot CH_2\cdot CMeR\cdot OH$. The alcohols formed are dehydrated by distillation either alone or with traces of iodine and anhydrous oxalic acid to the unsaturated ketones, R·CO·CH:CMeR. Magnesium butoxybromide causes the conversion of acetone into diacetone alcohol (cf. Grignard and Dubien, *loc. cit.*), but prolonged treatment or the use of magnesium bromodiacetone alcoholate gives phorone, *iso*phorone, and βζ-*dimethyl*-Δε-*hepten*-β-*ol*-δ-*one*, b. p. 95—96°/5 mm., d_4^{15} 0·9432, n_D^{15} 1·4577. Methyl ethyl ketone furnishes γ-*methyl*-n-*heptan*-γ-*ol*-ε-*one*, b. p. 85°/15 mm., d_4^{15} 0·9315, n_D^{15} 1·4367, dehydrated to γ-methyl-Δγ-hepten-ε-one, d_4^{15} 0·8511, n_D^{15} 1·4469 (*semicarbazone*, m. p. 115°). Methyl propyl

ketone gives δ-*methylnonan-δ-ol-ζ-one*, b. p. 110°/15 mm., d_4^{15} 0·9076, n_D^{15} 1·4424, dehydrated to δ-methyl-Δ^{δ}-nonen-ζ-one, b. p. 90°/14 mm., 202°/755 mm., d^{12} 0·8494, n_D^{12} 1·4512 (*oxime*, b. p. 130°/14 mm.). Methyl butyl ketone yields ε-*methylundecan-ε-ol-η-one*, b. p. 111°/4 mm., d_4^{16} 0·8975, n_D^{16} 1·4445, dehydrated easily to ε-*methyl-Δ^{ϵ}-undecen-η-one*, b. p. 120°/16 mm., d^{17} 0·8472, 1·4541 (*oxime*, b. p. 149—150°/12 mm.). From methyl *iso*butyl ketone there are obtained βδθ-*trimethylnonan-δ-ol-ζ-one*, b. p. 99°/3 mm., d^{11} 0·8962, n_D^{11} 1·4427, and βδθ-trimethyl-Δ^{δ}-nonen-ζ-one, b. p. 108°/15 mm., d_4^{12} 0·8447, n_D^{15} 1·4543 (*oxime*, b. p. 145°/14 mm.). Methyl amyl ketone gives ζ-*methyl-Δ^{ζ}-tridecen-θ-one*, b. p. 115°/4 mm., d_4^{12} 0·8510, n_D^{12} 1·4592, *R* 67·48 (*oxime*, b. p. 165°/12 mm.), which when ozonised yields methyl amyl ketone and probably amylglyoxal. The molecular refractions of the above unsaturated ketones show exaltation, due to conjugation.

Condensation of diethyl and dipropyl ketones proceeds with difficulty (cf. Ekeley and Carpenter, A., 1924, i, 369) under the influence of magnesium butoxybromide. There are formed δ-*methyl-γ-ethylheptan-γ-ol-ε-one*, b. p. 105°/14 mm., d_4^{18} 0·9175, n_D^{18} 1·4435, dehydrated to δ-methyl-γ-ethyl-Δ^{γ}-heptene-ε-one, b. p. 92°/14 mm., d^{17} 0·8515, n^{17} 1·4509, and ε-*ethyl-δ-propyl-Δ^{δ}-nonen-ζ-one*, b. p. 224°/755 mm., d^{11} 0·8506, n_D^{11} 1·4569, respectively.

Magnesium butoxybromide converts ethylidene- and propylidene-acetone into δ-*methyl-$\Delta^{\beta\delta\eta}$-nonatrien-ζ-one*, b. p. 102°/4 mm., d_4^{12} 0·9187, 1·4871, and ε-*methyl-$\Delta^{\gamma\epsilon\theta}$-undecatrien-η-one*, b. p. 120°/4 mm., 138°/18 mm., d_4^{18} 0·9103, n_D^{18} 1·4899, respectively. When ethylideneacetone is treated with a deficit of magnesium ethyl bromide there is formed in addition to the above condensation product some γ-*methyl-Δ^{δ}-hepten-γ-ol*, b. p. 62°/15 mm., d^{17} 0·8477, n_D^{17} 1·4421. Improved methods of preparation of ethylidene-, propylidene-, and butylidene-acetones, methyl butyl and methyl *iso*butyl ketones are given. *n*-Hexan-δ-ol-β-one has b. p. 83°/15 mm., d_4^{1} 0·9639, n_D^{13} 1·4353, *R* 31·42 (cf. Pastureau and Zamenhof, A., 1926, 272). βδ-*Dimethylhexane-βδ-diol*, prepared from magnesium ethyl bromide and diacetone alcohol, has b. p. 94—95°/5 mm., 0·9212, n_D^{15} 1·4437.

When methyl *iso*butyl ketone is treated with magnesium butoxybromide and benzoyl chloride there is formed in addition to the above trimethylnonenone, the *benzoate*, b. p. 123°/15 mm., d_4^{14} 0·9706, n_D^{1} 1·4898, of the enolic form of the initial ketone. The same benzoate is produced, together with methylethyl*iso*butylcarbinyl benzoate, from magnesium ethyl bromide and benzoyl chloride. These results demonstrate the enolising effect of the organo-metallic compound.

It is shown that magnesium butoxyiodide has a greater condensing action on butaldehyde than either the chloride or the bromide, whilst in a series of alkoxy-iodides the greatest effects are shown by Pr, Bu, and *iso*amyl. The benzyloxy-compound is of the same order as the butoxy-derivative, and the best results are obtained by using primary alcoholates. The corresponding ketolates are much less reactive.

The formation of esters from the aldehydes is explained by the production of a semi-acetal (I) (cf. Verley, A., 1925, i, 783) (probably isolated from benzaldehyde and magnesium butoxybromide) thus: R·CHO+BuO·MgBr ⟶ BuO·CHR·OMgBr (I), with subsequent condensation of 2 mols. into 2BuO·MgBr + CHR·O·CHR· ⟶ R·CO$_2$CH$_2$R. The production of
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the aldol (cf. Tischtschenko, A., 1907, i, 282, 284) is formulated CHO·CHR·H+BuO·CH(O·MgBr)·CH$_2$R ⟶ BuOH+CHO·CHR·CH(OMgBr)·CH$_2$R. When the aldehyde is reduced to the alcohol the following change takes place: CH$_2$PrO·CHR·OMgBr ⟶ CH$_2$R·OMgBr+Pr·CHO, and the formation of the enol form of the ketone is postulated as BuO·CR′(CH$_2$R)·OMgBr ⟶ BuOH+CHR:CR′·OMgBr.

H. BURTON.

Reactions of nitrosyl chloride. H. RHEINBOLDT and M. DEWALD (Annalen, 1928, **460**, 305—307).—It has been found (A., 1927, 229) that whilst some aldoximes and nitrosyl chloride gave crystalline chloronitrosohydrocarbons, higher aldoximes and *iso*valer- and phenylacet-aldoxime gave oils. Some higher aldoximes have now been converted into crystalline products, although the two other oximes named have not. With increase of mol. wt., the stability of the dimeric form of chloronitroso-compounds increases. (The higher members have only a feeble colour in benzene solution.) Again, the higher members pass much less readily than the lower into hydroxamic chlorides. α-*Chloro-α-nitroso*-n-*octane*, -n-*nonane*, -n-*decane*, and -n-*dodecane* melt, respectively, at 42°, 50—51°, 62°, and 63°. The last-named compound was obtained from *dodecaldoxime*, m. p. 73°.

E. E. TURNER.

[Preparation of] methyl *n*-amyl ketone. J. R. JOHNSON and F. D. HAGER (Org. Syntheses, 1927, 7, 60—62).

Mechanism of carbohydrate oxidation. VII. Action of potassium hydroxide on dihydroxyacetone. W. L. EVANS and W. R. CORNTHWAITE (J. Amer. Chem. Soc., 1928, **50**, 486—492; cf. A., 1926, 1226).—The action of aqueous potassium hydroxide on dihydroxyacetone under conditions precisely comparable with those previously applied to glyceraldehyde (*loc. cit.*) gives the same products, and the similarity between the variations of proportions of the different products with alkali concentration and temperature in the two cases is brought out by graphical methods. These results indicate that glyceraldehyde and dihydroxyacetone exist in alkaline solution in equilibrium with the same enediol. In presence of phenylhydrazine, the maximum production of pyruvaldehyde from glyceraldehyde and dihydroxyacetone occurs at the same alkali concentration, but the yields of pyruvaldehyde (as osazone) are not identical, from which it is concluded that the proportions of components present at equilibrium vary with the triose used, as previously noted by de Bruyn and van Eckenstein for dextrose, mannose, and lævulose. This is supported by the observation that the formation of pyruvaldehyde is a unimolecular reaction in each case, but that the rates of reaction are not identical.

F. G. WILLSON.

Catalytic hydrogenation of oximes and their transformation into β-hydroxylamines. G. VAVON and KRAJCINOVIC (Bull. Soc. chim., 1928, [iv], **43**, 231—237).—Hydrogenation of dipropyl ketoxime (1 mol.) in 70% aqueous-alcoholic solution in presence of platinum-black and hydrochloric acid (1 mol.) yields *δ-hydroxylaminoheptane*, m. p. 52°. When the *hydrogen oxalate*, m. p. 115°, of this base is treated with benzaldehyde in presence of aqueous-alcoholic sodium hydrogen carbonate, there is formed *N-benzylideneheptane-δ-nitrone*, m. p. 53—54°. *β-Hydroxylamino-δ-methylpentane*, m. p. 63° (*hydrogen oxalate*, m. p. 132—133°), and *β-hydroxylamino-β-phenylethane* (*hydrogen oxalate*, m. p. 150°), are obtained from methyl *iso*butyl ketoxime and acetophenoneoxime, respectively.

When aldoximes are hydrogenated by the same method, the main products are secondary hydroxylamines, probably formed thus: R·CH:N·OH ⟶ $R·CH_2·NH·OH$ ⇌ $R·CH_2·NO:CHR$ ⟶ $(CH_2R)_2N·OH$. Thus heptaldoxime furnishes *diheptylhydroxylamine* (90%), m. p. 74° (*hydrogen oxalate*, m. p. 137°); *iso*valeraldoxime yields *di-γ-methylbutylhydroxylamine* (*oxalate*, m. p. 167—168°); benzaldoxime affords dibenzylhydroxylamine, m. p. 123°, and piperonaloxime gives *dipiperonylhydroxylamine*, m. p. 123—124° (*hydrochloride*).

H. BURTON.

First phases of the chemistry of the dissimilation of the hexoses. A. J. KLUYVER and A. P. STRUYK (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 871—884).—The effect of the addition of disodium hydrogen phosphate on the rate of fermentation of dextrose by yeast juice varies with the sample of yeast employed; in one case (*A*) a rapid rise to a maximum velocity is followed by a fairly rapid and constant fall to the initial value, whilst in the other (*B*) the increase produced is smaller in magnitude but extends over a longer period. Isolation of the phosphoric ester produced by the method of Robison (A., 1923, i, 86) shows that in case *B* almost the whole of the phosphate is present as a hexose monophosphoric ester, but in case *A* a larger proportion of the diphosphoric ester is present. Attempts to prove the presence of a triose phosphoric ester were unsuccessful, although the application of the triose reaction of Neuberg, (A., 1918, i, 91) yielded methylglyoxal, isolated as its *p*-nitrophenylosazone. These results are shown to confirm the authors' theory of hexose dissimilation (A., 1926, 978). A critical summary of the literature is also given. J. W. BAKER.

Determination of reducing sugars by the ferricyanide method. A. IONESCO-MATIU (Bul. Soc. Chim. Romania, 1927, **9**, 68—75).—Dextrose and other reducing sugars may be rapidly and accurately determined by titration with potassium ferricyanide using picric acid as an indicator, the method employed varying in the case of relatively large or small sugar contents. In the former case 10 c.c. of the ferricyanide solution (46 g. of potassium ferricyanide and 46 g. of potassium hydroxide per litre, standardised by titration against a 5% solution of pure dextrose and diluted so that 10 c.c. are equivalent to 0·05 g. of dextrose), 20 c.c. of water, and 10 drops of a 1% solution of picric acid are heated to boiling and the sugar solution (approximately 5%) is added from a burette until the yellow colour changes to red. When the sugar content is less than 2% an indirect method must be employed. The ferricyanide solution (4 c.c.), 6 c.c. of water, and a measured volume (1—6 c.c.) of the sugar solution are boiled together for exactly 1 min., rapidly cooled, 100 c.c. of water and 5 c.c. of 20% sulphuric acid added, and the ferrocyanide produced is titrated with a 1% solution of potassium permanganate, the titre being compared with that of a 1% dextrose solution similarly treated. The method is applied to the following cases: invert-sugar, obtained by hydrolysis of a 5% sucrose solution with 1% hydrochloric acid and subsequent neutralisation before titration; 10 c.c. of ferricyanide solution = 0·0467 g. of sucrose or 0·0491 g. of invert-sugar; maltose, 10 c.c. = 0·637 g.; lactose, 10 c.c. = 0·0676 g. (the technique for the determination of lactose in milk is described); sugar in urine, previously defecated with lead acetate and diluted until the sugar content is 0·5%; blood-sugar previously treated with 20% trichloroacetic acid solution to remove albuminous matter, and subsequently neutralised. Reducing material in normal blood varies from 0·80 to 1·2%. J. W. BAKER.

Pentabenzoates of dextrose. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1928, **76**, 513—519).—Repetition of the work of Fischer and Freudenberg (A., 1912, i, 887) and of Schlubach and Huntenburg (A., 1927, 858) led to the preparation of *α-pentabenzoylglucose*, m. p. 187°, $[\alpha]_D^{20}$ +138·5° in chloroform, *β-pentabenzoylglucose*, m. p. 157°, $[\alpha]_D^{20}$ +24° in chloroform, *α-pentabenzoyl-γ-glucose*, m. p. 118°, $[\alpha]_D^{20}$ +79° in chloroform, *β-pentabenzoyl-γ-glucose*, m. p. 146—147°, $[\alpha]_D^{20}$ −82° in chloroform. These new values support the previous suggestion that the difference between the molecular rotations of the α- and β-forms of a sugar differs with the ring structure, and, further, that the sum of these rotations is less with a five-membered than with a six-membered ring. C. R. HARINGTON.

β-Acetylchloroglucose. II. H. H. SCHLUBACH, P. STADLER, and I. WOLF (Ber., 1928, **61**, [*B*], 287—293; cf. A., 1926, 600).—The use of a particularly active form of silver chloride enables the time required for the conversion of acetylbromoglucose into β-acetylchloroglucose to be reduced from 3—4 hrs. to 8—10 min. with consequent increase in the yield of β-product on which silver chloride has an isomerising action. The lowest value observed with the product is $[\alpha]_D^{20}$ −17·4° in carbon tetrachloride (Hudson's use of pharmaceutical chloroform in this connexion is adversely criticised); this datum differs by about 30° from that calculated by Hudson. A similar discrepancy is found with β-nitroacetylglucose, for which the values, m. p. 96°, $[\alpha]_D^{20}$ −8·4° in carbon tetrachloride, are now recorded. It is suggested that the principle of optical superposition is not valid in these cases and consequently that Hudson's methods of calculation cannot be applied.

The dielectric constant of the solvent appears to be intimately concerned with the rate of isomerisation

of β-acetylchloroglucose into dextrorotatory acetylchloroglucose in solution, but secondary reactions not involving the production of equilibrium mixtures inhibit mathematical treatment of the data. Ether is a potent stabiliser, whereas alcohols accelerate isomerisation; alkyl halides and acetonitrile occupy an intermediate position. Addition of small quantities of water, acids, or bases to the ethereal solution does not cause marked acceleration of the change, but silver chloride is a strong, positive catalyst. The formation of β-acetylchloroglucose in small amount by Fischer and Armstrong's method (A., 1901, i, 257, 671) is confirmed, as is its isomerisation when shaken in ethereal solution with sodium carbonate; the conversion of the crude material into tetramethyl-α-methylglucoside appears very improbable. Indications of the production of β-acetylbromoglucose by Fischer and Armstrong's method could not be observed. H. WREN.

α-Methylmannoside. C. S. HUDSON (Org. Syntheses, 1927, 7, 64—66).—The preparation of α-methylmannoside from "vegetable ivory" waste is described. A. A. ELDRIDGE.

Mannan acetate. I. Preparation of mannan acetate and some of its properties. R. SHINODA and C. ASHIZAWA (J. Cellulose Inst. Tokyo, 1928, 4, 3).—Mannan triacetate is prepared by treating raw Japanese konjaku powder (*Amorphophallus Konjac*) with an aqueous solution of chlorine peroxide, and heating the product (in the form of threads) with glacial acetic acid at 100°. It is claimed that the method is economical, the time of reaction is short, and that no decomposition of mannan takes place. Mannan triacetate may be used as a cellulose acetate substitute, since it yields a strong film; a 1% solution in a mixed solvent containing tetrachloroethane 40%, methyl acetate 40%, methyl alcohol 20% has a suitable viscosity. W. J. POWELL.

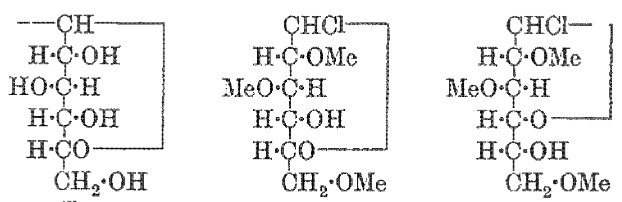
Epirhamnitol, reduction product of epirhamnose. E. VOTOCEK and J. MIKSIC (Bull. Soc. chim., 1928, [iv], 43, 220—224).—When epirhamnose (*iso*rhamnose) is reduced with sodium amalgam and acidulated water there is obtained *epirhamnitol*, a syrup, having $[\alpha]_D^{20}$ $+9{\cdot}18°$ in water when purified through the *dibenzylidene* derivative, $C_6H_{10}O\left(<{}^{O}_{O}>CHPh\right)_2$, m. p. 196°, $[\alpha]_D^{20}$ $-36{\cdot}7°$ in chloroform. Epirhamnitol and *iso*rhodeitol (following abstract) are optical antipodes. H. BURTON.

***iso*Rhodeitol, reduction product of *iso*rhodeose.** E. VOTOČEK and F. VALENTIN (Bull. Soc. chim., 1928, [iv], 43, 216—220).—Reduction of an aqueous solution of *iso*rhodeose, $[\alpha]_D$ $+30{\cdot}3°$ (cf. A., 1910, i, 274), with sodium amalgam gives *isorhodeitol*, a syrup, $[\alpha]_D$ $-8{\cdot}3°$ in water. When distilled in a high vacuum the alcohol has $[\alpha]_D$ $-9{\cdot}7°$, and its rotation is lowered when mixed with sodium borate. The crude alcohol reacts with benzaldehyde in presence of 50% sulphuric acid, yielding a *monobenzylidene* derivative, $C_6H_{12}O_3<{}^{O}>CHPh$, m. p. 158°, whilst the redistilled alcohol gives a *dibenzylidene* derivative, m. p. 196—197°, $[\alpha]_D^{18}$ $+35{\cdot}1°$ in chloroform. H. BURTON.

Cellulose formate. I. Formation [from hydrocellulose and cellulose regenerated from viscose]. Y. UEDA and K. HATA (J. Cellulose Inst. Tokyo, 1928, 4, 1—2).—Hydrocellulose with anhydrous formic acid and sulphuric acid yields a product containing 22·90% of formic acid (theory for monoformate 24·21%), whilst the product from cellulose regenerated from viscose contains 50·50% (cellulose triformate requires 56·09%). The ester is readily soluble in pyridine, but only sparingly soluble in other organic solvents. Results showing the effect of variations in the amount of sulphuric acid on the degree of esterification are given. W. J. POWELL.

Lignin and cellulose. II. Methylcellulose. K. FREUDENBERG and E. BRAUN (Annalen, 1928, 460, 288—304).—It was shown recently by Urban (cf. B., 1926, 531) that the methylation of cotton at 20° gives a trimethylcellulose essentially different from previously obtained trimethylcelluloses. It dissolves to a clear and very viscous solution in chloroform, tetrachloroethane, and glacial acetic acid, whilst the specimens of Denham (J.C.S., 1921, 119, 81) and of Irvine and Hirst (J.C.S., 1923, 123, 529) did not. Further, it differs from the product obtained by Hess (A., 1924, i, 142; 1927, 44) in being quite insoluble in water and not crystallising from other solvents. It is formed in 93% yield from unbleached cotton, whilst previous preparations were obtained only in about 75% yield. With methyl-alcoholic hydrogen chloride it gives a 91% yield of 2 : 3 : 6-trimethyl-methylglucoside and 9% of dimethyl-methylglucoside, corresponding with the original methoxyl content (44·4%) of the sample used (the highest OMe content obtained was almost 45% instead of calc. 45 No trace of tetramethylglucose was found. This establishes the structural identity and stereochemical similarity of all the glucose units (I) present in the cellulose molecule.

When trimethylcellulose (for the preparation of which a few further details are given) is treated with hydrogen chloride in presence of ether (sealed tube, 35°) 1-*chloro*-2 : 3 : 6-*trimethylglucose* (II or III) is formed. This gives a crystalline *pyridinium* salt, decomp. 180°, $[\alpha]_D^{15}$ $+26{\cdot}6°$ in water.



(I.) (II.) (III.)

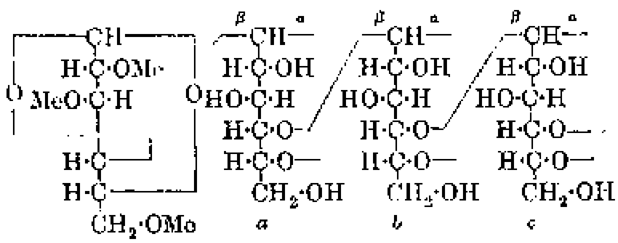
Powdered sodium converts the chloro-derivative in cold ethereal solution into 2 : 3 : 6-*trimethylglucose anhydride* (IV ?), a mobile oil, b. p. 83—85°/0·1 mm., $[\alpha]^{16}$ $-10{\cdot}1°$ (in water, $+16{\cdot}5°$, in chloroform $+14{\cdot}6°$), d^{15} 1·1593, n_D^{14} 1·4656. The anhydride contains no hydroxyl groups, is stable to Fehling's solution, to permanganate, and to bromine water, and when boiled with dilute hydrochloric acid gives 2 : 3 : 6-trimethylglucose, $[\alpha]_D^{15}$ $+90{\cdot}7°$, mutarotating to $+70{\cdot}2°$ (cf. Irvine and Hirst, J.C.S., 1922, 121, 1216).

The complete dissimilarity of trimethylcellulose and

trimethylglucose anhydride (the latter gives a filtrable mobile solution in chloroform and has a normal mol. wt. in benzene; a 2% chloroform solution of the former is too viscous to be poured and the mol. wt. is immeasurably large) shows that trimethylcellulose is not a trimethylglucose anhydride and therefore that cellulose is not a unimolecular glucose anhydride as suggested by Hess.

The results of Micheel and Hess (A., 1927, 1056) for the preparation of two 2 : 3 : 6-trimethylglucose anhydrides could not be confirmed. The anhydride had a considerable b.-p. range and two fractions obtained from it had $[\alpha]_D$ +23° and +50° respectively, the former giving rise to a trimethylglucose with $[\alpha]_D$ only +63·5°.

1-*Dimethylamino*-2 : 3 : 6-*trimethylglucose*, from trimethylglucose and dimethylamine in methyl alcohol, has b. p. 109°/0·1 mm., $[\alpha]_D$ +18·6° in water and +7·2° in methyl alcohol. The corresponding *quaternary ammonium iodide* and chloride had $[\alpha]_D^{15}$ −41·2° and $[\alpha]^{16}$ −9·4° in water, respectively, whereas the chloride prepared by Micheel and Hess had $[\alpha]_D$



(IV.) (V.)

A survey of the main facts shows that there can be no reversible interconversion of trimethylcellulose and trimethylglucose anhydride. Moreover, cellobiose must be a product of degradation of cellulose, not a product of re-synthesis from glucose. In short, ordinary co-valency linkings unite the glucose units in cellulose, which is probably (V). If cellulose contains the linkings $a_{1\alpha}$–a_5, $b_{1\alpha}$–b_5, and $c_{1\alpha}$–c_5, degradation would lead to reducing and tetramethylglucose fragments. With linkings $a_{1\alpha}$–b_5, $b_{1\alpha}$–c_5, and $c_{1\alpha}$–d_5, etc., the same might apply, but is not necessitated. More probable linkings are either (with a_β attached to OH and c_4 to H), $a_{1\alpha}$–a_5, $b_{1\alpha}$–b_5, and $c_{1\alpha}$ c_5, or $a_{1\beta}$ a_5, $a_{1\alpha}$ b_5, $b_{1\alpha}$ c_5, and $c_{1\alpha}$ c_4. An essential argument for the associative combination of glucose anhydride units in cellulose was the supposed associative dimerisation of acetylaldol. Bergmann has, however, shown that the " dimeride is a structural unit.

2 : 3 : 6-Trimethylglucose is converted by phosphorus pentachloride in ether into the *compound* $(C_9H_{16}O_6)_2PCl_3$, decomp. 160°. Trimethyl-methylglucoside reacts with phosphorus pentachloride in chloroform to give a syrupy *chlorohydrin*, $C_{10}H_{19}O_5Cl$ (Cl in position 4?), b. p. 88—95°/0·1 mm., $[\alpha]_D^{20}$ +16·4° in chloroform. The latter, when heated with hydrochloric acid, affords 2 : 3 : 6-*trimethylglucose*-4(?)-*chlorohydrin*, syrupy, b. p. 140—150°/0·1 mm., $[\alpha]_D$ +27·5° in chloroform. This in turn is converted by sodium into a 2 : 3 : 6-*trimethylhexose anhydride*, b. p. 84°/0·1 mm., $[\alpha]_D^{20}$ +106·8° (in water, +112·8°). Hydrolysis of the latter with hydrochloric acid gives a *trimethylhexose* with $[\alpha]_D$ +95·2° in water. Methylation of this gives a *methylhexoside* with $[\alpha]_D$ +33°, which when hydrolysed affords a *tetramethylhexose*, $[\alpha]_D$ +55°, not identical with tetramethylgalactose. The hexose anhydride, however, is not a derivative of glucose. E. E. TURNER.

Oxidation of amino-acids with sugars. S. AKABARI (Proc. Imp. Acad. Tokyo, 1927, **3**, 672—674).—When *l*-leucine is heated with *d*-glucose at 120—130° in glycerol there are formed carbon dioxide, *iso*valeraldehyde (15%), and a brown substance, probably melanoidin (cf. Maillard, A., 1912, i, 169). *l*-Phenylalanine and *dl*-alanine afford phenylacetaldehyde (*semicarbazone*, m. p. 154—155°) and acetaldehyde, respectively. Ammonia is not evolved during the reaction, probably because it is used in the formation of melanoidin. The glycerol solution of the brown substance contains a small amount of hydroxymethylfurfuraldehyde. The oxidation is formulated $NH_2\cdot CHR\cdot CO_2H+O=R\cdot CHO+CO_2+NH_3$. H. BURTON.

Crystallisation of lysine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **76**, 437—443).—Lysine was recovered from the carefully purified picrate, m. p. 266° (decomp.), by shaking the latter with dilute sulphuric acid and ether; the sulphuric acid was for the most part removed by addition of barium hydroxide, and the solution concentrated; with precautions against access of carbon dioxide, the remaining sulphuric acid was removed and the concentration continued; lysine separated in needles, darkening at 210°, m. p. 224—225° (decomp.), $[\alpha]_D^{20}$ +14·6°. C. R. HARINGTON.

Alkylation of α-cyano-β-alkylacrylic esters and of α-phenyl-β-alkylacrylonitriles. J. A. MCRAE and R. H. F. MANSKE (J.C.S., 1928, 484—491).—*Ethyl* α-n-*butyl*-Δ^1-cyclo*hexenylcyanoacetate* (I), b. p. 163—164°/15 mm., *ethyl* α-*ethyl*-Δ^1-cyclo*hexenylcyanoacetate* (II), b. p. 168°/22 mm., and *ethyl* α-*cyano*-α-n-*butyl*-Δ^β-*nonenoate* (III), b. p. 154—156°/11 mm., are prepared by treatment of ethyl *cyclo*hexylidenecyanoacetate or of ethyl heptylidenecyanoacetate with sodium ethoxide and the appropriate alkyl iodide. Ozone is rapidly absorbed by these compounds. Decomposition of the ozonisation products gives, in the three cases, ethyl *n*-butylcyanoacetate and adipic acid, adipic acid only, and hexaldehyde, formic acid, and *n*-butylmalonic acid. The compounds are therefore unsaturated in the βγ-position (cf. J.C.S., 1908, **93**, 1956), whereas the parent esters are unsaturated in the αβ-position (J.C.S., 1922, **121**, 274). The structural difference is further exemplified by the ease with which the alkyl derivatives take up bromine and by their failure to react with potassium cyanide or sodium hydrogen sulphite. Heptaldehyde condenses with phenylacetonitrile, giving α-*phenyl*-β-n-*hexylacrylonitrile* (IV), b. p. 168—170°/13 mm. Alkyl derivatives could not be prepared from the compound (IV) or from *cyclo*hexylidenephenylacetonitrile, m. p. 28°, b. p. 176—178°/12 mm. (cf. J.C.S., 1923, **123**, 2446). The last-named compound combines with hydrogen cyanide, giving 1-*cyano*cyclo*hexylphenylacetonitrile*, softening at 258°,

decomp. above 264°. Combination of the compound (IV) with hydrogen cyanide, followed by hydrolysis, gave *α-phenyl-α′-n-hexylsuccinic acid* and an *acid*, m. p. 170°. M. CLARK.

[Preparation of] chloroacetamide. W. A. JACOBS and M. HEIDELBERGER (Org. Syntheses, 1927, 7, 16—17).

Butenoic acid amides. P. BRUYLANTS and A. CASTILLE (Bull. Acad. Roy. Belg., 1927, [5], **13**, 767—781).—The amides of crotonic and *iso*crotonic acids have been prepared by the action of 66% sulphuric acid on the corresponding nitriles for several days at the ordinary temperature. The nitrile of b. p. 121° thus treated yields exclusively crotonamide (*trans*), m. p. 159—160°, whilst that of b. p. 108° yields a mixture of this amide and *iso*crotonamide, m. p. 100—101°. The nitrile of lower b. p. is therefore related to *iso*crotonic acid (*cis*), the reverse conclusion to that obtained by a comparative study of the ultra-violet absorption spectra and heats of combustion of the nitriles and acids. Physical evidence of the latter type is therefore untrustworthy as a basis for the determination of configuration (cf. Errera and Henri, A., 1925, ii, 1137; Auwers, A., 1923, i, 295). The same conclusion probably applies to the nitriles of α-methylcrotonic acids. In agreement with Stoermer (A., 1920, i, 614) and Auwers (*loc. cit.*), the b. p. of crotononitrile (*trans*) is 13° higher than that of *iso*crotononitrile (*cis*). Vinylacetamide is similarly prepared from the corresponding nitrile if excess of alkali (which causes isomerisation to crotonamide) is avoided in working up the product, the absorption spectrum of the amide in 0·1*N*-sodium hydroxide solution after 15 days closely resembling that of crotonamide in the same medium. The absorption curves of *cyclo*propanecarboxylic acid and its amide (obtained by alkaline hydrolysis of the nitrile) are plotted, and show a greater difference than is found in the corresponding crotonic acid derivatives. The amide of methylacrylic acid, obtained by acid hydrolysis of the nitrile, readily polymerises to an amorphous mass. J. W. BAKER.

Ureides of bromovaleric acids. II. Influence of branched chains on physiological properties. E. FOURNEAU and G. FLORENCE (Bull. Soc. chim., 1928, [iv], **43**, 211—216).—The effect of branching the chain in a series of α-bromovaleric ureides is to cause an increase in the hypnotic action. Bromopivalic ureide is a powerful hypnotic and as it contains the bromine atom in the β-position it is concluded that the group R·CHBr·CO– is not specific (Tiffeneau). The following data are recorded (percentage figures indicate solubility in water, and ordinary figures partition coefficients): α-bromo-*n*-valeric ureide, m. p. 162°, 0·833%, 0·42; α-bromo*iso*valeric ureide, 1·94%, 0·95; α-bromo-α-methylbutyric ureide, m. p. 132·5°, 5·3%, 1·98; *bromopivalic ureide*, m. p. 93·5°, 5·4%, 2·02. *n*-Valeric acid is obtained from magnesium butyl bromide and carbon dioxide in 78% yield. H. BURTON.

Additive compounds of allylthiocarbamide and silver halides. S. E. SHEPPARD and H. HUDSON (Z. wiss. Phot., 1928, **25**, 113—120).—See A., 1927, 755.

[Preparation of] guanidine nitrate. T. L. DAVIS (Org. Syntheses, 1927, 7, 46—48).

[Preparation of] nitroguanidine. T. L. DAVIS (Org. Syntheses, 1927, 7, 68—69).

[Preparation of] anhydrous hydrogen cyanide. K. ZIEGLER (Org. Syntheses, 1927, 7, 50—52).

Reaction of carbylamines and hydrocyanic acid with magnesium phenyl bromide. H. GILMAN and L. C. HECKERT (Bull. Soc. chim., 1928, [iv], **43**, 224—230).—Magnesium phenyl bromide reacts with methylcarbylamine forming a small amount of benzaldehyde (cf. Sachs and Loevy, A., 1904, i, 307). Definite reaction products were not obtained from hydrocyanic acid or ethyl-, *tert*.-butyl-, or *p*-tolyl-carbylamine. H. BURTON.

Preparation of magnesium *tert*.-butyl chloride. H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1928, **50**, 425—428; cf. A., 1924, i, 23).—Magnesium *tert*.-butyl chloride is obtained in 70% yield by adding *tert*.-butyl chloride (0·5 mol.) in ether (7 mols.) to magnesium powder (200-mesh), with stirring, during 3 hrs., the ether being maintained in gentle ebullition. F. G. WILLSON.

Lead tetraethyl. Y. TANAKA and T. KUWATA (Rep. Aeronautical Res. Inst., Tokyo, 1927, **2**, 409—417).—Crude lead tetraethyl, prepared from lead chloride and magnesium ethyl chloride, is best purified by the passage of air through a solution in dilute hydrochloric acid. This treatment converts the contaminating lead triethyl into crystalline *lead triethyl chloride*, which in turn affords lead tetraethyl with magnesium ethyl chloride (total yield 74%). Magnesium and ethereal ethyl chloride react readily if small amounts of iodine and ethyl iodide or bromide are added. Pure lead tetraethyl, b. p. 85·4—85·7°/13 mm., d_4^{18} (vac.) 1·6600, n_D^{18} 1·5206, decomposes at 400° giving metallic lead; at the ordinary temperature in sunlight it becomes turbid and alkaline, and when neutralised with hydrochloric acid yields some lead triethyl chloride. G. A. C. GOUGH.

Auto-oxidation. I. *cyclo*Hexene peroxide. H. N. STEPHENS (J. Amer. Chem. Soc., 1928, **50**, 568—571).—When oxygen is circulated continuously at atmospheric pressure and the ordinary temperature through *cyclo*hexene for 4 months, there is formed about 0·75% of cyclo*hexene peroxide*, b. p. 54—56°/0·5 mm., together with a non-volatile syrup, which appears to be a *dimeric* form of the peroxide, containing one peroxide group. F. G. WILLSON.

Oxidation of unsaturated hydrocarbons by free oxygen in presence of osmium. S. MEDVEDEV and E. ALEXÉEVA (Papers Pure Appl. Chem. Karpov Inst., Bach Festschr., 1927, 110—127; Chem. Zentr., 1927, ii, 1012).—The catalyst consisted of osmium dioxide deposited on alumina, ferric oxide, manganese sesquioxide, or cupric oxide; benzene was preferable to acetone as a solvent for the unsaturated hydrocarbon (*cyclo*hexene or Δ^2-methyl*cyclo*hexene), acetone solutions exhibiting an induction period of several hours. A catalyst inactivated by air is reactivated by benzene much more quickly than by acetone. The portion of the oxidation product of *cyclo*hexene which remained dissolved in the benzene contained peroxidic

compounds, an aldehyde (semicarbazone, m. p. 240—241°), and much Δ^2-*cyclo*hexenol (naphthylurethane, m. p. 156°). The portion on the catalyst contained adipic acid, and a compound, $C_6H_{10}O_2$, b. p. 108—110°/0·2 mm. A. A. ELDRIDGE.

Volume chemistry. II. Halogen derivatives of hydrocarbons. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 130—135, 172—174, 205—209; Chem. Zentr., 1927, ii, 777).—Abnormal "*E*-values" for cyclic hydrocarbons halogenated in a side-chain are avoided by supposing that the last hydrogen atom of the side-chain is attached to a nuclear carbon atom, with ring closure. A. A. ELDRIDGE.

Nitration by means of nitrogen peroxide. M. BATTEGAY (Bull. Soc. chim., 1928, [iv], **43**, 109—134).—A lecture.

Hydrogenation of cyclic compounds under pressure in presence of osmium and other catalysts. V. S. SADIKOV and A. K. MIKHAILOV (J.C.S., 1928, 438—448).—The rate of hydrogenation of benzene, quinoline, and pyridine in a modified Ipatiev apparatus has been investigated using as catalyst platinum, osmium, osmium–cerium oxide, or palladium deposited on asbestos. In every case a periodic absorption of hydrogen takes place, a period of activity being followed by a period of quiescence, whilst the activity of the catalyst gradually diminishes on account of the presence of impurities or of the formation of products of hydration inimical to the catalyst. This periodicity is attributed to removal of oxygen from the catalyst, followed by reactivation, and is compared with the periodic evolution of hydrogen when metals are dissolved in acids or alkalis (cf. Hedges and Myers, A., 1925, ii, 309). The addition of 1% of cerium oxide to a 20% osmium–asbestos catalyst for the reduction of quinoline causes considerable initial acceleration of the reaction, which proceeds throughout at a higher rate than when osmium alone is used; in the case of pyridine, the reverse effect results. In the reduction of benzene and pyridine in the presence of osmium, there is an initial period during which the rate of reaction is considerably greater for pyridine than for benzene, whilst the rate diminishes more rapidly with pyridine. The total amount of reduction over a period of hours is thus approximately the same for both (cf. this vol., 427). M. CLARK.

Comparative reactivities of some chloro-, bromo-, and iodo-nitrobenzenes. Mechanism of activation of halogen atoms by a nitro-group present in the same aromatic nucleus. A. BREWIN and E. E. TURNER (J.C.S., 1928, 332—334, 334—337).—The comparative reactivities of a number of halogenonitrobenzenes have been measured, using piperidine in benzene solution. It is concluded that reactions involving reactive halogen compounds are, as the majority of previous workers have assumed, dependent on the initial formation of additive compounds. A mechanism of activation by nitro-groups is developed, and correlated with one for aromatic substitution. M. CLARK.

Replaceability of nitro-groups from the nucleus of various aromatic compounds. R. H. CLARK and N. M. CARTER (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 323—338).—Data for the effect of heat on 119 aromatic nitro-compounds containing from one to five nitro-groups are recorded, and the results discussed from the point of view of the electronic conception of positive and negative valencies developed by Fry and others. In 96 of the compounds the results are in accordance with theory, in 9 the reaction appears to be with the unstable electromeride, whilst the behaviour of the remaining 14 cannot be accounted for on this hypothesis. M. S. BURR.

Replacement of halogen atoms from the nucleus of various aromatic compounds. R. H. CLARK and R. H. HALL (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 311—314).—The maximum replacement of halogen atoms, under the experimental conditions, has been determined for a number of aromatic halogen compounds, when heated under pressure with sodium methoxide of different concentrations. The yields are compared with those calculated on the basis of the electronic theory as elaborated by Fry. The results are not as conclusive as corresponding measurements on the nitro-groups. M. S. BURR.

Nature of the alternating effect in carbon chains. XXIII. Anomalous orientation by halogens, and its bearing on the problem of the *ortho-para* ratio, in aromatic substitution. C. K. INGOLD and C. C. N. VASS (J.C.S., 1928, 417—425).—The reaction mixture from *m*-fluoroacetanilide and bleaching powder yields, after treatment with hydrochloric acid, a mixture of 3-*fluoro*-4-*chloroacetanilide* (I), m. p. 115°, 3-*fluoro*-6(2 ?)-*chloroacetanilide*, m. p. 143°, and 3-*fluoro*-4 : 6(2 : 6 ?)-*dichloroacetanilide*, m. p. 124°. Hydrolysis of (I) gives 3-*fluoro*-4-*chloroaniline*, m. p. 61—62°, converted through the diazo-derivative into 3-*fluoro* 4-*chloronitrobenzene* (II), m. p. 63—64°, b. p. 114—116°/24 mm. Chlorination of *p*-fluoronitrobenzene in presence of anhydrous ferric chloride gives 4-fluoro-3-chloronitrobenzene (III), m. p. 41·5°, converted by elimination of the nitro-group into *o*-fluorochlorobenzene (IV), b. p. 138—140°/758 mm. Nitration of compound (IV) yields a mixture consisting essentially of compounds (II) and (III) present in the proportion corresponding with the ratio direction by F : direction by Cl=78·7% : 21·3%. An explanation of this anomaly is based on the hypothesis that the *op*-directive efficiencies of the halogens, which vary directly with the tendency of the halogen atom to share additional electrons (+T) and inversely as its attraction for electrons, shared and unshared (—T) (cf. this vol., 164), are also influenced by a third factor. The inductive effect is regarded as originating in a contracted electron shell round the halogen atom, and it is suggested that, as well as electron displacements relayed from linking to linking, modification of the existing electric fields might also occur by direct action through space in such a way that the potentially active electrons of the benzene ring would be subjected to additional electrostatic restraint. This "direct" effect of halogens would therefore be a deactivating influence (—D) and the full expression for the directive action of halogens in halogeno-

benzenes (+T—I—D). The variation of D as between different directing atoms would be the same as that of the inductive effect, but, since it is propagated through space, its distribution in the ring would be, not in the order $op > m$, but in the order $o > m > p$. The working of such an hypothesis in the case under discussion as well as in other cases cited is demonstrated. M. CLARK.

Nature of the alternating effect in carbon chains. XXIV. Directive action in aromatic substitution of certain groups containing triple linkings. J. W. BAKER, K. E. COOPER, and C. K. INGOLD (J.C.S., 1928, 426—431).—The nitration of two acetylene derivatives and two nitriles has been investigated with special reference to the proportion of *m*-isomeride formed, and the results are as follows: Phenylpropiolic acid (8% meta), ethyl phenylpropiolate (16%), benzonitrile (81%), phenylacetonitrile (14%). The results are discussed in relation to the other properties of the unsaturated groups contained in the side-chains of these compounds and an hypothesis is advanced to account for them. M. CLARK.

Preparation of *p*-nitrobenzyl bromide. I. V. HOPPER (J. Roy. Tech. Coll. Glasgow, 1927, (4), 58—60).—Addition of a solution of bromine in carbon tetrachloride to a boiling solution of *p*-nitrotoluene in the same solvent, in presence of a trace of iodine, and under the influence of ultra-violet light, gives excellent yields of *p*-nitrobenzyl bromide. L. M. CLARK.

Laws of aromatic substitution. VII. Constitution and substitution of phenylnitromethane and some of its derivatives. B. FLÜRSCHEIM and E. L. HOLMES (J.C.S., 1928, 453—483).—Contrary to the findings of Baker and Ingold (A., 1926, 1131), the statement by one of the authors (A., 1903, i, 79) that phenylbromocyanonitromethane (I) yields, on brief treatment with nitric acid (*d* 1·480) and subsequent oxidation with permanganate, a mixture consisting essentially of benzoic and *p*-nitrobenzoic acids is fully confirmed. Nitric acid of the strength used by Baker and Ingold (*d* 1·49) gives a similar result. The *p*-acid, amounting to 34—38% of the weight of the total acids, arises mainly by migration of the nitro-group during oxidation, and such migration can be prevented by prior treatment with alkali. The complex changes occurring on prolonged exposure of compound (I) to nitric acid (*d* 1·480) have been quantitatively elucidated. The main change—the migration of bromine into the *m*-position—occurs to the extent of 54% in 10 days and the rate of formation of the *m*-bromophenyl compound is independent of the concentration. With nitric acid of *d* 1·52, the nitromethane undergoes *m*-nitration (92—93%) (cf. Baker and Ingold, *loc. cit.*) and *p*(and *o*?)-nitration (8—7%). The compound (I) is decomposed by heat, giving 92% of benzoyl cyanide and 8% of *p*-nitrobenzoyl cyanide. m-*Nitrophenylbromocyanonitromethane* (II), m. p. 70—70·5°, gives 93·5% of *m*-nitrobenzoyl cyanide. Both the compound (I) and phenylcyano*iso*nitromethane (sodium derivative) are decomposed by concentrated sulphuric acid, giving a blue nitroso-compound formulated as $CN{\cdot}CPh(NO){\cdot}O{\cdot}SO_3H$, which breaks down into benzoyl cyanide and eventually into benzoic acid. The compound (II) undergoes analogous decomposition, yielding *m*-nitrophenylglyoxylic acid, m. p. 144·5—145° (lit. 77—78°). The compound (I) undergoes partial rearrangement in ethereal solution, a small percentage of bromine migrating to the *m*-position. The correlated behaviour of phenylcyano*iso*nitromethane (III), benzoyl cyanide (IV), and *m*-bromobenzoic acid (V) on nitration was also investigated quantitatively. The compound (III) gives more than 99% of *p*-nitrophenylcyano*iso*nitromethane in nitric acid (*d* 1·48); compound (IV) gives 87·6% of *m*-nitrobenzoyl cyanide and 12·4% of *o*- and *p*-nitrobenzoyl cyanides, using nitric acid of *d* 1·52; compound (V) gives 96% of *o*- and *p*-nitro-*m*-bromobenzoic acids and 4% of *m'*-nitro-*m*-bromobenzoic acid, using nitric acid of *d* 1·48. Migration of the nitro-group during oxidation of phenylcyanonitromethane is also shown to take place to the extent of 14 mol.-%. The mechanism of these various transformations is discussed. Both phenylbromocyanonitromethane, $CN{\cdot}CPh{<}\genfrac{}{}{0pt}{}{O}{N{\cdot}OBr}$, and its *m*-nitro-derivative possess a hypobromite constitution, with an oxygen bridge (cf. Willstätter and Hottenroth, A., 1904, i, 472). They react with dry ammonia with replacement of bromine by hydrogen and are quantitatively reduced by potassium iodide. Ethyl phenylbromomalonate, a true bromide, fails to give these reactions at the ordinary temperature; at 95°, however, there is equilibrium between the hypobromite and bromide forms, the latter greatly preponderating. M. CLARK.

Laws of aromatic substitution. VI. Quantitative method for the rapid determination of isomeric nitro-derivatives of laterally substituted toluenes. B. FLÜRSCHEIM and E. L. HOLMES (J.C.S., 1928, 448—453).—Isomeric nitro-derivatives of laterally substituted toluenes show almost identical resistance to destructive oxidation either by dilute permanganate solution (1 in 60) or by dilute nitric acid. The proportions of the corresponding acids obtained from mixtures of the isomerides are therefore essentially unaltered from those of the parent nitro-derivatives. For determination of these mixtures the nitro-acids may readily be separated from any benzoic or bromobenzoic acid present by reduction in dilute hydrochloric acid solution with titanous chloride. The non-amino-acids are removed by extraction with ether. The relative proportions of the residual isomeric amino-acids are then determined by prolonged exposure of the dilute hydrochloric acid solution to bromine. *o*- and *p*-Aminobenzoic acids are converted quantitatively into tribromoaniline, separation of which from the tribromo-*m*-aminobenzoic acid simultaneously formed from *m*-aminobenzoic acid is readily effected by alkaline reagents (cf. Francis and Hill, A., 1925, ii, 163). M. CLARK.

The parachor and chemical constitution. VII. Semipolar double bonds. A. FREIMAN and S. SUGDEN (J.C.S., 1928, 263—269).—Measurements have been made of the surface tension and density of *p*-toluenesulphonyl chloride, ethyl *p*-toluenesulphon-

ate, benzyl methyl sulphone, diphenyl sulphone, phenyl benzyl sulphone, chromyl chloride, sulphonal, and trional. Calculations of the parachor for the five simple sulphones, all of which are solid crystalline substances which can readily be purified, confirm the value $-1 \cdot 6$ obtained in an earlier investigation (A., 1925, ii, 936) for the effect of the semipolar double bond on the parachor. Measurements for chromyl chloride give a parachor for chromium of 54 units, assuming that the oxygen atoms in this compound are held by semipolar double bonds. This value is confirmed by calculation of the parachor for potassium dichromate from the observations of Jaeger (A., 1918, ii, 33). The parachor values for sulphonal and trional are 10—20 units lower than those predicted by theory. It is suggested that this is due to the production of a cyclic phase by the formation of singlet linkings between oxygen atoms of the SO_2 groups.

M. CLARK.

Houben's reaction. L. BERT (Compt. rend., 1928, **186**, 587—588).—The production of 1-benzyl-4-*iso*propylbenzene in the preparation of 1-propyl-4-*iso*propylbenzene from cuminyl chloride and magnesium ethyl iodide in the presence of toluene by Houben's method (A., 1903, i, 805) is attributed to the catalytic action of the magnesium halides which causes a Freidel–Crafts reaction to take place between the toluene and the cuminyl chloride. This conclusion is verified by substituting *cyclo*hexane or petroleum (b. p. 70—90°) for toluene; under these conditions the desired product (yield 50%) is obtained alone. In extending the modified reaction to the interaction of benzyl chloride with various magnesium alkyl bromides (yields 26—70%), concurrent reactions involving the production of dibenzyl, ethylene, and ethane (in the case of magnesium ethyl bromide) are noted.

G. A. C. GOUGH.

Aromatic compounds containing a *tert.*-butyl group. A. TSCHITSCHIBABIN, S. ELGASINE, and V. LENGOLD (Bull. Soc. chim., 1928, [iv], **43**, 238—242). —Bromination of *tert.*-butylbenzene in presence of a trace of iodine or iron gives mainly *p*-bromo-*tert.*-butylbenzene, b. p. 104—106°/14 mm., m. p. 10°. Hydrolysis of the reaction product of magnesium *p*-*tert.*-butylphenyl bromide and ethyl orthoformate yields p-tert.-*butylbenzaldehyde* (30—40%), b. p. 245—246° (corr.), d_4^0 0·9877, n_4^{20} 0·9733, oxidised by potassium permanganate to *p*-*tert.*-butylbenzoic acid, m. p. 164°. There is formed during the Grignard reaction some 4 : 4'-*di*-tert.-*butyldiphenyl*, b. p. 190—192°/13 mm., m. p. 128—129°. The above aldehyde condenses with acetone, forming p-tert.-*butylbenzylideneacetone*, b. p. 158—160°/11 mm., m. p. 49—50°. Magnesium *p*-*tert.*-butylphenyl bromide and magnesium β-chloroethoxy bromide give β-p-tert.-*butylphenylethyl alcohol*, b. p. 141—143°/15 mm., d_4^{15} 0·9782, d_4^{20} 0·9749, n^{17} 1·5209, R 55 1. Some of the above compounds have pungent odours.

H. BURTON.

Action of sodium–potassium alloy on certain hydrocarbons. J. B. CONANT and A. H. BLATT (J. Amer. Chem. Soc., 1928, **50**, 551—558).—*α-Phenyl-β-methyl*-n-*propyl bromide*, b. p. 116—119°/17 mm., and *α-phenyl*-n-*amyl bromide*, b. p. 120—123°/10 mm., are obtained by treating the corresponding carbinols with hydrogen bromide at 0°. From these, by treatment with magnesium and ether and subsequently with anhydrous cupric chloride and hydrolysis, *γδ-diphenyl-βε-dimethyl*-n-*hexane*, m. p. 150—150·5°, and *εζ-diphenyl*-n-*decane*, m. p. 80°, were prepared, *γδ-diphenyl-ββεε-tetramethyl*-n-*hexane*, m. p. 180—181°, being obtained analogously. These hydrocarbons and βγ-diphenyl-*n*-butane are unaffected by liquid sodium–potassium alloy. Treatment of Δ^{α}-phenylamylene with sodium–potassium and ether affords a red, metallic *derivative*, which is converted by carbon dioxide into the metallic salt of *αα'-diphenyl-ββ'-dipropyladipic acid*, m. p. 278°. ββ-Dimethylstyrene yields similarly *αα'-diphenyl-βββ'-tetramethyladipic acid*, m. p. 238—240° (decomp.), whilst treatment of the metallic derivative of the dimethylstyrene with water affords *αδ-diphenyl-ββγγ-tetramethyl*-n-*butane*, m. p. 131—132°.

F. G. WILLSON.

Supposed mechanism of polymerisations by alkali metals. K. ZIEGLER and K. BAHR (Ber., 1928, **61**, [*B*], 253—263).—The action of potassium β-phenyl*iso*propyl (Ziegler and Schnell, A., 1924, i, 851) on stilbene in the presence of ether followed by treatment of the product with dry carbon dioxide affords the two stereoisomeric forms of *αβγ-triphenyl-γ-methylvaleric acid*, m. p. 245—246° (*silver* salt) and 215—216° (*silver* salt). The primary product is therefore the compound, $CPhMe_2{\cdot}CHPh{\cdot}CHKPh$, formed simply by addition of the metallic compound to the double linking. When similarly treated, potassium β-phenyl*iso*propyl and αα-diphenylethylene give mainly *ααδ-triphenyl-γ-methylvaleric acid*, m. p. 154—156° (*silver* salt), with a little ααδδ-tetraphenyladipic acid, obtained also by the action of alkali metals on αα-diphenylethylene (cf. Schlenk, A., 1914, i, 396). Anthracene and potassium β-phenyl*iso*propyl yield 9-*phenyl*iso*propyl*-9 : 10-*dihydroanthracene*-10-*carboxylic acid*, m. p. 206—207°. With phenanthrene, addition of the potassium compound does not occur and the product of the change is the acid, $C_{30}H_{22}O_4$, m. p. 223—224° (*silver* salt), apparently identical with that obtained by Schlenk by the action of alkali metal and carbon dioxide on the hydrocarbon. The possibility of addition appears to depend on the presence of conjugated double linkings or a double linking vicinal to the benzene nucleus; thus *cyclo*hexene does not react. Polymerisation of an unsaturated organic compound, *e.g.*, butadiene, by an alkali metallic compound, *RK*, is explained by the hypothesis that the primary compound, $CH_2R{\cdot}CHK{\cdot}CH{:}CH_2$, is itself an alkali metallic compound and hence can react further with another molecule of butadiene, giving the substance $CH_2R{\cdot}CH(CH{:}CH_2){\cdot}CH_2{\cdot}CHK{\cdot}CH{:}CH_2$, and the process can continue until stopped by external agency, by process of the change in other directions, or by the increasing size of the molecule inducing extreme sluggishness in reaction. Although the additive compound from stilbene and potassium β-phenyl*iso*propyl does not further react with stilbene, it combines with styrene, giving, after treatment with carbon dioxide, *αγδε-tetraphenyl-ε-methylheptoic acid* (*silver* salt). Further, when potassium β-phenyl*iso*propyl is caused to react with increasing molecular proportions of

styrene or $\beta\gamma$-dimethylbutadiene and the products are treated with carbon dioxide the isolated acids exhibit increasing mol. wt. H. WREN.

α-Benzylnaphthalene. I. Reactions of 4-benzylnaphthalenesulphonic acid. K. DZIEWOŃSKI and S. DZIECIELEWSKI (Bull. Acad. Polonaise, 1927, *A*, 273—286).—*Sodium 4-benzylnaphthalenesulphonate* (corresponding *barium* and *lead* salts described), prepared by sulphonation of the hydrocarbon with sulphuric acid (*d* 1·84) at the ordinary temperature followed by treatment with brine, yields *4-benzylnaphthalenesulphonyl chloride*, m. p. 104—105° (corresponding *amide*, m. p. 164—165°). The constitution of this substance follows from the fact that *4-benzyl-α-naphthol*, m. p. 125—126° (*acetyl* derivative, m. p. 87—88°; *benzoyl* derivative, m. p. 103°; *methyl* derivative, m. p. 85—87°), prepared by fusion of the sodium sulphonate with potassium hydroxide at 240°, is identical with that prepared directly from α-naphthol and benzyl chloride in the presence of zinc chloride and chloroform. 4-Benzyl-α-naphthol affords *nitro-1-benzyl-4-naphthol*, m. p. 130—132°, with nitric acid (*d* 1·43) in acetic acid solution, *nitroso-4-benzyl-α-naphthol*, m. p. 170° (decomp.), with aqueous alcoholic zinc chloride and sodium nitrite, followed by decomposition of the resultant *zinc* salt with sodium hydroxide and the following arylazo-compounds on coupling with the appropriate diazotised amine: *benzeneazo-*, m. p. 191—193°; p-*nitrobenzeneazo-*, m. p. 252—253°; *α-naphthaleneazo-*, m. p. 201—203°; *β-naphthaleneazo-*, m. p. 207—208°. By heating 4-benzyl-α-naphthol at 240° with anhydrous calcium chloride saturated with ammonia, *4-benzyl-α-naphthylamine*, m. p. 114·5° (*acetyl* derivative, m. p. 208—209°), is obtained.

G. A. C. GOUGH.

Replaceability of the halogen atom in 1-chloro-2 : 4-dinitro- and -2 : 4 : 5-trinitro-naphthalenes. H. W. TALEN (Rec. trav. chim., 1928, **47**, 329—345).—The velocities of replacement of the chlorine atom by the action of sodium methoxide and ethoxide in 1-chloro-2 : 4-dinitrobenzene, 1-chloro-2 : 4-dinitronaphthalene, -2 : 4 : 6- and -2 : 4 : 5-trinitronaphthalene, and 2-chloro-1 : 6 : 8-trinitronaphthalene at 0°, 15°, and 25° have been determined. The values of the coefficients for a bimolecular reaction are constant except in the cases of 1-chloro-2 : 4 : 5-trinitronaphthalene and 1-chloro-2 : 4 : 6-trinitrobenzene, in which the value of the coefficient is initially very large and rapidly decreases, the reaction ceasing long before it is complete. It is assumed (cf. van de Vliet, A., 1924, i, 1293) that this is due to the occurrence of the concurrent reactions $RCl+NaOMe \longrightarrow ROMe+NaCl$: $ROMe+NaOMe \longrightarrow ROMe,NaOMe$ [$R=C_{10}H_4(NO_2)_3$ or $C_6H_2(NO)_3$], followed, in the latter case, by the slow reaction $ROMe,NaOMe+RCl \longrightarrow 2ROMe+NaCl$. An approximate value for this case, in which replacement is very rapid, was determined at —50°. The values of the velocity coefficient for the replacement of chlorine in 1-chloro-2 : 4-dinitrobenzene agree with those of Hollemann and Ter Weel (A., 1916, i, 22) and of Luloffs (A., 1902, i, 87), whose values must be halved, but the value obtained for k_{NaOEt} deviates from that found by Mattaar (A., 1922, ii, 275). At 0°, 15°, and 25°, the ratio k_{NaOMe}/k_{NaOEt} in this case is about 1 : 3. The chlorine atom in 1-chloro-2 : 4-dinitronaphthalene is much more reactive than in the corresponding benzene derivative, the ratio of the velocity coefficients for the two reactions at 0°, 15°, and 25° being, with sodium methoxide, 1 : 30·8, 1 : 14·0, and 1 : 13·9, and with sodium ethoxide, 1 : 24·9, 1 : 10·3, and 1 : 8·9, respectively. The chlorine in 1-chloro-2 : 4-dinitronaphthalene is thus replaced 2—3 times as rapidly with sodium ethoxide as with the methoxide, and, moreover, its mobility is of the same order of magnitude as that in 2-chloro-1 : 6 : 8-trinitronaphthalene. The introduction of another nitro-group in position 5 in the naphthalene nucleus increases the mobility of the chlorine considerably, but not to so great an extent as does the introduction of a third nitro-group in position 6 in the corresponding benzene derivative. The velocity of replacement in the latter case (1-chloro-2 : 4 : 6-trinitrobenzene) is so great that only at —50° is it of the same order of magnitude as for 1-chloro-2 : 4 : 5-trinitronaphthalene, and k^{15} for 1-chloro-2 : 4-dinitronaphthalene. The mobility of the chlorine in the chloro-di- and -tri-nitronaphthalenes investigated is thus intermediate between that in 1-chloro-2 : 4-dinitro- and -2 : 4 : 6-trinitrobenzene. The solubility of 1-chloro-2 : 4-dinitronaphthalene at 0° and 25°, is, in methyl alcohol, 0·1056 g. and 0·2378 g., and in ethyl alcohol, 0·0752 g. and 0·1780 g., in 100 c.c., respectively. J. W. BAKER.

Replacement of the halogen atom or the alkoxy-group in 1-chloro-, 1-methoxy-, or 1-ethoxy-2 : 4-dinitro- and -2 : 4 : 5-trinitronaphthalenes by various other groups. W. H. TALEN (Rec. trav. chim., 1928, **47**, 346—362).—By the action of amines and similar substances on 1-chloro-2 : 4-dinitro- and -2 : 4 : 5-trinitro-naphthalenes and on the corresponding 1-methoxy- and 1-ethoxy-derivatives a large number of α-naphthylamine derivatives have been prepared. From a review of the literature it is shown that by nitration of α-chloro- or α-bromo-naphthalenes the nitro-group first enters position 4 and subsequently positions 5 and 8, whilst in the case of α-alkoxy-derivatives the nitro-group is directed towards the 2-, 4-, and 5-positions. Thus nitration of α-naphthyl methyl ether yields 1-methoxy-2 : 4 : 5-trinitronaphthalene, m. p. 153° (Staedel, A., 1883, 861, gives 128°), identical with the product obtained by the action of sodium methoxide on the corresponding 1-chloro-compound. Similarly, nitration of α-naphthyl ethyl ether yields 1-ethoxy-2 : 4 : 5-trinitronaphthalene, m. p. 151° (Staedel, *loc. cit.*, gives 148°), identical with the product obtained from the 1-chloro-compound. The following derivatives of 2 : 4-dinitronaphthalene are obtained by heating 1-chloro- (or sometimes 1-alkoxy-)2 : 4-dinitronaphthalene with the calculated quantity of the appropriate amine in alcohol solution at 100° for several hours: α-2 : 4-dinitronaphthyl-amine, m. p. 242° (Ullmann and Bruck, A., 1909, i, 21) (*acetyl* derivative, m. p. 258—259°; $+1CH_3{\cdot}CO_2H$, m. p. 117°); *-methylamine*, m. p. 167·5° and 179—180°, the two modifications not being interconvertible and depressing each other's m. p.; -ethylamine, m. p.

172° (Meldola, J.C.S., 1906, **89**, 1435, gives 169—170°: *acetyl* derivative, m. p. 86—87°); -n-*propylamine*, m. p. 129°; -n-*butylamine*, m. p. 89°; -n-*amylamine*, m. p. 74°; -n-*heptylamine*, m. p. 58°. By similar methods are obtained 2 : 4-*dinitronaphthyl*-1-*semicarbazide*, decomp. 185—187°; and -1-*semioxamazide*, decomp. 227—228°. By nitration of 1-chloro-2 : 4-dinitronaphthalene the chief product is 1-chloro-2 : 4 : 5-trinitronaphthalene, m. p. 147—148° (Rindl, J.C.S., 1913, **103**, 1911, gives 143—144°), together with some 2 : 4 : 8-trinitro-compound. The 1-chloro- (or alkoxy-) group in the 2 : 4 : 5-trinitronaphthalene derivative is similarly replaced by amino-groups and thus are obtained α-2 : 4 : 5-*trinitronaphthyl-amine*, m. p. 310° (*acetyl* derivative, m. p. 275°); -*methylamine*, m. p. 206°; -ethylamine, m. p. 160° (Rindl, *loc. cit* gives 157—159°); -n-*propylamine*, m. p. 139°; -n-*butylamine*, m. p. 121°; -n-*amylamine*, m. p. 144—145°; -n-*heptylamine*, m. p. 99·5—100·5°; 2 : 4 : 5-*trinitronaphthyl*-1-*semicarbazide*, exploding 173°, and -1-*semioxamazide*, exploding 236°. The m. p. of the 1-*n*-alkylamino-derivatives of 2 : 4-dinitro- and 2 : 4 : 5-trinitro-naphthylamine decrease gradually with an increasing number of carbon atoms in the chain in a similar manner to that observed by Kam (A., 1926, i, 1240) in the case of the analogous derivatives obtained from 1-chloro-2 : 4-dinitrobenzene. J. W. BAKER.

Supposed stereoisomerism in the fluorene series. J. CEREZO (Anal. Fís. Quím., 1927, **25**, 567—587; cf. Wieland and Cerezo, A., 1927, 1183).—The alleged isomerism in the fluorene series is discussed and evidence put forward which demonstrates that no such isomerism is shown by 9-acetoxyfluorene, 9-aminofluorene, or 9-methylfluorenol. J. S. CARTER.

***meso*-Alkylanthracenes and "transannular tautomerism." IV.** E. DE B. BARNETT and J. W. COOK (Ber., 1928, **61**, [*B*], 314—319; cf. A., 1926, 1030; 1927, 140; this vol., 52).—1 : 5-Dichloroanthrone is converted by methyl iodide and potassium hydroxide at 100° into a mixture of approximately equal amounts of 1 : 5-dichloro-9-methoxyanthracene, m. p. 105°, and 1 : 5-*dichloro*-9-*methylanthrone*, m. p. 184°. The presence of the methyl group in the *meso*-position in the latter compound appears to hinder conversion into the enolic form, since 1 : 5-dichloro-9-methylanthrone cannot be etherified by treatment with potassium hydroxide and methyl toluene-*p*-sulphonate and only slowly yields an *acetate* with boiling acetic anhydride and pyridine. By treatment with the requisite Grignard reagent, 1 : 5-dichloro-9-methylanthrone is converted into the following substances: 1 : 5 - *dichloro*-9-*methyl* - 10 - *methylene*-9 : 10-*dihydroanthracene*, m. p. 143°; 1 : 5-*dichloro*-9-*methyl* - 10 - *ethylidene* - 9 : 10 - *dihydroanthracene*, m. p. 153°; 1 : 5-*dichloro*-9-*methyl*-10-iso*propylidene*-9 : 10-*dihydroanthracene*, m. p. 134°; 1 : 5-*dichloro* - 9 - *methyl* - 10 - *benzylidene*-9 : 10-*dihydroanthracene*, m. p. 165°. 1 : 5-*Dichloro*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthran*-10-*ol*, m. p. 144°, is converted by treatment with acetic acid containing hydrochloric acid at 100° into 1 : 5-*dichloro*-10-*phenyl*-9-*methylanthracene*, m. p. 104°. Further treatment of the latter compound with the same reagent produces 1 : 5-dichloro-10-phenyl-9-methylene-9 : 10-dihydroanthracene, m. p. 151°, thus placing beyond doubt the possibility of "transannular tautomerism." The constitution of the methylene derivative is established by its almost quantitative oxidation to 1 : 5-dichloro-9-phenylanthrone and conversion into 1 : 5-*dichloro*-9 : 10-*dibromo*-10-*phenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 122°. H. WREN.

9-Iodophenanthrene. J. SALKIND and F. LUBINSKAJA (Ber., 1928, **61**, [*B*], 269—271).—9-*Iodophenanthrene*, m. p. 87° (*picrate*, m. p. 137°), is prepared by the action of iodine on magnesium phenanthryl bromide in the presence of ether. It is oxidised to phenanthraquinone by chromic acid in glacial acetic acid. H. WREN.

Chlorination of anilides. II. Decomposition of *N*-chloroacetanilide by heat. A. E. BRADFIELD (J.C.S., 1928, 351—352).—In order to show that, contrary to the statement of Porter and Wilbur (A., 1927, 1041), the re-arrangement of fused *N*-chloroacetanilide at 100° is a two-stage process involving the intermediate production of chlorine, the reaction has been carried out with pure material in an open vessel in an air-bath, and in a sealed tube in boiling water. From the products 7·0% and 4%, respectively, of 2 : 4-dichloroacetanilide were isolated, in addition to *p*-chloro-, 41·0%, 50·7%; *o*-chloro-, 18·2%, 16·5%, and acetanilide, 6·3%, 0·0%. H. E. F. NOTTON.

[Preparation of] benzanilide. C. N. WEBB (Org. Syntheses, 1927, **7**, 6—7).

Interaction of sulphur and *p*-toluidine in presence of litharge: thio-*p*-toluidine and related compounds. M. T. BOGERT and L. SMIDTH (J. Amer. Chem. Soc., 1928, **50**, 428—436; cf. A., 1924, i, 166).—Separation of the products of the reaction between *p*-toluidine, sulphur, and litharge at 140° is conveniently effected by dissolution in 10% hydrochloric or sulphuric acid, followed by dilution to precipitate weakly basic resins, and fractional precipitation with ammonia solution. Purification of the products is effected by repeating this process. In this way 535 g. of *p*-toluidine afforded 70 g. of resins, 80 g. (17%) of dithio-*p*-toluidine, and 121 g. (26%) of monothio-*p*-toluidine, 167 g. of *p*-toluidine being recovered. Only small amounts of impure dithio-*p*-toluidine could be obtained by Hodgson's process (B.P. 15,466 of 1911). When heated at 205—210°, thio-*p*-toluidine evolves ammonia, hydrogen sulphide, and *p*-toluidine, leaving a brown, amorphous residue. Thio-*p*-toluidine yields only a small amount of *p*-toluidine when heated with concentrated hydrochloric acid or 25% sulphuric acid for 6 hrs. at 200°, and remains undecomposed when fused with sulphur. It is only slowly decomposed, with formation of basic tars, when heated with sulphur and litharge at 140—150°. Thio-*p*-toluidine could not be coupled with diazotised sulphanilic acid. Oxidation of the diacetyl derivative to the corresponding sulphone is conveniently effected by treatment with concentrated nitric and sulphuric acids (75 : 30) at the ordinary temperature. Treatment of thio-*p*-toluidine with acetic anhydride, glacial acetic acid, and hydrogen peroxide affords *bis*-2-*acetamido*-5-*methylphenylsulph*-

oxide, m. p. 212°. *Bis-2-chloro-5-methylphenylsulphone*, brown, amorphous, decomp. above 95°, is obtained by heating diazotised thio-*p*-toluidine with hydrochloric acid and copper powder, with subsequent oxidation with nitric and sulphuric acids; replacement of the copper powder in this process by potassium iodide affords analogously *bis-2-iodo-5-methylphenylsulphone*, pale brown, amorphous, decomp. about 82°. When diazotised thio-*p*-toluidine is kept over-night in excess of concentrated hydrochloric acid, and the solution then boiled, *2-chloro-5 : 5'-dimethyldiphenylsulphide-2 : 2'-oxide*, b. p. 265°/80 mm., is obtained. *2-Bromo-5 : 5'-dimethyldiphenylsulphone*, brown, amorphous, decomp. 69—72°, is obtained by diazotising thio-*p*-toluidine in aqueous sulphuric acid, with subsequent treatment with potassium bromide and copper powder, and oxidation as above. Thio-*p*-toluidine is not obtained when dithio-*p*-toluidine is heated with *p*-toluidine and litharge, or with sulphur and litharge, at 140—165° (cf. Hodgson, A., 1924, i, 1188). Diazotised and coupled with H-acid, dithio-*p*-toluidine yields a *dye* producing purplish shades on wool. *Dithio-*p*-toluidine picrate*, yellow, was prepared. Reduction of dithio-*p*-toluidine affords *2-amino-5-methylphenyl mercaptan* (*zinc* salt). F. G. WILLSON.

Condensation of ethyl cyanoacetate with some aryl- and alkyl-amines. Preparation of some aryl- and alkyl-substituted cyanoacetamides. K. G. NAIK and Y. N. BHAT (J. Indian Chem. Soc., 1927, **4**, 547—551).—The following new compounds are described: *cyanoaceto-*o*-toluidide*, m. p. 125°; *cyanoaceto-*m*-toluidide*, m. p. 132°; *cyanoaceto-α-naphthylamide*, m. p. 175°; *cyanoaceto-β-naphthylamide*, m. p. 174°; *cyanoaceto-*vic*-m-xylidide*, m. p. 107°; *cyanoacetomethylamide*, m. p. 101°; *cyanoacetoethylamide*, m. p. 74°. C. D. LANGFORD.

Properties of 2 : 5- and 2 : 8-naphthylamine-sulphonic acids. H. I. WATERMAN and J. GROOT (Chem. Weekblad, 1928, **25**, 40—42).—The four possible sulphonated β-naphthylamines having one sulphonic acid radical in the nucleus not containing the amino-group have been prepared in the pure condition. The solubilities in water at 20° are: 2 : 8- and 2 : 5-acids, as anhydrous, 1 part in 1680 and 3025 parts, respectively; 2 : 7- and 2 : 6-acids, as monohydrates, 1 in 5040 and 7790, respectively. The solubility products of the 2 : 5- and 2 : 8-acids are calculated from these data and from the dissociation constants recorded by Ebersbach (cf. A., 1893, ii, 450) as $1·08\times10^{-7}$ and $2·63\times10^{-7}$, respectively. These values are in accordance with the fact that the 2 : 5-acid separates first when an equimolecular mixture of the sodium salts of the two acids in solution is acidified; the solubility products calculated from the solubilities given by Forsling (A., 1887, 962) and the work of Levi (cf. B., 1921, 503A) indicate erroneously that the 2 : 8-acid separates first. S. I. LEVY.

Manufacture of anthracene derivatives [alkylaminoanthracenes] and of benzanthrene. I. G. FARBENIND. A.-G.—See B., 1928, 151.

Manufacture of aromatic oxamic acid halides. I. G. FARBENIND. A.-G.—See B., 1928, 151.

Transformation of diazoaminobenzene into aminoazobenzene. E. ROSENHAUER and H. UNGER (Ber., 1928, **61**, [*B*], 392—398).—Evidence in favour of the view that the conversion of diazoaminobenzene into aminoazobenzene is due to primary fission into diazonium salt and aniline followed by nuclear coupling and not to isomerisation is found in the following observations. Dimethylaminoazobenzene is obtained from diazoaminobenzene, dimethylaniline, and dimethylaniline hydrochloride. The conversion of diazoaminobenzene into aminoazobenzene is effected by glacial acetic acid, dilute aqueous acetic acid, or formic acid in satisfactory yield. Quinoline and its hydrochloride may replace aniline and aniline hydrochloride under the conditions usually employed, but reaction then occurs much more slowly. The weak point in the explanation appears to be in the assumption of nuclear coupling. This reaction is, however, general. Thus benzenediazonium chloride and aniline hydrochloride at 0° afford aminoazobenzene hydrochloride without intermediate formation of diazoaminobenzene. Further, crude diazoaminobenzene, obtained from diazotised aniline and aniline in aqueous solution containing acetic acid, sodium carbonate, or sodium hydroxide, invariably contains about 2% of aminoazobenzene, the proportion of which increases with rise of temperature. Coupling of diazotised aniline with aniline in neutral, feebly basic, or weakly acidic solution consists of two independent changes leading respectively to diazoaminobenzene and aminoazobenzene. Increasing acidity favours the production of the latter compound, which becomes exclusive at a certain degree of acidity. Beyond this point coupling does not occur. The yields of aminoazobenzene are better when aniline hydrochloride and aniline are used than when aqueous or alcoholic solutions are employed owing to the stabilising action on the diazonium salt of the aniline and its large excess. About 70% of aminoazobenzene can be obtained in acetic acid solution if 3—4 mols. of aniline are added.

The volatility of diazoaminobenzene with steam is incidentally recorded. H. WREN.

Sulphonation of phenolic ethers by means of aminosulphonic acid. A. QUILICO (Atti R. Accad. Lincei, 1927, [vi], **6**, 512—517).—Like anisole (cf. Hofmann and Biesalski, A., 1912, i, 444), both phenetole and phenyl ether are converted by the action of aminosulphonic acid into the ammonium salts of the corresponding *p*-sulphonic acids. Probably the first product of the reaction is an additive compound with the hydroxyl group of the aminosulphonic acid in the 1-position and the $NH_2·SO_2·$ in the 2-position, this then giving the ammonium salt of the *o*-sulphonic acid, which undergoes isomerisation into the salt of the *p*-acid. *Ammonium phenoxybenzene-*p*-sulphonate*, $OPh·C_6H_4·SO_3·NH_4$, the *barium* ($+H_2O$), *sodium*, and *potassium* salts, the free *acid*, m. p. 80°, the *sulphonyl chloride*, and the *sulphonamide*, m. p. 125° (? 88°), are described. T. H. POPE.

Fries' transformation. K. VON AUWERS [with W. MAUSS] (Ber., 1928, **61**, [*B*], 416—421; cf. A., 1926, 608).—The observation that *p*-chloroacetylphenol is not produced by the action of aluminium

chloride at 130—140° on a mixture of phenyl acetate and *p*-tolyl chloroacetate, whereas it is relatively freely produced from phenyl chloroacetate under precisely similar conditions, is strong evidence against Skraup's conception of the course of the Fries transformation (cf. A., 1925, i, 143; 1927, 659). Attempts to prepare the *o*-ββ-dimethylacrylylphenol, m. p. 88°, of Skraup and Beng (A., 1927, 560) were unsuccessful.

Phenyl *iso*valerate is converted by aluminium chloride at 130—140° into a mixture of *o*-iso*valerylphenol*, b. p. 138—140°/20 mm. (p-*nitrophenylhydrazone*, m. p. 121—122°; *methyl ether*, b. p. 142—144°/12 mm.; *acetate*, b. p. 164—166°/20 mm.), and *p-iso*-valerylphenol, m. p. 95·5—96·5°. Phenyl ββ-dimethylacrylate and aluminium chloride at 130—140° afford 7-*hydroxy*-3 : 3-*dimethylhydrindone* b. p. 138—142°/16 mm., d_4^{20} 1·098, n_e^{20} 1·5519 (*semicarbazone*, m. p. 261—263°). *o*-Dimethylacroyl-*p*-cresol is converted by protracted boiling with acetic anhydride into the corresponding *acetate*, m. p. 63—64°; the ketone is transformed by zinc chloride at 140° into 2 : 2 : 6-trimethylchromanone, identified as the *p*-nitrophenylhydrazone, m. p. 199—200°.

H. WREN.

Nitrosation of phenols. V. An *o*-nitrosophenol. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1928, 329—332).—5 - Chloro - 3 - hydroxyanisole is readily nitrosated to dark green 5-*chloro*-4-*nitroso*-3-*hydroxyanisole*, m. p. 132°, and nitrated to 5-*chloro*-4-*nitro*-3-*hydroxyanisole* (I), m. p. 105°, which is also formed by oxidising the nitroso-derivative with alkaline ferricyanide. 3 : 5-Dichloro-2-nitroanisole and 3 : 5-dichloro-4-nitroanisole yield with sodium methoxide 5-*chloro*-2-*nitroresorcinol dimethyl ether*, m. p. 171°, and 5-*chloro*-4-*nitroresorcinol dimethyl ether*, m. p. 123°, respectively. The constitution of (I) follows from its conversion by methyl sulphate and potassium carbonate into the latter ether. Oily 5-*chloro*-3-*methoxydimethylaniline*, prepared by heating 5-chloro-3-methoxyaniline with methyl sulphate and methyl alcohol at 165°, is nitrosated to green 5-*chloro*-4-*nitroso*-3-*methoxydimethylaniline*, decomp. 155° (*hydrochloride*), which forms methylamine and products of profound decomposition when boiled with 10% potassium hydroxide.

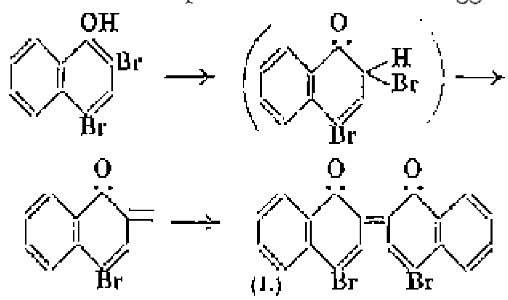
H. E. F. NOTTON.

Colour reactions of phenacetin. L. EKKERT (Pharm. Zentr., 1928, 69, 98—100).—A series of colour changes, obtained when phenacetin is warmed with resorcinol and sulphuric acid, and the mixture cooled, diluted, and treated with alkalis, with subsequent extraction, is described. S. I. LEVY.

[Preparation of] 3 : 5-dinitroanisole. F. REVERDIN (Org. Syntheses, 1927, 7, 28—29).

Action of niobium and tantalum pentachlorides on organic compounds. H. FUNK and K. NIEDERLANDER (Ber., 1928, 61, [*B*], 249—253; cf. Lindner and Feit, A., 1924, ii, 320).—Phenol is converted by niobium pentachloride in carbon disulphide solution and in absence of atmospheric moisture into the *compound* $Nb(OPh)_4Cl$, m. p. 233—235°; the analogous *substance* $Ta(OPh)_4Cl$, m. p. 240°, is described. β-Naphthol affords the *compounds* $Nb(O{\cdot}C_{10}H_7)_3Cl_2$, m. p. 215° (apparent decomp.), $Ta(O{\cdot}C_{10}H_7)_3Cl_2$, m. p. 210° (decomp.), and $Ta(O{\cdot}C_{10}H_7)_5$, m. p. 180°, if the action is very prolonged. From anthranol, the *products* $Nb(O{\cdot}C_{14}H_9)_2Cl_3$ and $Ta(O{\cdot}C_{14}H_9)_2Cl_3$ are derived. Careful regulation of the reaction between anthranol and tantalum pentachloride permits the isolation of the unstable, primary *adduct*, $C_{10}H_{14}O,TaCl_5$, and the intermediate *product*, $Ta(O{\cdot}C_{14}H_9)Cl_4$. The assumption that the metal in these compounds is united to oxygen is supported by their properties, analogies with known compounds such as those of zinc, and the established strong affinity of the metals for oxygen. H. WREN.

Formation of indigoid compounds from halogenated naphthols. R. WILLSTATTER and L. SCHULER (Ber., 1928, 61, [*B*], 362—372).—Halogenated α-naphthols readily pass into indigotin-like compounds owing to loss of hydrogen halide; for 2 : 4-dibromo-α-naphthol the scheme is suggested:

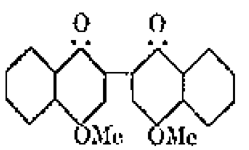


2 : 4-Dibromo-α-naphthol dissolves readily in solutions of alkali hydroxides or carbonates and an indigo-blue precipitate rapidly separates. Atmospheric oxygen takes no part in the change, but the product absorbs oxygen; it is decomposed by an excess of alkali, so that its formation is not observed in concentrated solution. It is also produced when solutions of 2 : 4-dibromo-α-naphthol in acetone, ether, or benzene are poured on to aqueous solutions of sodium carbonate or hydroxide, by contact of alcoholic solutions of the naphthol with metallic copper, and, most satisfactorily, by preserving the naphthol in cold pyridine. The *dye* does not appear to be quite homogeneous, but analyses indicate the composition $C_{20}H_{10}O_2Br_2$ (cf. I). Determinations of mol. wt. are untrustworthy, since the compound is unstable in solution. When suspended in ether and reduced with zinc dust and a little glacial acetic acid it gives *dibromo-α-dinaphthol* (constitution not decided), m. p. 219° (decomp.) (corresponding *diacetate*, $C_{24}H_{18}O_4Br_2$, m. p. 239°; *dimethyl ether*, $C_{22}H_{16}O_2Br_2$, m. p. 225—226°). α-Dinaphthol, obtained from α-naphthol and ferric chloride, is converted by bromine in glacial acetic acid solution into a *tribromo*-compound, transformed by boiling acetic acid into the dibromo-α-dinaphthol, m. p. 219—220° (decomp.). 2 : 4-Dichloro-α-naphthol is converted by alkali carbonate or hydroxide but not by pyridine into an analogous *dye*, $C_{20}H_{10}O_2Cl_2$.

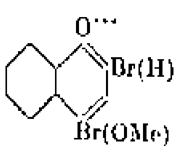
1 : 5-Dihydroxynaphthalene, in cold glacial acetic acid, is converted by chlorine into 4 : 8-*dichloro*-1 : 5-*diacetoxynaphthalene*, m. p. 154° (corr., decomp.), hydrolysed to 4 : 8-*dichloro*-1 : 5-*dihydroxynaphthalene*, m. p. 189—190° (corr.). The main product of

the action of a small excess of bromine on 1 : 5-dihydroxynaphthalene under similar conditions is the *monoacetate* of 4 : 8-dibromo-1 : 5-dihydroxynaphthalene, m. p. 165·5° (corr.), from which the *diacetate*, m. p. 131°, is obtained by pyridine and acetic anhydride. 4 : 8-*Dibromo*-1 : 5-*dihydroxynaphthalene* has m. p. 147·5° (decomp.). 4-*Bromo*-1 : 5-*dihydroxynaphthalene*, m. p. 116°, and its *diacetate*, m. p. 138°, are described. The colour reactions of certain halogenated naphthols are described in detail. 2-*Chloro*-4-*bromo*-α-*naphthol*, m. p. 112°, prepared by bromination of 2-chloro-α-naphthol, yields a blue dye with alkali hydroxide or carbonate with loss of hydrogen chloride and bromide. 4-*Chloro*-2-*bromo*-α-*naphthol*, m. p. 96°, behaves similarly to 2 : 4-dibromo-α-naphthol, but loses a little hydrogen chloride and mainly hydrogen bromide. 2-*Bromo*-1 : 4-*dihydroxynaphthalene*, m. p. 113—114°, is prepared by reduction of 2-bromo-α-naphthaquinone. H. Wren.

***oo*′-Diquinones of the naphthalene series.** S. Goldschmidt and H. Wessbecher (Ber., 1928, **61**, [*B*], 372—377).—4-Methoxy-α-naphthol dissolved in boiling benzene is readily oxidised by lead dioxide to a blue compound, m. p. 258°, for which Russig has established the formula $C_{22}H_{16}O_4$. Reduction of the product with zinc dust and glacial acetic acid in the presence of benzene affords the *leuco-compound*, $C_{22}H_{18}O_4$, m. p. 205° in an atmosphere of carbon dioxide (corresponding *diacetate*, m. p. 180°; mol. wt. 440 in boiling chloroform), readily reconverted by air into the dye, for which the quinonoid structure is thus established. Distillation of the dye with zinc dust yields two *hydrocarbons*, m. p. 257° and 175°, respectively (*picrate* of latter, m. p. 145°), which do not correspond with any of the expected products. Oxidation of the dye with nitric acid affords 2 : 2′-di-α-naphthaquinonyl, identical with the product obtained by Meldola and Hughes (J.C.S., 1890, **57**, 393, 631, 808) from 2 : 4-dibromo-α-naphthol, thus establishing the constitution (I). It is probable that the very unstable, violet-blue solutions obtained by the oxidation of α-naphthol contain *oo*′-dinaphthaquinone. Similarly, the substance obtained by the oxidation of 2 : 4-dibromo-α-naphthol by air in alkaline solution or by lead dioxide in benzene is probably constituted analogously to (I) (Br instead of OMe), since the change occurs with loss of bromine and the compound is oxidised to the product obtained by Meldola and Hughes. Reduction of it gives a leuco-compound and not the original material, and the amount of hydrazobenzene required to decolorise the violet solution is approximately that required theoretically. 4-Bromo-α-naphthol also appears to yield the same quinone. Production of *oo*′-dinaphthaquinones appears to be preceded by dehydrogenation of the naphthol to the radical (II) followed by rapid polymerisation to the bimolecular product (III). The very ready elimination of the bromine atom in position 2 can be explained only on the assumption that it is not aromatically combined during the change. It cannot be removed by powerful reducing agents from 2 : 4-dibromo-α-naphthol itself. H. Wren.



(I.)



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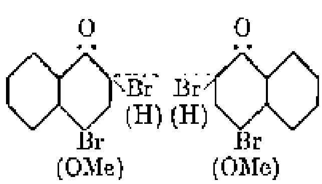


(III.)

Action of bromine on naphtholsulphonic acids. A remarkable colour reaction in solution. G. Heller [with W. Eisenschmidt, G. Reichardt, and H. Wild] (Z. angew. Chem., 1928, **41**, 171—177).—On treatment with 2 mols. of bromine in cold acetic acid solution naphthasultone gives 4-*bromonaphthasultone*, m. p. 199°; sodium naphthasultone-4-sulphonate and sodium 1-naphthol-4 : 8-disulphonate afford the same product when bromine in acetic acid is added to their aqueous solutions acidified with sulphuric acid. When treated with alkali in saturated solution in presence of excess of solid, undissolved crystals of *sodium* 2 : 4-*dibromo*-1-*naphthol*-8-*sulphonate* (obtained by brominating sodium 1-naphthol-8-sulphonate in a freezing mixture) develop a reddish-blue colour which diffuses through the solution and after some minutes fades to olive-brown. The coloration is due to the formation of the *quinhydrone* of 2-*bromo*-1 : 4-*naphthaquinone*-8-*sulphonic acid* (*sodium* salt, reddish-brown crystals with green reflex), the latter being also produced by the addition of potassium ferricyanide to the filtered solution of the dibromonaphtholsulphonate, and when the solution of sodium 1-naphthol-8-sulphonate is only cooled with ice for bromination. 1-Naphthol-2 : 4 : 8-trisulphonic acid affords the same quinhydrone. With excess of bromine (4 mols.) sodium 1-naphthol-8-sulphonate, -2 : 4 : 8-trisulphonate, and -3 : 8-disulphonate all afford *sodium* 2 : 3-*dibromo*-α-*naphthaquinone*-8-*sulphonate*, yellow, which is readily reduced to a colourless quinol, and with *p*-toluidine in alcohol yields 3-*bromo*-2-p-*toluidino*-α-*naphthaquinone*-4-p-*methylanil*-8-*sulphonic acid*, carmine-red, anthranilic acid giving an analogous *derivative*. With 1 mol. of bromine, sodium 1-naphthol-3 : 8-disulphonate gives *sodium* 4-*bromo*-1-*naphthol*-3 : 8-*disulphonate*, which couples with diazotised *p*-toluidine to give 4-*bromo*-2-p-*tolueneazo*-1-*naphthol*-3 : 8-*disulphonate*, and on treatment with a further mol. of bromine affords *sodium* 2-*bromo*-α-*naphthaquinone*-3 : 8-*disulphonate*, red needles, and traces of *sodium* 3 : 4-*dibromo*-1-*naphthol*-8-*sulphonate*, which forms no quinone. Bromination of sodium 1-naphthol-3 : 6-disulphonate gives the readily soluble *sodium* 2-*bromo*-α-*naphthaquinone*-3 : 6-*disulphonate*, yellow, which could not be obtained pure. Treatment of zinc 1-naphthol-4-sulphonate with 1 mol. of bromine affords 2-bromo-1-naphthol-4-sulphonic acid (*potassium* salt), the constitution of which follows from its inactivity towards alcoholic *p*-toluidine and diazonium salts. With a further mol. of bromine this potassium salt gives *potassium* 2 : 3-*dibromo*-1-*naphthol*-4-*sulphonate*. With 4 mols. of bromine zinc 1-naphthol-4-sulphonate gives 2-bromo-1 : 4-naphtha-

quinone, m. p. 127·5—128° (Zincke and Schmidt, A., 1895, i, 56), together with a little 2 : 3-dibromonaphthaquinone, m. p. 216—217°.

4-Bromonaphthasultone is converted by 10% sodium hydroxide into *sodium* 4-*bromo*-1-*naphthol*-8-*sulphonate*, which with 3 mols. of bromine gives sodium 2 : 3-dibromo-α-naphthaquinone-8-sulphonate, and with diazotised *p*-toluidine, *sodium* 4-*bromo*-2-p-*tolueneazo*-1-*naphthol*-8-*sulphonate*, analysis indicating displacement of bromine and coupling in the 4-position to a slight extent. *Sodium* 1-*naphthol*-2-p-*tolueneazo*-8-*sulphonate* is described.

Sodium 2-naphthol-6-sulphonate yields *sodium* 1-*bromo*-2-*naphthol*-6-*sulphonate* and a *dibromo*-2-*naphthol*-6-*sulphonate*. 2-Naphthol-3 : 6-disulphonic acid similarly affords mono- and di-bromo-derivatives, and 2-naphthol-6 : 8-disulphonic acid an easily soluble *sodium tribromo*-2-*naphtholsulphonate*. Sodium 2-naphthol-3 : 6 : 7-trisulphonate with 1 mol. of bromine gives *sodium* 1-*bromo*-2-*naphthol*-3 : 6 : 7-*trisulphonate* (sparingly soluble p-*toluidine* salt; does not couple with diazonium salts). In no case was quinone formation observed in the bromination of β-naphtholsulphonic acids. The quinone formation observed by Armstrong and Graham (J.C.S., 1881, **39**, 137) was probably due to the presence of α-naphthol in their β-naphthol. R. BRIGHTMAN.

***iso*Eugenol.** SCHIMMEL & Co. (Bericht, 1927, 138; Chem. Zentr., 1927, ii, 1472).—*iso*Eugenol was obtained in large crystals, m. p. 32°, stable at the ordinary temperature in absence of air. Structural isomerism is presumed. A. A. ELDRIDGE.

Molecular rearrangement in the *cyclo*heptane series. M. GODCHOT and (MLLE.) CAUQUIL (Compt. rend., 1928, **186**. 375—377).—Monochlorocarbamide reacts with *cyclo*heptene (cf. Detœuf, A., 1922, i, 236, 327) to form 2-*chlorocyclo*heptanol, b. p. 98°/16 mm., d^{19} 1·1351, n^{19}_{D} 1·4948, which when treated with magnesium methyl iodide (A., 1926, 164) yields *cyclo*hexylmethylcarbinol, b. p. 189·5° (corr.), together with a small amount of ethylidene*cyclo*hexane (nitrosate, m. p. 140°; nitrosochloride, m. p. 130°; *nitrosopiperidide*, m. p. 108—109°). A mechanism explaining the formation of a six- from a seven-membered ring is postulated. H. BURTON.

Colour reactions of cholesterol. L. EKKERT (Pharm. Zentr., 1928, **69**, 97—98).—The colorations obtained by treating alcoholic solutions of cholesterol with an alcoholic solution of an aldehyde and shaking with sulphuric acid are described. Using 0·1 mg. of cholesterol in 2 c.c. of alcohol, 2 drops of a 1% solution of furfuraldehyde in alcohol, and 2 c.c. of sulphuric acid, the alcohol layer becomes blue, and the acid layer rose. S. I. LEVY.

Sterol group. II. Formation of ψ-cholestene and cholestenone in the dry distillation of cholesterol. I. M. HEILBRON and W. A. SEXTON (J.C.S., 1928, 347—351).—Distillation of cholesterol in a carbon dioxide atmosphere at the ordinary pressure yields principally cholestenone and ψ-cholestene, with water, hydrogen, and a complex mixture of low-boiling hydrocarbons (cf. Diels and Linn, A., 1908, i, 164; Fischer, A., 1926, 399; Fantl and Kabos, A., 1927, 53; Windaus, A., 1927, 557). It is concluded that cholestenone and cholesterilene are the primary products, the hydrogen evolved in the formation of the former reducing the latter to ψ-cholestene. H. E. F. NOTTON.

Allophanates of certain sterols. U. TANGE and E. V. McCOLLUM (J. Biol. Chem., 1928, **76**, 445—456).—*Allophanates* of the following sterols were prepared by passing cyanic acid vapour into the cold benzene solution of the sterol; cholesterol, m. p. 235—236°, *iso*cholesterol, dihydrocholesterol, m. p. 255—256°, sitosterol, m. p. 246—247°, coprosterol, m. p. 210—211°; the esters, except that of *iso*cholesterol, are sparingly soluble in fat-solvents; they are very stable towards mineral acids but are fairly readily hydrolysed by alcoholic potassium hydroxide. C. R. HARINGTON.

Action of Grignard reagent on amino-acids. XIV. Decomposition of amino-alcohols by alkalis. F. BETTZIECHE (Z. physiol. Chem., 1928, **172**, 69—71).—The decomposition of amino-alcohols into ketone and amine by heating with alkali (cf. A., 1926, 154) has been investigated more fully. The small amount of ammonia formed under the influence of alkali at high temperatures is due to the side-reaction, $R{\cdot}CH(NH_2){\cdot}CR'_2{\cdot}OH \longrightarrow R{\cdot}CO{\cdot}CHR'_2+NH_3$, which accompanies the main reaction, $R{\cdot}CH(NH_2){\cdot}CR'_2{\cdot}OH \longrightarrow R{\cdot}CH_2{\cdot}NH_2+CO{\cdot}R'_2$. Thus two ketones, ammonia, and an amine are formed. No significant amount of ammonia is produced when the decomposition is effected by water at high temperatures and for this side-reaction alkali is necessary. The amounts of amine ammonia, ammonia, and the different ketones formed from various aminols with sodium hydroxide are given, and a general relationship is found between the relative amounts of ammonia and amine formed and the decomposition effected by heating with mineral acids. Amino-alcohols which are stable towards mineral acids give little or no ammonia, with the exception of "glycinephenylaminol" which is readily decomposed by acid but gives very little ammonia by decomposition with alkali. A. WORMALL.

***p*-Tolyl triphenylmethyl ether and its reaction with zinc chloride.** J. VAN ALPHEN (Ber., 1926, **61**, [*B*], 276—277).—Repetition of the author's experiments (A., 1927, 660) has confirmed the production of *p*-tolyl triphenylmethyl ether, m. p. 81°, by the action of *p*-cresol on triphenylmethyl chloride in pyridine (contrast Schorigin, this vol., 59). Probably the ether is trimorphous, giving forms of m. p. 81°, 95°, and 114°, respectively. The formation of triphenylmethane in addition to triphenylcarbinol by the action of zinc chloride on the ether has been overlooked by Schorigin. H. WREN.

Catalytic hydrogenation under pressure of *p*-hydroxytriphenylcarbinol and *p*-hydroxydiphenylmethane. V. IPATIEV and B. DOLGOV (Bull. Soc. chim., 1928, [iv], **43**. 242—248).—See this vol., 169.

Action of Grignard reagent on amino-acids. XIII. Phenylserine derivatives. F. BETTZIECHE and R. MEYER (Z. physiol. Chem., 1928, **172**, 64—

68; cf. A., 1927, 137).—By the action of magnesium phenyl bromide on phenylserine ester hydrochloride, *β-amino-ααγ-triphenylpropane-αγ-diol*, m. p. 154—155°, is obtained in 40% yield (N-*benzoyl* derivative, m. p. 174·5°). Magnesium benzyl bromide and phenylserine ester hydrochloride yield *β-amino-γ-phenyl-αα-dibenzylpropane-αγ-diol*, m. p. 126·5° (yield 13%; *hydrochloride*, difficult to obtain pure, m. p. of crude product, 115°). These aminols are not decomposed to any appreciable extent by heating with 12% hydrochloric acid or 20% sodium hydroxide.

A. WORMALL.

Permanganate oxidation in alkaline media. R. CORNUBERT and H. LE BIHAN (Bull. Soc. chim., 1928, [iv], **43**, 248—255; cf. A., 1921, i, 422).—Oxidation of 2-methyl-2-allyl*cyclo*hexanone with potassium permanganate in presence of sodium or potassium hydroxide, or sodium hydroxide and calcium oxide, yields in each case a glycol, m. p. 103° (corr.), together with an oil, probably a mixture of isomeric glycols (cf. A., 1927, 1075). The solid glycol when heated for 1 hr. in a vacuum yields the corresponding ethylene oxide, also formed in small quantity during the oxidation, which exists in a monomeric form, b. p. 110°/32 mm., and also in various polymeric forms. Dilute sodium hydroxide solution has practically no action on the monomeric oxide, and it is concluded that this compound is not an intermediate in the production of the glycol.

H. BURTON.

Union of benzoylacetonitrile with organic bases in presence of salicylaldehyde. II. P. KRISHNAMURTI (J.C.S., 1928, 415—417).—In presence of traces of salicylaldehyde and piperidine, benzoylacetonitrile combines (yield 40%, 20%, and 50%, respectively, of the theoretical) with aniline, *m*-4-xylidine, and *p*-, but not *o*- or *m*-toluidine. These compounds, unlike the corresponding piperidine derivative (A., 1927, 766), easily afford dibenzoyl derivatives, and their oximino-derivatives are decomposed by benzoylation, yielding the benzoyl derivative of the amine. The p-*toluidine* compound, $C_{16}H_{16}ON_2$, m. p. 182° (*hydrochloride*, m. p. 194—195°; *dibenzoyl* derivative, m. p. 166°), gives an orange *oximino*-derivative, m. p. 158° (*silver* salt). The *aniline* compound, $C_{15}H_{14}ON_2$, has m. p. 163° (*hydrochloride*, m. p. 94—96°; *dibenzoyl* derivative, m. p. 168°; red *oximino*-derivative, m. p. 182°), and the m-4-*xylidine* compound, $C_{17}H_{18}ON_2$, m. p. 145—146° (*benzoyl* derivative, m. p. 153°; *oximino*-derivative, m. p. 150—151°).

H. E. F. NOTTON.

Condensation of nitriles with thioamides. VI. Action of sulphur acid chlorides on thioamides. VII. Toluonitrile with thiotoluamide, naphthonitrile with thionaphthamide, and others. S. ISHIKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 237—248, 277—292; cf. A., 1925, 917, 1149).—VI. Thionyl chloride or sulphur monochloride reacts with thiobenzamide to give benziminoisothiobenzamide, 2 : 5-diphenyl-1 : 3 : 4-thiodiazole (dibenzenylsulphime), and sulphur; and with thioacetamide to yield acetamide and sulphur. Thionyl chloride reacts with thiobenzanilide to yield dibenzanilide sulphide, m. p. 111°, and aniline; with thioacetanilide to yield acetanilide, aniline, and sulphur. Sulphur monochloride reacts with α-benznaphthalide to yield dibenznaphthalide sulphide and α-benznaphthalide; with thiobenzanilide to yield benzanilide, sulphur, and dibenzanilide sulphide. The properties of the last-named compound uphold the formula ascribed by Rivier and Schneider (A., 1920, i, 229); it is very stable towards alkalis, and easily hydrolysed by acids to thiobenzanilide and benzanilide. Treatment with mercuric oxide yields only benzanilide, whilst it is easily reduced by sodium amalgam and alcohol to phenylbenzylamine. It is suggested that an ester of thiosulphuric acid is the unstable intermediate through which it is formed. Benzenesulphonyl chloride reacts with thiobenzamide to afford 1 : 5-diphenyl-1 : 3 : 4-thiodiazole, sulphur, and a red condensation compound; with thiobenzanilide to form dibenzanilide sulphide; with sodium thiobenzanilide to form benzenesulphonyl monosulphide, m. p. 101—102°, and benzenesulphonyl trisulphide, m. p. 133°. Hydrogen sulphide was detected in the last condensation only.

VII. Since the condensation of benzonitrile with *p*-thiotoluamide in the presence of hydrogen chloride proceeds normally to afford *benzimino*-p-iso*thiotoluamide* (*hydrochloride*, m. p. 132°; *picrate*, m. p. 116°; oxidised by iodine to *phenyl*-p-*tolyl*-1 : 3 : 4-*thiodiazole*, m. p. 56°), whereas a similar experiment with *p*-toluonitrile and thiobenzamide affords benzonitrile and the same benzimino-*p*-*iso*thiotoluamide, it is suggested that, in the latter condensation, an interchange of the aryl radicals takes place through the intermediate formation of the unstable di-iminosulphides, only part of which are converted into the benzimino-compound. The following condensations confirm this view: *p*-toluonitrile and *p*-thiotoluamide yield p-*toluimino*-p-iso*thiotoluamide*, m. p. 108° [*hydrochloride*, m. p. 161°; *picrate*, m. p. 160°; action of ethyl iodide affords S-*ethyl*-p-*toluimino*-p-iso*thiotoluamide hydriodide*, m. p. 154° (free base decomposes to give mercaptan and tri-*p*-tolylguanidine); 2 : 5-*di*-p-*tolyl*-1 : 3 : 4-*thiodiazole*, m. p. 129° (*hydrochloride*, m. p. 161°)]; *m*-toluonitrile and *m*-thiotoluamide yield m-*toluimino*-m-iso*thiotoluamide* (23%), m. p. 58° [*hydrochloride*, m. p. 114°; *chloroplatinate* (not obtained pure), m. p. about 121°; S-*ethyl*-m-*toluimino*-m-iso*thiotoluamide hydriodide*, m. p. 136° (corresponding *picrate*, m. p. 145°); corresponding *thiodiazole*, m. p. 49·5°]. The *S*-ethyl compound can be reduced by alcoholic hydrogen chloride and zinc to m-*methylbenzyl*-m-*toluamidine hydrochloride*, m. p. 199°.

p-Toluonitrile and *m*-thiotoluamide, β-naphthonitrile and thiobenzamide, and α-naphthonitrile and thioacetamide yield typical condensation compounds which were not further examined; benzonitrile and *m*-thiotoluamide yield probably a mixture of the possible products, from which a *hydrochloride*, m. p. 135° [corresponding *picrate* (B_2A), m. p. 140°; *hydrobromide*, m. p. 136°; corresponding *thiodiazole picrate*, m. p. 88°)], is obtained; *m*-toluonitrile and thiobenzamide yield a similar mixture from which a *hydrochloride*, m. p. 135°, a *hydrobromide*, m. p. 136°, and a *picrate*, m. p. 140°, are isolated.

G. A. C. GOUGH.

Condensation of nitriles with thio-acids. I. S. Ishikawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 293—300).—These condensations, carried out in ether saturated with hydrochloric acid, result in the production of the thio-amide from the nitrile and of the normal acid chloride from the thio-acid, together with the secondary condensation products of these substances. It is suggested that the reaction proceeds through the intermediate formation of a compound of the type R·C(:NH)·S·CO·R. In this way benzonitrile and thioacetic acid yield thiobenzamide, benziminoisothiobenzamide, and acetic acid; p-nitrobenzonitrile and thioacetic acid yield *p-nitrothiobenzamide*, m. p. 157°; m-nitrobenzonitrile and thioacetic acid yield *m-nitrothiobenzamide*, m. p. 130—131°; benzonitrile and thiobenzoic acid yield benzamide, benziminoisothiobenzamide, and benzoyl chloride. Nitriles react with hydrogen sulphide in ethereal hydrogen chloride to afford the aryliminoisothioarylamides, through the intermediate formation of the diarylimino-sulphide. Thus benzonitrile gives benziminoisothiobenzamide, also produced under similar conditions by the use of potassium, calcium, or zinc sulphide; and β-naphthonitrile gives β-thionaphthamide. G. A. C. Gough.

Action of metallic salts on thioamides and their derivatives. I. Mercuric chloride in ethereal solution. S. Ishikawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 301—312).—Mercuric chloride additive *compounds* of the type $B_2,HgCl_2$, are quantitatively formed when ethereal solutions of the following thioamides are titrated with ethereal mercuric chloride: thiobenzamide, m. p. 194—197° (decomp. with the liberation of mercuric chloride and hydrogen sulphide); m-thiotoluamide, m. p. 183—186° (decomp.); p-thiotoluamide, m. p. 191—194° (decomp.); m-nitrothiobenzamide, darkening at 206°; p-nitrothiobenzamide, m. p. 183° (decomp.); thioacetamide, m. p. 183°; phenylthioacetamide, m. p. 160° (decomp.); α-thionaphthamide, m. p. 184° (decomp.); β-thionaphthamide, m. p. 221° (decomp.); thiobenzanilide, m. p. 100—101° (re-solidifying at about 180° and unmelted at the b. p. of sulphuric acid); α-thioacetonaphthalide, decomp. 222° (previous darkening); β-thioacetonaphthalide, decomp. 225° (with previous darkening). *β-Thiobenznaphthalide mercuric chloride* has m. p. 184—187°. The following form additive compounds of the type $B,HgCl_2$: benziminoisothiobenzamide, m. p. 149° (decomp.): p-toluimino-p-isothiotoluamide, m. p. 118° (decomp. 163°); m-toluimino-m-isothiotoluamide, m. p. 110° (changing to a yellow solid at 159°); *acetophenonethiosemicarbazone mercuric chloride*. The first-named is decomposed by potassium hydroxide into potassium chloride, mercury, water, and the thiodiazole. G. A. C. Gough.

p-Iodobenzoic acid. F. C. Whitmore and (Miss) G. E. Woodward (Org. Syntheses, 1927, **7**, 58—59).—p-Iodobenzoic acid is prepared in 72—81% yield by the interaction of p-chloromercuribenzoic acid and iodine in alcoholic solution. A. A. Eldridge.

2-Bromo-3-nitrobenzoic acid. P. J. Culhane (Org. Syntheses, 1927, **7**, 12—14).—Interaction of anhydro-2-hydroxymercuri-3 nitrobenzoic acid, sodium bromide, and bromine, under conditions described in detail, produces sodium 2-bromo-3-nitrobenzoate. A. A. Eldridge.

Constitution of elemic acid. K. H. Bauer (Ber., 1928, **61**, [*B*], 343—344).—Determination of the iodine value of α-elemic acid, $C_{27}H_{42}O_3$ (cf. Tschirch and Cremer, A., 1902, i, 812; Buri, A., 1878, ii, 439; Lieb and Schwarzl, A., 1924, i, 1312), indicates the presence of a double linking which is confirmed by its catalytic hydrogenation in alcohol in presence of palladised kieselguhr to *dihydroelemic acid*, $C_{27}H_{44}O_3$, m. p. 238°. The *methyl* esters of elemic and dihydroelemic acid could not be caused to crystallise. H. Wren.

Addition of bromine to ethylenic compounds in non-hydroxylic solvents. D. M. Williams and T. C. James (J.C.S., 1928, 343—347; cf. Sudborough and Thomas, J.C.S., 1910, **97**, 715, 2450).—Three distinct types of reaction have been observed in dilute solutions in dry chloroform or carbon tetrachloride at 13° in the dark: (*a*) Addition to *cis*- and *trans-o*-methoxycinnamic acids, cinnamylideneacetic acid and its methyl ester, α-phenylcinnamylideneacetic acid, β-furfurylacrylic acid, oleic acid, and elaidic acid proceeds rapidly and is accompanied by substitution and formation of hydrogen bromide. The bimolecular velocity coefficient decreases as the reaction proceeds. (*b*) After an inhibition period addition to cinnamic acid, its methyl ester, crotonic acid, and methyl cinnamylidenemalonate proceeds slowly with increasing velocity. (*c*) No measurable addition to maleic anhydride, coumarin, and α-phenylcinnamonitrile is observed under these conditions. Reactions of type (*a*) are probably catalysed by the hydrogen bromide formed, since addition of this substance greatly accelerates those of type (*b*). In each case the inhibition period disappears and the reaction becomes bimolecular. Water and hydrogen chloride are less efficient catalysts. Reactions of type (*c*) are not accelerated by these substances. H. E. F. Notton.

Isomerism of phenylphthalimide [phthalanil] and a study of the nitro- and chloro-derivatives. M. L. Sherrill, F. L. Schaeffer, and E. P. Shoyer (J. Amer. Chem. Soc., 1928, **50**, 474—485).—By extraction with chloroform, Gabriel and Thorpe's "phthalanilic acid," m. p. 192° (cf. A., 1893, i, 466), can be separated into phthalanil (soluble) and phthalanilic acid, m. p. 169°. It is also shown that whilst van der Meulen's phthalphenylisoimide is the true *as*-phenylphthalimide (A., 1897, i, 414), Kuhara's βα-phenylphthalimide is a mixture of phthalphenylisoimide and phthalanilic acid (cf. A., 1911, i, 205), and his α-phenylphthalimide is a mixture of the normal and isophthalanils. The "p-isonitrophenylphthalimide" of Kuhara and Dobreff (A., 1895, i, 360) is identical with p-nitrophthalanilic acid (*ammonium* salt; *disilver* salt, brown); the "m-isonitrophenylphthalimide" is a mixture of m-nitrophenylphthalamide and m-nitrophenylphthalimide, whilst the "o-isonitrophenylphthalimide" is o-nitrophthalanilic acid, contaminated with o-nitrophthalanil and o-nitroaniline hydrochloride. p-Chlorophthalanilic acid is obtained by treatment of p-chloro-

aniline with phthalic anhydride in chloroform. m-*Chlorophthalanilic acid*, m. p. 183—184° (decomp.), and o-*chlorophthalanilic acid*, m. p. 147—148°, decomp. 155°, obtained analogously, are described. Fusion of phthalic anhydride with chloroanilines affords the respective *o*-, m. p. 132—140°, *m*-, m. p. 183—184° (decomp.), and *p*-chlorophenylphthalimide (cf. Gabriel, A., 1879, 323). F. G. WILLSON.

[Preparation of] 3-nitrophthalic acid. P. J. CULHANE and (MISS) G. E. WOODWARD (Org. Syntheses, 1927, 7, 70—72).

[Preparation of] 3-nitrophthalic anhydride. B. H. NICOLET and J. A. BENDER (Org. Syntheses, 1927, 7, 74—75).

[Preparation of] ethyl phthalimidomalonate. A. E. OSTERBERG (Org. Syntheses, 1927, 7, 78—79).

[Preparation of] β-bromoethylphthalimide. P. L. SALZBERG and J. V. SUPNIEWSKI (Org. Syntheses, 1927, 7, 8—10).

[Preparation of] α-cyano-β-phenylacrylic acid. A. LAPWORTH and W. BAKER (Org. Syntheses, 1927, 7, 20—22).

[Preparation of] diphenic acid. E. H. HUNTRESS (Org. Syntheses, 1927, 7, 30—33).—Vorlander and Meyer's method is applied to the preparation of large quantities. A. A. ELDRIDGE.

Hydroxyamino-acids. II. F. BETTZIECHE and R. MENGER (Z. physiol. Chem., 1928, **172**, 56—63; cf. A., 1926, 154).—*Benzoylphenylserine* (*α-benzamido-β-hydroxy-β-phenylpropionic acid*), m. p. 158°, when subjected to steam distillation in 8% sodium hydroxide yields benzaldehyde, benzoic acid, and glycine, but no ammonia or hippuric acid. *Hippurylphenylserine* (*α-hippurylamino-β-hydroxy-β-phenylpropionic acid*), m. p. 143°, in the same way yields benzoic acid, benzaldehyde, glycine, and traces of hippuric acid, but no ammonia; thus no splitting of the acid into hippurylamide and phenylpyruvic acid occurs. Toluenesulphonylphenylserine when heated with 3% sodium hydroxide for 5 hrs. at 200° is partly decomposed into benzaldehyde and toluenesulphonylglycine and partly into toluenesulphonamide and phenylpyruvic acid, the products of both changes being isolated; the yields, however, are minimal on account of the high temperature. By the action of benzoyl chloride on benzoylphenylserine in sodium hydrogen carbonate solution, the azlactone of benzamidocinnamic acid is formed and not the diacyl compound, which has not yet been obtained. The azlactone of benzamidocinnamic acid does not react with ethyl alcohol, but with methyl alcohol an almost quantitative yield of the *methyl* ester of the azlactone, m. p. 140°, is obtained. Benzamidocinnamic acid, in contrast with its azlactone, is indifferent to both methyl and ethyl alcohols. A. WORMALL.

Triple spiran. P. PFEIFFER and P. BACKES (Ber., 1928, **61**, [*B*], 434—435).—Pentaerythritol is converted when heated with ethyl *cyclo*hexanone-4-carboxylate into the triple *spiran*

$$C\left(<^{CH_2\cdot O}_{CH_2\cdot O}>C<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C<^{H}_{CO_2Et}\right)_2$$

, m. p. 139·5—140·5°, which is expected to afford an example of molecular asymmetry. H. WREN.

Auto-oxidation of benzaldehyde. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 286—300; cf. A., 1926, 519).—The oxidation of benzaldehyde to perbenzoic acid has been studied, using various metals and solvents. Iron powder considerably accelerates the oxidation, tin and aluminium powders having no particular accelerating action. On exposing benzaldehyde dissolved in acetone, carbon tetrachloride, benzene, or chloroform to diffuse light or to sunlight in the presence of oxygen, the formation of varying quantities of perbenzoic acid was observed, a conversion of 43% (determined by oxidation of iodide) being recorded with acetone solution. No perbenzoic acid was formed in pyridine solution. The oxidation of benzaldehyde in benzene solution produced a substance of sharp, penetrating odour and having the properties of a peroxide. The auto-oxidation being assumed as taking place in two stages: (i) $Ph\cdot CHO \longrightarrow Ph\cdot CO_3H$, (ii) $Ph\cdot CO_3H + Ph\cdot CHO$ —— $Ph\cdot CO_2H$, stabilisation of the intermediate product was necessary; acetone gave the best results (63·4% yield). A dilution of 10 vols. of benzaldehyde in 80 vols. of acetone should not be exceeded; the yield is then about 50%. Admission of water to the reaction greatly decreases the yield. Pure perbenzoic acid was obtained by oxidising a 10% acetone solution of benzaldehyde with oxygen until absorption ceased. After removal of acetone by distillation, the peroxide was isolated either by distillation at low pressure, or by removal of benzoic acid from the acetone solution with dilute sulphuric acid, followed by extraction with chloroform.

By oxidising benzaldehyde in carbon tetrachloride solution, it is shown that perbenzoic acid is not the first product of oxidation, since carbonyl chloride, hydrogen chloride, and carbon dioxide are formed. R. A. PRATT.

Auto-oxidation of benzaldehyde in presence of acetic anhydride. P. A. A. VAN DER BEEK (Rec. trav. chim., 1928, **47**, 301—308).—Equal volumes of benzaldehyde and acetic anhydride were mixed with the addition of one drop of phosphorus trichloride as catalyst, the mixture being kept over-night at a low temperature in the dark. Snow-white crystals of benzylidene diacetate, m. p. 40°, were formed in large yield. M.-p. curves, obtained by a method avoiding oxidation of benzaldehyde, were determined after the mixtures had been kept for 62 hrs. in an atmosphere of carbon dioxide. Two maxima were found, one corresponding with the *compound* $2Ph\cdot CHO,Ac_2O$, m. p. about 17°, and the other with $Ph\cdot CHO,Ac_2O$, m. p. 40°. Despite attempts to isolate the new compound in the pure state, it was impossible to preserve a solid substance with m. p. other than 45—46°. Apparently the new compound decomposes during purification into benzylidene diacetate and benzaldehyde. The addition of a trace of phosphorus trichloride to the pure diacetate, the reaction mixture being kept for some months in a sealed glass tube, also produces a compound of m. p. 40°, indicating that the reaction benzaldehyde+

acetic anhydride ⇌ benzylidene diacetate proceeds to an equilibrium. R. A. PRATT.

Mechanism of substitution of bromine in aromatic hydrazones. II. M. VANGHELOVICI (Bul. Soc. Chim. Romania, 1927, **9**, 59—67).—Bromination or chlorination of the phenylhydrazones of aromatic aldehydes occurs in accordance with the scheme CHPh.N·NHPh — CHPh:N·NH·C_6H.X(p) — CHPh:N·NH·$C_6H_3X_2$(2 : 4) ⟶ [CHXPh·NX·NH·$C_6H_3X_2$] ⟶ CXPh:N·NH·$C_6H_3X_2$ (X—Br or Cl), since the third halogen atom readily reacts with potassium cyanide to yield the corresponding cyano-derivative or with phenylhydrazine to yield intensely coloured azo-derivatives which are not isolated. The product, m. p. 114°, obtained by bromination of benzaldehydephenylhydrazone in glacial acetic acid has the structure CBrPh:N·NH·$C_6H_3Br_2$ (I), and is not p-*bromobenzaldehyde*-2 : 4-*dibromophenylhydrazone* as stated by Ciusa (A., 1916, i, 437). The latter, m. p. 125·5°, is synthesised from p-bromobenzaldehyde and 2 : 4-dibromophenylhydrazine. By treatment with potassium cyanide in boiling alcohol (I) yields α-*cyanobenzylidene*-2 : 4-*dibromophenylhydrazine*, m. p. 138°. By similar methods are prepared *salicylidene*-p-*bromophenylhydrazine*, m. p. 175°; α-*bromobenzylidene*-2-*bromo*-4-*nitrophenylhydrazine*, m. p. 169°; α-*chlorobenzylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 87°, from which is obtained α-*cyanobenzylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 128°; α *chloroanisylidene*-2 : 4-*dichlorophenylhydrazine*, m. p. 111°; the corresponding α-*cyano*-derivative, m. p. 150°.

J. W. BAKER.

Nitration of benzaldoxime and some derivatives. O. L. BRADY and B. E. M. MILLER (J.C.S., 1928, 337—342).—With nitric and sulphuric acids at 0° and 5°, respectively, benzaldoxime and its N-methyl derivative give exclusively m-nitro-derivatives, the yields being diminished by hydrolysis and oxidation. α-O-Methylbenzaldoxime is attacked by nitrating agents only with difficulty, even on warming, giving small amounts of the m-nitro-derivative. The absence of o- and p-derivatives is in accordance with Vorländer's rule (A., 1919, i, 319), but not with the suggestion of Ingold (Ann. Reports, 1926, **23**, 131; A., 1927, 236) that introduction of unsaturated carbon atoms between a positive pole and the nucleus should decrease the m-directing effect. When other strongly directive groups are present, nitration occurs more readily and the orienting effect of the aldoximino-group is not apparent. Thus, α-4-methoxybenzaldoxime yields a 3-nitro-derivative, and its O-methyl ether a 3-nitro- and a 3 : 5-*dinitro*-, m. p. 129°, derivative; α-3 : 4-methylenedioxybenzaldoxime and its O-methyl ether give 6-nitro-derivatives and α-4-hydroxy-3-methoxybenzaldoxime gives quantitatively a 5-nitro-derivative. H. E. F. NOTTON.

Dioximes. XLVI. G. PONZIO and C. CERRINA (Gazzetta, 1928, **58**, 26—35).—By the action of ammonia solution on dibenzoylglyoxime peroxide, Holleman (A., 1893, i, 206) obtained a substance, $C_9H_7O_2N_3$, (I), m. p. 135°, which Boeseken and van Lennep (A., 1912, i, 723) regarded as 5-amino-3-benzoyl-1 : 2 : 4-oxadiazole. The product (II) of the action of potassium ethoxide on (I) was considered to be the 5-hydroxy-compound. The latter has, however, been prepared (Ponzio, A., 1926, 1159), and has different properties. Actually, the action of ammonia solution in the cold yields benzamide and α-*benzoylaminoglyoxime*, m. p. 127° (decomp.), which forms a *silver* salt (explodes about 130°), and a *dibenzoyl* derivative CBz(N·OBz)·C(N·OBz)·NH_2, m. p. 158—159°; some 5-hydroxy-3-benzoyl-1 : 2 : 4-oxadiazole and benzoylmetazonic acid are also formed. On heating the above α-compound with dilute acetic acid, β-*benzoylaminoglyoxime*, m. p. 187° (decomp.), is obtained; the precipitates with nickel and copper acetate are described, as is the *dibenzoyl* derivative, m. p. 198°.

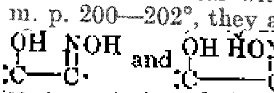
The compound (I) is obtained by the first-mentioned reaction only when the temperature rises, or by the action of acetic anhydride in the cold on the α-compound, or by heating the α- or the β-compound with ammonia solution; it is to be regarded as 3-amino-4-benzoyl-1 : 2 : 5-oxadiazole (derived through the intermediate formation of benzoyloximinoacetonitrile oxide). Its N-*oxide* ("benzoylaminoglyoxime peroxide"), m. p. 145° (decomp.), from which it can be obtained by reduction, is prepared by oxidation of α-benzoylaminoglyoxime by, *e.g.*, bromine water. Contrary to the statement of Boesoken, the compound (I) easily yields a *benzoyl* derivative, m. p. 139—140°.

Similarly, di-p-toluoylglyoxime peroxide yields α- and β-p-*toluoylaminoglyoximes*, m. p. 114° and 188° (each decomp.), respectively. 3-*Amino*-4-p-*toluoyl*-1 : 2 : 5-*oxadiazole* N-*oxide* ("p-toluoylaminoglyoxime peroxide") has m. p. 145° (decomp.), and can be reduced to the oxadiazole. The compounds regarded by Boeseken as 5-amino-3-p-toluoyl- and -3-p-anisoyl-1 : 2 : 4-oxadiazoles, m. p. 165° and 144° respectively, are renamed 3-amino-4-p-toluoyl- and -4-p-anisoyl-1 : 2 : 5-oxadiazoles.

The above-mentioned product (II) may have the structure CBz(N·OH)·$C\!\lessdot\!\begin{smallmatrix}NH\\ |\\ N\end{smallmatrix}$. E. W. WIGNALL.

Possibility of ring-chain valency tautomerism, and of a type of mobile-hydrogen tautomerism analogous to the Wagner–Meerwein re-arrangement. I. Derivatives of phorone. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1928, 365—410).—Further evidence (cf. Francis and Willson, *ibid.*, 1913, **103**, 2238) is adduced to show that, whilst phorone has an open-chain structure (I) $C\!<\!\begin{smallmatrix}\overset{(\alpha)}{C}{:}C\\ C{:}C\end{smallmatrix}$, its acyloxy- and alkyloxy-derivatives have cyclic formulæ, (II) $C\!<\!\begin{smallmatrix}C & \quad C\\ | & \quad |\end{smallmatrix}$ or (III) $C\!<\!\begin{smallmatrix}C{-}C\\ \quad\ |\\ C{-}C\end{smallmatrix}$, and its halogeno-derivatives are in an intermediate state, (IV) $C\!<\!\begin{smallmatrix}C{-}C\\ |\quad\\ C{-}C\end{smallmatrix}$. A formula of type (IV) for dichloro- and dibromophorone is favoured by refractivity measurements and by the reduction of the latter by Clemmensen's method to phorone and deoxyphorone, and by phosphorus and hydriodic acid to 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone (IX). Further, since compounds of types (II) and (III) are obtainable from the same

hydroxyphorone, the latter must be capable of a tautomerism, $\mathrm{CO}<\begin{matrix}\mathrm{CR}\text{——}\mathrm{CMe_2}\\ \mathrm{C(OH)\cdot CMe_2}\end{matrix}$ (V, R=Br; VI, R=H) $\rightleftharpoons \mathrm{C(OH)}<\begin{matrix}\mathrm{CR\cdot CMe_2}\\ \mathrm{O\cdot CMe_2}\end{matrix}$ (VII, R—Br; VIII, R—H), similar to the Wagner–Meerwein transformation. The electronic interpretation of these and analogous reactions is discussed, and it is shown that the tendency of a phorone derivative to undergo the changes (I) ⟶ (IV) ⟶ (II), which are accompanied by a decrease in unsaturation and visible colour, and by depression of the mol. refractivity and parachor (cf. Sugden, this vol., 416), runs parallel with the *op*-directing power in aromatic substitution of the group in position (*a*). The structure of the ketone (IX) (cf. Farmer and Kracovski, A., 1927, 447) has been confirmed by its synthesis by heating βγ-dibromo-βγ-dimethylbutane and ethyl acetonedicarboxylate with sodium ethoxide and hydrolysing the product with hydrochloric acid. It gives a *di*-3 : 4-*methylenedioxybenzylidene* derivative, m. p. 125°, and a 2 : 5-*dioximino*-derivative, m. p. 223°, which is hydrolysed by hydrochloric acid in presence of formaldehyde to oily *tetramethyl*cyclo*pentane*-1 : 2 : 3-*trione* (*trioxime*, m. p. 168—169°). The ketone (IX) absorbs bromine (3 mols.) in anhydrous solvents, forming probably 2 : 5-dibromo- and 2 : 2 : 5-tribromo-3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone. The latter is decomposed by water to bromohydroxyphorone (V) or (VII) (d-*bromocamphorsulphonyl* derivative, m. p. 150°; p-*nitrobenzyl ether*, m. p. 111°). This is reduced by zinc dust and acetic acid to the hydroxyphorone (VI) or (VIII) and the products of direct alkylation and acylation of the latter are also preparable by this method from the corresponding derivatives of (V) or (VII). The ethers and esters described below fall into two groups, (i) derivatives of (V) or (VI), which are fairly stable towards reduction, oxidation, and bromination, and (ii) derivatives of (VII) or (VIII), which yield dihydro-derivatives and are easily oxidised and brominated.

(i) Bromohydroxyphorone does not form ketonic derivatives, but hydroxyphorone (VI) gives a *semicarbazone*, m. p. 211—213°, an *anil*, m. p. 104°, a p-*dimethylaminoanil*, m. p. 90°, and an α-*oxime*, m. p. 96° [*monohydrate*, m. p. 76°; *sodium* salt, m. p. 200° (decomp.); *hydrochloride*, m. p. 189—190° (also $+\mathrm{CCl_4}$, m. p. 174—175°); *benzoyl* derivative, m. p. 134—135°], which is converted by cold ethereal hydrogen chloride into the *hydrochloride*, m. p. 69—70°, of a β-*oxime*, m. p. 114—115°. The α- and β-forms are readily interconvertible, and since the latter gives by the Beckmann reaction a *substance* [(?) 2 : 3-*diketo*-4 : 4 : 5 : 5-*tetramethylpiperidine*], m. p. 113°, not identical with ααββ-*tetramethylglutarimide*, m. p. 200—202°, they are probably stereoisomerides, , respectively. The α-oxime is shown to be a derivative of (VI) by its reduction by sodium amalgam and acetic acid or palladium and hydrogen to 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentylamine*, m. p. 100—102° [*picrate*, m. p. 255°; *chloroaurate*, m. p. -30° (decomp.); *hydrochloride*, m. p. 308° (decomp.); *acetyl* derivative, m. p. 95°], which is obtained by the same methods from 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanoneoxime*, m. p. 107° (*hydrochloride*, m. p. 119°), or its *acetyl* derivative. On further treatment with hydroxylamine, the α-oxime yields 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentane*-1 : 2-*dionedioxime*, m. p. 211°, dehydrated by heating with aqueous ammonia to a *furazan*, m. p. 209°. The hydroxyketone (VI) and *o*-phenylenediamine yield in boiling glacial acetic acid a *quinoxaline*, $\mathrm{C_{15}H_{18}N_2}$, m. p. 100°. The benzoate (X) of hydroxyphorone (VI) is converted by hydroxylamine into the (γ)-*oxime* (2-*oximino*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*), m. p. 115°, of (VIII), which is also formed on regulated nitrosation of the ketone (IX) in chloroform. In methyl-alcoholic solution (IX) yields a δ-*oxime*, m. p. 170—172° (*monohydrate*, m. p. 83°; *sodium* salt, m. p. 200°), which is probably stereoisomeric with the γ-oxime, since it affords with hydrochloric acid and formaldehyde ααββ-tetramethylglutaric acid. The γ-oxime is converted by hydroxylamine into the above dioxime, m. p. 211°, by sodium and alcohol into (?) 5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentylamine*, isolated as the *picrate*, m. p. 220—221°, and by the Beckmann reaction into (?) 2 : 3-*diketo*-5 : 5 : 6 : 6-*tetramethylpiperidine*, m. p. 200°. If the oximino-group directly displaces the benzoyl group in (X), the latter has thus been shown to be a derivative of (VI). Bromohydroxyphorone is converted by sodium ethoxide and *p*-bromobenzyl bromide into an oily *by-product* (XI) and the p-*bromobenzyl ether*, m. p. 65°, of (V), which is reduced by zinc dust and acetic acid to the p-*bromobenzyl ether*, m. p. 86°, of (VI). This is fairly stable towards bromine and alkaline permanganate and does not yield a dihydro-derivative (cf. the methyl ether, below). With boiling hydriodic acid it gives (IX) and with ozone, bromine, and an ozonide which is hydrolysed to *p*-bromobenzaldehyde and tetramethylsuccinic acid. The *acetyl* derivative, m. p. 84°, of its *oxime*, m. p. 175° (*hydrochloride*, m. p. 133°), is reduced to (?) 2-*hydroxy*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentylamine* [*picrate*, m. p. 215° (decomp.)], besides neutral *substances*, m. p. 161—162°, and oils. 1-*Cyano*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-*dicyclopentan*-4-*ol*-5-*one* (V or VII, R=CN) has m. p. 172—173°.

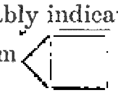
(ii) The constitution of the acetate (1-bromo-5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*penten-4-one) (Francis and Willson, *loc. cit.*) of bromohydroxyphorone is established as follows: it is reduced by zinc and acetic acid, first to 5-*acetoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*, b. p. 120°/15—16 mm., d_4^{20} 1·0190, n_D^{20} 1·4549, then to 5-*acetoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (XII), b. p. 127°/15—16 mm. (hydrolysed to a *hydroxyketone*, $\mathrm{C_9H_{16}O_2}$, m. p. 140°), and by sodium amalgam and acetic acid to 2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (XIII), b. p. 100°/16 mm., m. p. 119° (*semicarbazone*, m. p. 222°), and a little of the isomeride (IX). The *oxime*, m. p. 101—102° (*hydrochloride*, m. p. 125°), of (XIII) is reduced by sodium and alcohol to 2 : 2 : 3 : 3-*tetramethyl*cyclo*pentylamine* (XIV) (*picrate*, m. p. 242—243°; *acetyl* derivative, m. p. 115°), which is also obtained by oximation and reduction from (XII). Similarly, the *methyl ether* (1-*bromo*-5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*), b. p. 120°/14 mm., 1·5131—1·5147, d_4^{20} 1·3159, of (VII) is reduced by zinc dust and

acetic acid to 5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-4-*one*, m. p. (on one occasion) 37°, b. p. 112—115°/21 mm., 1·4687 [reducible through its *oxime*, b. p. 140—150°/22 mm. to (XIV)], and to 5-*methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone*, b. p. 88—90°/10 mm., n_D^{18} 1·4580, which is reduced by hydriodic acid to (IX) and through its *oxime* to (XIV). The by-product (XI) appears to contain the *p*-bromobenzyl ether of (VII), since it is reduced by zinc and acetic acid to a substance, the oxime of which is reduced by sodium and alcohol to (XIV).

The oxidation and halogenation of bromohydroxyphorone are best explained in terms of formula (VII). With sodium perchlorate and osmium tetroxide it affords the lactonic acid (XV) of γγ-dihydroxy-ααββ-tetramethylglutaric acid and the lactonic acid (*dilactone anhydride*, m. p. 177—178°) of γ-hydroxy-ααββ-tetramethylglutaric acid. The methyl ether of (VII) is ozonised to bromine and ozonides which yield on hydrolysis a product containing the *lactonic* ester,

$CMe_2 \cdot CMe_2 \cdot C(OH) \cdot CO_2Me$
CO———O

b p 155—165°/13 mm., and its *methyl ether*, m. p. 103°, previously regarded by Rothstein and Shoppee (A., 1927, 447) as methyl γ-keto-ααββ-tetramethylglutarate. The acetate of (VII) does not yield bromine when ozonised; it is oxidised by permanganate to (XV). Hydroxyphorone (VI) or (VIII) and the ketone (XIII) are both oxidised to ααββ-tetramethylglutaric acid. The constitution, 1 : 1 - dibromo - 2 : 2 : 3 : 3 - tetramethyl*cyclo*pentanedione, proposed by Francis and Willson for the bromination product of (VII) is supported by the observation that chlorination of (VII) and bromination of 1-*chloro*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (V or VII, R=Cl), m. p. 116° (*acetyl* derivative, m. p. 47°), yield the same 1-*chloro*-1-*bromo*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione*, m. p. 178°, which is reduced by carbamide to the chlorohydroxy-derivative. The close similarity between dibromo-, chlorobromo-, and 1 : 1-*dichloro*-, m. p. 187°, -tetramethyl*cyclo*pentanediones indicates that they are analogously constituted. H. E. F. NOTTON.

Parachor and chemical constitution. VIII. Ring-chain valency tautomerism in phorone derivatives. S. SUGDEN (J.C.S., 1928, 410—415).—The constitutions assigned to these derivatives on chemical grounds by Ingold and Shoppee (this vol., 414) are, in general, confirmed. The parachor and the calculated value for the formula, CMe_2:CR·CO·CR':CMe_2, with two non-polar double linkings, are given for the following compounds: (*a*) phorone, 367·9, 372·2; (*b*) dichloro-, 427·7, 446·6; (*c*) dibromo-, 463·2, 474·0; (*d*) acetoxy-, 459·4, 476·0; (*e*) bromoacetoxy-, 506·4, 526·9; (*f*) bromomethoxy-, 455·3, 482·1; (*g*) benzoyloxy-, 583·9, 609·9; (*h*) bromobenzoyloxy-, 642·4, 660·8; (*i*) *p*-bromobenzyloxy-, 630·7, 655·0; (*j*) bromo-*p*-bromobenzyloxy-, 684·0, 705·9, also for distyryl ketone, 564·5, 562·0, and αα'-dibromodistyryl ketone, 650·7, 663·8. Thus, (*a*) agrees well with an open-chain structure, whereas the maximum deviations at (*f*), (*g*), and (*i*) probably indicate complete conversion into the dicyclic form . The mean structural constant for this system is therefore 20·7. The difference between this and the value (25·2) calculated for superimposed three- and five-membered rings is ascribed to the stabilising effect of the *gem*-dimethyl groups. The anomaly of (*d*) is in accordance with the structure, 5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*penten-4-one, and that of (*c*) with an equilibrium between cyclic and open-chain forms, which must have nearly the same energy content, since the parachor does not vary appreciably with temperature. Similarly, whilst distyryl ketone has a normal structure, its dibromo-derivative appears to exist partly in the dicyclic form. H. E. F. NOTTON.

Orientation phenomena with 2-methyl*cyclo*hexanone. R. CORNUBERT (Compt. rend., 1928, **186**, 441—442).—Alkylation of 2-methyl*cyclo*hexanone by means of sodamide yields mainly the 2 : 2-dialkyl derivative, with a small proportion of the 2 : 6-dialkyl compound (cf. Haller and Cornubert, A., 1927, 152; Cornubert and Le Bihan, *ibid.*, 1075). That this is not due to an inversion of the latter is shown by the stability of both 2 : 2- and 2 : 6-dimethyl*cyclo*hexanones towards sodium hydroxide and hydrochloric acid; also, both ketones can be isolated without using sodium hydrogen sulphite. It is concluded that sodium, unlike chlorine, substitutes in the 2- preferentially to the 6-position. The "tetrahydropyrone" compound of 2 : 6-dimethyl*cyclo*hexanone has m. p. 175°, not 197—198°, as previously stated. E. W. WIGNALL.

2 : 6-Dimethyl*cyclo*hexanones. R. CORNUBERT (Compt. rend., 1928, **186**, 585—586; cf. preceding abstract).—The mixture of dimethyl*cyclo*hexanones, obtained by the methylation of 2-methyl*cyclo*hexanone by the method of Kotz and Blendermann (A., 1913, i, 1069), is separated by crystallisation of the oximes affording the *oxime A*, m. p. 119° (hydrolysed with difficulty to yield the *ketone A*, b. p. 85°/41 mm., d^{18} 0·914, n_D^{18} 1·4486), and the *oxime B*, m. p. 64—65° (softening at 63°; easily hydrolysed to afford the *ketone B*, b. p. 80·5°/41 mm., d^{18} 0·911, 1·4482). The ketone *A* gives pyrone-like *compounds*, m. p. 197—198°, 175°, and 216°, of the common formula $C_{22}H_{24}O_2$, when treated with benzaldehyde in the presence of hydrogen chloride (A., 1925, i, 1070, 1071), whilst the ketone *B* similarly affords the compound, m. p. 175°, b. p. 271°/20 mm., and the compound, m. p. 216°. Oximation of the ketones in the presence of sodium acetate yields in each case mixtures of the oximes *A* and *B*, whilst in the presence of alkali the ketone *A* gives the oxime *A* alone and the ketone *B* again gives a mixture. Both ketones give mixtures of semicarbazones (Zelinsky, A., 1897, i, 462). The results are attributed to the rapid interchange of the *cis–trans* isomerides. G. A. C. GOUGH.

Relative ease of formation of rings. II. J. VON BRAUN (Ber., 1928, **61**, [*B*], 441—443; cf. this vol., 174).—It is shown in two instances that a six-membered carbon ring is more readily allied to a benzene nucleus than a five-membered carbon ring (cf. Leuchs and others, this vol., 287).—*Benzyl-β-phenylethylacetyl chloride*, b. p. 198—202°/15 mm., is converted by aluminium chloride in presence of carbon disulphide into 1-keto-2-benzyl-1 : 2 : 3 : 4-

tetrahydronaphthalene, b. p. 220—225°/13 mm. (*oxime*, m. p. 119°), the constitution of which is established by converting it by Clemmensen's method into 2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 194—195°/13 mm., transformed by heated lead oxide into naphthalene. Benzylsuccinic acid is converted by phosphorus pentachloride into *benzylsuccinyl chloride*, b. p. 115—117°/0·5 mm., which, with aluminium chloride, affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene-3-carboxylic acid*, m. p. 144°, b. p. 218—220°/16 mm. (also obtained from benzylsuccinic anhydride and aluminium chloride); the *ethyl* ester, b. p. 175—177°/15 mm., and the *semicarbazone*, m. p. 264°, are described. The acid is reduced by amalgamated zinc and hydrochloric acid to 1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m. p. 97°.

H. WREN.

Preparation of benzophenone. G. DOUGHERTY (J. Amer. Chem. Soc., 1928, **50**, 571—573).—*o*-Benzoylbenzoic acid (300 g.) is stirred with its *copper* salt (20 g.) at 200—260° for about 4 hrs., or until evolution of carbon dioxide has ceased, in a distilling flask, and the benzophenone then distilled from the mixture. The yield is 82—84%, calculated on the *o*-benzoylbenzoic acid, after crystallisation from alcohol, m. p. 47—48°. F. G. WILLSON.

Preparation of benzophenone by organo-magnesium compounds. Mechanism of the reaction between organo-magnesium compounds and their carbonated derivatives. D. IVANOFF (Compt. rend., 1928, **186**, 442—444).—When phenyl magnesium bromide is treated at −20° with half an equivalent of carbon dioxide for 8 hrs., a 60% yield of benzophenone is obtained on hydrolysis, with 2—3% of triphenylcarbinol; the reaction is unsuccessful with other ketones. From anhydrous magnesium benzoate and magnesium phenyl bromide a 35% yield of benzophenone is obtained. If the product of the first reaction is treated, before hydrolysis, with benzoyl or acetyl chloride, no trace of an ester is obtained; it is therefore concluded that the complex $CPh_2(OMgBr)_2$, is not formed, but rather the complex $Ph_2CO,MgBr_2$, from which benzophenone can be obtained by distillation, although not by extraction.

E. W. WIGNALL.

[Preparation of] *p*-dimethylaminobenzophenone. C. D. HURD and C. N. WEBB (Org. Syntheses, 1927, 7, 24—26).

Wandering of alkyl groups in the Fries transformation. K. VON AUWERS and W. MAUSS (Annalen, 1928, **460**, 240—277).—A continuation of previous work (A., 1927, 608). The Fries transformation has been effected with a number of other polyalkylphenyl acetates, using the methods of rapid or of slow heating with aluminium chloride. In order to determine whether wandering of alkyl has occurred or not during the transformation, the acetyl group is removed from the resulting hydroxyacetophenone and the new phenol identified. Phosphoric acid used formerly for this removal is often less effective than boiling glacial acetic–hydrobromic acid. In general *o*- and *p*-hydroxyacetophenones are separable by steam distillation.

The new results show that an alkyl group in the *meta*-position to the acetoxyl group favours the formation of *o*-hydroxyacetophenones. Two *meta*-groups produce an even greater tendency in the same direction. Thus, when 3 : 5-dimethyl- and 3 : 5-diethyl-phenyl acetate undergo the Fries change, no 4-hydroxyacetophenones are formed. Similarly, 3 : 5-dimethylphenyl alkyl ethers give only 2-derivatives in Friedel–Crafts reactions. When one *meta*-alkyl group is present (*e.g.*, *m*-tolyl acetate), the Fries change gives a little *p*-compound. A second methyl group in the *ortho*-position (3-*o*-xylyl acetate) does not weaken the effect of the *meta*-grouping in this respect.

Phenyl acetates with a free *ortho*-position give a Fries change only if one alkyl group is in position 2 and a second in position 5 (homologues of *p*-xylenol or *ψ*-cumenol, 4 : 5-dimethyl-2-ethyl-, 2 : 4-dimethyl-5-ethyl-, and 5-methyl-2 : 4-diethyl-phenyl acetates).

The ethyl group is much more readily displaced than methyl (cf. 2 : 6-dimethyl-4-ethylphenyl acetate, where the Fries change is abnormal in giving rise to a *p*-compound). When ethyl groups are present in both *ortho*- and *para*-positions, the *ortho*-group is eliminated, the displaced ethyl group wandering into the *para*-position to that it originally occupied (2-methyl-4 : 6-diethyl- and 2 : 4 : 6-triethyl-phenyl acetates). Other new facts which show the greater valency requirement of ethyl over methyl are the abnormal Gattermann aldehyde and Friedel–Crafts ketone syntheses recorded with 2-methyl-4-ethyl- and 5-methyl-2 : 4-diethylanisole.

When 2 : 4-dimethyl-6-ethylphenyl acetate undergoes the Fries change, both a methyl and an ethyl group are displaced by the entering acetyl groups, but in 2-methyl-4 : 6-diethylphenyl acetate only the ethyl is displaced. Again, whilst 2-methyl-6-ethylphenyl acetate gives mainly 4-hydroxy-3-methyl-5-ethylacetophenone, some ethyl is displaced, giving 2-hydroxy-3-methyl-4-ethylacetophenone. Yet with 2 : 6-diethylphenyl acetate no ethyl displacement occurs. A further fact showing that methyl is more firmly attached than ethyl is that acetyl groups are more readily removed from a hydroxymethyl- than from a hydroxyethyl-acetophenone, *i.e.*, ethyl takes up more of the nuclear affinity than does methyl.

2 : 4-*Dimethyl*-6-*ethylphenyl acetate*, b. p. 242°, gives a mixture of 2-*hydroxy*-3 : 5-*dimethyl*-4-*ethylacetophenone*, m. p. 52—53°, b. p. 153—155°/11 mm. (*oxime*, m. p. 157·5—158·5°; *semicarbazone*, m. p. 235—236°; p-*nitrophenylhydrazone*, m. p. 212—214°), and 2-*hydroxy*-4 : 5-*dimethyl*-3-*ethylacetophenone* (*semicarbazone*, m. p. 219—221°, p-*nitrophenylhydrazone*, m. p. 179—183°). The former acetophenone is converted into 2 : 4-*dimethyl*-3 : 6-*diethylphenol*, m. p. 59·5—60·5°, b. p. 250—252°. 4 : 5-*Dimethyl*-2-*ethylanisole*, b. p. 218—220°, from the corresponding phenol, alkali, and methyl sulphate, is converted by acetyl chloride and aluminium chloride into an oil from which only 2-*hydroxy*-5 : 6-*dimethyl*-3-*ethylacetophenone*, a yellow oil, b. p. 143—145°/11 mm. (*oxime*, m. p. 153—154°; p-*nitrophenylhydrazone*, m. p. 251—253°), is obtained. It gives the original dimethylethylphenol when boiled with hydrobromic–acetic acid and when reduced (Clemmensen) affords 3 : 4-*dimethyl*-2 : 6-*diethylphenol*, m. p. 47—48°, b. p. 246—

248°. 3-o-*Xylyl acetate*, b. p. 226—228°, is converted only into 2-*hydroxy*-3 : 4-*dimethylacetophenone*, a steam-volatile yellow oil, b. p. 122—124°/12 mm. (p-*nitrophenylhydrazone*, m. p. 216—218°), undergoing reduction to 2 : 3-*dimethyl*-6-*ethylphenol*, m. p. 53—54°. The *methyl ether*, b. p. 216—218°, of the latter gives 4-*methoxy*-2 : 3-*dimethyl* - 5 - *ethylacetophenone*, steam-volatile, b. p. 138—140°/12 mm., which on reduction affords 2 : 3-*dimethyl*-4 : 6-*diethylanisole*, b. p. 234—236°, demethylated to 2 : 3-*dimethyl*-4 : 6-*diethylphenol*, b. p. 244—246°. 4 : 5-*Dimethyl*-2-*ethylphenyl acetate*, b. p. 247—249°, is converted (Fries) into a steam-volatile mixture of hydroxyacetophenones, b. p. 145—147°/12 mm., which when reduced gives 3 : 4-dimethyl-2 : 6-diethylphenol, but is not separable. Fractionation of the *p*-nitrophenylhydrazones shows the presence of 2-hydroxy-5 : 6-dimethyl-3-ethyl- and 2-hydroxy-4 : 5-dimethyl-3-ethyl-acetophenone.

2 : 4-*Dimethyl*-6-*ethylanisole*, b. p. 210—211°, slowly reacts with acetyl chloride ($AlCl_3$) to give some 2 : 4-dimethyl-6-ethylphenol, and, as the main product (semi-solid, b. p. 178—182°/15 mm.), 3-*hydroxy*-2 : 6-*dimethyl*-4-*ethylacetophenone* (possibly containing some 3-hydroxy-4 : 6-dimethyl-6-ethyl isomeride, and converted by phosphoric acid into 2 : 4-dimethyl-6-ethylphenol), the constitution of which follows from its reduction to 2 : 4-dimethyl-3 : 6-diethylphenol.

Reduction of 3-hydroxy-4 : 6-dimethylacetophenone affords 2 : 4-*dimethyl*-5-*ethylphenol*, m. p. 39—40°, b. p. 242—244°, the *acetate*, b. p. 254—256°, of which is transformed (Fries) mainly into 2-hydroxy-3 : 5-dimethyl-4-ethylacetophenone (converted in poor yield by phosphoric acid into 2 : 4-*dimethyl*-3-*ethylphenol*, m. p. 70—71°) together with some 2-hydroxy-3 : 5-dimethyl-6-ethylacetophenone, isolated only as the impure *oxime*, m. p. 120—125°.

In an attempt to synthesise 2 : 6-dimethyl-4-ethylphenol, 2-methyl-4-ethylanisole was treated with hydrogen cyanide and chloride in presence of aluminium chloride and benzene. The main product was 4-methoxy-3-methylbenzaldehyde, since it was reduced to 4-*m*-xylenol, the by-product being 2-*hydroxy*-3-*methyl*-5-*ethylbenzaldehyde*, a yellow oil, b. p. 120—122°/12 mm. (p-*nitrophenylhydrazone*, m. p. 167—169°). The dimethylethylphenol was successfully synthesised from 2-*m*-xylenol. The *acetate*, b. p. 214—216°, of the latter was treated in the cold with aluminium chloride and the mixture then slowly heated to 120° (see below). Some 2-*m*-xylenol and (mainly) 4-*hydroxy*-2 : 6-*dimethylacetophenone*, m. p. 150—151° (*sodium* salt, sparingly soluble), were formed. The latter was deacetylated normally to the original xylenol and reduced to 2 : 6-*dimethyl*-4-*ethylphenol*, m. p. 36—37°, b. p. 228—230°. The *acetate*, b. p. 245—247°, of this substance is converted (Fries) mainly into 4-hydroxy-3 : 5-dimethyl- and some 2-hydroxy-3 : 5-dimethyl-4-ethylacetophenone. Reduction of 2-hydroxy-5-methyl-3-ethylacetophenone gives 4-*methyl*-2 : 6-*diethylphenol*, m. p. 48—48·5°, b. p. 229—230° (*benzoate*, m. p. 103—103·5°), the *acetate*, b. p. 242—243°, of which affords (Fries) 2-*hydroxy*-5-*methyl*-3 : 4-*diethylacetophenone*, a yellow oil, b. p. 136—137°/12 mm. [*oxime*, m. p. (?) 108—109°; *semicarbazone*, m. p. 228—229°; p-*nitrophenylhydrazone*, m. p. 254—256°], undergoing reduction to 4-*methyl*-2 : 3 : 6-*triethylphenol*, a yellow oil, b. p. 242—244°.

5-*Methyl*-2-*ethylanisole*, b. p. 200°, gives a very little 2-*hydroxy*-6-*methyl*-3-*ethylphenol*, b. p. 137—138°/12 mm., and mainly 4-*methoxy*-2-*methyl*-5-*ethylacetophenone*, m. p. 29—30°, b. p. 139—140°/12 mm., converted by hydrobromic-acetic acid into 5-methyl-2-ethylphenol and reduced to 5-*methyl*-2 : 4-*diethylanisole*, b. p. 222—224°. The latter is demethylated normally to give 5-*methyl*-2 : 4-*diethylphenol*, b. p. 247—249° (*carbamate*, m. p. 109—110°), the *acetate*, b. p. 258—260°, of which under Fries' conditions affords a mixture of 2-hydroxy-5-methyl-3 : 4-diethylacetophenone and (?) 2-hydroxy-3 : 5-dimethyl-6-ethylacetophenone. Acetyl chloride ($AlCl_3$) and 5-methyl-2 : 4-diethylanisole give a mixture of 2-*hydroxy*-4-*methyl*-5-*ethylacetophenone*, m. p. 94—95°, and 2-*methoxy*-6-*methyl*-3 : 5-*diethylacetophenone*, a pale yellow oil, b. p. 146—148°/11 mm., the oily oxime of which when boiled with 20% hydrochloric acid gives a base (cf. A., 1924, i, 743; 1925, i, 264, 265). Reduction of the methoxyacetophenone gives 3-*methyl*-2 : 4 : 6-*triethylanisole*, b. p. 252—254°, converted by aluminium chloride into 3-*methyl*-2 : 4 : 6-*triethylphenol*, b. p. 256—258° (*sodium* salt, sparingly soluble).

Reduction of 4-hydroxy-2-methylacetophenone gives 3-*methyl*-4-*ethylphenol*, b. p. 228—230°, the *acetate*, b. p. 239—240°, of which undergoes Fries transformation into 2-hydroxy-4-methyl-5-ethylacetophenone, reduced to 5-methyl-2 : 4-diethylphenol. 2-Methyl-4-ethylphenol gives a *benzoate*, m. p. 47—49°, and an *acetate*, b. p. 238—240°. The latter is converted (Fries) into 2-*hydroxy*-3-*methyl*-5-*ethylacetophenone*, a yellow oil, b. p. 129—131°/11 mm. (p-*nitrophenylhydrazone*, m. p. 196—198°), which is reduced to 2-*methyl*-4 : 6-*diethylphenol*, b. p. 234—236°. The *acetate*, b. p. 250—252°, of the latter undergoes Fries change to 2-*hydroxy*-3-*methyl*-4 : 5-*diethylacetophenone*, m. p. 50—51° (*oxime*, m. p. 125—126°, gives no base, when boiled with hydrochloric acid; p-*nitrophenylhydrazone*, m. p. 187—190°), which on reduction affords 2-*methyl*-3 : 4 : 6-*triethylphenol*, m. p. 28—29°, b. p. 252°.

Whilst phenyl acetate under Fries' conditions gives a 50% yield of *p*- in addition to *o*-hydroxyacetophenone, the method of Wha (Diss., Kiel, 1928: acetyl chloride and aluminium chloride on phenol in nitrobenzene solution) gives a 70% yield of *p*-compound. Reduction of the latter gives *p*-ethylphenol, the acetate of which (Fries) gives 2-*hydroxy*-5-*ethylacetophenone*, a yellow oil, b. p. 119—121°/12 mm. (*oxime*, m. p. 118—119°), reduced to 2 : 4-*diethylphenol*, b. p. 228—230° (*phenylcarbamate*, m. p. 96—99°). The *acetate*, b. p. 242—244°, of this substance under Fries' conditions passes into 2-*hydroxy*-3 : 5-*diethylacetophenone*, a yellow oil, b. p. 138—140°/12 mm. (p-*nitrophenylhydrazone*, m. p. 136—138°), which is reduced to 2 : 4 : 6-*triethylphenol*, b. p. 244—246°. 2 : 4 : 6-*Triethylphenyl acetate*, b. p. 261—262°, undergoes Fries transformation into 2-*hydroxy*-3 : 4 : 5-*triethylacetophenone*, a yellow oil, b. p. 153—155°/12 mm., together with (?) some 2-hydroxy-3 : 5 : 6-triethylacetophenone, not isolated.

2-*o*-Xylyl acetate when heated rapidly with

aluminium chloride at 130—140° gives only 4-hydroxy-3 : 5-dimethylacetophenone, whereas *2-methyl-6-ethylphenyl acetate*, b. p. 220—222°, under Fries' conditions gives some *2-hydroxy-3-methyl-5-ethylacetophenone*, steam-volatile, b. p. 130—132°/12 mm. (p-*nitrophenylhydrazone*, m. p. 191—195°), but chiefly *4-hydroxy-3-methyl-5-ethylacetophenone*, m. p. 95·5—96·5°.

Fries' conditions convert *o*-ethylphenyl acetate into *2-hydroxy-3-ethylacetophenone*, b. p. 213° (p-*nitrophenylhydrazone*, m. p. 213—217°), reduced to 2 : 6-diethylphenol, the *acetate*, b. p. 238—240°, of which when rapidly heated under Fries' conditions gives a little *o*-hydroxyketone (?), but mainly *4-hydroxy-3 : 5-diethylacetophenone*, m. p. 92—92·5°.

3 : 5-*Diethylphenyl acetate*, b. p. 250—251°, is converted (Fries) into *2-hydroxy-4 : 6-diethylacetophenone*, b. p. 140°/12 mm. (*sodium* salt, sparingly soluble), which with boiling 84% phosphoric acid gives 3 : 5-diethylphenol.

The colour reactions of the hydroxy-compounds with ferric chloride are noted. Some compounds such as 4-hydroxy-3 : 5-diethylacetophenone give no colour with this reagent. E. E. TURNER.

Benzoylmethylcarbinol and acetylphenylcarbinol. II. K. VON AUWERS and H. MAUSS (Biochem. Z., 1928, **192**, 200—229; cf. A., 1924, i, 384).—Benzoylmethylcarbinol (α-ketol) and acetylphenylcarbinol (β-ketol) furnish the same semicarbazone, m. p. 193°, thiosemicarbazone, m. p. 197°, and *phenylurethane*, m. p. 143—144°. To explain these reactions it is assumed that each ketol reacts as a mixture of OH·CPh·O·CHMe and Ph·CH·O·CMe·OH. Oxidation of the semicarbazone prepared from α-ketol with lead peroxide and acetic acid at 50° affords phenylmethylglyoxalsemicarbazone, m. p. 211° (cf. Diels and van Dorp, A., 1903, i. 862). α-Ketol (benzoate, m. p. 106—107°, cf. Zincke and Zahn, A., 1910, i, 316) reacts with *p*-nitrobenzoyl chloride in pyridine to yield *p*-nitrobenzoic anhydride and *α-ketol* p-*nitrobenzoate*, m. p. 120—121°, also formed from potassium or silver *p*-nitrobenzoate and α-bromopropiophenone. Phenyl magnesium bromide and α-ketol give αα-diphenylpropane-αβ-diol, m. p. 95—96° (*monobenzoate*, m. p. 184·5—185·5°), which when treated with boiling 10% sulphuric acid gives benzhydryl methyl ketone. From β-ketol (regenerated from the semicarbazone) and phenyl magnesium bromide there is obtained αβ-diphenylpropane-αβ-diol (*monobenzoate*, m. p. 141—142°), which, contrary to the statement of Neuberg and Ohle (A., 1922, i, 480), yields with boiling 10% sulphuric acid mainly αα-diphenylpropaldehyde, b. p. —178°/12 mm., which when oximated and treated with acetic anhydride affords *αα-diphenylpropionitrile*, b. p. 178—180°/12 mm. Favorsky's conversion of α- into β-ketol by treatment with alcohol and sulphuric acid at 120—130° (A., 1926, 500) has not been confirmed.

α-Anilinopropiophenone reacts with ethyl chloroformate yielding *α-N-carbethoxyanilinopropiophenone*, m. p. 81°, which when treated with alkali in ice-cold alcoholic solution gives *3 : 5-diphenyl-4-methyloxazolone*, m. p. 113—114°. Similarly the N-*carbethoxy*-derivative, m. p. 56—58°, of *α-anilinobenzyl methyl ketone*, m. p. 90—91°, yields *3 : 4-diphenyl-5-methyloxazolone*, m. p. 162·5°, also formed by the action of 50% sulphuric acid on a hot alcoholic solution of the above phenylurethane. Hydrolysis of this oxazolone with alcoholic potassium hydroxide regenerates α-anilinobenzyl methyl ketone. Benzoinphenylurethane affords 3 : 4 : 5-triphenyloxazolone, m. p. 214—214·5° (McCombie and Parkes, J.C.S., 1912, **101**, 1994, give m. p. 210°).

α-Bromo*iso*butyrophenone is decomposed by sodium hydroxide in dilute alcoholic solution into *benzoyldimethylcarbinol* (*semicarbazone*, m. p. 188°; *acetate*, b. p. 148—150°/14 mm., m. p. 61°). Acetylphenylmethylcarbinol (*semicarbazone*, m. p. 183—184°) is acetylated by acetyl chloride, forming the *acetate*, b. p. 152—154°/14 mm. (*semicarbazone*, m. p. 183°). *Benzoylcarbinolsemicarbazone acetate* has m. p. 148—149°. Numerous spectrochemical data for the above ketols and esters are tabulated.

H. BURTON.

Tautomerism of α-diketones. Two forms of benzylmethylglyoxal and their reversible transformation. H. MOUREU (Compt. rend., 1928, **186**, 380—382; cf. A., 1927, 246, 1173).—Distillation of the hydrolytic product of the intermediate piperidide (Dufraisse and Moureu, this vol., 180) gives *benzylmethylglyoxal* (I), yellow, b. p. 104°/10 mm., m. p. 17—18°, which when kept in a sealed tube undergoes after several hours or days spontaneous transformation into a colourless form (II), b. p. 134°/10 mm., m. p. 69—70° (Dufraisse and Moureu, *loc. cit.*). Treatment of (I) with traces of alkali in the cold causes transformation into (II), the rates of change being a few seconds for diethylamine and piperidine, 12 min. for potassium hydroxide, and 3 days for benzylamine. When (II) is heated with the same catalysts and then distilled there is formed (I).

H. BURTON.

Tautomerism of α-diketones. Constitution of the two forms of benzylmethylglyoxal. H. MOUREU (Compt. rend., 1928, **186**, 503—505).—Benzylmethylglyoxal exists in two tautomeric forms, *A* and *B*. *A* has the constitution $CH_2Ph{\cdot}CO{\cdot}COMe$. The enolic form, *B*, CHPh:C(OH)·COMe, is far more reactive than *A* with Grignard reagents, bromine, and ferric chloride; it gives an *antimony* derivative, m. p. 184—185°, and *benzoyl* derivative, m. p. 82—83°; with *o*-phenylenediamine it forms *benzylmethylquinoxaline*, m. p. 57—58°. The "α-phenylacetoacetaldehyde" of Weitz and Scheffer (A., 1921, i, 869) was in reality the above *B* tautomeride.

B. W. ANDERSON.

Influence of anti-auxochromic groups on the halochromy of ketones. P. PFEIFFER and B. SEGALL (Annalen, 1928, **460**, 123—137).—It is shown that the nitro- and sulpho-groups, and to a lesser extent halogen atoms, exert a hypsochromic effect on the halochromy of unsaturated ketones. The *meta*-directing nitro-group exerts its effect most markedly when it is in the *meta*-position with respect to the ethylenic linking, and least when it is in the *para*-position. The *ortho–para* directive groups, OH,

OMe, and NH_2, best exert their effect, which is bathochromic, when in the *para*-position to the unsaturated side-chain.

The preparation of 3-nitro-4-methoxybenzaldehyde by the nitration of anisaldehyde is described. The nitro-compound when condensed (this and other condensations now described were carried out in aqueous-alcoholic sodium hydroxide) with acetophenone, gave *phenyl 3-nitro-4-methoxystyryl ketone*, yellow, m. p. 146°, whilst with *p*-methoxyacetophenone, p-*anisyl 3-nitro-4-methoxystyryl ketone*, yellow, m. p. 160°, resulted. The *perchlorate*, m. p. 177—180° (decomp.), of the latter is orange-red, whilst the *perchlorate* of *p*-anisyl *p*-methoxystyryl ketone is red. Condensation of *o*-nitrostyryl methyl ketone with *o*-nitrobenzaldehyde affords 2 : 2'-*dinitrodistyryl ketone*, yellow, m. p. 170·5—171°. The known 3 : 3'-isomeride is greenish-yellow, and forms an orange-yellow *perchlorate*, decomp. 143—145° (softening at about 125°). 3-*Nitro*-4 : 4'-*dimethoxydistyryl ketone*, obtained either from 3-nitro-4-methoxystyryl methyl ketone or from *p*-methoxystyryl methyl ketone, is yellow and has m. p. 158·5°. 3 : 3'-*Dinitro*-4 : 4'-*dimethoxydistyryl ketone*, yellow, has m. p. 220°, and forms an orange-red *perchlorate*, m. p. 198° (decomp.).

3-*Chloro*-4-*methoxystyryl methyl ketone*, bright yellow from aqueous alcohol or colourless from water, has m. p. 111·5° and is formed together with some of the distyryl ketone (next below) when acetone is condensed with 3-chloroanisaldehyde, m. p. 62·5—63° (prepared by the hydrogen cyanide method from *o*-chloroanisole; Gattermann gave m. p. 53°). With different proportions of reactants, 3 : 3'-*dichloro*-4 : 4'-*dimethoxydistyryl ketone*, yellow, m. p. 177·5—178·5° (*perchlorate*, chocolate-brown, subl. 153°, m. p. 205—207° decomp.), is formed. The similarly obtained *phenyl 3-chloro-4-methoxystyryl ketone*, bright yellow, has m. p. 113—114°.

3-Bromo-4-methoxybenzaldehyde, prepared by an improved method, is converted by acetone into a mixture of 3-*bromo*-4-*methoxystyryl methyl ketone*, m. p. 101°, with some 3 : 3'-*dibromo*-4 : 4'-*dimethoxydistyryl ketone*, yellow, m. p. 181° (*perchlorate*, deep brownish-red, but lighter in shade than the bromine-free compound, has m. p. 168—169°, decomp.), obtainable better from bromoanisaldehyde and bromostyryl methyl ketone. *Phenyl 3-bromo-4-methoxystyryl ketone*, bright yellow, has m. p. 112—113°, and p-*anisyl 3-bromo-4-methoxystyryl ketone*, bright greenish-yellow, has m. p. 120° (*perchlorate*, orange-red, m. p. 138—139°). E. E. TURNER.

Behaviour of methoxy-compounds towards aluminium bromide. P. PFEIFFER and E. HAACK (Annalen, 1928, **460**, 156—179).—Previous work has shown that when perchloric acid or stannic chloride forms additive compounds with unsaturated ketones containing methoxyl groups, neither the latter nor the ethylenic linking are concerned in the compound formation, which is controlled by the carbonyl group solely. Aluminium bromide is now shown to form, with unsaturated ketones, compounds in which each methoxyl and each carbonyl group can cause the union of a molecule of bromide, although here again the ethylenic linking plays no part. 4-Methoxydiphenyl is exceptional in giving the *compound* $3C_6H_4Ph{\cdot}OMe,2AlCl_3$, the composition of which cannot be accounted for.

The aluminium bromide additive compounds of methoxylated ketones have much less deep colours than those of the methoxyl-free ketones, a result due to the depression of the bathochromic effect of the methoxyl group by its combination with aluminium bromide, and analogous to the similar depression of the bathochromic effect of an amino- or a derived amino-grouping in perchlorate formation, with unsaturated amino-ketones (Pfeiffer, Kollbach, and Haack, following abstract). The group $\cdot OMe,AlBr_3$, in fact, exerts a hypsochromic action.

The discovery that phenol ethers in general form additive compounds with aluminium bromide suggests that the probable mode of action of aluminium halides as demethylating agents is to be represented as follows: $R{\cdot}OMe \longrightarrow R{\cdot}OMe,AlBr_3 \longrightarrow R{\cdot}O{\cdot}AlBr_2+MeBr \longrightarrow R{\cdot}OH$. In actual fact, the additive compounds now described usually decompose smoothly when heated in benzene solution to give the aluminium alkyloxybromides, which with water afford the corresponding phenols. It is pointed out that aluminium bromide is probably preferable to the chloride, since it is readily soluble in benzene etc., whilst the chloride is not.

Precise directions are given for the purification of the benzene and other solvents used for the preparation of the aluminium bromide additive compounds, a special apparatus being described. Most of the additive compounds derived from methoxylated compounds lose methyl bromide merely on keeping, passing thereby into the aluminium alkyloxybromides. The same decomposition occurs more rapidly in a vacuum at 100—130°, but is accompanied by side reactions. Quantitative demethylation is effected by heating the additive compound with excess of benzene, avoiding ingress of moisture. The above additive compound of aluminium bromide and methoxydiphenyl is thus converted into a crystalline *aluminium methoxydibromide*, which with water affords 4-hydroxydiphenyl. The additive *compound* of β-naphthyl methyl ether with $1AlBr_3$ behaves similarly.

Quinol dimethyl ether forms two additive *compounds*, one with $1AlBr_3$, one with $2AlBr_3$. Decomposition of the latter in boiling benzene affords the yellow crystalline *compound*, $AlBr_2{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}AlBr_2$, from which quinol was readily obtained.

p-Methoxyacetophenone gives a *compound* with $2AlBr_3$, readily converted into *p*-hydroxyacetophenone. 4 : 4'-Dimethoxybenzophenone gives a *compound* with $2AlBr_3$. If this ketone is heated in benzene solution with aluminium bromide, the yellow $R{\cdot}O{\cdot}AlBr_2$ *compound* separates and may be converted into the corresponding phenol. 4-Methoxy-α-naphthyl methyl ketone forms yellow *compounds* (1) with $1AlBr_3$, and (2) with $2AlBr_3+C_6H_6$. The latter decomposes to give an oily $R{\cdot}O{\cdot}AlBr_2$ *compound*, convertible into the corresponding phenol.

p-Methoxystyryl methyl ketone affords a red *compound* with $1AlBr_3$ and a deep yellow *compound* with $2AlBr_3$, through which demethylation was effected. Phenyl *p*-methoxystyryl ketone gives a deep red

compound with $1AlBr_3$, decomposing in hot benzene without demethylation, and a honey-yellow *compound* with $2AlBr_3$, decomposing particularly readily in hot benzene to give the yellow *compound*, $Br_2AlO{\cdot}C_6H_4{\cdot}CH{:}CHBz,AlBr_3$, from which the *p*-hydroxy-ketone was obtained.

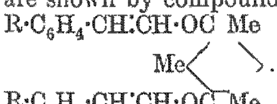
p-Anisyl *p*-methoxystyryl ketone forms a cinnabar-red *compound* with $1AlBr_3$, not undergoing demethylation in hot benzene, and a honey-yellow *compound* with $3AlBr_3$, demethylating with great readiness.

4 : 4′-Dimethoxydistyryl ketone forms a bright red *compound* with $1AlBr_3$, and a honey-yellow *compound* with $3AlBr_3$, the latter undergoing demethylation with moderate facility. E. E. TURNER.

Halochromic compounds of polyketones. P. PFEIFFER, K. KOLLBACH, and E. HAACK (Annalen, 1928, **460**, 138—156).—An investigation devised to test Pfeiffer's theory that additive compounds of ketones and inorganic chlorides etc. are not merely "molecular" compounds but that the oxygen of the keto-group is definitely the prime factor causing combination. The theory is apparently proved, for in the case of polyketones, additive compounds with aluminium bromide have been obtained which contain as many molecules of bromide as there are keto-groups in the polyketone. In the case of unsaturated ketones, no addition occurs at the ethylenic linking. Perchlorates of the polyketones were also isolated, but their composition did not uniformly correspond with the requirements of the above theory.

Some further observations are made on the halochromy of "double chalkones," viz., compounds of type I:

When R=H, R=*p*-OMe, and R=*o*-Cl, the diketone is straw-yellow, bright yellow, and pale yellow, respectively; the solution in concentrated sulphuric acid is deep orange-red, deep reddish-violet, and orange-red, respectively. Paler halochromy colours are shown by compounds of type II,



. Thus, when R=H, R=*p*-Me, R=*p*-OMe, R=*p*-NMe_2, R=*o*-Cl, and R=*p*-Cl, the diketone is yellowish-white, yellowish, yellowish, yellowish-green, pale straw-yellow, and pale yellow, respectively. When R=H, *o*-Cl, or *p*-Cl, the concentrated sulphuric acid solution is greenish-yellow. When R=*p*-Me, this solution is deep yellow, and when R=*p*-OMe, it is orange. In concentrated sulphuric acid solution, the bathochromic effect of a *p*-NMe_2 group is destroyed owing to salt formation, and the solution is only yellowish-brown in consequence. The halochromy colours of the "double chalkones" of the diacetylmesitylene series (II) correspond with those of the simple chalkones, whilst the colours of the "double chalkones" of the 1 : 4-diacetylbenzene series (I) are markedly deeper than those of the latter.

1 : 4-Diacetylbenzene, difficult to prepare by Ingle's method (Diss., München, 1894) from ethyl terephthaloyldimalonate, is also obtained in poor yield by the action of magnesium methyl iodide on terephthalonitrile, prepared by distilling lead terephthalate with lead thiocyanate. Benzaldehyde converts diacetylbenzene in aqueous-alcoholic sodium hydroxide solution (the condensing method used generally in this investigation) into 1 : 4-*dicinnamoylbenzene* (I, R=H), m. p. 205·5—207·5° (no perchlorate obtainable). 1 : 4-*Di*-p-*methoxycinnamoylbenzene* (I, R=*p*-OMe), prepared from anisaldehyde, has m. p. 212° (*perchlorate*, violet-black), and 1 : 4-*di*-o-*chlorocinnamoylbenzene* (I, R=*o*-Cl), from *o*-chlorobenzaldehyde, has m. p. 251°, and was not obtained quite pure.

Acetophenone-4-carboxylic acid has m. p. 210°, not 205° as lit., and is converted normally into p-*cinnamoylbenzoic acid*, pale yellow, m. p. 234°, 4-p-*methoxycinnamoylbenzoic acid*, yellow, m. p. 223° (*perchlorate*, chocolate-brown, exploding when heated), 4-o-*chlorocinnamoylbenzoic acid*, yellow, m. p. 214—215°, and 4-p-*dimethylaminocinnamoylbenzoic acid*, reddish-brown, m. p. 248°. These four substances dissolve in concentrated sulphuric acid to give reddish-orange, deep bluish-red, orange, and deep greenish-yellow solutions, respectively.

2 : 4-Diacetylmesitylene is readily converted into 2 : 4-*dicinnamoylmesitylene* (II, R=H), m. p. 135°, 2 : 4-*di*-p-*methylcinnamoylmesitylene* (II, R=*p*-Me), m. p. (+½EtOH) 97°, 2 : 4-*di*-p-*methoxycinnamoylmesitylene* (II, R=*p*-OMe), m. p. (+½EtOH) 105—106° or (+$\frac{1}{2}C_6H_6$) 93°, 2 : 4-*di*-o-*chlorocinnamoylmesitylene* (II, R=*o*-Cl), m. p. 161°, 2 : 4-*di*-p-*chlorocinnamoylmesitylene* (II, R=*p*-Cl), m. p. 116° (*perchlorate*, yellowish-grey, exploding when heated), and 2 : 4-*bisdimethylaminocinnamoylmesitylene* (II, R=*p*-NMe_2), m. p. 234° (*perchlorate*, yellow, exploding when heated). The six last-named ketones give, in concentrated sulphuric acid solution, the following colours, respectively: deep greenish-yellow, deep yellow, orange, greenish-yellow, greenish-yellow, and yellowish-brown.

p-Tolyl 4-diphenylyl ketone forms a lemon-yellow additive *compound* with $1AlBr_3$, xanthone a yellow additive *compound* with $1AlBr_3+1C_6H_6$, phenyl styryl ketone an orange *compound* with $1AlBr_3$, distyryl ketone a blood-red *compound* with $1AlBr_3$, αε-diphenyl-$\Delta^{\beta\delta}$-pentadien-α-one (cinnamylideneacetophenone) a blood-red *compound* with $AlBr_3$, 1 : 4-dibenzoylbenzene a *compound* with $2AlBr_3+C_6H_6$, 2 : 4-diacetylmesitylene a reddish-yellow *compound* with $2AlBr_3$, and *s*-triacetylbenzene a pale yellow *compound* with $3AlBr_3$. E. E. TURNER.

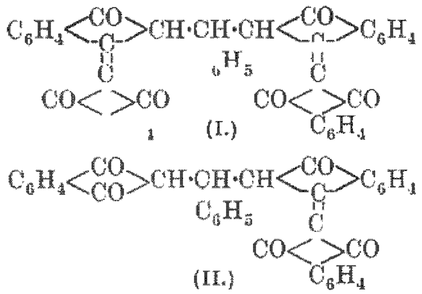
Unusual substitution reaction. I—III. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1926, 3, 54—59, 210—229, 230—239; Chem. Zentr., 1927, i, 602, ii, 69, 70).—I. Condensation of dimethyldihydroresorcinol with ethyl benzylideneacetoacetate by means of piperidine in absolute alcohol affords *benzylidenebisdimethyldihydroresorcinol*, m. p. 192°, which is also produced from dimethyldihydroresorcinol and ethyl benzylidenebisacetoacetate, and is converted by sulphuric or acetic acid into Vorlander's phenyltetramethyloctahydroxanthendione, m. p. 200—201° (A., 1900, i, 100).

II. This substitution,

$$(CO{\cdot}R')_2CH{\cdot}CHR{\cdot}CH(CO{\cdot}R'')_2+CH_2(CO{\cdot}R''')_2 \longrightarrow (CO{\cdot}R')_2CH{\cdot}CHR{\cdot}CH(CO{\cdot}R''')_2+CH_2(CO{\cdot}R'')_2,$$

is

determined by the activity of the methylene compounds, which rises in the series: ethyl malonate, ethyl acetoacetate, acetylacetone, indandione, dimethyldihydroresorcinol, di-indone. Evidence is adduced in support of the author's view of the reaction. *Benzylidenebisdi-indone* (I), yellow, m. p. 256°, is obtained by interaction of indandione and ethyl benzylideneacetoacetate, ethyl benzylideneindandionemalonate, benzylidenebisdimethyldihydroresorcinol, or (together with benzylideneindandionedi-indone) benzylideneindandione in absolute alcohol



(I.) (II.)

in presence of piperidine. *Benzylideneindandionedi-indone* (II), m. p. 302°, is also obtained from ethyl benzylideneindandionemalonate and dimethyldihydroresorcinol.

III. [with V. N. Georgescu]. Methylenebisdi-indone, $C_{37}H_{20}O_6$, yellow, m. p. 273°, gives with alkali in boiling alcohol an indigo-blue, then reddish-violet colour. Methyleneindandionedi-indone, $C_{28}H_{16}O_5$, has m. p. 305—311° (decomp. and subl.), and gives a reddish-violet solution in alcoholic potash.

A. A. Eldridge.

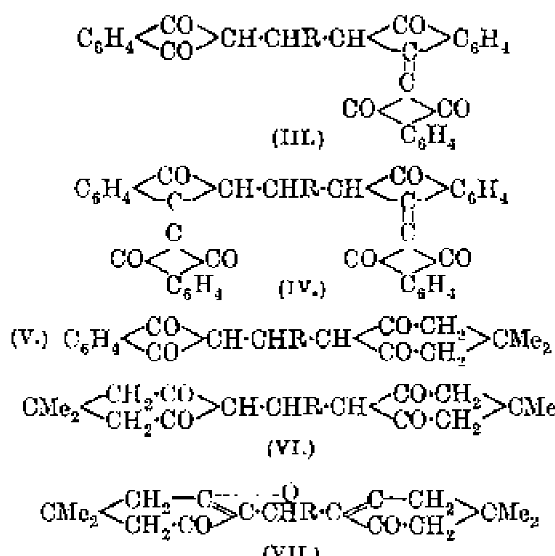
Factors disturbing valency fields. Action of substances with an active methylene group on the carbindogenides. I—II. M. V. Ionescu and S. Secareanu (Bul. Soc. Stiinte Cluj, 1926, 3, 112—128, 250—284; Chem. Zentr., 1927, i, 601—602, ii, 71—72).—I. It has already been shown (Bul. Soc. Stiinte Cluj, 1925, 2, 280) that the absorption spectrum of a chromogen is modified by the introduction of a co-ordinatively unsaturated group, in a measure determined by the extent of the unsaturation. According to the character of the absorption spectra, the carbindogenides (I) can be divided into (*a*) those where R=phenyl, *o*-tolyl, *m*-tolyl, or *p*-acetoxyphenyl, the absorption curve lying below 4800 Å.,

(I.) $C_6H_4<^{CO}_{CO}>C:CHR$

(II.) $C_6H_4<^{CO}_{CO}>CH\cdot CHR\cdot CH(CO_2Et)_2$

and (*b*) those where R=*p*-anisyl, 3 : 4-methylenedioxyphenyl, *p*-hydroxyphenyl, or *p*-dimethylaminophenyl, the curve passing 4800 Å. Only group (*a*) gives products (II) by addition with ethyl malonate on account of the presence of the co-ordinatively unsaturated groups OMe, O_2CH_2, OH, and NMe_2. The *p*-tolyl derivative, when heated at 175° or treated with cold, concentrated sulphuric acid, does not yield a lactone, but is decomposed into its components. *Ethyl α-carbethoxy-β-indandionyl-β-phenylpropionate*, m. p. 108°; *ethyl β-indandionyl-β-phenylpropionate*, m. p. 109°; *ethyl α-carbethoxy-β-indandionyl-β-*p*-tolylpropionate*, m. p. 111—112° [dicarboxylic *acid*, $C_{20}H_{16}O_6$, m. p. 182° (decomp.); *lead* and *copper* salts]; the *diphenylhydrazonediphenylhydrazide* from II, $C_{44}H_{40}O_2N_8$, m. p. 178°; *β-indandionyl-β-*p*-tolylpropionic acid*, m. p. 173° (*lead* and *copper* salts); *ethyl α-carbethoxy-β-indandionyl-β-*m*-tolylpropionate*, m. p. 135°, and *ethyl α-carbethoxy-β-indandionyl-β-*p*-acetoxyphenylpropionate*, m. p. 154°, are described.

II. The following compounds have been prepared: p-*toluylidene-*, m. p. 310°; p-*acetoxybenzylidene-*, m. p. 320; *anisylidene-*, m. p. 310°; m-*toluylidene-*, m. p. 340°; and p-*hydroxybenzylidene-*, m. p. 275°, *-indandionedi-indones* (cf. III); p-*acetoxybenzylidene-*, m. p. 162°; p-*toluylidene-*, m. p. 151°; m-*toluylidene-*, m. p. 156°, and *α-naphthylidene-*, m. p. 172°, *-indandiones* (cf. I); p-*toluylidene-*, m. p. 253°; m-*toluylidene-*, m. p. 236°; *anisylidene-*, m. p. 233°; *piperonylidene-*, m. p. 242°; and *α-naphthylidene-*, m. p. 230°, *-bisdi-indones* (cf. IV); the *compounds* $C_{23}H_{26}O_3$ (VII, R=Ph), m. p. 202°; $C_{24}H_{28}O_3$ (VII, R=*p*-C_7H_7), m. p. 202°; $C_{24}H_{28}O_4$ (VII, R=*p*-anisyl), m. p. 247°; *compound* (VII) (R=*p*-acetoxyphenyl), not analysed, has m. p. 234°. Inadequate boiling in the preparation of the compound $C_{23}H_{26}O_3$ leads to the production of (VI).

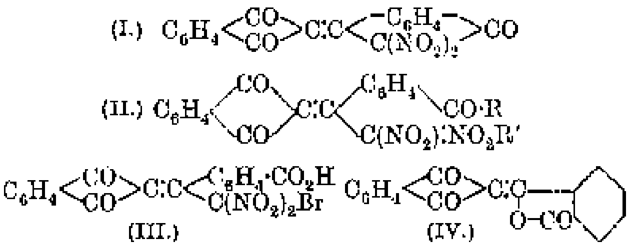


(III.) (IV.) (V.) (VI.) (VII.)

A. A. Eldridge.

Dinitrobindone and its scission products. W. Wislicenus and H. Schlichenmaier (Annalen, 1928, 460, 278—288).—Nitric acid (*d* 1·5) converts bindone (indandionylidenehydrindone; Wislicenus, Ber., 1887, 20, 598) in boiling glacial acetic acid solution into *dinitrobindone* (I), m. p. 183°. The latter in alcoholic potassium hydroxide affords the red *dipotassium* salt of the unstable *acid* (II, R=OH, R′=H), m. p. 94°, whilst bromine and aqueous potassium hydroxide convert (I) into *compound* (III), pale yellow, exploding at 117°. When dinitrobindone is treated with ice-cold potassium hydroxide and the red solution formed is at once acidified, *phthalideneindandione* (IV,) m. p. 253°, is formed, dinitromethane being eliminated at the acidification stage. By prolonged heating of dinitrobindone with aqueous potassium

hydroxide at 100°, the *potassium* salt of dinitromethane, exploding at 204°, is obtained.



Alcoholic potassium ethoxide converts (I) into the deep red *potassium* salt–*ethyl* ester (II, R=OEt, R′=K) (+2MeOH). Acidification of this affords the *ethyl hydrogen* ester (II, R=OEt, R′=H), m. p. initially 132°, rapidly changing to 124°. The *potassium* salt–*methyl* ester (II, R=OMe, R′=K) (+2MeOH) and the *methyl hydrogen* ester (II, R=OMe, R′=H) are formed similarly. The last-named potassium salt is converted by bromine water into the corresponding *tribromodinitro-methyl* ester, yellow, m. p. 139°.

Aqueous ammonia converts dinitrobindone into the *lactam* corresponding with (IV), m. p. 265°, and dinitromethane, whilst if ammonia gas is passed into a cold benzene solution of dinitrobindone, the red *ammonium* salt–*amide* (II, R=NH_2, R′=NH_4), decomp. 183°, results. The latter undergoes decolorisation when treated with anhydrous ether. Cold aniline slowly converts dinitrobindone into the red *phenylammonium* salt–*anilide* (II, R=NHPh, R′=NH_3Ph), transformed by anhydrous ether into the free *anilide* (II, R=NHPh, R′=H) and by warm methyl-alcoholic hydrogen chloride into dinitromethane and the *phenylimide*, orange-yellow, m. p. 234°, stable to acids and only slowly hydrolysed by alkalis. When the above lactam, m. p. 265°, is warmed with aqueous sodium hydroxide, 2-o-*carboxybenzoylindandione*, obtained anhydrous and +1MeOH, m. p. 155—160°, results (*copper* salt; *methyl* ester, m. p. 123°). Bromination of (II) in chloroform gives the 2-*bromo*-derivative, which rapidly passes over into *dibromodiketohydrindene*, m. p. 176°, which is also formed by treating a solution of the acid in sodium hydrogen carbonate with bromine water. E. E. TURNER.

Tautomerism of hydroxyquinones. L. F. FIESER (J. Amer. Chem. Soc., 1928, **50**, 439—465).—Tautomeric equilibrium between 2-hydroxy-α-naphthaquinone (α-form) and 4-hydroxy-β-naphthaquinone (β-form) has previously been evidenced (cf. Fieser, A., 1927, 59). Since both tautomerides yield the same trihydroxynaphthalene on reduction, the value of the tautomeric equilibrium constant (K) can be deduced from their respective normal reduction potentials, and it is shown that $\log K=(E^{\beta}-E^{\alpha})/0{\cdot}0296$. The normal reduction potentials of certain alkyl ethers of the α- and β-isomerides were determined, the values for the methyl ethers being 0·353 and 0·433 volt, respectively, and K was evaluated assuming that the difference between these two values approximates to that between those for the two tautomeric hydroxynaphthaquinones. The measured normal reduction potential of naphthapurpurin (0·243 volt) is in good agreement with that calculated from the corresponding constants of related compounds, whilst the value similarly calculated for the tautomeride of naphthapurpurin (0·308 volt) is considerably higher, thus confirming that the tautomeride of lower reduction potential predominates in the equilibrium mixture, according to the above expression, and this is also supported by available data for two indophenols (cf. Clark, A., 1924, ii, 597). From determinations of normal reduction potentials of lapachol, its derivatives, and a large number of similar compounds it is concluded that both lapachol and *iso*-β-lapachol are derivatives of α-naphthaquinone (cf. Hooker, J.C.S., 1896, **69**, 1381). With regard to the influence of p_H on the position of tautomeric equilibrium, it is shown mathematically that the ratio of the equilibrium constant of the undissociated tautomeride to that of the completely ionised substance is equal to the ratio of the dissociation constants of the two tautomerides.

4-n-*Propoxy*-β-*naphthaquinone*, orange-yellow, m. p. 116°, and 2-n-*propoxy*-α-*naphthaquinone*, pale yellow, m. p. 91°, are described. The following 3-methoxy-2-alkyl-α-naphthaquinones were prepared by treating the corresponding hydroxy-derivatives with diazomethane: 3-*methoxy*-2-γ-*methyl*-Δ^{β}-*butenyl*-, m. p. 53°; -2-γ-*phenyl*-Δ^{β}-*propenyl*-, m. p. 90·5°; -2-*benzyl*-, m. p. 83·5°, and -2-*diphenylmethyl*-α-*naphthaquinone*, m. p. 112·5°. Details are given of the preparation of a number of polyhydroxynaphthaquinones (cf. Charrier and Tocco, A., 1923, i, 1028); the *barium* salt of naphthapurpurin is described. iso*Naphthazarin dimethyl ether*, yellow, m. p. 115°, is hydrolysed by aqueous 1% sodium hydroxide solution to a *monomethyl ether*, yellow, m. p. 152°, which is very resistant to further hydrolysis. 3-Hydroxy-2-β-hydroxypropyl-α-naphthaquinone yields 1-methyl-4 : 5-benzocoumaran-3 : 6-quinone (I) when treated with hydrobromic acid in glacial acetic acid, and 1-methyl-5 : 6-benzocoumaran-3 : 4-quinone (II) when treated with concentrated sulphuric acid, reverse changes being effected in each case by the action of aqueous sodium hydroxide, whilst (II) yields (I) when treated with hydrobromic acid (cf. Fieser, A., 1927, 462).

F. G. WILLSON.

2-Hydroxy-1 : 4-anthraquinone. L. F. FIESER (J. Amer. Chem. Soc., 1928, **50**, 465—474).—When treated with aqueous sodium hydrogen sulphite, 1 : 2-anthraquinone yields *sodium* 1 : 2-*dihydroxyanthracene*-4-*sulphonate*, from which, by oxidation with chromic acid, *sodium* 1 : 2-*anthraquinone*-4-*sulphonate*, red, is obtained. The corresponding *ammonium* salt (I) is also obtained by treatment of nitroso-β-anthrol with aqueous sodium hydrogen sulphite, and oxidation, with 25% nitric acid, of the resulting 1-*amino*-2-*anthrol*-4-*sulphonic acid*, (+$\frac{1}{2}H_2O$), yellow. Treatment of (I) with methyl alcohol and concentrated sulphuric acid affords 2-*methoxy*-1 : 4-*anthraquinone*, yellow, m. p. 217°, which is hydrolysed by boiling aqueous sodium hydroxide to 2-*hydroxy*-1 : 4-*anthraquinone* (II), yellow, m. p. 243° (decomp.) (*sodium* salt, orange; *silver* salt, red; *acetate*, yellow, m. p. 195°). When boiled with acetic anhydride, sodium acetate, and zinc dust, (II) yields

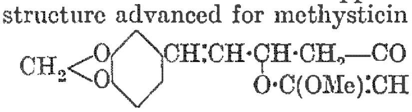
1 : 2 : 4-*triacetoxyanthracene*, m. p. 191°, which, on oxidation with chromic acid in glacial acetic acid, affords triacetylpurpurin, m. p. 202—203° (cf. Schunk and Roemer, A., 1877, ii, 624). Treatment of the silver salt of (II) with methyl iodide in benzene affords 4-*methoxy*-1 : 2-*anthraquinone*, yellow, m. p. 198°, together with about half its weight of the above 2-methoxy-1 : 4-anthraquinone, the former being completely isomerised to the latter when boiled with methyl alcohol and sulphuric acid. Allyl bromide yields, similarly, the following three derivatives, in the proportions given: 4-*allyloxy*-1 : 2-*anthraquinone* (70%), yellow, m. p. 173°, 2-*allyloxy*-1 : 4-*anthraquinone* (11%), yellow, m. p. 139°, and 3-*hydroxy*-2-*allyl*-1 : 4-*anthraquinone* (10%), yellow, m. p. 215°. The *o*-quinonoid derivative is isomerised to the *p*-quinone when heated at 175°, whilst treatment with cold, concentrated sulphuric acid affords 1-*methyl*-5 : 6-(ββ-*naphtha*)*coumaran*-3 : 4-*quinone*, orange-red, m. p. 186—187°. When treated with warm, dilute, aqueous alkali, the latter yields 3-*hydroxy*-2-β-*hydroxypropyl*-1 : 4-*anthraquinone*, yellow, m. p. 211—212°. The reduction potentials of α- and β-anthraquinones are from 81 to 101 millivolts lower than those of the corresponding naphthaquinones, whilst that of α-anthraquinone is 246 millivolts higher than that of 9 : 10-anthraquinone. It is concluded that there is complete analogy between α-anthraquinone and α-naphthaquinone, but that α-anthraquinol is analogous to 9 : 10-anthraquinol. F. G. Willson.

[Fritzsch's reagent.] Correction. E. Bornstein (Ber., 1928, **61**, [*B*], 443; cf. A., 1927, 155).—The terms α- and β-methylanthracene should be interchanged. H. Wren.

Salicylic acid primeveroside. M. Bridel and P. Picard (Compt. rend., 1928, **186**, 98—99).—Monotropitoside, when hydrolysed by aqueous potassium hydroxide, and then treated with the calculated quantity of sulphuric acid, yields *salicylic acid primeveroside*, α_D −61·6°, a crystalline, non-reducing substance. When hydrolysed by dilute sulphuric acid, the primeveroside yields salicylic acid and equimolecular proportions of xylose and dextrose.

B. W. Anderson.

Methysticin. V. Lampe, J. Zielinska, and J. Majewska (Bull. Soc. chim., 1928, [iv], **43**, 62—71; cf. Borsche, Meyer, and Peitzsch, A., 1927, 1192).—*Methyl piperoylacetate*, m. p. 132—134°, has been synthesised by boiling *methyl α-piperoylacetoacetate*, m. p. 166—167° (from piperoyl chloride, b. p. 175—185°, and methyl sodioacetoacetate), with dilute acetic acid and proved identical with ψ-methysticin. Pomeranz's structure for methysticin (A., 1889, 278; 1890, 257) is therefore abandoned. Heating at 3 atm. pressure for 3 hrs. converts methyl α-piperoylacetoacetate into piperoylacetone, m. p. 119—120°. *Ethyl α-piperoylacetoacetate*, m. p. 92—94°, with 10% ammonia affords *ethyl piperoylacetate*, m. p. 73—75° (cf. Winzheimer, A., 1908, i, 804). Potassium piperoylacetate and methyl iodide in alcoholic solution also afford ψ-methysticin, together with a substance, m. p. 156—157°. Alcoholic potassium hydroxide converts ψ-methysticin into an indefinite amorphous, orange substance; with 10% alcoholic sulphuric acid or on heating with water under 3 atm., methysticol is obtained. With sodium in anisole ψ-methysticin yields a sodium derivative giving, with acetyl chloride, methyl α-piperoylacetoacetate. On reduction with hydrogen in acetone solution in presence of palladium–barium sulphate, 4 atoms of hydrogen are absorbed, affording an oil which gives no copper salt, and agitated with 2% sodium hydroxide in ether gives an orange-brown solution from which carbon dioxide precipitates an oil. Under similar conditions methysticin absorbs 2 atoms of hydrogen, giving a product m. p. 113—115°. On bromination with the hydrobromide of pyridine dibromide in chloroform, methysticin affords a *dibromo*-derivative, m. p. 156° (decomp.); ψ-methysticin under similar conditions gives a monobromo-derivative, probably *methyl α-bromopiperoylacetic acid*, m. p. 98°, since under similar conditions cinnamoylacetone gives *α-bromo-α-cinnamoylacetone*, m. p. 93—95°, identical with the product obtained by the action of bromine on the copper salt of cinnamoylacetone in chloroform solution. These relations between methysticin and ψ-methysticin are parallel to those obtaining between the chalkones and flavones and support the 1 : 4-pyrone structure advanced for methysticin:



R. Brightman.

Photochemical oxidation of ergosterol. A. Windaus and J. Brunken (Annalen, 1928, **460**, 225—235).—Ergosterol undergoes photo-oxidation in 95% alcohol solution in presence of eosin when submitted to radiation from a powerful filament lamp. Eosin may be replaced by other fluorescent substances, *e.g.*, erythrosin, methylene-blue, chlorophyll, or hæmatoporphyrin. Acridone is feebly sensitising, but rosaniline has no effect. Potassium cyanide inhibits the photo-oxidation, and the latter does not occur at all in the dark.

The product of oxidation is *ergosterol peroxide*, $C_{27}H_{42}O_3$, m. p. 178°, having a normal *M* in camphor or naphthalene, and $[\alpha]_D^{19}$ −35·7° (in chloroform, $[\alpha]_D^{18}$ −35·5°). The peroxide is very unstable in presence of acids. Its chloroform solution becomes greenish-blue, then deep blue, and finally violet when treated with arsenic trichloride. Antimony trichloride and tin tetrachloride give brownish-violet and wine-red colorations, respectively. Concentrated sulphuric acid becomes deep red when shaken with a chloroform solution of the peroxide. When distilled in a high vacuum, the latter affords a crystallisable distillate, not examined, but is for the most part unchanged up to 180—185°. Digitonin precipitates an additive *compound*, $[\alpha]^{15}$ −38° in pyridine, from an alcoholic solution of the peroxide; the latter is converted by acetic anhydride into *ergosteryl acetate peroxide*, m. p. 202°, also obtained by the photo-oxidation of ergosteryl acetate in alcoholic (eosin) solution. Alcoholic potassium hydroxide converts the acetate into ergosterol peroxide. The latter on reduction with sodium and alcohol affords ergosterol and then, slowly, *dihydroergosterol*, m. p. 173—174°, $[\alpha]_D$ −20·4° in chloroform (the

readily hydrolysed *acetate*, m. p. 180—181°, has $[\alpha]_D^{16}$ —20° in chloroform), also obtainable direct from ergosterol. Traces of the latter may be removed from dihydroergosterol by treatment with blood charcoal in alcohol, or by photo-oxidation. Dihydroergosterol gives no colour reactions with arsenic or antimony trichlorides, but sulphuric acid gives a yellow, then an orange, solution. Dihydroergosteryl acetate, when reduced with hydrogen in presence of acetic acid and platinum-black, affords γ-ergostyl acetate (Reindel, A., 1927, 241).

Ergosterol peroxide, whether irradiated or otherwise, has neither antixerophthalmic nor antirachitic action, whilst ergosterol prepared from the peroxide is still capable of activation. This suggests that it is ergosterol itself and not an impurity present in it which forms the antirachitic provitamin. Dihydroergosterol, before or after irradiation, is physiologically inactive. E. E. TURNER.

Photochemical dehydrogenation of ergosterol. A. WINDAUS and P. BORGEAUD (Annalen, 1928, **460**, 235—239).—Ergosterol dissolved in alcohol containing eosin or erythrosin (chlorophyll has a feeble sensitising action, whilst methylene-blue and rosaniline have none) undergoes photo-dehydrogenation in a glass vessel in sunlight to give *ergopinacol*, $C_{54}H_{82}O_2$, m. p. 202—203° (decomp.), $[\alpha]_D^{16}$ —209° in pyridine. Concentrated sulphuric acid becomes orange when shaken with a chloroform solution of the pinacol. On distillation at 0·1 mm. (bath at 210°) the latter affords *neoergosterol*, $C_{27}H_{42}O$ ($C_{27}H_{40}O$ not impossible), m. p. 151—152°, *M* normal in camphor, $[\alpha]_D$ —12° (*acetate*, m. p. 122—123°), also formed by reducing ergopinacol with zinc dust and glacial acetic acid. Neither ergopinacol nor neoergosterol possesses antirachitic action, whether previously irradiated or not. E. E. TURNER.

Santenonequinone and a general method for the preparation of diketones. J. PALMEN (Finska Kemistamfundets Medd., 1927, **36**, 11—21; Chem. Zentr., 1927, ii, 1691).—In the preparation of *iso*nitrosocamphor, sodamide and benzene were substituted for sodium and ether. Treatment with formaldehyde and hydrogen chloride then yields a diketone, the method being convenient for diketones having an unsubstituted CH_2-group next to the CO-group. In this way were obtained *iso*nitrososantenone and an oil, possibly a geometrical isomeride. Thence were obtained santenonequinone hydrate, m. p. 137—138°, and santenonequinone (annexed formula), m. p. 84—85° [disemicarbazone, m. p. 238° (uncorr.)]. The dioxime, $C_9H_{14}O_2N_2$, has m. p. 144—145°. Oxidation of the quinone with 2% potassium permanganate solution yields santenic acid, $C_9H_{14}O_4$. A. A. ELDRIDGE.

CHMe·CH·CO
| CH_2 |
CHMe·CH·CO

Higher terpene compounds. XXXI. Second double linking in *d*-pimaric acid. L. RUZICKA, H. W. HUYSER, and C. F. SEIDEL (Rec. trav. chim., 1928, **47**, 363—369; cf. this vol., 297, 298).—Catalytic reduction of *d*-pimaric acid with hydrogen at 220—235°/48 atm. in the presence of platinum-black for 3 days yields a mixture, m. p. 200—203°, of stereoisomeric dihydro-acids. When a platinum oxide catalyst in ethyl acetate at 15° is employed, two stereoisomeric dihydro-acids, m. p. 238—239° (less soluble) and m. p. 228—229°, can be separated by fractional crystallisation of the product from ethyl acetate. Reduction in acetic acid solution with the same catalyst at 50°, however, yields a mixture of stereoisomeric *tetrahydro*-d-*pimaric acids* from which one form, m. p. 236—237°, is isolated in a pure state, and proved by crystallographic data [by NIEUWENKAMP] to be different from the dihydro-acid. Further proof of the presence of a second, unreactive, double linking in *d*-pimaric acid is obtained by comparative measurements of the velocity of oxidation, with perbenzoic acid, of *d*-pimaric and abietic acids. In each case one double linking is rapidly attacked with approximately the same velocity, whilst the second reacts only extremely slowly. Dihydroabietic acid, m. p. 167—168° (Ruzicka and Meyer, A., 1922, i, 544), as expected, reacts with only 1 mol. of perbenzoic acid, whilst the isomeric product, m. p. 130°, obtained by the action of hydrogen bromide in acetic acid on the dihydro-acid, and which later (unpublished) work has shown to be an isomeric lactone, is unattacked. J. W. BAKER.

Higher terpene compounds. XXXIV. Sesquiterpene compounds of vetiver, West Indian sandalwood, and galangal oils. L. RUZICKA, E. CAPATO, and H. W. HUYSER (Rec. trav. chim., 1928, **47**, 370—381).—The constituents of vetiver, sandalwood, and galangal oils have been investigated. The samples of vetiver oil (cf. Semmler, Risse, and Schroter, A., 1912, i, 882), obtained either from Reunion or Java stock, contain essentially the same constituents. The fraction of b. p. 110—140°/12 mm. contains mainly dicyclic sesquiterpenes together with a small quantity of tricyclic, and on dehydrogenation with sulphur yields cadalene. The fraction of b. p. 140—180°/12 mm. contains the sesquiterpene alcohols. Esterification by means of phthalic anhydride and subsequent hydrolysis of the esters separates the primary alcohols, the less volatile fraction of which is mainly dicyclic (together with small amounts of tricyclic); on dehydrogenation the alcohols yield a mixture of cadalene and eudalene. The intermediate fraction consists of a mixture of tricyclic alcohols with a little dicyclic, and the fraction of higher b. p. contains only tricyclic alcohols, $C_{15}H_{24}O$; when heated with dilute sulphuric acid these lose water to yield sesquiterpenes, but no hydrocarbon picrate could be isolated after dehydrogenation. The unesterified portion consists of a mixture of tertiary alcohols, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, which by heating with 80% formic acid afford a mixture of dicyclic sesquiterpenes, $C_{15}H_{22}$ and $C_{15}H_{24}$, and yield cadalene on dehydrogenation. The fraction of b. p. above 180°/12 mm. after hydrolysis with 10% alcoholic solution of potassium hydroxide contains the tricyclic vetivenic acid $C_{15}H_{22}O_2$ and primary sesquiterpene alcohols.

The second runnings of West Indian sandalwood oil (cf. Deussen, A., 1912, i, 368; von Soden, A., 1900, i, 401) contain no sesquiterpenes, but consist of a mixture of tertiary, dicyclic sesquiterpene alcohols, chiefly $C_{15}H_{26}O$. When they are heated with phthalic anhydride, water is eliminated and a sesquiter-

pene, $C_{15}H_{24}$, is produced which yields a dihydrochloride identical with that of *l*-cadinene, hence the original constituents are probably a mixture of cadinols.

The more volatile fraction of galangal oil consists of dicyclic sesquiterpenes, mainly cadalene, probably mixed with hydronaphthalene derivatives, and by dehydrogenation yields cadalene. The higher fraction yields a small quantity of a solid, m. p. 167°, and liquid sesquiterpene alcohols, $C_{15}H_{24}O$, which by heating with 90% formic acid yield sesquiterpenes which are dehydrogenated to cadalene. The original oil, therefore, probably contains hydrated hexahydrocadalenes.

J. W. BAKER.

Furan. W. C. WILSON (Org. Syntheses, 1927, 7, 40—41).—Furan is obtained in 72—78% of the theoretical yield by heating furan-2-carboxylic acid at 200—205°. A. A. ELDRIDGE.

[Preparation of] furfurylideneacetone. G. J. LEUCK and L. CEJKA (Org. Syntheses, 1927, 7, 42—43).

[Preparation of] 2-furylmethyl acetate. MINER LABORATORIES (Org. Syntheses, 1927, 7, 44—45).

Alkylations. K. VON AUWERS [with T. BAHR, G. WEGENER, and C. WIEGAND] (Ber., 1928, 61, [*B*], 408—416; cf. A., 1912, i, 484, 486; 1921, i, 806; 1924, i, 992).—Treatment of ethyl 3-hydroxycoumarone-2-carboxylate or its 5-methyl derivative with alkyl halides shows that production of *C*-compounds is favoured by the use of halides containing an alkyl group of low valency demand (allyl or benzyl), whereas the formation of *O*-derivatives is facilitated by "true" alkyls (ethyl and propyl); the methyl group occupies an intermediate position. The particular halogen present also influences the course of the change. The observations are confirmed with 2-cyano*cyclo*hexanone, with which it is found that *C*-derivatives are produced in greater proportion when the change proceeds most rapidly. The following compounds are incidentally described: 2-*propylcoumaranone*, b. p. 125·5—126°/13 mm., d_4^{20} 1·094, n_{He}^{20} 1·5459, converted by semicarbazide acetate into the *disemicarbazone* of o-*hydroxyphenyl propyl diketone* (+H_2O), m. p. 210—211°; 3-*propoxycoumarone-2-carboxylic acid*, m. p. 154—155°; 2-*allylcoumaranone*, b. p. 132°/13·5 mm., d_4^{20} 1·101, n_{He}^{20} 1·5614; 2-*benzylcoumaranone*, b. p. 193—195°/11 mm., d_4^{20} 1·166, n_{He}^{20} 1·6034 [*disemicarbazone* of *o*-hydroxyphenyl benzyl diketone (+$2H_2O$), m. p. 219—220° (decomp.)]; 3-*benzyloxycoumarone-2-carboxylic acid*, m. p. 159—160°; 3-*propoxy-5-methylcoumarone-2-carboxylic acid*, m. p. 159—160° (decomp.); 5-*methyl-2-allylcoumaranone*, m. p. 56—57° [*disemicarbazone* (+H_2O), m. p. 200°, and *di-*p*-nitrophenylosazone*, decomp. 165—170°, of *p*-tolyl allyl diketone].

H. WREN.

Condensation of certain β-ketonic esters with *o*-hydroxymonostyryl ketones. R. HILL (J.C.S., 1928, 256—259).—In agreement with Heilbron and Hill (A., 1927, 565) it is found that the interaction of α-substituted-β-ketonic esters with *o*-hydroxymonostyryl ketones yields only γ-pyran derivatives and, contrary to the findings of Forster and Heilbron (A., 1924, i, 1323), no trace of the substituted dihydrocoumarin is detected. Interaction of the appropriate ketone with the β-ketonic ester in alcoholic sodium ethoxide at the ordinary temperature for 8 days yields 4-*acetonyl*-2 : 3-*dimethyl*-, m. p. 141°; 4-*phenacyl*-2 : 3-*dimethyl*-, m. p. 179°; 4-*acetonyl-3-phenyl-2-methyl*-, m. p. 186—187°; and 4-*phenacyl-3-phenyl-2-methyl*-, m. p. 219—221°, -1 : 4-*benzopyran*. Ethyl cyanoacetate, ethyl oxaloacetate, and ethyl malonate do not react with *o*-hydroxymonostyryl ketones, whilst when ethyl malonate is allowed to react with 2-hydroxystyryl phenyl ketone in the presence of sodium ethoxide at the ordinary temperature for 10 weeks, coumarin-3-carboxylic acid is the sole product, scisson of the ketone occurring in the presence of the alkali. J. W. BAKER.

[Preparation of] xanthydrol. A. F. HOLLEMAN (Org. Syntheses, 1927, 7, 88—89).

[Preparation of] xanthone. A. F. HOLLEMAN (Org. Syntheses, 1927, 7, 84—86).

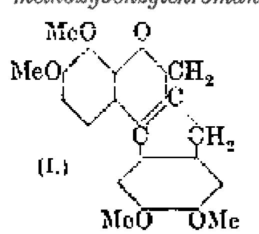
Synthesis of myricetin. M. NIERENSTEIN (Ber., 1928, 61, [*B*], 361—362).—The observations of Hattori (A., 1927, 883) show that the flavanone, $\begin{matrix}CO\text{———}CH_2 \\ C_6H_2(OMe)_2{\cdot}O\end{matrix}{>}CH{\cdot}C_6H_2(OMe)_3$, is converted by amyl nitrate into myricetin 5 : 7 : 3′ : 4′ : 5′-pentamethyl ether (cf. Dean and Nierenstein, A., 1925, i, 951) without possible isolation of the intermediate oximino-compound (contrast Sonn, A., 1925, i, 932).

H. WREN.

Gossypol. II. Carruth's *D*-gossypol. E. P. CLARK (J. Biol. Chem., 1928, 76, 229—235).—The *D*-gossypol obtained by Carruth from heated cottonseed meal (A., 1918, i, 266) gives, with aniline, dianilinogossypol. *D*-Gossypol cannot therefore be a degradation product of gossypol; it is suggested that it may be gossypol in amide linking with free amino-groups of the cottonseed proteins.

C. R. HARINGTON.

Brazilin and hæmatoxylin. VI. Synthesis of tetramethylanhydrohæmatoxylin. P. PFEIFFER, E. HAACK, and J. WILLEMS (Ber., 1928, 61, [*B*], 294—299; cf. A., 1927, 1198).—Pyrogallol 1 : 2-dimethyl ether condenses with β-chloropropionic acid to β-2 : 3-*dimethoxyphenoxypropionic acid*, m. p. 101°, converted by phosphoric oxide in presence of benzene into 7 : 8-dimethoxychromanone, b. p. 196°/17 mm., m. p. 98—100°. The latter compound is converted by veratraldehyde and hydrogen chloride in glacial acetic acid into 7 : 8-*dimethoxy*-3 : 3′ : 4′-*dimethoxybenzylidenechromanone*, m. p. 137—137·5°, catalytically hydrogenated in acetic acid solution in the presence of spongy platinum to 7 : 8-*dimethoxy*-3 : 3′ : 4′-*dimethoxybenzylchromanone*, m. p. 90—90·5° (*hydrate*, m. p. 115°; *oxime*, m. p. 167°). Treatment of the benzyl derivative with phosphoric oxide in presence of benzene yields tetramethylanhydrohæmatoxylin (I.), m. p. 170—173° (decomp.), according to the rate of heating, identical with the tetramethyldeoxyhæmatoxylone of Herzig and Pollak (A., 1905, i, 605).



(I.)

H. WREN.

Acylation of thiophen in presence of tin tetrachloride. G. Stadnikov and V. Rakovski (Ber., 1928, **61**, [*B*], 268—269).—Addition of tin tetrachloride to a solution of acetyl chloride and thiophen in light petroleum at 0° causes immediate separation of a crystalline complex compound, decomposed by water into thiophen and 2-acetothienone, b. p. 213—214°/760 mm. [semicarbazone, m. p. 188° (cf. A., 1917, i, 278); oxime, m. p. 81°; phenylhydrazone, m. p. 94·5°]. 2-Benzothienone, m. p. 55° (oxime, m. p. 93°), is prepared similarly. H. Wren.

Bromination of tertiary β-ketonic bases and synthesis of 3-hydroxy-1-methylpyrrolidine. C. Mannich and T. Gollasch (Ber., 1928, **61**, [*B*], 263—268).—α-Dimethylaminobutan-γ-one does not react simply with bromine, whereas its hydrobromide is converted by bromine and hydrogen bromide in glacial acetic acid into *δ-bromo-α-dimethylaminobutan-γ-one hydrobromide*, m. p. 103°, in 65% yield from which potassium carbonate liberates the corresponding unstable *base*, whereas barium hydroxide converts it into 3-*keto*-1 : 1-*dimethylpyrrolidinium bromide*, m. p. 213—215° [*oxime*, m. p. 209°; 3-*keto*-1 : 1-*dimethylpyrrolidinium chloride*, m. p. 185°, and *chloroaurate*, m. p. 183° (decomp.)]. Reduction of the chloride by sodium amalgam in hydrochloric acid solution affords α-dimethylaminobutan-γ-ol, which is also produced by electrolytic reduction at a lead cathode together with small quantities of 3-*hydroxy*-1 : 1-*dimethylpyrrolidinium chloride* (*chloroaurate*, decomp. 260°), more readily prepared by catalytic hydrogenation in aqueous solution under pressure in presence of spongy platinum. 3-*Hydroxy*-1-*methylpyrrolidine*, b. p. 77°/16 mm., obtained by thermal decomposition of the above chloride in an atmosphere of nitrogen, gives a *chloroaurate*, m. p. 191° (decomp.), very hygroscopic *hydrochloride*, *methiodide*, m. p. 260°, and *benzoate hydrochloride*, m. p. 146°. γ-Piperidinomethyl-Δ^{ϵ}-hexen-β-one hydrobromide is hydrogenated in aqueous solution in the presence of palladised charcoal to *γ-piperidinomethylhexan-β-one hydrobromide*, m. p. 151° (corresponding *base*, b. p. 126°/16 mm.). The salt is transformed by bromine in chloroform solution into *α-bromo-γ-piperidinomethylhexan-β-one hydrobromide*, m. p. 142°, converted by barium hydroxide into spiro-1-(4′-*keto*-3′-*propylpyrrolidinium*)-1-*piperidinium bromide*,

$$\begin{array}{l}CHPr^{a}\cdot CH_2\\ CO\text{—}\cdot CH_2\end{array}\!\!>\!NBr\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>\!CH_2,$$ m. p 221°.

H. Wren.

By-products of the hydrogenation of pyridine under pressure. V. S. Sadikov and A. K. Mikhailov (Ber., 1928, **61**, [*B*], 421—427).—Hydrogenation of pyridine under pressure in presence of osmium deposited on asbestos affords ammonia, piperidine (up to 70%), and products of high b. p. from which the *compounds* $C_9H_{19}N$ and $C_{15}H_{30}O_2$ are isolated. The former compound, regarded as 1-*methyl*-3-*propylpiperidine*, b. p. 195—200°, *d* 0·8415, mol. wt. 151, yields a *picrate*, m. p. 106—107°, and *methiodide*, $(C_9H_{19}N)_2$,MeI, m. p. 81°. With hydroferrocyanic and hydrochloric acids it appears to give the *substances* $(C_8H_{17}N)_2,H_4FeC_6N_6$ and $C_8H_{17}N$,HCl, m. p. 200°. The latter compound, considered to be 2 : 2′-*dimethyl*-3-*propyl*-1 : 1′-*dipiperidyl*, b. p. 295—300°, is characterised by its *hydroferrocyanide*, $C_{15}H_{30}N_2,H_4FeC_6N_6$, *methiodide*, $C_{15}H_{30}N_2$,2MeI, m p 269—270°, and *picrate*, m. p. 191° (attempts to recover the base from the picrate are accompanied by extensive resinification and the volatile product gives a *hydrochloride*, $C_{15}H_{26}N_2$,2HCl, m. p. 157°); when evaporated with hydrochloric acid the base loses its methyl groups and affords the *salt*, $C_{15}H_{26}N_2$,2HCl, m. p. 258°. If asbestos impregnated with 20% of osmium and 1% of cerium dioxide is used, the hydrogenation is extraordinarily accelerated and the product contains 34·6% of piperidine, 55·8% of methylpropylpiperidine, and 9 1% of 2 : 2′-dimethyl-3-propyl-1 : 1′-dipiperidyl. If reduction is effected in an autoclave provided with a cooled side tube in which volatile products of the reaction can be condensed during the progress of the change, the less volatile bases are obtained in high yield, thus indicating that alkylation of the piperidine occurs in the early stages of hydrogenation. H. Wren.

Local anæsthetics derived from β-piperidylcarbinol. L. T. Sandborn and C. S. Marvel (J. Amer. Chem. Soc., 1928, **50**, 563—567).—3-*Piperidylcarbinol*, b. p. 106—107°/3·5 mm., d_4^{20} 1·0263, n_D^{20} 1·4964, is obtained in 40—43% yield by reduction of ethyl nicotinate with sodium and alcohol. The following alkyl derivatives were prepared by the action of the appropriate alkyl bromides or iodides in boiling benzene: N-*methyl*-, b. p. 110—112°/7 mm., d_4^{20} 1·0125, n_D^{20} 1·4988; N-*ethyl*-, b. p. 110—111°/6·5 mm., d_4^{20} 0·9904, n_D^{20} 1·4911; N-iso*propyl*-, b. p. 93—94°/3·5 mm., d_4^{20} 0·9881, n_D^{20} 1·4916; N-n-*butyl*-, b. p. 100—102°/4 mm., d_4^{20} 0·9484, n_D^{20} 1·4838; and N-*allyl*-3-*piperidylcarbinol*, b. p. 110—111°/7 mm., d_4^{20} 0·9873, n_D^{20} 1·4982. These were converted into the *p*-nitrobenzoate hydrochlorides and *p*-aminobenzoate hydrochlorides by the usual methods, the m. p. of the two derivatives of each carbinol, taken in the above order, being as follows: 187—190°, 174—177°; 194—195°, 188—190°; 196—200°, 235·5—237·5°; 197—198°, 205—207°; 186—187·5°, —. The aminobenzoate hydrochlorides possess relatively low toxicity and strong local anæsthetic action. F. G. Willson.

2-Dimethylaminopyridine and its derivatives. A. E. Tschitschibabin and I. L. Knunianz (Ber., 1928, **61**, [*B*], 427—434).—2-Dimethylaminopyridine, b. p. 88°/15 mm., is obtained in 40—50% yield by the action of sodamide and methyl sulphate on 2-aminopyridine in the presence of ether. Unchanged primary and secondary amine are removed from the crude mixture by means of acetic anhydride. The compound differs from dimethylaniline in its inability to afford a nitroso-derivative or to couple with diazonium compounds. Nitration yields 5-*nitro*-2-*dimethylaminopyridine*, m. p. 154—155°, and 3 : 5-*dinitro*-2-*dimethylaminopyridine*, m. p. 125—126°. The mononitro-compound is reduced by tin and hydrochloric acid to 5-*amino*-2-*dimethylaminopyridine*, m. p. 55—56° (*dihydrochloride*, m. p. 225—226°; *chlorostannite*, m. p. 148—150°), which gives the customary diazo-reactions and yields 5-*iodo*-2-*dimethylaminopyridine*, m. p. 55°, and 5-*bromo*-2-*dimethylaminopyridine*, m. p. 42—43°. Bromination of

2-dimethylaminopyridine in dilute sulphuric acid gives the 5-bromo-derivative (*picrate*, m. p. 208°) and 3 : 5-dibromo-2-dimethylaminopyridine, isolated as the *picrate*, m. p. 185—186°. The 5-bromo-compound is also obtained by methylation of 5-bromo-2-aminopyridine with sodamide and methyl sulphate. 2-Dimethylaminopyridine is converted by sodamide at 190° into dimethylamine and 2 : 6-diaminopyridine.
H. WREN.

Constitution of vasicine. I. Synthesis of 4-hydroxy-2-propyl-(and *iso*propyl)quinazoline. A. K. DE and J. N. RAY (J. Indian Chem. Soc., 4, 541—545).—Butyranilide and *iso*butyranilide condense with ethyl carbamate in boiling xylene solution in presence of phosphoric oxide to give 4-hydroxy-2-propylquinazoline, m. p. 197° (*picrate*, m. p. 184°), and 4-hydroxy-2-*iso*propylquinazoline, m. p. 227° (decomp.) (*picrate*, m. p. 215—216°), respectively. The natural product has m. p. 196° (picrate, m. p. 199°) and depresses the m. p. of the propyl derivatives above, and thus Ghose's suggested constitution (A., 1927, 785) is incorrect. Bischler and Lang (A., 1895, i, 250) give the m. p. of the propyl and *iso*propyl derivatives as 205° and 195—196°, respectively, whilst Niementowski gives the m. p. of the latter as 224°.
C. D. LANGFORD.

Reactivity of *ortho*-diketonic groups placed between two nitrogen atoms. P. K. DE and A. C. SIRCAR (J. Indian Chem. Soc., 4, 531—534).—2-Thio-1 : 3-diphenylparabanic acid and *o*-phenylenediamine (2 mols.) react in boiling pyridine to give *o*-phenyleneoxamide, aniline, and (?) thionyl-*o*-phenylenediamine. *s*-Diphenylthiocarbamide is probably formed as an essential intermediate. *s*-Diphenylthiocarbamide and *o*-phenylenediamine under similar conditions afford aniline and thionyl-*o*-phenylenediamine. Dinitrothiophenylparabanic acid behaves like the parent acid. Diphenylparabanic acid affords *o*-phenyleneoxamide and *s*-diphenylcarbamide.
C. D. LANGFORD.

Reaction of organic halogen compounds with copper and pyridine. P. KARRER, W. WEHRLI, E. BIEDERMANN, and M. DALLA VEDOVA (Helv. Chim. Acta, 1928, 11, 233—239).—When *p*-toluenesulphonyl chloride is treated with copper bronze and dry pyridine there are formed di-*p*-tolyl disulphoxide, di-*p*-tolyldisulphone, dipyridine copper chloride, $[(C_5H_5N)_2Cu]Cl_2$, and a compound, probably $C_6H_4Me\cdot SO_3Cu(C_5H_5N)_2$. Similar treatment of hippuryl chloride yields *NN*-dibenzoyldiketopiperazine, m. p. 137°, hydrolysed by concentrated hydrochloric acid to *N*-benzoyldiketopiperazine, m. p. 205°. Phthalyl chloride furnishes a small amount of diphthaloyl, m. p. 335°.
H. BURTON.

Formation of derivatives of dihydrobenziminazole and tetrahydroquinoxaline by the action of acetic anhydride and zinc chloride on nitro-derivatives of alkylanilines. P. VAN ROMBURGH and H. W. HUYSER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 844—849).—When dinitrodimethylanilines are boiled with zinc chloride and acetic anhydride for 4—5 hrs., acetyl derivatives of 2-keto-1 : 2-dihydrobenziminazole are obtained. Thus 3 : 6- and 2 : 4-dinitrodimethylanilines yield, respectively, 6-*nitro*- (I), m. p. 185—186°, and 5-*nitro*-, m. p. 175—176°, -2-*keto*-3-*acetyl*-1-*methyl*-1 : 2-*dihydrobenziminazoles*, which by boiling with alkali are converted into 6-*nitro*- (II), m. p. 272°, and 5-*nitro*-, m. p. 300°, -2-*keto*-1-*methyl*-1 : 2-*dihydrobenziminazoles*. The latter are readily re-acetylated to the parent substances and, by reduction with iron and hydrochloric acid, yield the *hydrochlorides* ($+H_2O$) of the corresponding 6- and 5-amino-derivatives, whilst by treatment with phosphorus pentachloride in phosphoryl chloride as a solvent they are converted into 2-*chloro*-6-*nitro*- and 2-*chloro*-5-*nitro*-1-*methylbenziminazoles*. Synthesis of (II) is effected by the interaction of carbonyl chloride and 4-nitro-2-aminomethylaniline. By a similar treatment for 72 hrs. 3 : 4 : 6-trinitrodimethylaniline yields 5 : 6-*dinitro*-2-*keto*-1-*methyl*-1 : 2-*dihydrobenziminazole*, m. p. 294°, which yields a 3-*acetyl* derivative, m. p. 191°, identical with that obtained by nitration of (I). A similar reaction applied to nitrodiethylanilines leads to the formation of derivatives of 3-keto-1 : 2 : 3 : 4-tetrahydroquinoxaline. Thus 3 : 6-dinitrodiethylaniline yields 7-*nitro*-3-*keto*-4-*acetyl*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 127°, from which, by hydrolysis, 7-*nitro*-3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 206° (*nitroso*-derivative), is obtained. Similarly, from 2 : 4-dinitrodiethylaniline, 6-*nitro*-3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 157°, is obtained.
J. W. BAKER.

Derivatives of *iso*indigotin. A. WAHL and FERICEAN (Compt. rend., 1928, 186, 378—380; cf. A., 1927, 470).—Treatment of 5-chloro- and 7-chloroisatin with hydrogen sulphide (A., 1925, i, 588) affords 5 : 5′-*dichloro*- and 7 : 7′-*dichloro-disulphoisatide*, which are transformed in boiling pyridine into 5 : 5′-*dichloro*- and 7 : 7′-*dichloro*-iso*indigotins*, together with small amounts of 5-*chloro*- and 7-*chloro-oxindoles* (the corresponding *benzylidene* derivatives have m. p. 204° and 185°, respectively). The formation of the oxindoles is explained thus: $2C_{16}H_{10}O_2N_2Cl_2S_2 \longrightarrow C_{16}H_8O_2N_2Cl_2+2C_8H_6ONCl+4S$. Reduction of the dichloro*iso*indigotins by zinc and acetic acid gives the corresponding *leuco*-compounds. Condensation of the chloroisatins with oxindole in presence of piperidine affords the corresponding *chloroisatans*, which are dehydrated by boiling acetic–hydrochloric acids (cf. A., 1924, i, 322) into 5-*chloro*- and 7-*chloro*-iso*indigotins*.
H. BURTON.

Syntheses in the phenazine series. H. McCOMBIE, H. A. SCARBOROUGH, and W. A. WATERS (J.C.S., 1928, 353—359).—The method of Fischer and Heiler (A., 1893, 266) has been applied to the synthesis of various 1- and 2-substituted phenazine derivatives, the use of anhydrous sodium acetate (Kehrmann and Havas, A., 1913, i, 298) not being suitable for the preparation of substituted phenazines. The yields in all cases are only of the order of 5% of the theoretical. By heating a mixture of *o*-chloronitrobenzene, *o*-toluidine, and anhydrous sodium acetate for 20 hrs. at 220—240° a 10% yield of 2-*nitro*-2′-*methyldiphenylamine*, m. p. 76°, is obtained. This, by reduction with alcoholic stannous chloride, yields the corresponding 2-*amino*-compound, m. p. 64°, which is converted by heating with litharge at 200—240°

under reduced pressure into 1-*methylphenazine*, m. p. 108° (*chloroplatinate*, decomp. above 200°). The same compound is obtained by the action of sodium sulphate on 2 : 3-tolylenediamine and *o*-benzoquinone in anhydrous ether for 2 days. 2-*Chlorophenazine*, m. p. 139°, is similarly obtained by the litharge method from 4-chloro-2-nitrodiphenylamine, whilst 2-*bromophenazine*, m. p. 150°, is obtained from 4′-*bromo*-2-*aminodiphenylamine*, m. p. 128°, obtained by the reduction of 4′-*bromo*-2-*nitrodiphenylamine*, m. p. 167°, which is prepared by the interaction of *o*-chloronitrobenzene and *p*-bromoaniline. By similar methods, 2-*nitro*-4′-*methoxydiphenylamine*, m. p. 89° (for which crystallographic data are given), is prepared and reduced to the corresponding 2-*amino*-compound, m. p. 78°, from which 2-*methoxyphenazine*, m. p. 126° (*chloroplatinate*, decomp. above 250°), is synthesised. This compound is not identical with hemipyocyanine (Wrede and Strack, A., 1925, i, 844). A similar attempt at ring closure with 2-*amino*-2′-*methoxydiphenylamine*, m. p. 58°, obtained by reduction of the 2-*nitro*-compound, m. p. 83°, leads only to the production of phenazine, instead of the 1-methoxy-derivative. Reduction of 2-nitrodiphenylamine-2′-carboxylic acid yields the 2-*amino*-derivative, m. p. 204° (*ammonium* and *double tin* salts; *hydrochloride*, decomp. 240°), but attempts to effect ring closure in order to synthesise a substance having the seven-membered ring lactam structure, assigned by Wrede and Strack (*loc. cit.*) to hemipyocyanine, were unsuccessful. The free amino-acid by heating or by treatment with concentrated sulphuric acid yields a green *substance*, m. p. 255° (decomp.). J. W. BAKER.

I. 8-Iodoxanthines. II. Preparation and properties of xanthine. III. Alkylation in the xanthine series. IV [with R. LEMBERG] **Ethylation of ψ-uric acid.** H. BILTZ and A. BECK (J. pr. Chem., 1928, [ii], **118**, 149—224).—In continuation of previous work (cf. A., 1922, i, 380—384) it is shown that 8-thiouric acids which have a hydrogen atom in the 7- or 9-position (8-thiolxanthines) are converted by iodine and sodium hydrogen carbonate into 8-iodo*iso*xanthines and 8-iodoxanthines, respectively. Thus, 8-thio-1 : 9-dimethyluric acid (A., 1921, i, 612) yields 8-*iodo*-1 : 9-*dimethyl*-$\Delta^{7 \cdot 8}$-*isoxanthine*, decomp. 280—320°, darkening from 230°, which is reduced by hydriodic acid to 1 : 9-dimethyl*iso*xanthine; 8-thio-1 : 3 : 9-trimethyluric acid yields 8-*iodo*-1 : 3 : 9-*trimethyl*-$\Delta^{7 \cdot 8}$-*isoxanthine*, m. p. 260—265°, losing iodine from 225° (*periodide*, $C_8H_9O_2N_4I_2$), which is reduced to *iso*caffeine; 8-*thio*-3 : 7-*dimethyluric acid*, m. p. 335—337° (decomp.), prepared from 8-chloro- or 8-bromo-theobromine and potassium hydrogen sulphide, yields 8-*iodotheobromine*, m. p. 330—335°, decomp. from 250°; 8-thio-1 : 3-dimethyluric acid, decomp. 320° (cf. Boehringer & Söhne, A., 1903, i, 868), prepared from 8-bromotheophylline (A., 1914, i, 586), yields 8-*iodotheophylline*, decomp. 303—305°, altering from 250°, which is reduced to theophylline; 8-thio-1 : 3 : 7-trimethyluric acid yields 8-*iodocaffeine*, m. p. 230°, and 8-thiouric acid (cf. Fischer and Tüllner, A., 1902, i, 664), prepared by an improved method, yields 8-*iodoxanthine*, decomp. from 200° (*potassium*, *sodium*, and *ammonium* salts). Unlike xanthine, this last exhibits acidic properties only. Attempts to prepare 8-iodo-9-phenyl*iso*xanthine and 2 : 6-di-iodo-7-methylpurine from the corresponding thiol derivatives by this method were unsuccessful.

A large number of experiments on the production of xanthine from uric acid and 8-thiouric acid are described. The optimum conditions, which must be closely followed, for its preparation by Sundvik's method (A., 1912, i, 321), are: a mixture at 170° of 500 c.c. of glycerol, 50 c.c. of 95% formic acid, and 20 g. of crude uric acid is warmed during 30—40 min. to 230°, maintained at this temperature until 3—10 min. after dissolution is complete, cooled rapidly, and poured into water. The xanthine (6 g.) is extracted from the unchanged uric acid by $2N$-hydrochloric acid and completely freed from the latter by prolonged digestion with 23% nitric acid. Coloured impurities are removed by recrystallising the sodium salt. The physical properties of xanthine, its lack of reactivity, and its insolubility in all chemically indifferent solvents (except "polyglycol," from which it separates in microscopic crystals) indicate that, like cellulose, it is probably in a highly associated molecular condition. It affords a characteristic *perchlorate* ($+H_2O$), m. p. 262—264°, sintering from 250° (crystallographic data), also a *hydrobromide* ($+H_2O$), *hydriodide* ($+H_2O$), decomp. 220°; *fluoborate*; *hydrofluoride*, $C_5H_4O_2N_4,2HF$; *chlorostannite*, $(C_5H_4O_2N_4)_2,H_2SnCl_4,H_2O$, and *zincichloride*, $[Zn(C_5H_4O_2N_4)_2]Cl_2$, decomp. 310—350°. *Theobromine perchlorate* ($+H_2O$), decomp. 271—273°, sinters from 250°. Unsuccessful attempts to chlorinate, brominate, and acetylate xanthine are described.

The literature relating to the alkylation of xanthine derivatives is comprehensively reviewed. Further examples of the use of (*a*) diazomethane, (*b*) methyl sulphate and alkali, are given. Ethyl bromide may be used instead of the iodide with alkali in a sealed tube at 100° (*c*), or under reflux (*d*). The thiol group in 8-thiolxanthines may be alkylated in alkaline solution at the ordinary temperature by means of methyl iodide (*e*) or ethyl sulphate (*f*). The following compounds have been prepared by these methods: caffeine from xanthine (*a*)(*b*), or theophylline (*b*); 8-bromocaffeine from 8-bromotheophylline (*b*); 7-ethyltheophylline from theophylline (*c*); 8-bromo-7-ethyltheophylline from 8-bromotheophylline (*c*); 8-*methylthioltheobromine*, m. p. 263°, from 8-thioltheobromine (*e*); 8-*methylthioltheophylline*, m. p. 307—310°, from 8-thioltheophylline (*e*); 8-methylthiolcaffeine from 8-thiolxanthine and its lower methylation products (*a*)(*b*); 8-*ethylthiolxanthine*, m. p. 302° (decomp.), from 8-thiolxanthine (*f*); 8-*ethylthioltheobromine*, m. p. 217°, from 8-thioltheobromine (*d*)(*f*); 8-*ethylthioltheophylline*, m. p. 249°, from 8-thioltheophylline (*d*)(*f*); 8-*ethylthiolcaffeine*, m. p. 137°, from 8-thiolcaffeine (*d*)(*f*); 8-*ethylthiol*-1-*ethyltheobromine*, m. p. 136°, from 8-thioltheobromine (*c*, at 80°). 8-Bromo-7-ethyltheophylline and potassium hydrogen sulphide afford 8-*thiol*-7-*ethyltheophylline*, m. p. 264°, from which 8-*ethylthiol*-7-*ethyltheophylline*, m. p. 115°, is obtained by methods (*c*) and (*f*) and the 8-*methylthiol derivative*, m. p. 128°, by (*b*). When 8-thioltheobromine is refluxed with allyl bromide and 10% potassium hydroxide it yields a mixture of

8-*allylthioltheobromine*, m. p. 212°, and 8-*allylthiol*-1-*allyltheobromine*, m. p. 118°, whilst 8-thiolcaffeine is similarly converted into 8-*allylthiolcaffeine*, m. p. 97—100°. Diallyl ether is obtained in high yield by heating allyl bromide with 50% potassium hydroxide in a sealed tube at 100°.

Attempts to ethylate ψ-uric acid or potassium ψ-urate using ethyl sulphate or bromide, to methylate it with diazomethane or with methyl alcohol and hydrogen chloride, and to prepare carbethoxy- and carbomethoxy-derivatives from it, were unsuccessful. H. E. F. NOTTON.

Transformation of hæmin and *meso*hæmin into isomerides. R. KUHN and C. SEYFFERT (Ber., 1928, **61**, [*B*], 307—314).—Attempts to acetylate α-chlorohæmin by acetic anhydride in the presence of chloroform and pyridine result in its isomerisation to allo*hæmin*. The anhydride is the essential reagent and the same effect may be (less advantageously) produced by a large excess of boiling acetic anhydride. *allo*Hæmin differs from hæmin I in crystalline habit, free solubility in chloroform, and insolubility in cold 2*N*-sodium carbonate or boiling 0·02*M*-disodium hydrogen phosphate. The spectra of the two compounds are identical in dry or moist pyridine within the limits of experimental error. *allo*Hæmin loses the FeCl group very slowly when acted on by formic acid and iron powder under the conditions laid down for the preparation of protoporphyrin. With phosphonium iodide and hydriodic acid it gives *meso*porphyrin much more easily and in a purer form than does hæmin. When boiled with methyl alcohol containing sulphuric acid it affords tetramethylhæmatoporphyrin isolated as complex iron salt agreeing in m. p. 178—180° and crystalline form with the product obtained by Fischer and Lindner (A., 1927, 886) from hæmin. Catalytic hydrogenation in chloroform causes loss of iron. With methyl-alcoholic hydrogen chloride it affords a crystalline dimethyl ester similar to that obtained from hæmin dimethyl ester and acetic anhydride in pyridine–chloroform; it is uncertain whether the compounds are identical with one another and with Küster's hæmin dimethyl ester. If a solution of *allo*hæmin in chloroform is poured into hot, glacial acetic acid, *hæmin* II is precipitated. In solubility and spectroscopic behaviour, hæmin II is very similar to acetic acid hæmin (hæmin I), but differs from it in crystalline habit and probably is a modification of the latter substance. In pyridine–acetic anhydride, hæmins I and II yield the same *allo*-hæmin. *allo*Hæmin, unless carefully freed from enclosed acetic anhydride, is gradually isomerised if exposed to moist air, whereas the homogeneous compound is stable.

Under similar conditions, *meso*hæmin is isomerised to allomeso*hæmin*, $C_{34}H_{38}O_4N_4ClFe$, differentiated from the initial material by insolubility in 2*N*-sodium carbonate and free solubility in chloroform. It is re-converted into *meso*hæmin by crystallisation from glacial acetic acid. Manganese*meso*hæmin is isomerised by boiling acetic anhydride to allo*manganese*-meso*hæmin*, $C_{34}H_{36}O_4N_4ClMn$, readily soluble in chloroform but insoluble in cold 2*N*-sodium carbonate. H. WREN.

Diphenyl*iso*oxazolone. Tautomerism of *iso*-oxazolones. E. P. KOHLER and A. H. BLATT (J. Amer. Chem. Soc., 1928, 504—516).—When an ethereal solution of diphenyl*iso*oxazolone is shaken with aqueous copper acetate, the mixed *copper* salt, $C_{15}H_{10}O_2N{\cdot}CuO{\cdot}OAc$, deep blue or purple, is precipitated. A *magnesium bromide* salt is obtained by adding the *iso*oxazolone to excess of ethereal magnesium ethyl bromide. Treatment of diphenyl*iso*oxazolone with bromine in carbon tetrachloride affords 4-*bromo*-3 : 4-*diphenyl*iso*oxazolone*, m. p. 72°, whilst phosphorus pentachloride in chloroform yields similarly 4-*chloro*-3 : 4-*diphenyl*iso*oxazolone*, m. p. 77—78°. Diphenyl*iso*oxazolone is readily oxidised by ferric chloride, aqueous bromine, nitrous and nitric acids, potassium permanganate, and potassium ferricyanide, with formation of the *ether*

CPh:C—O—CPh·CO
  >O | >O, m. p. 154—156° (decomp.),
CPh:N   CPh=N

the constitution of which is established by its formation by condensation of the sodium salt of diphenyl*iso*oxazolone and the above 4-bromo-derivative in ether. Bromine titration of alcoholic solutions of diphenyl*iso*oxazolone indicates the presence, in solution, of the enolic tautomeride to the extent of about 90% after equilibrium is established, whilst the lower results obtained with fresh solutions indicate that the solid substance is not the enolic modification. Methylation of diphenyl*iso*oxazolone by a variety of methods yields always N-*methyl*-3 : 4-*diphenyl*iso-*oxazolone*, m. p. 92°. The latter is unaffected by boiling concentrated hydrochloric acid, but yields deoxybenzoin and benzoic acid when boiled with methyl-alcoholic potassium hydroxide. The N-*benzyl* derivative has m. p. 123°, and behaves similarly. Treatment of the methyl derivative with ozone in carbon tetrachloride yields benzoylformic acid. Treatment of diphenyl*iso*oxazolone with benzoyl chloride yields a *benzoyl* derivative, m. p. 138—139°, whilst treatment of the sodium salt with ethereal ethyl chloroformate affords a *carbethoxy*-derivative, m. p. 109—110° after softening at 103°. Neither of these derivatives forms an ozonide, but both are readily hydrolysed with regeneration of the *iso*-oxazolone, from which it is concluded that the acyl derivatives have probably an *O*-acyl structure. Diphenyl*iso*oxazolone is very slowly attacked by 6% ozone, but does not yield an ozonide or any normal decomposition products of such a derivative, from which it appears that the possible tautomeride,

CPh–CO
  || >O does not exist. F. G. WILLSON.
CPh·NH

Preparation of thiolbenzthiazoles. L. B. SEBRELL and J. TEPPEMA.—See B., 1928, 152.

Heterocyclic dyes. K. FUCHS and E. GRANANG (Ber., 1928, **61**, [*B*], 57—65).—Heterocyclic dyes are described analogous to pinacyanol but containing the group :CH·N:N· in place of :CH·CH:CH·. They act as powerful desensitisers towards the photographic plate whether in pre-treatment or as an addition to the developer. *as*-Phenylethylthiocarbamide is transformed by bromine in chloroform solution into

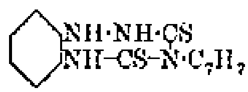
1-imino-2-ethylbenzthiazoline, $C_6H_4<{}^{NEt}_{S}>C{:}NH$, m. p. 83—84° (cf. Besthorn, A., 1910, i, 507), converted by nitrous acid into the corresponding *nitroso*-derivative, decomp. 131—131·5°, passing in boiling xylene into 2-*ethylbenzthiazolone*, b. p. 170°/14 mm., and reduced by zinc dust and 50% acetic acid to 2-*ethylbenzthiazolonehydrazone*, m. p. 77·5—78·5°.

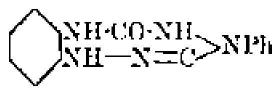
2-Iodoquinoline methiodide, prepared from 2-chloroquinoline and methyl iodide at a temperature not exceeding 80°, is transformed by methyl hydrazinecarboxylate in boiling alcohol into *methyl* 1-*methyl*-2-*quinolonehydrazonecarboxylate*, m. p. 167—168° (decomp.), converted by boiling hydrochloric acid into 1-*methyl*-2-*quinolonehydrazone*, m. p. 126—127° (decomp.) [*hydrochloride*; *hydriodide*]. Treatment of 2-quinolylhydrazine with methyl iodide does not afford a ready method for preparing the quinolone derivative. The action of a large excess of hydrazine hydrate on 2-iodoquinoline methiodide leads mainly to the production of the corresponding *ketazine*, $C_{20}H_{18}N_4$, m. p. 257—258° (*perchlorate*). 2-Iodoquinoline methiodide and 2-ethylbenzthiazolonehydrazone in boiling alcohol afford the 2-*ethylbenzthiazolonehydrazone* of 1-*methyl*-2-*quinolone*, m. p. 137—138° (*perchlorate*).

The necessary aldehydic components for the preparation of the dyes are obtained by the action of *p*-nitrosodimethylaniline in the presence of piperidine on the quaternary perchlorates or bromides of the methylquinoline or methylbenzthiazole derivatives followed by fission of the condensation products by boiling dilute acid. The dyes from 2-ethylbenzthiazolonehydrazone are derived by treating a hot aqueous solution of its hydrochloride or perchlorate with a solution of the corresponding Schiff's base in dilute perchloric acid. Those from methyl 1-methyl-2-quinolonehydrazonecarboxylate are obtained by hydrolysing the latter with boiling, fuming hydrochloric acid and adding a solution of the requisite aldehyde. The following compounds are described: 2-*ethylbenzthiazolenylhydrazone* of *pyridine*-2-*aldehyde methobromide*, decomp. (indef.) 234—237°, *quinoline*-2-*aldehyde methoperchlorate*, decomp. (indef.) 230—235°, and *benzthiazole*-1-*aldehyde methoperchlorate*, decomp. 260—262°; 1-*methyl*-2-*quinolenylhydrazone* of *quinoline*-2-*aldehyde methoperchlorate*, decomp. (indef.) 210—212°; 1-*methyl*-2-*quinolenylhydrazone* of *benzthiazole*-1-*aldehyde methoperchlorate*, decomp. 253—255°.

H. Wren.

o-Aminophenylhydrazine and heterocyclic compounds derived from it. III. Lengthened o-di-derivatives of benzene and their ring-closure. P. C. Guha and T. N. Ghosh (J. Indian Chem. Soc., 4, 561—572).—The following compounds are described: 1-o-*nitrophenyl*-4-p-*tolylthiosemicarbazide*, m. p. 176°; 1-o-*aminophenyl*-4-p-*tolylthiosemicarbazide*, m. p. 252—253° (decomp.); 4-p-*tolyl*-3-*thiol*-1 : 4-*dihydrobenz*-1 : 2 : 4-*triazine*, m. p. 182° (corresponding *disulphide*, m. p. 97—98°, decomp.); 1-o-*nitrophenyl*-4-(1′ : 3′ : 4′)-*xylylthiosemicarbazide*, m. p. 112°; 1-o-*aminophenyl*-4-(1′ : 3′ : 4′)-*xylylthiosemicarbazide hydrochloride*, m. p. 255—256° (decomp.); 1-*xylylthioldihydrobenztriazine*, m. p. 173—174°; 1-o-*nitrophenyl*-4-*allylthiosemicarbazide*, m. p. 160°; 1-o-*aminophenyl*-4-*allylthiosemicarbazide hydrochloride*, m. p. 247—248° (decomp.); 1-*phenylthiocarbamido*-2-*phenylthiosemicarbazidobenzene*, m. p. above 290°; 1-p-*tolylthiocarbamido*-2-*phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*xylylthiocarbamido*-2-*phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*allylthiocarbamido*-2-*phenylthiosemicarbazidobenzene*, not melting at 290°; 1-p-*tolylthiocarbamido*-2-p-*tolylthiosemicarbazidobenzene*, m. p. 281—282°; the *substance* (I or II), m. p. 200°; 1-*carbamido*-2-*phenylthiosemicarbazidobenzene*, not melting at 290°; 1-*phenylcarbamido*-2-*phenylthiosemicarbazidobenzene*, m. p. above 290°; the *substance* III, m. p. 145°; the *substance* IV (R=Ph) as *hydrochloride*, m. p. 140°; the *substance* IV ($R=C_7H_7$) as *hydrochloride*, not melting at 290°; the substance V (R=Ph), m. p. 83—84°; the substance V (R=allyl), m. p. 81—82°; 1-o-*benzylideneaminophenyl*-4-*phenylthiosemicarbazide*, m. p. 168—169°; 1-o-(o′-*nitrobenzylideneaminophenyl*-4-*phenylthiosemicarbazide*, m. p. 260°; the substance VI as *hydrochloride*, m. p. 216—217°.

(I.)   (II.)


(III.)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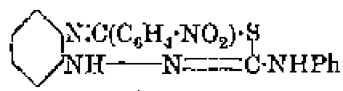
(V.)


(VI.)

C. D. Langford.

Synthesis of nicotine, and Nagai's work on ephedrine. E. Spath and H. Bretschneider (Ber., 1928, 61, [B], 327—334).—Pyrrolid-2-one, prepared by the reduction of succinimide at a lead cathode, is converted by methyl sulphate and sodium in presence of benzene into 1-methylpyrrolid-2-one, b. p. 82—84°/10 mm., transformed by ethyl pyridine-3-carboxylate in presence of sodium ethoxide and benzene into 3′ : 1′-*methylpyrrid*-2-*onyl* 3-*pyridyl ketone*, b. p. 152—154°/0·02—0·03 mm. (*picrate*, m. p. 154—155°). The ketone is converted by hydrochloric acid at 130° into 3-*pyridyl* γ-*methylamino*-n-*propyl ketone* (*chloroplatinate*, partial decomp. 180—185°), which is reduced by zinc dust in alcoholic alkaline solution to 3-*pyridyl*-γ-*amino*-n-*propylcarbinol* (*chloroplatinate*, decomp. 306—310° after darkening at 200° and shrinking at 285°). With fuming hydriodic acid at 100°, α-3-pyridyl-δ-methylamino-*n*-butyl iodide is formed from the secondary alcohol and passes in alkaline solution into *dl*-nicotine, identical with the base obtained by racemising *l*-nicotine sulphate in aqueous solution at 200°; the *picrate*, m. p. 217—218°, *picrolonate*, m. p. 238° (decomp.), and 2 : 4 : 6-*trinitro*-m-*tolyloxide*, m. p. 205—206° (decomp.), are described. The weak link in the chain is the reduction of the amino-ketone to the amino-alcohol, which is accompanied by extensive resinification. This can be obviated by using the catalytic method in aqueous suspension in the presence of palladised charcoal.

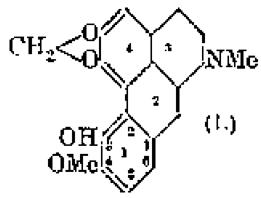
Nagai's claim to the elucidation of the constitution and to the synthesis of ephedrine (Ber., 1927, **60**, [*A*], 173) is adversely criticised. H. WREN.

Synthesis of evodiamine. Y. ASAHINA and T. OHTA (Ber., 1928, **61**, [*B*], 319—321; cf. A., 1924, i, 665).—*N*-Methylanthranilic acid is converted by ethyl chloroformate into N-*methylisatic anhydride*, $C_6H_4<\begin{matrix}NMe\cdot CO\\ CO—O\end{matrix}$, m. 177°, which is transformed by aniline and 3-β-aminoethylindole, respectively, into o-*methylaminobenzanilide*, m. p. 126°, and 3-β-o-*methylaminobenzoylaminoethylindole*, m. p. 113°. The indole derivative and ethyl orthoformate at 175—180° afford *r*-evodiamine, m. p. 278°, converted by boiling alcoholic hydrogen chloride into *iso*evodiamine, m. p. 147°. H. WREN.

Yohimba alkaloids. IV. G. HAHN and W. STENNER (Ber., 1928, **61**, [*B*], 278—286; cf. A., 1926, 1263; 1927, 471).—Decarboxylation of yohimbenic, *iso*yohimboaic, and yohimboaic acids affords in each case *yohimbol*, $C_{19}H_{21}ON_2$, decomp. 306—307°, $[\alpha]_D^{20}$ $-100{\cdot}0°$ in pyridine, so that the isomerism of the three acids and hence of the corresponding alkaloids depends on difference of position of the carboxy-group in the molecule. *allo*Yohimboaic acid, on the other hand, is decarboxylated to an isomeric *compound*, $C_{19}H_{21}ON_2$, decomp. 230°, $[\alpha]_D^{13}$ $+144{\cdot}6°$ in pyridine. The difference between the four alkaloids does not appear profound, and it is suggested that *allo*yohimbine is a hydrogenated product of one of the three isomerides. Yohimbol (*methiodide*) is also obtained by decarboxylation of quebrachoic acid (cf. Hahn, A., 1927, 888).

Yohimbenic acid methylbetaine is converted by ethyl alcohol and hydrogen chloride into *ethyl yohimbenate methochloride*, $C_{23}H_{31}O_3N_2Cl,4H_2O$, which is readily reconverted into the betaine by short treatment with potassium hydroxide; similarly, formation of the betaine takes place when the additive product from methyl iodide and yohimbene or ethyl yohimbenate is treated with alkali. Since a like result is obtained with yohimboaic acid methylbetaine (Spiegel's "methylyohimboaic acid"), the betaine structure of the two compounds is regarded as established. The attempted Hofmann degradation of ethyl yohimbenate methylbetaine affords ill-defined products, but, under certain conditions, isomerisation to the corresponding methyl ester takes place; this type of change has been observed previously only with *d*-betaines, so that the carboxy-group in yohimbenic acid appears to be in the α-position to the nitrogen atom. It is highly probable that a quinoline or at any rate a pyridine ring is present in the yohimbene skeleton and the assumption is made that methyl iodide or sulphate is added to this ring nitrogen atom, to which the carboxy-group stands in the α-position. The acidities of the amino-acids increase in the order yohimbenic, *allo*yohimboaic, yohimboaic, and *iso*yohimboaic, in such a manner that the differences are very marked between the pairs yohimbenic and *allo*yohimboaic acids, on the one hand, and yohimboaic and *iso*yohimboaic acids, on the other, whereas the difference between the individual members of the same pair is slight but distinct. The more strongly acidic character of the *iso*acid in comparison with yohimboaic acid is shown by the separation of the former from solutions with p_H 4·4, whereas the latter requires p_H 4·8 for separation; this behaviour, combined with the different intervals of time required for crystallisation of the acids, forms a basis for their ready separation. Comparison of the strengths of the yohimba acids with those of simple pyridinemonocarboxylic acids confirms the position 2 for the carboxy-group in yohimbenic acid and possibly in *allo*yohimboaic acid. In *iso*yohimboaic and yohimboaic acids the carboxy-group appears to occupy positions 3 and 4 respectively. These views receive support in the physiological action of the acids compared with that of the pyridinecarboxylic acids. H. WREN.

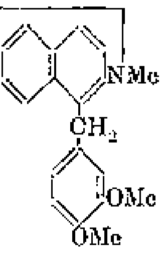
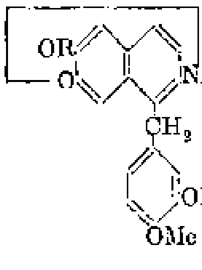
Alkaloids of *Corydalis cava*. XI. Constitution of bulbocapnine. E. SPÄTH, H. HOLTER, and R. POSEGA (Ber., 1928, **61**, [*B*], 322—327).—Oxidative degradation of bulbocapnine under varied conditions confirms the constitution (I) assigned to the alkaloid


(I.)

by Gadamer (A., 1911, i, 1012 and previous abstracts). Oxidation by nitric acid of the methiodide of the methine base obtained by the Emde degradation of bulbocapnine yields benzene-1 : 2 : 3 : 4 - tetracarboxylic acid, m. p. 233—236° (decomp.), identical with the acid prepared similarly from thebenene and identified as the methyl ester, m. p. 129°. Gentle oxidation of bulbocapnine by potassium permanganate in alkaline solution affords hydroxyhydrastinine, m. p. 96—97°. Bulbocapnine methyl ether, m. p. 129—130°, is converted by permanganate into hemipinic acid (identified as the anhydride and ethylimide) and 2 : 3-*methylenedioxy*-2′ : 3′-*dimethoxydiphenyl*-5 : 6 : 6′-*tricarboxylic acid*, m. p. 258—260° (decomp.) (*anhydride*, m. p. 266—267°). *Bulbocapnine ethyl ether*, from the alkaloid and diazoethane in alcohol-ether, is oxidised to 4-methoxy-3-ethoxybenzene-1 : 2-dicarboxylic acid, thus establishing the relative position of the hydroxy- and methoxy-groups in bulbocapnine. The possibility that the groups are in the 5 : 6-position in nucleus (I) (see formula) is not excluded, but is unlikely if the constitution of analogous alkaloids is taken into account. H. WREN.

Opium alkaloids. IX. Constitution of protopapaverine and synthesis of *dl*-codamine. E. SPÄTH and H. EPSTEIN (Ber., 1928, **61**, [*B*], 334—343; cf. A., 1927, 163).—Protopapaverine, $C_{19}H_{19}O_4N$, m. p. 279—280°, is prepared by the thermal decomposition of papaverine hydrochloride at 235° and subsequently at 215—216° (cf. Hesse, A., 1903, i, 773; Pictet and Kramers, *ibid.*, 358). It is not a partly demethylated papaverine, since the alkaloid is not re-formed by treatment with diazomethane. Contrary to previous assumption, it contains only two methoxy-groups, the third methyl radical being attached to nitrogen. Reduction of protopapaverine by tin and hydrochloric acid followed by treatment of the base with diazomethane affords

dl-laudanosine, thus establishing the close similarity of the skeletons of papaverine and protopapaverine. Its solubility in alkali hydroxide establishes the presence of at least one hydroxy-group. Oxidation of protopapaverine by permanganate affords veratric acid, whilst treatment with diazomethane gives the substance (I) (R=Me) (cf. Decker and others, A., 1908, i, 204; 1913, i, 289; Späth and Epstein, *loc. cit.*), reduced to ψ-laudanine. The constitution (I) (R=H) is therefore ascribed to protopapaverine.

(I.)


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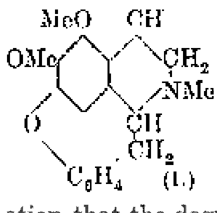
Protopapaverine is converted by methyl iodide into 7-*hydroxy*-6-*methoxy*-3′ : 4′-*dimethoxybenzyl*iso*quinoline methiodide*, which, when converted into the corresponding *methochloride* and then reduced with tin and hydrochloric acid, gives *dl*-codamine (*picrate*, m. p. 187—188°). The identity of the base is confirmed by its methylation to *r*-laudanosine and oxidation of its ethylated product to 1-keto-6-methoxy-7-ethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline.

In addition to protopapaverine (41%), the thermal decomposition of papaverine hydrochloride affords 29% of the hydrochloride of the base (I) (R=Me), about 10% of the isomeric compound (II) (R=Me), and probably about 10% of the substance (II) (R=H). The latter compounds have not been isolated as such but as their reduction products, *dl*-codamine and 6 : 7-dihydroxy-3′ : 4′-dimethoxybenzyl-2-methyl*iso*quinoline. The latter base is oxidised to veratric acid and converted by diazomethane into *r*-laudanosine, m. p. 114—115°. Ethylation with diazoethane followed by oxidation gives 4 : 5-diethoxybenzene-1 : 2-dicarboxylic acid, identified as the ethylimide, m. p. 199—200°. For purposes of comparison, *m*-hemipinic acid is demethylated by hydriodic acid (*d* 1·7) at 100° to 4 : 5-dihydroxybenzene-1 : 2-dicarboxylic acid and then converted by diazoethane into 4 : 5-*diethoxybenzene*-1 : 2-*dicarboxylic acid*, m. p. 165—166° (decomp.), from which the corresponding *anhydride*, m. p. 157—158°, and *ethylimide*, m. p. 199—200°, are derived.

H. Wren.

Constitution of *iso*chondodendrine. F. Faltis and A. Troller (Ber., 1928, **61**, [*B*], 345—355).—Oxidation of the product, $C_{18}H_{16}O_3$, obtained from *iso*chondodendrine by a combination of the Emde and Hofmann methods of degradation has yielded an acid, $C_{12}H_5O(OMe)_2(CO_2H)_3$, derived from diphenyl ether and converted by fusion with potassium hydroxide into *p*-hydroxybenzoic acid (cf. Faltis and Neumann, A., 1922, i, 569). Direct comparison shows the acid not to be identical with 3 : 4′-carboxyphenoxy-5 : 6-dimethoxybenzene-1 : 2-dicarboxylic acid. Since the isomeric acids theoretically possible are not synthetically available, attention has been directed to the synthetic dimethoxydicarboxylic acid for purposes of comparison with the acid produced from the tricarboxylic acid and hydriodic acid (*loc. cit.*). Methyl 3-hydroxy-4 : 5-dimethoxybenzoate is converted into its sodium derivative, which is heated with methyl *p*-bromobenzoate, copper powder, and copper acetate at 180—200°, whereby, after hydrolysis, 3-p-*carboxyphenoxy*-4 : 5-*dimethoxybenzoic* [2 : 3-*dimethoxydiphenyl ether* 5 : 4′-*dicarboxylic*] *acid*, m. p. 217—218°, is produced, identical with the acid derived from *iso*chondodendrine; the non-crystalline *methyl* ester is described. Similarly, using *o*-bromobenzoic ester, the isomeric 3-o-*carboxyphenoxy*-4 : 5-*dimethoxybenzoic* [2 : 3-*dimethoxydiphenyl ether* 5 : 2′-*dicarboxylic*] *acid*, m. p. 228·5—229° (*methyl* ester, m. p. 72—73°), is obtained; fusion with potassium hydroxide gives salicylic acid unaccompanied by *p*-hydroxybenzoic acid. Since migration of the carboxy-group is not observed, the "degradation acid" cannot contain the *o*′-carboxyphenoxy-group. The reactions of the other product of the alkaline fission of the isomeric acids are identical with those of the similar product from the "degradation acid."



There is therefore no reason to assume that the latter is not derived from pyrogallol (cf. *loc. cit.*). The constitution (I) can therefore almost certainly be assigned to methyl*iso*chondodendrine. Confirmation of this conception is found in the observation that the degradation product (II), obtained by reduction of the hydromethine prepared from the alkaloid by Emde and Hofmann's method (*loc. cit.*), is converted by mild oxidation into the carboxylic *acid* (III) (*barium* salt; *methyl* ester, m. p. 252—253°), which does not yield *p*-hydroxybenzoic acid when fused with potassium hydroxide. The unusually high m. p. and the value obtained for the mol. wt. of α-methyldihydro*iso*chondodendrimethine

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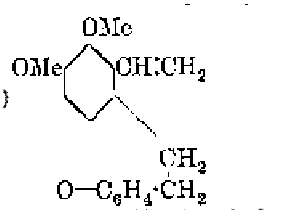
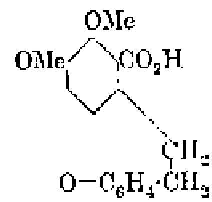


(III.)

and α-methyl*iso*chondodendrimethine by Rast's method suggest a complex constitution for the parent alkaloid, but chemical evidence is adduced in favour of the simple composition $C_{18}H_{19}O_3N$; the phenomena of association appear to be characteristic of the peculiar oxygen ring system.

H. Wren.

***p*-Arsinophenoxyacetic acid.** C. S. Palmer and E. B. Kester (Org. Syntheses, 1927, 7, 4—5).—The product of interaction of sodium hydroxide, *p*-hydroxyphenylarsinic acid, and chloroacetic acid is treated with hydrochloric acid.

A. A. Eldridge.

Pure arsenobenzene and the molecular complexity of arsenobenzene and arsenomethane. C. S. Palmer and A. B. Scott (J. Amer. Chem. Soc., 1928, **50**, 536—541).—Pure arsenobenzene, m. p. 195°, prepared by a modification of the method of

Binz, Bauer, and Hallstein (A., 1920, i, 401), is unimolecular in boiling carbon disulphide, but partly associated in boiling benzene (cf. Michaelis and Schafer, A., 1913, i, 783), and probably bimolecular in molten naphthalene. Both the yellow, liquid and red, solid modifications of arsenomethane appear to exist as $(MeAs)_5$ in boiling carbon disulphide.

F. G. Willson.

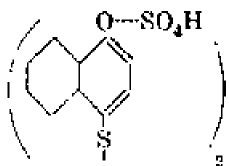
Manufacture of organic compounds of arsenic [oxazinearsinic acids]. G. Newbery, and May and Baker.—See B., 1928, 211.

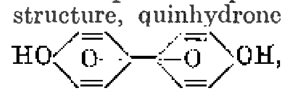
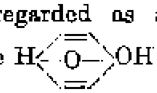
Arsenical derivatives of quinoline. S. Berlingozzi (Annali Chim. Appl., 1928, **18**, 31—36).—When coupled with diazotised arsanilic acid derivatives, hydroxyquinolines yield the following red or brown hydroxyazo-compounds, which are being examined as to pharmacological properties: *2-Methyl-3-azo-4-hydroxyquinoline-*p*-phenylarsinic acid* (not melted at 300°), *5-azo-8-hydroxyquinoline-*p*-phenylarsinic acid*, *2-phenyl-4-azo-3-hydroxyquinoline-*p*-phenylarsinic acid*, and *2-methyl-4-azo-3-hydroxyquinoline-*p*-phenylarsinic acid*. All of these acids give red colorations with concentrated sulphuric acid.

T. H. Pope.

[Preparation of] triphenylstibine. G. S. Hiers (Org. Syntheses, 1927, **7**, 80—82).

Cyclic organo-metallic compounds. V. Phenoxselenine and phenoxthionine from phenoxtellurine. Selenylium and thionylium compounds. H. D. K. Drew (J.C.S., 1928, 511—524).—When phenoxtellurine or its derivatives (with the exception of nitro-compounds) are heated with sulphur or selenium, the tellurium is replaced by these elements and the analogous phenoxthionine or phenoxselenine is obtained. These form mixed crystals and yield -ylium compounds analogous to the tellurylium salts. Thus when phenoxtellurine is boiled with sulphur it yields phenoxthionine, m. p. 58° unchanged (Mauthner, A., 1906, i, 447, gives 60—61°), contaminated with 6—7% of unaltered phenoxtellurine, from which it is separated by addition of a few drops of bromine to its chloroform solution and subsequent treatment with acetone and ether. It is converted by hydrogen peroxide in glacial acetic acid into *phenoxthionine oxide*, m. p. 158—159°, whilst prolonged action of the reagent yields the *dioxide*, m. p. 147—148°. *Phenoxselenine*, m. p. 87—88°, is obtained in a similar manner. The original complex, composed of phenoxselenine (2 mols.) and phenoxtellurine (1 mol.), is separated by boiling the mixed dibromides with acetone and treating the residue with ether, the phenoxtellurine dibromide being insoluble. When treated with the appropriate halogen in chloroform solution it yields a *dichloride*, m. p. 127° (decomp.), and *dibromide*, m. p. 147—148° (decomp.). Oxidation with hydrogen peroxide converts it into *phenoxselenine dihydroxide*, which readily loses 1 mol. of water, yielding the *oxide*, m. p. 171—172°, which is quantitatively converted into phenoxselenine by heating it above its m. p. The intensely coloured solutions of phenoxthionine in sulphuric (or phosphoric) acid are due to the presence, not, as suggested by Hilditch and Smiles (J.C.S., 1911, **99**, 408), of thionium salts, but of the *thionylium* compound (annexed formula), since by subsequent



decomposition with ice, half the phenoxthionine is recovered as oxide (donor) and half unchanged (acceptor). Cautious dilution of the corresponding solution of phenoxselenine in concentrated sulphuric acid yields copper-red crystals of pure *triphenoxselenylium dibisulphate sulphuric acid dihydrate* (changing, in a sealed tube, at 155° and m. p. 168°), of analogous structure to the corresponding tellurylium compound (cf. following abstract), and, subsequently, a mixture of this with dark purple crystals. Crystallisation of this mixture from acetic acid containing a few drops of sulphuric acid yields the pure copper-red compound, which is decomposed quantitatively by cold water into sulphuric acid, phenoxselenine, and its oxide. Decomposition with ice of the violet solution obtained by dissolving phenoxthionine oxide in sulphuric acid yields phenoxthionine, the tendency towards the formation of thionylium salts being sufficiently great to cause the sulphuric acid to act either as an oxidising or a reducing agent as required. Mechanisms of the various reactions are given. It is deduced that, in their compounds, sulphur may be associated with 18 or 20 electrons, selenium with 36 or 38, and tellurium with 54 or 56, the tendency to become associated with the higher number increasing in this order. An attempt is made to interpret the quinhydrones on a carbonylium structure, quinhydrone itself being formulated as , its generator, quinol, being regarded as able to assume the carbonium structure .

J. W. Baker.

Cyclic organometallic compounds. IV. Tellurylium compounds. H. D. K. Drew (J.C.S., 1928, 506—510).—The author's method of ascertaining the relative proportions of donor and acceptor in the molecule of a tellurylium compound (A., 1927, 164) has been improved to give quantitative results, and its application to the compounds previously described (*loc. cit.*) proves the correctness of the formulæ assigned except in the case of the compound previously described as diphenoxtellurylium hydroxybisulphate monohydrate, obtained by crystallising diphenoxtellurylium dibisulphate or its complex with 2 mols. of sulphuric acid from glacial acetic acid. This is really *triphenoxtellurylium dibisulphate*, $\left(C_6H_4<^{O}_{Te}>C_6H_4\right)_3(HSO_4)_2$. An expanded formula for this is suggested in which the three tellurium atoms are held together by four electrons. There exists, therefore, a series of compounds of the type $[R_x](HSO_4)_2$ in which x may be 1, 2, or 3, some of which have addenda of water or sulphuric acid molecules. The compound of m. p. 59° described by Thomason and Drew (A., 1927, 267) as a complex of phenoxtellurine and chloromethylphenoxtellurine has been separated into these components by fractional precipitation of its chloroform solution with bromine. Phenoxtellurine dibromide separates

first and then the *dibromide*, m. p. 315° (decomp.), of *chloromethylphenoxtellurine*, m. p. 46—47° [*dichloride*, m. p. 300° (decomp.); *diacetate*, m. p. 230—232° (decomp.); *disulphate*; di-α-bromocamphor-π-sulphonate which could not be purified owing to its tendency to hydrolyse], which is obtained from the dibromide by reduction with potassium metabisulphite, and from which a *tellurylium* compound was obtained. J. W. Baker.

***cyclo*Telluropentane.** G. T. Morgan and H. Burgess (J.C.S., 1928, 321—329).—The action of aluminium telluride on αε-pentamethylene dihalides under varying conditions according to the halide employed, yields cyclo*telluropentane*, b. p. 82—83°/12 mm., 44—45°/1—2 mm., in accordance with the equation $Al_2Te_3+3CH_2X\cdot[CH_2]_3\cdot CH_2X=3C_5H_{10}{:}Te+2AlX_3$ (X=Cl, Br, or I), but this product is not isolated at this stage, since it interacts with more of the pentamethylene dihalide to yield compounds of the type $C_5H_{10}{:}TeX\cdot CH_2\cdot[CH_2]_3\cdot CH_2X$ (I) and $C_5H_{10}{:}TeX\cdot CH_2\cdot[CH_2]_3\cdot CH_2\cdot TeX{:}C_5H_{10}$ (II). A small amount of the *cyclo*telluripentane dihalide, $C_5H_{10}{:}TeX_2$, is also obtained in the case of the bromine and iodine compounds, but this is best prepared by the addition of halogen to the compounds (I) or (II) or their products of thermal decomposition (below). Thus are obtained: 1-ε-*chloroamyl*-cyclo*telluripentane*-1-*chloride*, m. p. 149—151°, -1-*bromide*, m. p. 143—145°, and -1-*iodide*, m. p. 135—136°, resolidifying almost immediately and then having m. p. 197—198°; *pentamethylene*-αε-*bis*cyclo-*telluripentane*-1 : 1′-*dichloride*, decomp. 224—225°, -1 : 1′-*dibromide*, exploding on rapid heating, and -1 : 1′-di-iodide, m. p. 216—217° (decomp.). cyclo-*Telluripentane*-1 : 1-*dichloride*, m. p. 106—107° (*dichromate*), is prepared either by thermal dissociation, or by the action of a slight excess of chlorine, from (I). The corresponding -1 : 1-*dibromide*, m. p. 105—107°, is best prepared by heating either (I) or (II) to 160—190°/25—30 mm. and the action of excess of bromine on the *cyclo*telluropentane thus liberated, or by the direct action of bromine on (I) in carbon tetrachloride solution. By treatment with bromine in carbon tetrachloride it yields the corresponding -1 : 1-*bisperbromide*, m. p. 102—104°. The -1 : 1-*di-iodide*, m. p. 135—136°, which is obtained in two forms, one deep red with purplish-blue reflex (stable) and the other orange, transformation of the latter into the former occurring slowly at the ordinary temperature, and at 105° on heating, is obtained by addition of iodine to *cyclo*telluropentane in carbon tetrachloride. By reduction with potassium metabisulphite in aqueous solution, *cyclo*telluripentane-1 : 1-dibromide is converted into *cyclo*telluropentane (above), which must be distilled in an inert atmosphere, since it is rapidly oxidised either by air or hydrogen peroxide to cyclo*telluripentane*-1 : 1-*dioxide*, $+H_2O$, a white, amorphous powder which explodes on rapid heating. J. W. Baker.

Valency problem of boron. III. Valency phenomena of boron in boron tri*cyclo*hexyl and boron tri-*p*-tolyl. E. Krause and H. Polack (Ber., 1928, 61, [*B*], 271—276; cf. A., 1922, i, 694; 1924, i, 436; 1926, 628).—*Boron tri*-p-*tolyl*, m. p. above 175°, resembles boron triphenyl in that it is sensitive towards air but forms stable additive compounds with nitrogenous bases which are indifferent towards oxygen; the *substances* $B(C_7H_7)_3,NH_3$, m. p. 225—226° in a sealed capillary; $B(C_7H_7)_3,C_5H_5N$, m. p. 201—202°, and $B(C_7H_7)_3,C_5H_{11}N$, m. p. 202° after softening, are described. Like the phenyl derivative, boron tri-*p*-tolyl reacts with sodium and potassium, but the products crystallise with difficulty. *Boron tri*cyclo*hexyl*, m. p. 98—100°, is much more sensitive to air than the phenyl compound. Its additive *compounds* with ammonia, $B(C_6H_{11}),NH_3$, m. p. 105—106°, and pyridine, $B(C_6H_{11})_3,C_5H_5N$, are readily affected by atmospheric oxygen, whereas the *compound* $B(C_6H_{11})_3,C_5H_{11}N$, m. p. 135—136°, is stable when solid, but rapidly oxidised when dissolved. Like boron tri-*n*-propyl, m. p. −56°, it does not react with the alkali metals. H. Wren.

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid. F. C. Whitmore, P. J. Culhane, and H. T. Neher (Org. Syntheses, 1927, 7, 1—3).—Experimental details for the preparation of anhydro-2-hydroxymercuri-3-nitrobenzoic acid from sodium 3-nitrophthalate and mercuric acetate are recorded. A. A. Eldridge.

Proteins. V. Glutamic acid. C. Okinaka (Sexagint [Osaka celebration], Kyoto, 1927, 27—59). Glutamic acid probably plays an important part in the metabolism of proteins in plants. Ethyl glutamate passes readily into ethyl pyrrolidine-1-carboxylate and the free acid gives the corresponding acid; this reaction is accelerated by heat or dilute alkali but retarded by excess of strong acid or alkalis. The reaction does not go to completion but attains an equilibrium. The optical properties of its solutions of various p_H values indicate that the acid exists normally to some extent in the form of an internal salt and this is probably the first step in the formation of the pyrrolidinecarboxylic acid. C. D. Langford.

Combination of gelatin with organic bases. A. Petrunkin and M. Petrunkin (Arch. Sci. biol., 1927, 27, 219—234).—See this vol., 190.

Degradation of gelatin with acetic anhydride. A. Fodor and C. Epstein (Z. physiol. Chem., 1927, **171**, 222—241).—Various crystalline *products*, very hygroscopic and varying in solubility in alcohol, have been obtained from the syrupy product of the degradation of gelatin with boiling acetic anhydride. Investigations were confined to the more soluble portions over the range $[\alpha]_D^{20}$ −76·92° to −101·4°. These are identified by their chemical behaviour, mol. wt., and analysis as: hydroxyprolylalanine, $C_8H_{14}N_2O_4$, $[\alpha]_D^{20}$ −76·92°; $(C_8H_{14}N_2O_4)_4$ (polymerised hydroxyprolylalanine, ?), $[\alpha]_D^{20}$ −78·2°; $4(C_8H_{14}N_2O_4),3H_2O$, $[\alpha]_D^{20}$ −78·2°; $4(C_8H_{14}N_2O_4),H_2O$, $[\alpha]^{20}$ −88·8°; and (hydroxyprolylalanine +3-hydroxyprolylglycine $-3H_2O$), $[\alpha]_D^{20}$ −101·4°. Depolymerisation of these by barium hydroxide or by sodium hydroxide to dipeptide and amino-acid furnishes evidence on which suggested structural formulæ for the polymerides are based. J. Stewart.

Decomposition of soya-bean protein. V. Decomposition of soya-bean protein by sulphuric acid. VI. Decomposition of soya-bean pro-

tein by organic acids. VII. Decomposition by Japanese acid clay. M. MASHINO and T. SHISHIDO (J. Soc. Chem. Ind. Japan, 1927, **30**, 552—560, 561—564, 565—568; cf. A., 1927, 474).—V. Soya bean from which oil had previously been extracted with light petroleum was treated for 6 hrs. with dilute sulphuric acid (1—20%) at 4·7 atm. The action of the acid was much more rapid and the amounts of ammonia and amino-nitrogen formed were much larger than at atmospheric pressure. The amount of nitrogen appearing as ammonia increased with increasing time of treatment, reaching 11·63—20·05% of the total nitrogen at the end of 6 hrs. With 20% sulphuric acid the amount of amino-nitrogen formed increased rapidly at first, reached a maximum (about 80% of the total nitrogen), and then decreased gradually to about 60% at the end of 6 hrs. With more dilute acid no maximum was found.

VI. When soya-bean protein was treated with acetic, lactic, citric, tartaric, or oxalic acid for several hours at 2·66—5·8 atm., the ammonia-nitrogen liberated was nearly the same in every case (10—13% of the total nitrogen). The amino-nitrogen liberated varied from 3·1 to 25·1% of the total nitrogen, according to the acid used, and increased in the order: acetic, lactic, citric, tartaric, oxalic acid.

VII. When soya-bean protein was heated under pressure with acid clay and water, or with acid clay and sodium chloride solution, the ammonia-nitrogen and amino-nitrogen liberated was about 8·5% and about 5% of the total nitrogen, respectively. With acid clay and hydrochloric acid the amount of amino-nitrogen liberated was somewhat less than with the acid alone. Y. NAGAI.

Nitrogen distribution of soya-bean protein. M. MASHINO and S. NISHIMURA (J. Soc. Chem. Ind. Japan, 1927, **30**, 607—610).—The nitrogen distribution of several varieties of soya-bean protein has been determined by the Van Slyke method. Y. NAGAI.

Purification of soya-bean protein. M. MASHINO (J. Soc. Chem. Ind. Japan, 1927, **30**, 610—617).—Soya bean, from which oil had previously been extracted with light petroleum, was treated with various solvents to remove constituents other than the protein. Methyl alcohol proved best. The amount of extraction increased with temperature. Extraction by methyl or ethyl alcohol at 67—68° or at 82—83° was almost complete in 1 hr. Soya-bean protein purified with methyl alcohol is no longer hygroscopic, is odourless, and has only a light colour. Y. NAGAI.

Behaviour of proteins with alkali with some conclusions in regard to their structure. J. TILLMANS and P. HIRSCH (Biochem. Z., 1928, **193**, 216—236).—The changes of "molecular binding power, δ" of egg-albumin and gliadin solutions on addition of acids and alkalis is investigated. These proteins, especially gliadin, have very low δ values, but the latter increases considerably on adding sodium hydroxide (especially in the case of albumin), due to the liberation of new acid and basic groups, the strengths of which correspond with those of peptides. Peptides, however, are only difficultly attacked by sodium hydroxide and the results favour, therefore, the ring (diketopiperazine) rather than the peptide structure of the proteins. Although the δ values for albumin increase much more quickly than for gliadin, the final values, after more prolonged digestion with alkali, are bigger for gliadin than for albumin. P. W. CLUTTERBUCK.

Rapid determination of carbon, nitrogen, and hydrogen in organic compounds. R. VANDONI and M. ALGRAIN (Bull. Soc. chim., 1928, [iv], **43**, 255—260).—A modified Dumas apparatus is described for the volumetric determination of carbon and nitrogen at the same time. The combustion is carried out using oxygen in slight excess of the calculated amount, and the apparatus is arranged so that the gaseous products can be passed over heated copper oxide as many times as are necessary for complete burning. A similar apparatus is described for the gravimetric determination of hydrogen. The methods are quick and give trustworthy results. H. BURTON.

Determination of halogens in organic compounds. M. PRONER (Rocz. Farm., 1926, **4**, 99—106; Chem. Zentr., 1927, ii, 1596).—The method is specially suitable for naphthalene derivatives, terpenes, and heterocyclic compounds. The substance (0·1—0·2 g.) is slowly warmed with 95% alcohol, and small pieces of sodium (1 g.) are added; the mixture is warmed with 30% hydrogen peroxide solution (5 c.c.) until evolution of oxygen ceases, acidified with nitric acid, reduced with sodium sulphite, warmed, and the chloride precipitated with silver nitrate. A. A. ELDRIDGE.

Determination of selenium in organic compounds. W. E. BRADT and R. E. LYONS (Proc. Indiana Acad. Sci., 1926, **36**, 195—201).—The (halogen-free) substance is heated with nitric acid in a sealed tube, the solution being made alkaline with potassium hydroxide (free from halide), slightly acid with nitric acid, and then neutral with excess of zinc oxide, and finally titrated with siver nitrate in presence of sodium chromate. CHEMICAL ABSTRACTS.

Thalleioquinine reaction. B. OLSZEWSKI (Rocz. Farm., 1926, **4**, 119—130; Chem. Zentr., 1927, ii, 1598).—Optimally, 1 mol. of quinine is treated with 4—8 atoms of bromine for 15 sec. In the micro-reaction, the precipitate is dissolved in 30% acetic acid, the acid removed by evaporation, and the residue. after dissolution in water, treated with 1 drop of dilute bromine water. A. A. ELDRIDGE.

Determination of the isoelectric point of amino-acids, asparagine, or glycine. M. D. BACH (Bull. Soc. Chim. biol., 1928, **9**, 1233—1243).—The compound to be examined is added in equal amounts to each of a series of tubes containing suitable buffer solutions chosen so as to extend over a range of p_H including the isoelectric point required. An identical set of buffer tubes is also prepared to which none of the compound is added. By electrometric methods or by the addition of a suitable indicator to each of the two sets of tubes the particular p_H is found which is such that the addition of the compound causes no change in hydrogen-ion concentration. By this method it has been found that the isoelectric points of glycine and of asparagine are at p_H 4·3 and 5·8, respectively. W. O. KERMACK.

Biochemistry.

Glycerol and potassium hydroxide in the microscopical detection of blood. K. Meixner (Deuts. Z. ges. gericht. Med., 1927, **10**, 253—254; Chem. Zentr., 1927, ii, 1742).—A mixture of concentrated aqueous potassium hydroxide and glycerol, or a glycerol solution of potassium hydroxide is preferred to aqueous potassium hydroxide; the formation of hæmatin and hæmochromogen takes place completely, but more slowly. The use of reducing agents for this purpose is objectionable.
A. A. Eldridge.

Value of benzidine reaction and the clinical significance of the hæmatoporphyrin test in fæces. D. E. Schouten (Ned. maandschr. geneesk., 1926, **13**, 651—668; Chem. Zentr., 1927, ii, 963).—The pigment of the blood is partly or completely converted in the intestinal canal into hæmatoporphyrin; spectroscopic detection of the porphyrin is preferred. The test is not less sensitive than the benzidine reaction. A. A. Eldridge.

Effect of posture on the composition and volume of blood in man. W. O. Thompson, P. K. Thompson, and M. E. Dailey (Proc. Nat. Acad. Sci., 1928, **14**, 94—98).—In the standing-still position there occurs a net loss of approximately protein-free fluid from the blood. This seems to be due to an increase in capillary pressure. The loss amounts to about 11% of the total plasma volume, and is probably greatest in the lower extremities.
W. E. Downey.

Origin of the pigment of *Chironomus* larvæ. M. Comas (Compt. rend. Soc. Biol., 1927, **96**, 866—868; Chem. Zentr., 1927, ii, 100).—Hæmoglobin in *Chironomus* larvæ does not arise from ingestion of chlorophyll, but is hereditary. It is associated with a green pigment similar in its properties to biliverdin.
A. A. Eldridge.

Coagulation of hæmoglobin in presence of organic substances. B. Jirgensons (Biochem. Z., 1928, **193**, 109—121).—The coagulation of hæmoglobin with potassium chloride and magnesium chloride is sensitised by the presence of small amounts of capillary-active substances having small dielectric constants (ether, chloroform, amyl and *iso*butyl alcohols, acetone, methylurethane), whilst in larger concentrations these substances may act either as sensitisers if the salt concentration is small, or as stabilisers if it is large. Some capillary-inactive substances (mannitol and dextrose) have a slight stabilising action (cf. A., 1927, 512, 624).
P. W. Clutterbuck.

Amino-acids in blood of insects. M. Duval, P. Portier, and A. Courtois (Compt. rend., 1928, **186**, 652—653).—Amino-acids have been determined by the Sørensen titration method in the blood of insects, in the chrysalid, larval, and fully-grown states. The value is high in each case, and particularly in the chrysalis. W. K. Slater.

Blood-creatinine. O. H. Gaebler and A. K. Keltch (J. Biol. Chem., 1928, **76**, 337—359).—Addition of a 10% solution of phosphotungstic acid, saturated with picric acid, to a saturated picric acid solution containing creatinine causes precipitation of the latter; the precipitate can be decomposed with a mixture of alcohol and ether and the creatinine re-precipitated by addition of picric acid to the filtrate. Picric acid is removed by shaking the precipitate with dilute sulphuric acid and ether, the creatinine is re-precipitated with basic lead acetate, recovered with hydrogen sulphide in the usual manner, and finally isolated as potassium creatinine picrate; in order to obtain the maximum yield of the latter it is important to have the correct concentration of potassium in the solution. The above method has been applied to the isolation of creatinine from blood which has been freed from protein by treatment with picric acid. Treatment of such protein-free blood-filtrates with kaolin removes the creatinine but leaves in solution other substances which give the Jaffe reaction and also accumulate in those pathological conditions which lead to retention of creatinine. Creatinine may also be separated from blood-filtrates by treatment with Lloyd's reagent, and decomposition of the precipitate by means of lead hydroxide. C. R. Harington.

Determination of cholesterol in small amounts of blood. S. M. Ling (J. Biol. Chem., 1928, **76**, 361—365).—Blood is dried on filter-paper and extracted for 40 min. with chloroform in a special apparatus; cholesterol in the extract is determined colorimetrically. C. R. Harington.

Determination of dihydroxyacetone in blood and urine. W. S. McClellan (J. Biol. Chem., 1928, **76**, 481—486).—The utility of the method of Campbell (A., 1926, 443) for the determination of dihydroxyacetone in blood is confirmed; the method can be applied to urine, after preliminary removal of phosphates. C. R. Harington.

Methylglyoxal as intermediate product in glycolysis in blood. H. K. Barrenscheen (Biochem. Z., 1928, **193**, 105—108).—The formation of methylglyoxal during glycolysis in blood is detected by addition of semicarbazide with isolation and identification of methylglyoxal disemicarbazone.
P. W. Clutterbuck.

Glycolysis of dextrose and lævulose in the blood of normal and diabetic dogs. E. Turgatti (Rev. Soc. Argentina Biol., 1927, **3**, 716—720).—Venous blood from dogs was incubated for 6 hrs., alone, and with the addition of dextrose or lævulose. The greatest amount of glycolysis occurred in blood of low blood-sugar level, and *vice versa.* Glycolysis was retarded considerably by the addition of dextrose and moderately by the addition of lævulose. Glycolysis was slower in the blood of dogs from which the pancreas had been removed, and was retarded or even inhibited by addition of dextrose, but the addition of lævulose had, on the whole, little effect. It is suggested that hyperglycæmia can be considered not only as a symptom, but also as itself a cause of disturbance. R. K. Callow.

"Protein"-blood-sugar. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, 97, 186—187; Chem. Zentr., 1927, ii, 1162).—Hydrolysis of plasma-protein yields a small fraction of a reducible and fermentable substance, having a reducing power about 6% of that of the sugar-free hydrolysate; the ratio of protein to the substance is about 1 : 0·0044.

A. A. Eldridge.

Reducing and fermentable substances in combination with proteins of the blood-plasma. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, 97, 187—191; Chem. Zentr., 1927, ii, 1162—1163; cf. preceding abstract).—Pure constituents of the blood-serum were submitted to hydrolysis. Proteins give by acid hydrolysis 7·4% of reducing substance expressed as dextrose and calculated on the original quantity of sheep blood-proteins; the fermentable fraction is only 0·8—1·2%, and is ascribed to traces of nucleoproteins.

A. A. Eldridge.

Presence of two reducing carbohydrates in blood. G. Fontès and L. Thivolle (Compt. rend. Soc. Biol., 1927, 96, 994—996; Chem. Zentr., 1927, ii, 449).—The use of mercuric nitrate and of tungstic acid (the former, but not the latter, precipitating creatinine and uric acid) indicates the presence in blood, in addition to that of "glucose," of an ethereal component the reducing power of which is unchanged by hydrolysis. The amount is not increased by muscular work or insulin. A. A. Eldridge.

Distribution of the carbohydrate reducing substances between plasma and blood-corpuscles. G. Fontès and L. Thivolle (Compt. rend. Soc. Biol., 1927, 96, 997—998; Chem. Zentr., 1927, ii, 449).—Hirudin does not affect the natural distribution of reducing carbohydrates in the corpuscles; other anticoagulants affect the plasma and corpuscles in the same sense. A. A. Eldridge.

Determination of blood-sugar. II. S. R. Benedict (J. Biol. Chem., 1928, 76, 457—470).—Evidence was obtained of the presence in protein-free blood filtrates of substances which affect the dissociation of the complex copper salt, in the solutions usually employed for the determination of blood-sugar, rendering it more easily reduced by dextrose; this effect has been overcome by the addition of alanine to a new reagent of the Fehling type. The new reagent gives results for the blood-sugar about 22 mg.% lower than the reagent of Folin and Svedberg (A., 1926, 1282); further, dextrose added to protein-free filtrates of blood which have been subjected to yeast fermentation can be quantitatively determined by the new reagent, which therefore appears not to be affected by the non-dextrose reducing substances present in such filtrates. The work of Somogyi (A., 1927, 1214) is criticised on the ground that insufficient time was allowed for fermentation; good results are obtained by diluting blood with a suspension of washed yeast and keeping the mixture for 15 min. before precipitation with tungstic acid. C. R. Harington.

Micro-determination of blood-sugar. H. Citron (Deutsch. med. Woch., 1927, 53, 1216—1217; Chem. Zentr., 1927, ii, 1598).—The Hagedorn-Jensen method is improved. A. A. Eldridge.

Serum-calcium. I. Oral administration. J. C. Hoyle (J. Pharm. Exp. Ther., 1928, 32, 309—320).—No definite differences in the normal serum-calcium content of male and female rabbits have been detected, but a seasonal variation occurs. Loss of blood equivalent to about one fifth of the body-weight causes a fall in the serum-calcium of approximately 14%. Administration by mouth of single or repeated doses of 1 g. of calcium carbonate per kg. body-weight causes an increase of serum-calcium up to 16% which, when allowance is made for effect of hæmorrhage, is equal to an increase of 20—25%. By administration of 2 g. of calcium carbonate per day a permanent increase of serum-calcium of 5—15% has been obtained. Single doses of calcium lactate (3 g. per kg. body-weight) cause an increase in serum-calcium of 15—22%, whilst repeated daily doses of 6 g. of the salt cause a maximum increase of only 5%, or 12% if allowance be made for the effects of repeated bleeding. W. O. Kermack.

Replacement of the serum-calcium and thyroid gland in rabbits after intravenous injections of oxalate. H. W. C. Vines (Endocrinol., 1927, 11, 290—296).—The speed of replacement of calcium, which has been removed from the blood following the intravenous injection of ammonium oxalate, was determined. Chemical Abstracts.

Blood-phosphorus in health and disease. I. Distribution of phosphorus in human blood in health. H. D. Kay and F. B. Byrom (Brit. J. Exp. Path., 1927, 8, 240—253).—The distribution of phosphorus in venous blood is fairly constant; the ester phosphorus is greater, and the portion thereof hydrolysable by phosphatase is less, in men than in women. After a meal there is a slight diminution in inorganic phosphorus, a diminution in phosphoric ester hydrolysable by phosphatase, and a corresponding increase in the ester fraction resistant to enzyme hydrolysis; there is also possibly a slight rise in lipin-phosphorus. The phosphorus index (mg. of ester phosphorus in 100 c.c. of red cells) is a more stable constant than the p_H of the blood.

Chemical Abstracts.

Use of the quinhydrone electrode for the determination of the p_H of whole blood and serum. J. Gewecke (Biochem. Z., 1928, 193, 181—186).—The experiments of F. Schmidt (Z. Immun. exp. Ther., 1926, 46, 386) were repeated using rabbit's in place of guinea-pig's blood, but the results were not consistent and often very different from those obtained by the hydrogen electrode. With inactivated human serum the initial potential was highest and quickly fell, and the results again differed from those obtained by the hydrogen electrode.

P. W. Clutterbuck.

Determination of p_H of blood. I. Accuracy of quinhydrone electrode for determining p_H of blood-plasma or serum. G. E. Cullen and I. P. Earle. **II. Comparison of colorimetric method with hydrogen and quinhydrone electrodes.** I. P. Earle and G. E. Cullen (J. Biol. Chem., 1928, 76, 565—581, 583—590).—I. A modified technique

for the use of the quinhydrone electrode (cf. Cullen and Biilmann, A., 1925, i, 1201) is described, by the employment of which reproducible results for the p_H of normal blood-plasma or -serum may be obtained, these results being always 0·06 p_H more acid than the corresponding figures obtained with the hydrogen electrode.

II. Figures obtained for the p_H of normal diluted human blood-serum by the colorimetric method of Cullen (A., 1922, ii, 672) were 7·41—7·50, and were 0·14 p_H more alkaline than those obtained with the quinhydrone electrode. C. R. HARINGTON.

Calculation of cell volume changes as a function of p_H. D. B. DILL (J. Biol. Chem., 1928, **76**, 543—545).—By mathematical extension of the calculations of Van Slyke, Wu, and McLean (A., 1923, i, 1249) a relationship is developed between the relative volume of the red blood-corpuscles and the p_H of the serum. C. R. HARINGTON.

Effect of carbon dioxide equilibration on surface tension of blood-serum. J. M. JOHLIN (J. Biol. Chem., 1928, **76**, 559—564).—Neither the absolute magnitude of the surface tension of blood-serum nor the change in surface tension with time is significantly affected by equilibration with varying tensions of carbon dioxide. C. R. HARINGTON.

Hæmoclastic changes *in vitro* from agents causing anaphylactoid reactions. P. J. HANZLIK, F. DE EDS, L. W. EMPEY, and W. H. FARR (J. Pharm. Exp. Ther., 1928, **32**, 273—294).—Various anaphylactoid reagents, copper sulphate, arsphenamine, peptone, acacia, agar, and toxified serum added *in vitro* to oxalated blood-plasma or serum cause a decrease in surface tension and an increase in the albumin–globulin ratio. Albumin, peptone, and agar increase the viscosity of blood-serum, acacia and gelatin increase the rate of sedimentation of blood-corpuscles suspended in plasma. The fragility of the corpuscles is decreased by acacia and gelatin and increased by arsphenamine and copper sulphate. The results are considered to support the view that anaphylactoid changes are of the nature of a disturbance in the equilibrium of the body colloids. W. O. KERMACK.

Variations in the coagulability of the blood normally and after ingestion of food. C. A. MILLS and H. NECHELES. **Relation of blood coagulability to body metabolism and to the specific dynamic action of food.** H. NECHELES and C. A. MILLS (Chinese J. Physiol., 1928, **2**, 19—23, 25—32).—The coagulation time of blood is decreased after a meal containing protein, but not after one containing only carbohydrate or fat. It is decreased also after administration of glycine, which, like proteins, has a marked specific dynamic action. The decrease in coagulation time appears to be related, not directly to the increase of metabolism which occurs after a meal, but rather to the presence in the blood-stream of substances which exert specific dynamic action. W. O. KERMACK.

Action of soluble iron salts on coagulation of blood. P. BORDET (Compt. rend. Soc. Biol., 1927, **96**, 1061—1063; Chem. Zentr., 1927, ii, 450).—Ferrous sulphate and chloride, aluminium sulphate, and chrome alum hinder the coagulation of blood owing to interaction with the blood constituents. A. A. ELDRIDGE.

Chemistry of specific hæmagglutination. A. KONIKOV (Žurn. eksp. biol. med., 1926, 128—145; Chem. Zentr., 1927, ii, 1046).—The erythrocytes can be regarded as an amphoteric protein of isoelectric point p_H 5. Probably only between p_H 6 and 9 are the stroma and agglutinin oppositely charged. The presence of electrolyte is necessary in the first phase of hæmagglutination; the action of the salt is expressed by the scheme stroma—Na—Cl—agglutinin, in which auxiliary valencies function. The subject is discussed from this point of view. A. A. ELDRIDGE.

Rapid preparation of crystalline egg-albumin. W. LA ROSA (Chemist-Analyst, 1927, **16**, No. 2, 3).—The whites of fresh eggs are beaten well and mixed with an equal volume of saturated ammonium sulphate solution. After 15 hrs. the liquid is centrifuged and the clear supernatant liquid is siphoned off. Acetic acid (10%) is then added, with stirring, until a permanent turbidity appears, an additional 1 c.c. for each 100 c.c. of liquid being finally added. CHEMICAL ABSTRACTS.

Physiology of the fœtus. T. SUGANO (Kinki Fuji. Gak. Zassi, 1926, **9**, 97—100; Chem. Zentr., 1927, ii, 945).—Pepsin appears in the fœtus at the fifth or sixth month. A. A. ELDRIDGE.

Oxidising substances in animal cells. W. LOELE (Arch. path. Anat. Physiol., 1926, **261**, 484—502; Chem. Zentr., 1927, ii, 943).

Microchemistry of the cell. I. Chromatin content of normal and malignant cells. R. J. LUDFORD (Proc. Roy. Soc., 1927, B, **102**, 397—406).—The chromatin content of various normal and abnormal animal cells has been investigated by means of Feulgen's "nucleal" reaction" During oogenesis in the rat and in the mouse there is no increase in the chromatin content of the nuclei, and when formation of the chromosomes takes place no chromatin is extruded into the cytoplasm; the heads of the spermatozoa of the rat and the mouse contain chromatin. Experiments on the nuclei of gland cells before and after secretory activity indicate no appreciable diminution in chromatin content. There is no correlation between the amount of chromatin in the nuclei of tumour-cells and the rate of growth of the tumour; the nuclear extrusions occurring in certain tumours do not consist of chromatin. E. A. LUNT.

Oxidising and reducing powers of mitochondria. P. JOYET-LAVERGNE (Compt. rend., 1928, **186**, 471—473).—Histological studies have been made on the effect of certain comparatively non-toxic substances which become coloured on oxidation, *e.g.*, quinol, "metol," pyrogallol, and of aqueous solutions of gold chloride and of silver nitrate on fresh liver cells, and are held to indicate the oxidising and reducing properties of the chondriosome system. E. A. LUNT.

Spectrophotometric studies of the two components of trypan-blue. (Adsorption theory of

vital staining.) N. Okuneff (Biochem. Z., 1928, **193**, 70—84).—Aqueous solutions of trypan-blue possess a definite absorption constant (max. 0·911) and a definite absorption maximum (580—590 $\mu\mu$). The absorption constant is independent of the concentration within certain limits (1/5000—1/100,000), but differs with the different commercial samples of the dye. When strips of filter-paper are dipped in dilute solutions of the dye, the solution gradually becomes red and the paper blue, the absorption constant then showing a progressive decrease and the absorption maximum a displacement to the left. The blue component is adsorbed much more firmly than the red. Addition of gelatin, protein, or plasma-colloids increases the adsorption constant and displaces the absorption maximum to the right. The fate of the two components in the organism is therefore conditioned, not only by their different diffusibilities, but also by their different adsorbabilities.

P. W. Clutterbuck.

Microchemical detection of potassium and calcium in histological sections. W. Jacobi and W. Keuscher (Arch. Psych. Nerv., 1927, **79**, 323—326; Chem. Zentr., 1927, ii, 1985—1986).—The tests depend, respectively, on the formation of potassium chloroplatinate and calcium sulphate.

A. A. Eldridge.

Chemical composition and histological structure of normal and atrophied muscle. T. Cahn (Ann. physiol. physicochim. biol., 1926, **2**, 646—681; Chem. Zentr., 1927, ii, 846—847).—A critical review.

Composition of human epidermis. Y. Jono (J. Biophys., 1927, **2**, xlviii).—Human epidermis contained water 20%, ash 1·5% (the silica content being high; sulphur content of ash 0·78%), fat 2%. Hydrolysis of the protein yielded tyrosine, leucine, alanine, valine, *iso*leucine, proline, glutamic acid, arginine, and lysine. Chemical Abstracts.

Ferments of human skin. N. Melczer (Dermatol. Z., 1926, **49**, 252—261; Chem. Zentr., 1927, ii, 945).—Diastase, phenolase, catalase, peroxidase, and glycolytic ferment are present in human skin; lipase is produced by the epidermal cells. In fatal pulmonary or peritoneal tuberculosis the skin lipase is practically or completely absent.

A. A. Eldridge.

Organic content of human enamel. C. Sprawson and F. W. Bury (Proc. Roy. Soc., 1927, **B**, **102**, 419—426).—The protein content of human enamel calculated from the nitrogen and the carbon contents of enamel is, respectively, 0·15% and 0·21%; it is suggested that the discrepancy in these results is due to the contamination of the enamel with carbon from the steel used in filing the enamel from the tooth. The organic content of enamel is independent of the dentition or the age of the tooth.

E. A. Lunt.

Determination of glutathione. A. Blanchetière and L. Melon (Compt. rend. Soc. Biol., 1927, **97**, 242—244; Chem. Zentr., 1927, ii, 1495).—Tunnicliffe's method is preferred to that of Thompson and Voegtlin. The lower limits of sensitiveness are for cysteine, 200 mg. per litre, and for reduced glutathione 125 mg. per litre. A. A. Eldridge.

Osmotic concentration of secretions. J. Straub and L. Soep (Arch. Neerland. Physiol., 1928, **12**, 346—367).—A series of analyses of secretions and sera before and after dialysis, with an interpretation of the results in the light of modern theories.

W. Robson.

Bacterial growth as a factor in the deposition of calcium from saliva. W. A. Peabody, I. C. Hall, and R. C. Lewis (Dental Cosmos, 1927, **69**, 1087).—Direct precipitation of calcium in centrifuged saliva determines at least 93% of the total calcium. Incubation of raw saliva with or without excess of fermentable carbohydrate produces, respectively, an acid reaction with an increase of soluble calcium, or an alkaline reaction with a decrease of soluble calcium. Chemical Abstracts.

Composition of synovial fluid. F. A. Cajori and R. Pemberton (J. Biol. Chem., 1928, **76**, 471—480).—The concentrations of the non-protein nitrogenous compounds of synovial fluid and of blood-plasma are similar; synovial fluid has a variable content of globulin, and usually a higher albumin : globulin ratio than plasma. Glycolysis is rapid in synovial fluid containing many leucocytes, and probably accounts for the high acidity and low sugar content of such fluid; glycolysis does not occur in the absence of leucocytes. C. R. Harington.

Differences in the behaviour of raw, pasteurised, boiled, evaporated, and dried milk at the hydrogen-ion concentration of the stomach. A. M. Courtney (J. Can. Med. Assoc., 1927, **17**, 919—922).—The characters of the casein precipitated by acid, but not the soluble calcium and protein contents, differed. Chemical Abstracts.

Detection of lactic acid in stomach contents. B. Bisbini (Rinasc. med., 1926, **3**, 514—516; Chem. Zentr., 1927, ii, 964).—The stomach liquor (20 c.c.) is evaporated at 70° to 2 c.c., thoroughly extracted with ether (40—50 c.c.), the residue after removal of the ether is dissolved in lukewarm distilled water (30—40 c.c.), made alkaline with calcium oxide, filtered, and the filtrate evaporated to dryness. The residue is treated with a little water, the solution filtered, evaporated on the water-bath to 0·5 c.c., and the solution placed on an object slide in a desiccator. The formation of calcium lactate crystals is observed with a microscope; 0·05% of lactic acid can be detected. A. A. Eldridge.

Detection of reducing sugars in urine by Castellani's mycological method. P. Pietra (Giorn. batteriol. immunol., 1927, **2**, 1—10; Chem. Zentr., 1927, ii, 963).—Characteristic organisms suitable for symbiotic fermentation with yeast of dextrose, lævulose, maltose, galactose, lactose, pentoses, sucrose, and inositol by Castellani's method are described. Within limits, several sugars present together in urine can be detected. A. A. Eldridge.

Determination of bismuth in urine. H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou (Biochem. Z., 1928, **193**, 53—61).—See A., 1927, 788.

Pigment obtained from fæces. L. F. Hewitt (Brit. J. Exp. Path., 1927, **8**, 333—335).—The rose-

red pigment obtained when fæces are subjected to prolonged heating with alcoholic hydrogen chloride is believed to be a dye of the diphenylmethane type, derived by oxidation of the product of condensation of a pyrrole derivative, *e.g.*, skatole, with aldehyde present in the alcohol. CHEMICAL ABSTRACTS.

Chemical changes of the blood in asphyxia. I. R. RITTMANN (Z. ges. exp. Med., 1927, **56**, 262—270; Chem. Zentr., 1927, ii, 951).—The blood-calcium rises, and -potassium falls; the residual nitrogen is not increased. Fibrinogen, globulin, and albumin are scarcely affected. A. A. ELDRIDGE.

Carbon dioxide tension in tissues in relation to cancerous cells. J. C. MOTTRAM (Nature, 1928, **121**, 420—421).—A mechanism whereby localised increase of the carbon dioxide tension in the tissues may induce abnormal cell division is indicated.

A. A. ELDRIDGE.

Fractionation of the Rous chicken sarcoma. K. SUGIURA and S. R. BENEDICT (J. Cancer Res., 1927, **11**, 164—186).—The nitrogen content of the Rous chicken sarcoma (dried) was 11·0—12·2% and the ash 5·69—8·01%. The tumour-producing substance is carried down with the globulin fraction of the tumour proteins on addition of ammonium sulphate.

CHEMICAL ABSTRACTS.

Lipin metabolism in the transplanted tumour. J. HOMMA and T. ISSIKI (Gann, 1927, **31**, 38—40).—The blood-lipin and -lipase of tumour chickens is subnormal; the blood-lipin and serum-lipase in the tumour wing are also less than that in the normal wing. CHEMICAL ABSTRACTS.

Effect of radiation on blood-cholesterol in malignant disease. W. L. MATTICK and K. BUCHWALD (J. Cancer Res., 1927, **11**, 86—100).—A solution of cholesterol in chloroform is affected by radiation of short wave-length, the amount of change depending on the condition of the solute.

CHEMICAL ABSTRACTS.

Hyperallantoinuria in experimental polyuria and diabetes insipidus in man. A. E. Y COSTA (Compt. rend., 1928, **186**, 650—652).—Allantoin is determined by a variation of Wiechowski's method. The precipitate with mercury is decomposed by hydrogen sulphide and half the solution used for the determination of carbamide by xanthydrol. The other half is hydrolysed with hydrochloric acid in an autoclave and the ammonia determined. The difference between total and carbamide ammonia represents 92% of the nitrogen of the allantoin. Polyuria produced by the ingestion of water, injection of "novasurol," and in diabetes insipidus is always accompanied by a high allantoin excretion.

W. K. SLATER.

Acetates in normal and diabetic blood. A. A. BRUNO (Rev. Soc. Argentina Biol., 1927, **3**, 617—620). The blood of normal dogs contained 1·0—1·5 mg.-% of acetic acid. Higher proportions were found in diabetic dogs and lower proportions in dogs after the injection of insulin. It is concluded that acetic acid is not formed directly from carbohydrates.

R. K. CALLOW.

Reaction of tissues. I. Hydrogen-ion concentration of tissues during fever. J. OGAWA (Proc. Imp. Acad. Tokyo, 1927, **3**, 699—701).—Injection of *Leptospira icterohæmorrhagiæ*, *icteroides*, and *hebdomadis*, coli and typhus vaccines, and tetrahydro-β-naphthylamine in aqueous emulsion, into the rabbit, guinea-pig, rat, and mouse, or overheating the animal at 40—41°, and subsequent determination of the p_H values of the tissues of various organs, shows that there is a decrease in the normal value of 7·0—7·3 to 6·7—6·9. H. BURTON.

Iodine metabolism. I. Urinary excretion of iodine by the inhabitants of a Norwegian goiterous district. G. LUNDE (Biochem. Z., 1928, **193**, 94—104).—The urinary iodine excretions of a large number of men are tabulated and the high values correlated with the type of diet.

P. W. CLUTTERBUCK.

Excretion of hippuric acid in renal disease. I. SNAPPER and A. GRUNBAUM (Presse med., 1926, **34**, 1524—1526; Chem. Zentr., 1927, ii, 1977).—Oral administration of 5 g. of sodium benzoate to healthy men results in 12 hrs. in its quantitative excretion as hippuric acid. In renal disease with nitrogen retention the excretion (but not the formation) is incomplete. A. A. ELDRIDGE.

Metabolic changes in rickets. H. HENTSCHEL and E. ZOLLER (Monatsschr. Kinderheilk., 1926, **34**, 248—253; Chem. Zentr., 1927, ii, 952).—In rachitic rats the total phosphoric acid was unchanged; the ability to synthesise a lactacidogenic substance from inorganic phosphoric acid and hexose was diminished.

A. A. ELDRIDGE.

Role of calcium in the nutrition and biological processes of the animal organism. A. W. POPOVA (Arch. Sci. Biol., 1927, **27**, 377—392).—The variations in blood-calcium have been determined in the guinea-pig as an index of the progress of the diseases of scurvy and tuberculosis, and it is concluded in the latter case that these variations give results which can be correlated with the corresponding variations in temperature and body-weight; the author regards hypercalcæmia as an index of serious pathological catabolism. E. A. LUNT.

Blood-sugar level in pulmonary tuberculosis. G. SAYAGO, T. DE V. LASTRA, and C. M. VOCOS (Rev. Soc. Argentina Biol., 1927, **3**, 585—595).—It was found that the mean blood-sugar level was lower in acute cases of pulmonary tuberculosis than in mild cases, but the range of variation was much greater in acute cases. Administration of dextrose *per os* caused a prolonged subnormal reaction in acute cases and a subnormal or normal reaction of normal duration in mild cases. Both rise and fall of blood-sugar level were observed following pneumothorax of different origin, but no definite conclusion could be reached as to the cause of variation. R. K. CALLOW.

Buffering power of serum and immunity. W. KOPACZEWSKI (Compt. rend., 1928, **186**, 635—637).—The physico-chemical properties of the medium in which pathogenic organisms are grown begin to change only when the number of organisms has increased to such an extent that the regulating mechanisms of the medium are exhausted. It is suggested that the periods of incubation in, and

immunity from, certain diseases are to be attributed to this effect. W. K. SLATER.

Respiration of the frog's heart. I. Oxygen consumption of the surviving frog's heart perfused with Ringer, Tyrode, and Locke solutions. T. HIRAOKA. **II. Influence of acid and alkali on the oxygen consumption of the surviving frog's heart.** W. ARNOLDI and T. HIRAOKA (Biochem. Z., 1928, **193**, 197—202, 203—206).—I. The oxygen consumption of the frog's heart is much more constant with Tyrode than with Ringer solution. No difference in oxygen utilisation was obtained on perfusing with Tyrode solution (p_H 7·7) with or without dextrose, the oxygen usage being 0·1 c.c. per g. per hr. more than during perfusion with Ringer solution (p_H 6·7).

II. The oxygen consumption of the surviving frog's heart perfused with 121 c.c. of Tyrode solution (without dextrose), on addition of 0·001*N*-hydrochloric acid, at first rapidly decreases (with 0·5 c.c.), then rises to the original value (0·5—3 c.c.), then again decreases (3—8 c.c.), and finally increases again (8—11 c.c.). Similar addition of 0·001*N*-sodium hydroxide causes with the first 0·5 c.c. a rapid fall, followed by a more gentle fall (0·5—7 c.c.) of oxygen utilisation. P. W. CLUTTERBUCK.

Gas and sugar metabolism of the vivi-perfused stomach. T. G. NI and R. K. S. LIM (Chinese J. Physiol., 1928, **2**, 45—86).—In the vivi-perfused stomach there is an increase in oxygen consumption during secretion from 3- to 9-fold as compared with the quiescent oxygen consumption of 0·007 c.c. per g. per min. (corresponding with a basal coefficient of the gastric mucosa of 0·013 c.c. of oxygen). The respiratory quotient of the stomach may vary from 0·6 during motility to 1·31 during secretion. After a meal the metabolism of the stomach may account for an increase of 10—12% of the basal metabolism.
W. O. KERMACK.

Relation between glutathione and the intracellular oxidation-reduction potential. P. JOYET-LAVERGNE (Compt. rend. Soc. Biol., 1927, **97**, 140—142; Chem. Zentr., 1927, ii, 1168).—Glutathione is an important factor in the r_H value, and therefore influences intracellular respiration. In organs the regions rich in glutathione appear to be those of the most intensive carbohydrate metabolism.
A. A. ELDRIDGE.

Urinary excretion of ketonic substances by the fasting dog. F. MAIGNON and E. KNITHAKIS (Compt. rend., 1928, **186**, 463—465).—The daily average urinary excretion of β-hydroxybutyric acid falls from 0·077 to 0·023 g. during 8—16 days' starvation, during which water only was administered, whilst that of acetone rises from 0·001 to 0·005 g.
E. W. WIGNALL.

Variations of the p_H and the alkaline reserve of the blood of the fasting dog. [F.] MAIGNON and E. KNITHAKIS (Compt. rend., 1928, **186**, 600—602).—In dogs given nothing but water the acidosis leads generally to a fall in the p_H and to only slight variations in the alkaline reserve and the total carbon dioxide content of the blood; in a few cases rapid adjustment is observed. In prolonged fasting, when water only was administered, diminishing alternations of the rise and fall of the two first-named variables were observed. G. A. C. GOUGH.

Metabolism with regard to calcium supply. W. KRANE (Pflüger's Archiv, 1927, **217**, 24—35; Chem. Zentr., 1927, ii, 1166).—The requirement for calcium equilibrium is 1·2—1·5 g. of calcium per day. The value is higher for a diet rich in meat. Calcium administration has no influence on the nitrogen metabolism. Fæcal nitrogen diminishes during administration of calcium. Deposition of calcium in the body causes loss of chlorine and removal of sodium and potassium from the body.
A. A. ELDRIDGE.

Effect of variations in calcium, magnesium, and phosphorus of the diet. J. R. HAAG and L. S. PALMER (J. Biol. Chem., 1928, **76**, 367—389).—Normal growth in rats could be obtained only so long as a balance was preserved between the above-mentioned elements in the diet; in particular, it was found that a high concentration of magnesium, in combination with low concentrations of calcium and phosphorus, retarded growth and calcification.
C. R. HARINGTON.

Action of sugar in the organism. IV. Behaviour of blood-sugar after intravenous injections of methylglyoxal, dihydroxyacetone, and dextrose. F. FISCHLER and O. HIRSCH (Arch. exp. Path. Pharm., 1928, **127**, 287—307).—The authors advance a scheme of the mechanism of sugar regulation in the body. Methylglyoxal is considered to be an intermediate in the decomposition of sugar. It is produced whenever there is a large and rapid breakdown of sugar, and then it acts as a central nervous stimulant whereby the store of glycogen is mobilised and sugar produced. Dihydroxyacetone is able to prevent the excessive action of methylglyoxal in this direction. W. ROBSON.

Relation between vegetable and animal carbohydrate degradation. A. GOTTSCHALK (Ergebn. Physiol., 1926, **25**, 643—663; Chem. Zentr., 1927, ii, 953).—A discussion. Three types of carbohydrate degradation are differentiated. A. A. ELDRIDGE.

Is there a proportionality between the performance of work and the lactic acid, phosphorus, and sugar contents of blood? N. P. RIABOUSCHINSKY (Biochem. Z., 1928, **193**, 161—175).—By increasing the performance of work, the percentage content of lactic acid which reaches the blood from the muscles increases in direct proportion. The lactic acid is not distributed throughout the body uniformly immediately after the work or in the resting period. After lifting weights, the lactic acid content of the blood of the active arm is increased, the increase being conditioned by congestion and insufficient oxygen supply. During this static work, the lactic acid content of the blood of the inactive arm remained almost unchanged. Immediately after the work, a considerable increase of inorganic phosphorus is found which is proportional to the amount of work done. In the resting period, the inorganic phosphorus of the blood in the working arm decreases below the original level, the decrease being the greater the larger the amount of work done. Immediately after work,

a slight increase of blood-sugar is usually observed, and in the resting phase, a decrease, but these changes are not in proportion to the amount of work done.

P. W. CLUTTERBUCK.

Metabolism after extirpation of [dog's] liver. V. M. VESSELKINA (Z. ges. exp. Med., 1927, **55**, 198—213; Chem. Zentr., 1927, ii, 453).—After extirpation of the livers of fasting dogs (after which death occurred in 3—16 hrs.), the urine was free from albumin and was strongly acid. The ammonia, amino-nitrogen, uric acid, and purine- and allantoin-nitrogen were increased.

A. A. ELDRIDGE.

Growth on diets practically devoid of arginine. Relation of glutamic and aspartic acids to nutrition. W. E. BUNNEY and W. C. ROSE (J. Biol. Chem., 1928, **76**, 521—534).—Good growth was obtained in rats on a diet in which the source of nitrogen was hydrolysed caseinogen from which practically all the arginine had been removed by precipitation with flavianic acid; in some experiments, in which a large proportion of the dicarboxylic amino-acids had also been removed, growth continued to be satisfactory.

C. R. HARINGTON.

Nitrogen minimum. Effect of protein-free diet on urinary nitrogen and on heat production. Effect of thyroxine following protein-free diet. H. J. DEUEL, jun., I. SANDIFORD, K. SANDIFORD, and W. M. BOOTHBY (J. Biol. Chem., 1928, **76**, 391—406, 407—414).—After 30 days on a protein-free diet the urinary nitrogen excretion of a normal man was 2·1 g. per day; the basal metabolic rate fell about 20%; at this stage thyroxine was administered, and exerted its characteristic effect in increasing the basal metabolic rate and the excretion of carbamide. Continuance of the protein-free diet after treatment with thyroxine finally reduced the daily excretion of nitrogen to 1·75 g. Practically all variations in nitrogen excretion were due to variations in carbamide. The total excretion of nitrogen throughout the whole protein-free period was 291 g. and indicates that the reserve protein of the body is greater than has been previously supposed.

C. R. HARINGTON.

Limit of acid taste and hydrogen-ion concentration. A. BERLATZKY and T. GUEVARA (Rev. Soc. Argentina Biol., 1927, **3**, 721—724).—The values of p_H at the limiting concentrations for perception of acid taste were: sulphuric acid, 2·9; nitric, 3·2; citric, 3·9; tartaric, hydrochloric, and lactic, 4·3; acetic, 4·5; phosphoric, 4·7. If acid taste is due to hydrogen ions, this series is explicable if the anion has an antagonistic cation, which is probably dependent on the ionic mobility. Thus sulphate ions depress the sensitivity of the nerves more than chloride ions, magnesium sulphate having a higher concentration limit of bitter taste (due to magnesium ions) than the chloride. Similar results were obtained with sodium and potassium nitrates and chlorides.

R. K. CALLOW.

Effect of β-indolethylamine on blood-sugar. S HASEGAWA (J. Biophys., 1927, **2**, xlvi—xlvii).—With small, but not large, injections, hyperglycæmia occurred.

CHEMICAL ABSTRACTS.

Influence of climatic factors on the cholesterol of the blood and suprarenal capsule. I—III. A. RABBENO (Arch. sci. biol., 1926, **9**, 161—167, 168—177, 178—183; Chem. Zentr., 1927, ii, 1163).—The effect of life at a high altitude, and that of maintenance at a constant temperature throughout the year, on the cholesterol and neutral fat content are investigated.

A. A. ELDRIDGE.

Biological activity of the porphyrins. K. REITLINGER and P. KLEE (Arch. exp. Path. Pharm., 1928, **127**, 277—286).—Hæmato-, copro-, and uroporphyrin increase the tonus of the surviving small intestine of the guinea-pig, cat, and rabbit. The action is strongest in the case of the dibasic hæmatoporphyrin and the tetrabasic coproporphyrin, weakest in the case of the octabasic uroporphyrin. Atropine is unable to inhibit the action of porphyrin. No relationship between the actions of porphyrin and choline has been found. The porphyrins are unable to sensitise the intestine to light rays.

W. ROBSON.

Alcohol. III. Variations in the alcohol content of human blood. H. KIONKA. **IV. Determination of ethyl alcohol in urine.** P. HIRSCH. **V. Excretion of alcohol by the kidneys.** H. KIONKA and M. HAUFE (Arch. exp. Path. Pharm., 1928, **128**, 133—145, 146—149, 150—164; cf. A., 1924, i, 1366).—III. The concentration of alcohol in the blood has been determined in individuals fasting and after the administration by mouth of various quantities of alcohol. The maximum concentration found in the blood increases with the quantity of alcohol taken from a mean fasting value of 0·0031% to a mean value of 0·0452% after administration of 114 c.c. of alcohol. The effect of various factors on the blood-alcohol curve has been investigated, and in particular the previous consumption of a meal and also the induction of marked diuresis causes the maximal values attained to be lower.

IV. The interferometer method previously devised by Kionka and Hirsch (A., 1924, i, 1366) for the determination of alcohol in blood has been developed so as to be applicable to the determination of alcohol in urine.

V. The quantity of alcohol excreted in the urine, always a small percentage of that administered, increases relatively when the quantity administered is very small. The major part of the alcohol excreted in the urine is eliminated during the 3—4 hrs. following consumption. Relatively more appears in the urine when it is administered in a concentrated form. The maximum urine concentration never exceeds about 0·1%. With increased diuresis the quantity of alcohol excreted is increased. The concentration of alcohol in the urine depends on the concentration in the blood, but no simple relationship appears to exist.

W. O. KERMACK.

Higher toxicity of methyl alcohol in presence of ethyl alcohol. M. PANTALEONI (Ann. Igiene, 1927, **37**, 537—540; Chem. Zentr., 1927, ii, 1980—1981).—A mixture of equal parts of methyl and ethyl alcohols is much more toxic to cats than either alcohol alone.

A. A. ELDRIDGE.

Effect of chloralose on blood-sugar level. M. A. MAGENTA (Rev. Soc. Argentina Biol., 1927, **3**, 681—686).—The blood-sugar level of dogs injected

with chloralose, after slight irregular variation, fell to a minimum after 5—7 hrs. and then regained the normal value. The variation from normal is small, and chloralose is therefore a good anæsthetic for use in the study of hyperglycæmia. R. K. CALLOW.

Elimination of morphine. F. DE CAMELIS (Arch. Farm. sperim., 1927, **44**, 77—92).—Only a very small proportion of a dose of morphine is eliminated in the fæces. The urine contains morphine 24 or 48 hrs., but not on the third day, after the administration. Repeated administration of morphine results in the appearance of reducing substances, probably owing to the presence of morphine-glycuronic acid.
T. H. POPE.

Pharmacological assay of ergot. I. B. VON ISSEKUTZ and M. VON LEINZINGER. II. M. VON LEINZINGER and J. VON KELEMEN (Arch. exp. Path. Pharm., 1928, **128**, 165—172, 173—178).—I. The antagonistic action of ergotamine and adrenaline on the isolated rabbit intestine may be used to determine the activity of the alkaloids of ergot.

II. Determination of the alkaloid content of ergot by the Keller–Fromme method (cf. Z. anal. Chem., 1894, **34**, 115; 1907, **46**, 743) gives a very good indication of its biological activity. W. O. KERMACK.

Comparative behaviour of animal charcoal and activated aluminium in toxicology. G. SENSI and C. DE ROSA (Annali Chim. Appl., 1928, **18**, 3—18).—Aqueous alcoholic extracts of alkaloids obtained from animal organs in toxicological investigations may be conveniently purified by means of activated aluminium, prepared by immersion of sheet metal or turnings in 10% mercuric chloride solution for 3 min., washing with much water, then with alcohol, and finally with ether, and storing the dried metal under light petroleum; the latter is removed and the metal weighed immediately before use. Activated aluminium is easier to prepare, and more convenient to use, than animal charcoal. From none of the alkaloid solutions tested is more alkaloid removed by the aluminium than by animal charcoal, and in some cases considerably less is removed. T. H. POPE.

Effect of sodium fluoride on blood-sugar level. M. A. MAGENTA (Rev. Soc. Argentina Biol., 1927, **3**, 691—693).—Injection of sodium fluoride into dogs had little effect on the blood-sugar level, increasing it only when the toxic dose (50 mg. per kg.) was reached. R. K. CALLOW.

Degree of dispersity and pharmacological action of colloidal sulphur. M. MESSINI (Arch. exp. Path. Pharm., 1928, **127**, 366—382).—The toxicity of colloidal sulphur depends on the mode of its preparation, its age, its concentration, and on the rate of its injection. With these factors the degree of dispersity of the colloidal sulphur varies, and with the latter in turn its surface of contact with the body fluids which reduce it to hydrogen sulphide. The pharmacological and toxic actions of colloidal sulphur depend on its conversion into hydrogen sulphide, and hence its therapeutic action must be assigned chiefly to the hydrogen sulphide and in general its application limited to those cases in which hydrogen sulphide is of use. W. ROBSON.

Detoxication of hydrogen cyanide. A. W. FORST (Arch. exp. Path. Pharm., 1928, **128**, 1—66).—The toxic action of hydrogen cyanide is inhibited (except in the case of white rats) by previous administration of sodium thiosulphate or, even more effectively, of colloidal sulphur. These compounds are quite ineffective against poisoning by aromatic nitriles. Administration of dextrose protects against four times the lethal dose of hydrogen cyanide. Insulin alone has very little action, whilst insulin and dextrose are practically no more effective than is dextrose alone. Dihydroxyacetone effectively protects against nine times the lethal dose of the poison. If dihydroxyacetone is administered after the symptoms have developed, the symptoms disappear but death is not averted. When, however, dihydroxyacetone and sulphur are administered together (after poisoning by 9—10 times the lethal dose of hydrogen cyanide), recovery is effected even after the symptoms of poisoning have developed. W. O. KERMACK.

Barium and sulphate as antidotes. L. SCREMIN (Arch. int. pharmacodyn. ther., 1926, **32**, 207—215; Chem. Zentr., 1927, ii, 954).—When injected slowly, but not when injected rapidly, colloidal barium carbonate is somewhat less toxic than barium chloride. The toxicity is not reduced by simultaneous injection of equimolecular sodium sulphate; a solution five times as concentrated is required. Barium hydrogen carbonate is apparently formed in the blood. On slow injection elimination of sulphate runs parallel with injection, and in dilute solutions the conditions do not favour the formation of complex salts containing anionic barium. A. A. ELDRIDGE.

Chemical changes in blood in mercuric chloride poisoning. H. M. TRUSLER, W. S. FISHER, and C. L. RICHARDSON (Arch. Int. Med., 1928, **41**, 234—243).—Mercuric chloride poisoning by intravenous injection causes a lowering of the blood-chlorides in dogs, but not in rabbits. The dogs suffer from violent vomiting, whilst the rabbits do not. Other symptoms are similar, hence it is concluded that the chlorides are lost by vomiting. Hypochloræmia was found to cause gastric tetany associated with acidosis. Intravenous injection of 2% sodium chloride solution prevents tetany but does not influence the other symptoms. The clinical aspect is discussed. W. K. SLATER.

Preventive action of metals against syphilis. C. LEVADITI, V. S. BAYARRI, R. SCHOEN, and Y. MANIN (Ann. Inst. Pasteur, 1928, **42**, 105—169; cf. A., 1927, 587).—Administration of finely-divided tellurium and bismuth and of certain derivatives of these metals to rabbits renders them resistant to subsequent experimental infection with syphilis. The protection given by bismuth may exceed that conferred by arsenobenzene and other arsenicals. The degree and duration of immunity depend both on the dose and on the nature of the metal derivative administered. W. O. KERMACK.

Azo-dyes containing antimony in the treatment of trypanosomiasis. F. DUNNING and

D. I. MACHT (J. Pharm. Exp. Ther., 1928, **32**, 205—213).—Azo-dyes of the general formulæ $Na_2O_3Sb\cdot C_6H_4\cdot N{:}N\cdot C_6H_3R\cdot OH$ or $Na_2O_3Sb\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NR_2$ do not cure rats infected with *Trypanosoma equiperdum*. Of the dyes formed by coupling diazotised stibanilic acid with α-naphthol-4-sulphonic acid, β-naphthol-3 : 6-disulphonic acid, 1 : 8-dihydroxynaphthalene-2 : 6-disulphonic acid, 8-amino-α-naphthol-3 : 6-disulphonic acid, 6-amino-α-naphthol-3-sulphonic acid, and β-naphthylamine-3 : 6-disulphonic acid, respectively, the sodium salts of the last three possess marked curative action, the ratio of the maximum tolerated dose to the minimum curative dose being 6—7, 4—5, and 4—5, respectively. W. O. KERMACK.

Effect of catalase injected into the circulating blood. Catalase and anticatalase content of various tissues. L. BELKINE, R. FALK, and L. KREMLEV (Compt. rend. Soc. Biol., 1927, **97**, 525—526; Chem. Zentr., 1927, ii, 1480).—Catalase, when injected into the blood, disappears in 3 hrs. The catalase content of tissue is at first increased, particularly in the kidneys and muscles, and then gradually falls to the normal value. Anticatalase changes show no such regularity. A. A. ELDRIDGE.

Action of light on the decolorisation process in a dehydrogenase–methylene-blue system. A. KRESTOVNIKOV (Skand. Arch. Physiol., 1927, **52**, 199—208; Chem. Zentr., 1927, ii, 1478).—The decolorisation of methylene-blue in the presence of dehydrogenase and a hydrogen donator is accelerated by light; hence in Thunberg's method the illumination must be weak and uniform. A. A. ELDRIDGE.

Preparation of succinodehydrogenase. N. ANDERSSON (Skand. Arch. Physiol., 1927, **52**, 187—198; Chem. Zentr., 1927, ii, 1479).—Chopped muscle (100 g.) is washed with 100 c.c. quantities of 0·25% sodium chloride solution until the mass is colourless; it is then ground with $M/15$-disodium hydrogen phosphate solution, shaken for 1 hr., and the ferment solution separated by centrifuging. A. A. ELDRIDGE.

Purification of the lactic acid-forming enzyme. K. MEYER (Biochem. Z., 1928, **193**, 139—160).—Purification of the lactic acid-forming enzyme of muscle from protein may be effected either by repeated acetate precipitation at p_H 5 with subsequent elution by dilute phosphate at p_H 7·5—8, or by adsorption of the enzyme on alumina followed by phosphate elution. The first method occasionally gives an enzyme of high degree of activity (50 times the original), but the result is difficult to reproduce. The second method gives much more consistent results, the activity being increased 20 times. The amount of the increased activity depends on various factors, especially on the dilution of the alumina adsorbate and on the distribution of enzyme between precipitate and solution. To elute the enzyme, short, gentle shaking with phosphate is used, since vigorous shaking inactivates it. In this case only the heat-sensitive part of the enzyme is freed from protein. Addition of the heat-stable co-enzyme (boiled muscle extract) is always necessary for the formation of lactic acid. The purified enzyme is relatively more stable than the extract. Whereas the latter becomes inactive on keeping for a few hours, the purified enzyme solution loses only about half its activity in 24—48 hrs. Sodium fluoride acts on the purified enzyme much less than on the extract, attacking probably the protein substances accompanying the enzyme. The action of arsenate is, however, the same for both. P. W. CLUTTERBUCK.

Lipase. I. Optimum action of gastric lipase. II. Lipase of organs and its resistance to acids and alkalis. III. Action of quinine on lipase of organs. K. GYOTOKU (Biochem. Z., 1928, **193**, 18—26, 27—38, 39—52).—I. The optimal p_H for the action of rabbit's and human gastric lipase is 6·0, and after purification 7·6—7·8. When pig's gastric lipase, the optimal p_H of which lies on the alkaline side, is kept in the dry condition, its optimal p_H is displaced to 6·0—6·5, the change not being obtained with the gastric lipase of rabbit, dog, and man. When the enzyme is kept in solution, the optimum is displaced to the alkaline side. Normal gastric lipase is probably combined with substances which activate the lipolytic action in acid, and inhibit in alkaline medium.

II. Gastric lipase is more resistant to acids than alkalis and pancreatic and liver lipases are more resistant to alkalis, but gastric lipase is much more stable than other organ lipases to such reagents. Purification of gastric lipases of man, dog, and pig causes decrease of resistance to acids, the enzyme becoming no more stable than pancreatic lipase. Pancreatic and liver lipases also lose their resistance to alkalis on purification. Unpurified gastric lipase retains its resistance to acids for a long time on keeping. Strong acids and alkalis cause great injury to lipases, the degree of injury being directly related to the concentration of hydrogen or hydroxyl ions; addition of proteins or peptones protects the enzyme to some extent.

III. Pancreatic, liver, and gastric lipases are often sensitive to quinine and may be either activated or inhibited. Refractory lipases, on purification, become considerably inhibited by quinine. When dried lipases of organs are kept for several months, the extent of the quinine inhibition decreases. With pig's liver lipase an 80—90% activation is obtained. The action of quinine on the lipase is the sum of two opposed effects, that on the enzyme itself and that on the substances accompanying it which are lost on purification. The organ lipases of man and dog are much more sensitive to quinine than those of rabbit, pig, cat, sheep, and guinea-pig, and serum-lipases of man and dog are much more sensitive than pancreatic lipase. P. W. CLUTTERBUCK.

Influence of cations on the action of lipase. S. UENO (J. Biophys., 1927, **2**, xxxiv).—Potassium and (to a smaller extent) sodium retard, whilst manganese and cobalt accelerate, the action of pancreatic lipase on cream. Strontium, calcium, barium, magnesium, nickel, uranyl, copper, and mercury depress the action in that order. The depressing action of sodium is neutralised by strontium, barium, calcium, and magnesium.

CHEMICAL ABSTRACTS.

Melibiase. II. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 99—110; cf. *ibid.*, 1927, 699).—Purified yeast melibiase has a maximum activity at p_H 4·8, but it does not vary much between p_H 3·5 and 5·5. With varying concentrations of enzyme the same percentage of melibiose is hydrolysed in times inversely proportional to the concentration of the enzyme provided the other conditions are kept constant. The activity of melibiase in certain preparations is within limits approximately represented by the formula for a unimolecular reaction. Suitable units in which to measure the activity of melibiase and the concentration of it in any particular material are suggested, following the principles used by Willstatter (A., 1920, 1, 795) in relation to maltase. Methods are described for the preparation of melibiase solutions and for the determination of melibiase in yeast. W. O. KERMACK.

Decomposition of urea by urease. S. MORI (J. Biophys., 1927, 2, xxiii).—When the solution is sufficiently buffered against the ammonia formed, the reaction is shown to be unimolecular.
CHEMICAL ABSTRACTS.

Decomposition of caseinogen by trypsin. S. MORI (J. Biophys., 1927, 2, xxiii).—The velocity is proportional to the amount of enzyme. The optimal reaction takes place at 55° with p_H 7·76—7·78. CHEMICAL ABSTRACTS.

Denaturation of proteins. VI. Effect of denaturation on the digestibility of ovalbumin by pepsin and trypsin. K. H. LIN, H. WU, and T. T. CHEN (Chinese J. Physiol., 1928, 2, 107—130).—Natural and denatured egg-albumins are digested by pepsin or trypsin at different rates. The optimal p_H varies according to the method of denaturation. The results are considered to support the view that the fundamental change in denaturation is similar in nature to some of the early stages of tryptic digestion.
W. O. KERMACK.

Digestibility of racemised caseinogen and egg-albumin. K. H. LIN, H. WU, and T. T. CHEN (Chinese J. Physiol., 1928, 2, 131—137).—Racemised egg-albumin and racemised caseinogen are subject to putrefaction, and are hydrolysed by enzymes provided the hydrogen-ion concentration of the medium is suitable, but the rates of hydrolysis are less than those of the natural proteins. These results do not agree with those of Dakin and Dudley (cf. A., 1913, i, 1249), who claim that racemised protein undergoes neither hydrolysis by enzymes nor putrefaction. The racemised egg-albumin is purified by utilising its low solubility at the isoelectric point, p_H 4·45. W. O. KERMACK.

Specificity of animal proteases. XII. Specificity of pancreatic trypsin and intestinal erepsin. E. WALDSCHMIDT-LEITZ, A SCHAFFNER, H. SCHLATTER, and W. KLEIN (Ber., 1928, 61, [B], 299—306; cf. A., 1927, 1112).—Investigation has been made of the hydrolytic action of intestinal erepsin, trypsin kinase, and, in some cases, of trypsin towards glycylglycine, leucylglycine, leucyl-leucine, glycylserine, alanylserine, leucylmethyl*iso*serine, glycylcystine, dileucylcystine, leucylglutamic acid, phenylalanylglutamic acid, glycyltyrosine, diarginine trinitrate, alanyl- and leucyl-β-amino-*n*-butyric acids, glycyl- and alanyl-α-amino-*n*-hexoic acids, leucyl-ε-amino-*n*-hexoic acid, glycyl anhydride, glycylalanine anhydride, alanylphenylalanyl anhydride, glycylserine anhydride, phenyldiketopiperazine, leucyltriglycyl-leucine, leucylheptoglycine, leucylnonaglycine, α-bromo*iso*hexoylnonaglycine, α-bromo*iso*hexoyltriglycyl-leucylnonaglycine, leucyltriglycyl-leucyltriglycyl-leucylnonaglycine, leucylglycyltyrosine, glycylalanyltyrosine, glycyltyrosylglycine, glycylalanylglycyltyrosine, and β-naphthalenesulphonylglycyltyrosine. The dipeptides occupy an exceptional position, since, independently of the nature of the amino-acids from which they are derived, they act as specific substrates for erepsin; a possible exception is diarginine trinitrate, which may not have the constitution ascribed to it by Fischer and Suzuki (A., 1906, i, 73). Fission of higher peptides by pancreas trypsin, which is inactive towards all dipeptides, depends on the presence of certain amino-acids, of which tyrosine is an example. An indication of the cause of the specific differences in the actions of trypsin and erepsin is found in the alteration of the behaviour of glycyltyrosine consequent on the introduction of the β-naphthalenesulphonyl group; glycyltyrosine is hydrolysed only by erepsin, β-naphthalenesulphonylglycyltyrosine only by trypsin. Erepsin appears to require the presence of a free amino-group, which is unnecessary for trypsin.
H. WREN.

Growth of the yeast *Saccharomyces cerevisiæ*. I. The growth curve and the effect of temperature on the yeast growth. O. W. RICHARDS (Ann. Bot., 1928, 42, 271—283).—The growth curve is an asymmetrical S-shaped curve in which, in the medium employed, maximum growth is attained within 100 hrs. following seeding. Cell-volume increase exceeds cell-number increase for the first 15 hrs. and then decreases; both have the same value after 90 hrs. Analyses of the curve indicate that the limiting master reaction is quinquemolecular.
E. A. LUNT.

Acetylmethylcarbinol formation in the alcoholic fermentation of sugar. L. ELION (Ned. tijdschr. hyg. microbiol., 1926, 1, 171—179; Chem. Zentr., 1927, ii, 1042).—The appearance of acetylmethylcarbinol as a product of the fermentation of sugar fixes the acetaldehyde, which can no longer act as hydrogen-acceptor. Free hydrogen, however, is not evolved, but a complex reduction process takes place, the nature of which is under investigation.
A. A. ELDRIDGE.

Comparison of the actions of arsenate and organic derivatives of arsenic acid on alcoholic fermentation of sugar. P. MAYER (Biochem. Z., 1928, 193, 176—180).—A number of aromatic derivatives of arsenic acid can accelerate fermentation of hexosediphosphate, especially phenylarsinic and arsanilic acids, but none of these substances has as great an effect as potassium arsenate.
P. W. CLUTTERBUCK.

Thermophilic and thermoduric micro-organisms, with special reference to species isolated from milk. I. Review of literature. III. Description of non-spore-forming, thermoduric

organisms isolated. A. H. ROBERTSON (New York Agric. Exp. Sta., Tech. Bulls. 130 and 131, Aug. 1927, 56 and 62 pp.).

Thermophilic fermentation processes. C. COOLHAAS (Ned. tijdschr. hyg. microbiol., 1926, **1**, 338—350; Chem. Zentr., 1927, ii, 1159).—A rapid thermophilic fermentation of formate, acetate, oxalate, gluconate, and lactate, and a slower fermentation of butyrate and propionate to carbon dioxide and methane took place with spore-forming rod-bacteria of very different lengths. In a fermentation of peptone to carbon dioxide and methane, most of the nitrogen was converted into ammonia. A motile, spore-forming, aerobic bacterium caused the extraordinarily rapid conversion of starch into maltose and dextrin; another bacterium fermented various carbohydrates to carbon dioxide, hydrogen, butyric acid, and active lactic acid. A. A. ELDRIDGE.

Action of digestive juices on lactic organisms. C. A. SAGASTUME and A. SOLARI (Rev. Soc. Argentina Biol., 1927, **3**, 573—580).—When a mixture of *B. acidi lacti*, a lactic streptococcus, and a torula from milk was incubated in acid and alkaline media (p_H 1·2—1·9 and 10·4—10·8), the first two alone were affected, being killed at $p_H < 1·4$. *B. acidophilus* and *B. bulgaricus* were tested in the same media and in hypochlorhydric, normal, and hyperchlorhydric gastric juice, and in duodenal juice. Whilst *B. acidophilus* was practically unaffected, *B. bulgaricus* was killed in the acid media and in hyperchlorhydric gastric juice.

Since the nutritive requirements of *B. acidophilus* and *B. bulgaricus* are similar, the difficulty of adaptation of the latter to the human intestine which is generally recorded can be attributed to its lower resistance to the digestive juices, combined with the bacterial antagonism of the intestinal medium. R. K. CALLOW.

Fermentation of dextrose by *Bacillus coli*. ROSNATOVSKY (Zentr. Bakt. Par., 1927, I, **102**, 145—148; Chem. Zentr., 1927, ii, 1481).—When *B. coli* is grown on acid or neutral bouillon in presence of 0·5—2·0% of dextrose, the amount of gas produced (hydrogen : carbon dioxide=6 : 1 to 10 : 1 in acid, always 2 : 1 in neutral bouillon) is variable, and independent of the sugar content. Intermediate products therefore appear to be concerned. A. A. ELDRIDGE.

Biochemical preparation of a disaccharide-monophosphoric ester. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1928, **193**, 237—244).—Dephosphorylation of sodium hexosediphosphate by the action of *B. coli* and *B. lactis aërogenes* gave poor results, the action being slow and incomplete. With the lactic acid bacterium, *B. Delbrücki*, however, a disaccharidemonophosphoric ester was obtained, determinations of carbon, hydrogen, barium (of barium salt), and phosphorus agreeing with the formula for the barium salt of $C_{12}H_{21}O_{14}PBa$, $\alpha_D +55·2°$. P W. CLUTTERBUCK.

Influence of sodium chloride on the formation of volutin in the cells of spore-forming bacteria. P. SMIRNOV (Zentr. Bakt. Par., 1927, II, **70**, 29—36; Chem. Zentr., 1927, ii, 1480—1481).—The formation of volutin by *Bacillus alvei* depends on the size of the cell, and hence on the sodium chloride content. A. A. ELDRIDGE.

Fat metabolism of *Hyphomycetæ*. I. A. VON MALLINCKRODT-HAUPT (Zentr. Bakt. Par., 1927, I, **103**, 73—87; Chem. Zentr., 1927, ii, 1041).—*Trichophyton gypseum* grows on Uschinsky's medium with butter or lard, but not cod-liver oil; growth was poor on beef- or mutton-fat. Olive and castor oils were suitable, as well as pure triacetin and triolein. The optimum p_H for tributyrin hydrolysis is 6·0, and for peptone 7·0. A. A. ELDRIDGE.

Oxidation of waxes by micro-organisms. W. O. TAUSSON (Biochem. Z., 1928, **193**, 85—93).—*Aspergillus flavus* can utilise as a source of carbon the esters of higher fatty acids with glycerol and with the higher alcohols. There is a close correspondence between the power of the mould to use these substances and to oxidise paraffin. The absolute amount of wax oxidised by the mould is proportional to the age of the culture and is smaller than the amounts of paraffin oxidised under the same conditions. The results support the view that such esters are formed as an intermediate stage in the oxidation of paraffin. P. W. CLUTTERBUCK.

Formation of citric acid by *Aspergillus niger*. F. CHALLENGER, L. KLEIN, V. SUBRAMANIAM, and T. K. WALKER (Nature, 1928, **121**, 244).—Potassium citrate has been isolated from cultures of *A. niger* on potassium hydrogen adipate and on potassium muconate. A. A. ELDRIDGE.

Formation of an *o*-diphenol at the expense of sugars by certain microbes of the soil. LEMOIGNE (Compt. rend., 1928, **186**, 473—475).—*B. subtilis* and other soil bacteria which give a butyleneglycol fermentation are cultivated on an acid medium containing sugar as the sole organic constituent; the product gives with ferric chloride, after precipitation and re-dissolution of ferric phosphate, a green coloration attributed to the presence of an *o*-diphenol. The product on concentration shows all the reactions of *o*-diphenols, but no chemical individual is isolated. E. W. WIGNALL.

Nitrate reduction by *Azotobacter*. S. KOSTYTSCHEV and O. SCHVEZOVA (Z. wiss. Biol., Abt. 3. Planta, Arch. wiss. Bot., 1926, **2**, 527—529; Chem. Zentr., 1927, ii, 1159).—A discussion. A. A. ELDRIDGE.

Biological reduction of mineral phosphate. K. I. RUDAKOV (Zentr. Bakt. Par., 1927, II, **70**, 202—214; Chem. Zentr., 1927, ii, 947).—Reduction of phosphoric acid in soil to phosphorous and hypophosphorous acids and phosphine by micro-organisms in soil has been observed. The reduction process is diminished by addition of potassium nitrate and magnesium sulphate. A pure culture of the reducing organism was obtained. A. A. ELDRIDGE.

Decomposition of fats by the tubercle bacillus. A. SEDYCH and G. SELIBER (Compt. rend. Soc. Biol., 1927, **97**, 57—58; Chem. Zentr., 1927, ii, 1158).—Fats are hydrolysed by the tubercle bacillus. A. A. ELDRIDGE.

Electrodialysis of tuberculin. VIII. F. B. SEIBERT and M. T. HANKE (J. Biol. Chem., 1928,

76, 535—541).—Electrodialysis causes a more efficient removal of the last traces of electrolytes from tuberculin than does ordinary dialysis, although the initial stages of the process are no quicker; no loss of activity is brought about by the electric current, but under its influence small amounts of the protein diffuse through parchment; in the absence of the electric current such diffusion takes place only through collodion membranes prepared from a solution of collodion in a mixture of ether and 95% (not absolute) alcohol. C. R. Harington.

Antigens. F. Przesmycki (Z. Immunitatsforsch., 1927, 51, 408—420; Chem. Zentr., 1927, ii, 1717—1718).—For the preparation of the residual antigens of bacteria, an aqueous extract is boiled with 10% acetic acid for 5 min., and the precipitate is separated in a centrifuge; 10 vols. of 95% alcohol are added, the precipitate is dissolved in water and reprecipitated with alcohol. The process is repeated 6 times in alternately alkaline and acid medium. The aqueous dialysate is then precipitated with acetone. A. A. Eldridge.

Does adrenaline act through calcium? L. Jendrassik and A. Czike (Klin. Woch., 1927, 6, 1521; cf. Jendrassik and Antal, *ibid.*, 1338; Chem. Zentr., 1927, ii, 1722—1723).—Zondeck's theory of parallelism between the action of adrenaline and calcium ions is unsupported by experiment. A. A. Eldridge.

Influence of amino-acids and their derivatives on adrenaline hyperglycæmia. M. Chikano (J. Biophys., 1927, 3, xlv—xlvi).—Dihydroxyphenylalanine and pyrocatechol cause considerable, and tryptophan slight, hyperglycæmia. Tyrosine, hydroxyphenylpyruvic acid, and tryptophan augment adrenaline hyperglycæmia; leucine and histidine counteract it, and phenylalanine exerts no action. Glycine and glutamic acid have no influence on blood-sugar. Chemical Abstracts.

Influence of some protein derivatives on the regulation of blood-sugar. I. Effect on the blood-sugar curve and the hyperglycæmic reaction after adrenaline. F. Nord (Acta med. scand., 1926, 65, 1—115; Chem. Zentr., 1927, ii, 1717).—Glycine, glutamic acid, and Witte's peptone exercise a sugar-mobilising effect, but do not increase the action of adrenaline on the blood-sugar. Glycine and glutamic acid can completely suppress insulin hypoglycæmia; the action of Witte's peptone is irregular. A. A. Eldridge.

Inner secretion of the pancreas. VI. Substance in human urine which diminishes the blood-sugar. K. Kozuka (Tohoku J. Exp. Med., 1927, 9, 130—147).—Human urine contains a very variable quantity of a hypoglycæmic substance. The substance cannot be isolated in diabetes unless sugar is eliminated from the urine by treatment with the pancreatic hormone, with which the substance is probably identical. Chemical Abstracts.

Mode of action of insulin. C. Lundsgaard (Acta med. scand., Suppl. Bd., 1926, 16, 473—484; Chem. Zentr., 1927, ii, 1974).—The action of insulin depends on an intramolecular rearrangement of the sugar, with formation of neoglucose; sufficient insulin for the purpose is normally present. The effect of insulin depends on the presence of some substance present in fresh muscle; if this is provided, the action can be reproduced *in vitro*. A. A. Eldridge.

Hormonal processes after administration of dextrose. IV. Detection of insulin in human blood after peroral administration of dextrose. H. Hausler and R. Weeber (Klin. Woch., 1927, 6, 1521—1522; Chem. Zentr., 1927, ii, 1974).—Insulin was detected. A. A. Eldridge.

Colorimetric determination of iodine in homœopathic and biochemical preparations. C. A. Rojahn (Apoth.-Ztg., 1927, 42, 551; Chem. Zentr., 1927, ii, 149).—An aqueous extract (5 c.c.) is filtered, and the filtrate is treated with sulphuric acid, potassium iodate, and chloroform; after shaking, the colour of the chloroform layer is compared with that of a standard solution. A. A. Eldridge.

Determination of uric acid [in body fluids]. C. Currado (Pediatria, 1926, 2, 216; Chem. Zentr., 1927, ii, 306).—Benedict's method is preferred. A. A. Eldridge.

Rapid volumetric determination of amino-acids, organic acids, and bases. I. Determination of ammonia and volatile amines in biological fluids and determination of the different classes of acid radicals represented in the total alcohol titration value. II. Quantitative removal and determination of the carbonic acid radical especially in bacterial cultures. F. W. Foreman (Biochem. J., 1928, 22, 208—221, 222—229).—I. A detailed description of the methods which are an extension of the author's original method (cf. A., 1920, ii, 564).

II. The method is based on the observation that concentrated alcohol in which carbonic acid and small quantities of "free" volatile acids are dissolved very readily parts with the whole of the carbon dioxide, but completely retains the volatile acids on aeration. Hydrogen carbonates of "weak" nitrogenous bases lose their carbon dioxide by this treatment. S. S. Zilva.

Stain solubilities. III. W. C. Holmes (Stain Tech., 1928, 3, 12—13).—The solubilities in water and 95% alcohol of 45 dyes are tabulated. H. W. Dudley.

Fast-green, a substitute for light-green S. F. yellowish. R. Haynes (Stain Tech., 1928, 3, 40).—Fast-green, a triphenylmethane dye (see Johnson and Staub, B., 1927, 404), is slightly greener, stains more intensely in a shorter time, destains safranine more slowly (making differentiation easier), and is much more permanent than light-green. H. W. Dudley.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1928.

General, Physical, and Inorganic Chemistry.

Spectrometer or monochromator with lenses or mirrors for use with one or two prisms of glass, quartz, rock salt, etc. C. Leiss (Z. Physik, 1928, **47**, 137—142).—A new form of constant-deviation spectrometer is described which can be used according to requirements with one or two prisms of glass (for visible region), quartz (up to 4 μ), or rock salt (up to 16 μ). The arrangement of mirrors (or lenses) and prisms is such that the prisms are always used in the position of minimum deviation. The instrument is very compact and simple of adjustment. J. W. Smith.

Direct-vision spectroscopic apparatus and monochromator with two prisms and constant deviation. C. Leiss (Z. Physik, 1928, **47**, 143—146).—A direct-vision spectroscope is described which can be used with either one or two prisms. Mirrors are mounted in permanent connexion with the prisms, which can be adjusted together with one movement. It is so arranged that any line focussed on the cross-wires or on the emergence slit has passed through the prism with minimum deviation. J. W. Smith.

Spark producer as an atomiser of salt solutions for flame spectra and the photography of their spark spectra. W. Hirschel (Z. Physik, 1928, **47**, 147—150).—A method is described whereby the atomising properties of the spark producer can be employed for maintaining a continuous flame spectrum. A small amount of the solution of a salt is placed in the bottom of the spark producer and sparking maintained while a stream of coal gas is passed through the apparatus and burnt in a Bunsen burner. Only a few mg. of a salt solution are required to produce a good spectrum photograph, so that the method is particularly applicable to small quantities of material. Methods of obtaining visible and ultra-violet spark spectra by the use of the same apparatus are also described. J. W. Smith.

Luminosity of flames containing sodium vapour. G. L. Locher (Physical Rev., 1928, [ii], **31**, 466—469).—Except for small concentrations of sodium vapour, the luminosity of a sodium flame is proportional to the square root of its thickness. The luminosity of a flame is independent of the distribution in it of the emitting vapour. A. A. Eldridge.

Doublet components of H_α in the absorption spectrum of hydrogen. L. S. Ornstein, F. Zernike, and J. L. Suvek, jun. (Z. Physik, 1928, **47**, 627—630).—It is shown experimentally that the durations of the two final states of H_α are approximately equal. It is concluded that the cause cannot be the metastability of the lower states. W. E. Downey.

Relation between the spectral lines of hydrogen and of ionised helium, and the movements of the electrons. A. M. Titov (Ann. Inst. Polyt. Oural, 1926, **5**, 37—48).—Mathematical. C. W. Gibby.

Structure of band spectrum of helium. IV. W. E. Curtis (Proc. Roy. Soc., 1928, **A**, **118**, 157—169; cf. A., 1925, ii, 722).—Details are given of three new bands having the same final electronic state ($2P$) as the three previously investigated (*loc. cit.*). Two of the new bands are closely associated with the neighbouring strong bands 6400 and 4546, the weak bands being due to the vibration transition $1 \longrightarrow 1$, with the initial electronic levels $3S$ and $4S$, whilst the strong bands arise from the vibrationless molecule. The third new band has an initial electronic level of effective quantum number 2·96. The combination result indicates that the final state is identical with that of the $R'P$-branches of 5730, *i.e.*, $2P_A(0)$, but its electronic designation is uncertain. The term constants have been accurately calculated for the new bands and for 6400, 4546, and 5730. The molecular constants are thence determined and their relations discussed. Further support is afforded to Lenz's suggestion that the structure of the helium molecule is related to that of the hydrogen molecule (Verh. Physikal. Ges., 1919, **21**, 632). It is probable that a satisfactory method of distinguishing between the A- and B-rotational sub-states could be based on the effects on them of increasing excitation, for the electronic term value becomes greater for A than for B, and the moment of inertia for the A-state remains almost constant, whilst that for the B-state shows a fairly rapid increase. L. L. Bircumshaw.

Distribution of intensity in the band spectrum of helium: the band at 4650. W. H. J. Childs (Proc. Roy. Soc., 1928, **A**, **118**, 296—317).—A method is described for measuring the intensity distribution in the helium band at 4650 Å. (first of the main series). The spectrum is photographed in the usual way, but each plate is calibrated by exposure (for the same time as was necessary for the band spectrum) to a number of sources of known relative intensity. The densities of both the lines and calibration marks, obtained by means of a stepped aperture, are found, and from the measurements on the calibration marks a curve connecting light intensity with photographic density is drawn. This is then used to translate the

densities of the band-line images into relative densities. Chance errors are eliminated by the policy of obtaining several records by entirely different methods and taking weighted means. The observed values are compared with the predicted energy distribution calculated by means of the summation rule. Quantitatively, the agreement is not good, although the observed intensity curves are of the predicted type. Notably the prediction that the Q-branch at its greatest should be twice as strong as the maximum intensity of the P-branch is not fulfilled, the ratio being more nearly 10 : 7. The observed distribution is adequately described by an expression of the form $ie^{-E'/kT}$, where i is a linear function of j'. The effective temperature of the source, estimated by assuming the distribution of angular momentum to be governed by the Boltzman factor, is much higher than the true temperature. A higher temperature is obtained from the Q-branch than from the P- or R' branches. Examination of the Doppler width of the band lines indicates, however, that the distribution of translational velocities among the emitting molecules is that corresponding with the true temperature of the gas in the tube.

L. L. BIRCUMSHAW.

Emission spectrum of the chromosphere. A. UNSOLD (Z. Physik, 1928, **46**, 782—787).—The intensity distribution in the spectral lines emitted by the chromosphere is discussed, and an expression is derived for this distribution which leads to values for H_α which show a satisfactory agreement with observation. R. W. LUNT.

Conditions of emission of forbidden lines. A. S. EDDINGTON (Month. Not. Roy. Astron. Soc., 1927, **88**, 134—138).—Possibilities are discussed to account for the brightness of forbidden lines in nebulæ in comparison with ordinary lines. It is suggested that the stimulating radiation must be so weak that the atom is unlikely to absorb a quantum during the full duration of the metastable state. A similar explanation would hold if nebular light were due to ordinary temperature collisions, but the latter is regarded as improbable. It is shown to be unlikely that the coronium spectrum can consist of forbidden lines. J. W. SMITH.

Density necessary to produce the nebular spectrum. D. H. MENZEL (Nature, 1928, **121**, 618).—A criticism (cf. Elvey, this vol., 98).

A. A. ELDRIDGE.

Arc spectrum of carbon. A. FOWLER and E. W. H. SELWYN (Proc. Roy. Soc., 1928, **A**, **118**, 34—51; cf. Merton and Johnson, A., 1923, ii, 446).—Photographs of the spectrum of an oxide of carbon in helium, covering the region 1250—2760 in the first order and 1250—1380 Å. in the second order, have been taken with the vacuum grating spectrograph. The effect of admixture with helium is to emphasise the known lines of C I with respect to those of C II which appear with them, and to introduce additional lines, many probably due to C I. Results similar to those of Ryde (this vol., 97), but excluding some of the fainter lines, have been obtained with currents much smaller than those used by him, and this method has been utilised to extend the observations as far as 10120 Å. in the near infra-red. It appears that all the ordinary sources yield lines of C I which arise from combinations of the deeper terms of the spectrum, and special methods become necessary only for the excitation of lines due to combinations of terms representing higher energy levels. The terms of C I predicted by the Heisenberg–Hund theory are similar to those of N II and O III. The deepest term is a triplet P_0, the value of which is estimated at 91,017, corresponding with an ionisation potential of 11·2 volts. A close similarity between the spectra of C I, N II, and O III is to be expected, since the three atoms are similarly constituted. Each has six external electrons, but the nuclear charges are different. A regular progression is clearly shown in most of the term values in passing from O III to C I.

L. L. BIRCUMSHAW.

Intensities in the spark spectrum of oxygen. W. R. VAN WIJK (Z. Physik, 1928, **47**, 622—626).—The extended summation rule of Ornstein and Burger (A., 1927, 81) has been experimentally found to apply to the spark spectrum of oxygen (O II).

W. E. DOWNEY.

Line spectrum of oxygen. C. MIHUL (Ann. Physique, 1928, [x], **9**, 261—380).—428 lines of the second order spectrum of oxygen, and 315 lines of the third order spectrum between 7000 and 2050 Å. have been classified. C. W. GIBBY.

Spark spectrum of neon. II. T. L. DE BRUIN (Z. Physik, 1928, **46**, 856—872; cf. A., 1927, 910).—The spark spectrum excited by damped wave-trains of unspecified frequency and voltage in neon at 2 cm. has been examined by a grating method. A large number of lines have been recorded and classified.

R. W. LUNT.

Spectrum of ionised argon (A II). T. L. DE BRUIN (Nature, 1928, **121**, 576).—A considerable number of the lines of A II have been classified, and a doublet and a quadruplet term system has been found. The term structure is analogous to that of F I and Ne II. A. A. ELDRIDGE.

Spark spectrum of silver (Ag II). A. G. SHENSTONE (Physical Rev., 1928, [ii], **31**, 317—322).—Tabulated values are given of terms, intervals and limits, and intensities in multiplets. The lines (3372·51—1932·88 Å.) are classified with their intensities, frequencies, and designations. The calculated ionisation potential is 17·1 volts from $5s^3D_3$.

A. A. ELDRIDGE.

Intensity of forbidden multiplets. L. S. ORNSTEIN and H. C. BURGER (Naturwiss., 1927, **15**, 670—671; Chem. Zentr., 1927, ii, 2263).—The summation rule and intensity formula for normal multiplets are valid for forbidden multiplets of the cadmium arc spectrum. The relation pf/pd is approximately proportional to the 0·4 power of the pressure, and increases with increasing current. At atmospheric pressure pf/pd is 0·01 and 0·10 for the first and second members respectively, the ratio 10 being characteristic for the cadmium atom.

A. A. ELDRIDGE.

Mercury spectra. M. PONTE (Compt. rend., 1928, **186**, 633—635).—The special type of discharge produced at a tungsten electrode in an intense high-

frequency field, using oscillations of very short wave-length (this vol., 212), has been examined spectroscopically for mercury vapour. At 80° the discharge is of the arc type, but shows some first order spark rays, whilst at 150° it becomes molecular in type, and band spectra, due probably to rapid distillation of the mercury, appear. A list of bands obtained between 2345 and 4132 Å. is given. These could be produced by feeble or strong excitations which resulted in a green or white radiation, respectively, corresponding with different stages of atomic excitation. With respect to the ray 3300 Å., the former was the more intense. The measurements agree with those of Stark, but bands of higher wave-lengths were not identified. J. GRANT.

Apparent failure of the Hund theory. A. G. SHENSTONE (Nature, 1928, **121**, 619).—(*a*) The Paschen *s* terms in Ne I are ^3P and ^1P, arising from an electron structure $2p^5ns$ ($n \geqq 3$). The $1s$ terms can be arranged thus: $^3P_2=1s_5$, $^3P_\cdot=1s_4$, $^3P_0=1s_3$, $^1P_1=1s_2$. Consequently $^3P_2$ and $^3P_1$ converge to one limit, and $^3P_0$ and $^1P_1$ to a higher limit, the two limits together being the $^2P(p^5)$ of Ne II. This is in disagreement with the theory. (*b*) Ni I, Cu II, Pd I, and Ag II show sequences of ^3D, ^1D terms of origin d^9s converging to the $^2D(d^9)$ of the higher ion. In Cu II, Ni I, and Ag II only two series members are known, but they are well verified. In all cases the calculated limits of $^3D_3$ and $^3D_2$ fall close together, as do those of $^3D_1$ and $^1D_2$, contrary to the theory.

A. A. ELDRIDGE.

Excitation of spectra by high-frequency oscillations. J. R. CLARKE (Nature, 1928, **121**, 282).—Explanatory (cf. Ponte, this vol., 212).

A. A. ELDRIDGE.

Natural width of the lines of *X*-ray spectra. D. COSTER (Z. Physik, 1927, **45**, 797—800).—A theory of natural width of the lines of *X*-ray spectra is advanced to explain the apparent discrepancies between the experimental results of Ehrenberg, Mark, and Susich (*ibid.*, **42**, 807, 823) and those of Wien (A., 1927, 707). R. W. LUNT.

Dispersion and absorption of *X*-rays. J. A. PRINS (Z. Physik, 1928, **47**, 479—498).—On the assumption that the resonators in the *K*-level are distributed according to a λ^3-law, the theoretical dispersion and absorption of *X*-rays are calculated. Two sets of formulæ are deduced, for long and short waves, respectively. Application of the formula derived to the measurements of Richtmyers on molybdenum, silver, tin, and gold shows that for reasonable agreement one electron instead of two must be assumed in the *K*-level. Various curves showing absorption and dispersion as functions of frequency for different degrees of damping are given. Next, consideration is given to the so-called total reflexion. Application of Fresnel's formula yields an expression for the relative intensity at different glancing-angles, and is shown that the absorption at any particular wave-length must exert a perceptible influence on the reflexion conditions for that wave-length. In particular, if the reflexion is considered as a function of the wave-length, the effect is most noticeable on passing through an absorption edge for the reflecting element. There are described some new experiments on so-called total reflexion of *X*-rays, the first reflexion from a steel mirror being studied in the neighbourhood of the *K*-absorption edge for iron. In the first experiment, unfiltered rays from copper, nickel, cobalt, and iron were used, giving tests in both long and short wave-ranges. In the second and third experiments, analysed rays were used, and in the latter a double mirror was utilised, the separation being varied during the experiment. Photographs of all three experiments are given, from which the abrupt alteration at the absorption edge and disappearance of the critical glancing-angle for reflexion in the long-wave case are evident. The dispersion and absorption show a clear influence on the reflexion in good agreement with the theory. However, to get moderately complete numerical agreement for the actual dispersion it is necessary to assume that the number of dispersion electrons in the *K*-level of iron is about 1·3 instead of 2. A. J. MEE.

Absorption of carbon *K*-radiation by carbon, nitrogen, and oxygen. H. KURTZ (Ann. Physik, 1928, [iv], **85**, 529—551).—Mass absorption coefficients for air, oxygen, nitrogen, carbon dioxide, carbon monoxide, and ethane have been determined for carbon *K*-radiation. Atomic absorption coefficients have been evaluated as follows on the basis of the validity of the simple additivity law for the atomic absorption coefficients in the molecule: oxygen, $1·58\pm0·06$, nitrogen $0·88\pm0·05$, carbon, in carbon dioxide $0·42\pm0·06$, in carbon monoxide $0·48\pm0·06$, in ethane $0·54\pm0·03\times10^{-19}$. The additivity law is thus valid for very soft radiation, and no definite influence of the chemical linking can be ascertained. The absorption coefficients follow the rule $\alpha_{At}=kZ^{4·4\pm0·4}$, k being $(1·7\pm0·2)\times10^{-23}$ and Z the atomic number. R. A. MORTON.

Additional lines in the *K*-series of molybdenum and the natural breadth of spectral lines. B. DAVIS and H. PURKS (Proc. Nat. Acad. Sci., 1928, **14**, 172—178; cf. A., 1927, 804).—Additional lines have been observed near the β_2-line and near the α_1- and α_2-lines. The width of the lines is less than the value to be expected from the classical theory of damping by radiation.

W. E. DOWNEY.

***L*-Series of rhenium.** H. BENTHE (Z. Physik, 1928, **46**, 873—877).—The following values have been assigned to the *L*-series of rhenium from measurements with a calcite grating for α_1, α_2, β_1, β_2, β_3, β_4, β_5, β_6, β_8, γ_1, γ_2, γ_3, γ_6: 1429·8, 1440·7, 1235·9, 1203·8, 1217·6, 1256·3, 1174·7, 1248·1, 1198·0, 1058·7, 1029·8, 1023·5, 1034·3 X, respectively.

R. W. LUNT.

Precision measurements in the rhodium *K*-series. F. EUGER (Z. Physik, 1928, **46**, 826—832).—The wave-lengths of the following rhodium *K*-lines have been determined, using a calcite grating and a new form of the Siegbahn–Larsson spectrometer: α_2, $\alpha_\cdot$, $\beta_\circ$, $\beta_\cdot$, β_2, respectively 616·371, 612·023, 545·093, 544·491, and 533·957 X. R. W. LUNT.

Zeeman effect at intermediate strengths of magnetic field. K. DARWIN (Proc. Roy. Soc.,

1928, **A**, **118**, 264—285; cf. C. G. Darwin, A., 1927; 707).—Mathematical. Darwin's new formulæ (*loc. cit.*) for obtaining the frequency and intensity of any component in the standard Zeeman effect in any strength of field are applied to the $s-p$ and $p-d$ doublets and the $s-p$ triplets, involving 10, 34, and 19 lines, respectively. L. L. BIRCUMSHAW.

Zeeman effect of an intercombination line. W. C. VAN GEEL (Z. Physik, 1928, **47**, 615—621).—The positions and intensities of the Zeeman-effect components of the mercury, p_2D_2, intercombination line have been measured. The intensity formula of Honl (*ibid.*, 1925, **31**, 340) was found to hold for the components of an intercombination line.
W. E. DOWNEY.

Method of determining ionisation and resonance potentials. I. H. BARTELS (Z. Physik, 1928, **47**, 61—67).—A new method of measurement is described based on the Hertz differential method for resonance potentials which enables the determination of a function, I_r, of the voltage, V, accelerating the electrons which exhibits a maximum whenever V attains a value corresponding with an ionisation or a resonance potential. An electron stream is allowed to flow at one end into a metal cylinder which is maintained at a potential V above the filament; the filament must be placed relatively to the cylinder so that the electrons lose no appreciable fraction of their energy V_e before entering the cylinder. An electrode placed in the cylinder, but insulated from it, is maintained at a small potential V' (generally a fraction of a volt) above that of the cylinder; the current, I_m, flowing from this electrode to the cylinder is measured. It is shown that $I_r=(I_m-I_0)/I_0$ is a measure of the number of electrons of low energy liberated in the cylinder as a result of inelastic collisions suffered by electrons of energy $V-2V'$; if I_r reaches a maximum at V, this signifies a resonance or an ionisation potential at $V-2V'$. I_0 is the current flowing from the collector electrode to the cylinder when the electrode is at the same potential as the cylinder, V, and V is the value of this potential at which I_m has been determined. Lack of uniformity in the velocities of the electrons entering the cylinder does not shift the position of the maxima but reduces their sharpness. R. W. LUNT.

Resonance and ionisation potentials of argon. H. BARTELS and W. GLIWITZKY (Z. Physik, 1928, **47**, 68—71).—The following values of resonance potentials in argon at pressures of 0·22 and 0·12 mm. have been obtained by Bartels' method (cf. preceding abstract): 11·5, 12·8, and 14·0 volts, in good agreement with the data of Hertz. Ionisation potentials were observed at 15·86 and 16·25 volts, in good agreement with the values 15·66 and 15·84 calculated from spectroscopic data. These measurements indicate the advantages of the new technique of Bartels, since, in the older methods, it was impossible to distinguish between two ionisation potentials so closely placed. R. W. LUNT.

Thermionic emission and electron reflexion by metals. L. NORDHEIM (Z. Physik, 1928, **46**, 833—855).—By assuming that the electrons in metals behave as a gas to which the Fermi–Dirac statistical calculus may be applied, the Richardson–Dushman formula has been derived. The quantum mechanics of the reflexion of electrons from metal surfaces are also discussed. R. W. LUNT.

Electronic discharge from cold wires in intense electric fields. R. J. PIERSOL (Physical Rev., 1928, [ii], **31**, 441—447).—The curves obtained by plotting the potential gradient against the logarithm of the electronic current for outgassed tungsten at 27° and −180° are not linear. A. A. ELDRIDGE.

Velocity distribution of photo-electrons. F. HEROLD (Ann. Physik, 1928, [iv], **85**, 587—611).—The velocity distribution of electrons liberated by radiation of wave-length 254 $\mu\mu$ from copper, platinum, aluminium, and lampblack indicates that although the curves are closely similar for the different materials, definite deviations are shown and are greatest at the smallest and greatest velocities. The velocity distribution with platinum varies with the gas content, since outgassing shifts the curve at first in the direction of greater velocities and later again in the direction of smaller velocities. From the change in the form of the curve in the region of moderate velocities, it would appear that the nature of the excited substance definitely influences the velocity distribution. The use of platinum films of various thicknesses shows that the velocity distribution curves are identical for thicknesses varying from 35 to 5·5 $\mu\mu$, but that for thinner films, the slowest electrons (of about 0·1 volt) undergo retardation. The absolute values and the distribution of velocities with tungsten layers are independent of the angle of incidence of the light. R. A. MORTON.

Influence of the gas layer on the photo-electric sensitivity of metals. H. KLUMB (Z. Physik, 1928, **47**, 652—670).—Small pieces of tantalum, tungsten, molybdenum, nickel, and palladium were, in turn, heated in an evacuated tube. It was found that in each case the effect of this heating was to move the limit of the photo-electrically effective wave-lengths towards the short ultra-violet. The ordinarily observed photo-electric effects are ascribed as being due to a surface layer of gaseous impurity. Further experiments suggested that water vapour is peculiarly effective in this respect. W. E. DOWNEY.

Inner photo-electric effect with silver halides. S. E. SHEPPARD (Nature, 1928, **121**, 574—575).—A discussion of two possible views of the photolysis of silver halide, based on considerations of lattice energy.
A. A. ELDRIDGE.

Photo-electric threshold frequency and the thermionic work function. R. H. FOWLER (Proc. Roy. Soc., 1928, **A**, **118**, 229—232).—Mathematical. Richardson's suggestions as to the nature of the "free" electrons necessary to explain the existence of a sharp photo-electric threshold frequency ν_0 are unnecessarily complicated. It is shown to follow generally from Sommerfeld's revived electron theory of metals, and independently of any particular assumptions as to the nature of the surface action, that there exists a sharp photo-electric threshold frequency ν_0, and that the energy corresponding with this threshold frequency is equal to the therm-

ionic work function, *i.e.*, $h\nu_0=\chi$. Sommerfeld's theory gives an equally satisfactory account of the currents extracted from cold metals by intense fields.
L. L. BIRCUMSHAW.

Directions of emission of photo-electrons. P. AUGER (Compt. rend., 1928, **186**, 758—760).—Experiments on the photo-electric effects produced by the $K\alpha$-rays of tungsten in argon diluted with hydrogen indicate the need for revision of the theory proposed by the author and F. Perrin (cf. A., 1926, 876). The distribution in space of the directions of emission of the photo-electrons is unsymmetrical and the emission shows a principal maximum at an angle of 80°, and secondary and tertiary maxima at 60° and 120°, respectively. An orientation in the absorbing atom may determine the directions of emission of the photo-electrons. J. GRANT.

Electric fields near metallic surfaces. J. A. BECKER and D. W. MUELLER (Physical Rev., 1928, [ii], **31**, 431—440).—A study of the fields near metallic surfaces which affect the escape of electrons.
A. A. ELDRIDGE.

Secondary electron current as a function of crystal structure. H. E. FARNSWORTH (Physical Rev., 1928, [ii], **31**, 419—422).—The view that the secondary electron characteristics of copper, in the low-voltage region, are a function of the arrangement of the atoms at the surface, and are not directly dependent on the structure of the atoms themselves, is supported by the results of comparative experiments with phosphor-bronze, sheet copper, and single-crystal copper. A. A. ELDRIDGE.

Energy distribution of secondary electrons from copper, iron, nickel, and silver. H. E. FARNSWORTH (Physical Rev., 1928, [ii], **31**, 405—413).—The energy-distribution curves vary with the metal and with its heat treatment. There is no evidence of the existence of inelastic collisions.
A. A. ELDRIDGE.

Large angle scattering of low-velocity electrons from copper, iron, nickel, and silver. H. E. FARNSWORTH (Physical Rev., 1928, [ii], **31**, 414—418).

Electronic collisions in a gas-filled space. M. PIRANI and H. SCHONBORN (Naturwiss., 1927, **15**, 767—768; Chem. Zentr., 1927, ii, 2261).—The *P.D.* produced when two concentric cylindrical electrodes of tungsten and molybdenum, respectively, are placed in an atmosphere of hydrogen or nitrogen at 1600—2000° Abs. is 30 millivolts or 50 millivolts, an electron current passing from the tungsten to the molybdenum. When the circuit is closed, the current increases with rise of temperature. With an applied potential nitrogen, but not hydrogen, exhibits a saturation value. A. A. ELDRIDGE.

Collisions between electrons and gas molecules. I. LANGMUIR and H. A. JONES (Physical Rev., 1928, [ii], **31**, 357—404).—By the use of positive ion sheaths as perfect grids, data have been obtained regarding the probability of collisions between electrons of 30—250 volts velocity and mercury, hydrogen, nitrogen, helium, neon, and argon molecules; the mean angular deflexion for elastic and inelastic collisions between electrons and gas molecules has been calculated. The current density of positive ions has been measured, and the space potential both measured and calculated. The maximum number of positive ions produced by an electron is dependent only on its velocity and the nature of the gas. Values of the mean free path for inelastic collisions are tabulated, and the small angular scattering of electrons is discussed. The following resonance and ionisation potentials (volts), respectively, were observed: mercury 6·7, 10·4; neon 18·5, 21·5; argon 13·0, 15·3; helium 21·1, 24·5; nitrogen 13·0, 16·8; hydrogen 12·8, 16·1. A. A. ELDRIDGE.

Relation between effective molecular diameter and quantum changes. E. BRÜCHE (Z. Physik, 1928, **47**, 114—130).—The significance of various definitions of the effective molecular diameter of gases as a function of the velocity of colliding electrons is discussed. A relation is sought between the variation of the effective molecular diameter with electron velocity and the quantum energy changes that may occur corresponding with resonance and ionisation potentials. R. W. LUNT.

Recombination of ions and electrons. J. FRANCK (Z. Physik, 1928, **47**, 509—516).—Using the hypothesis that an electron set free by some ionisation process from the positive ion can recombine with the emission of radiation before it has got out of the sphere of influence of the atom, the investigations of variation of intensity of a spectral line with the kinetic energy of the electron stimulating it are considered: (*a*) those in which the energy of the primary electron only just exceeds the necessary energy for the excitation of the given line; (*b*) those in which fast electrons are employed. The explanation of the form of variation at high electron velocities is made possible by the original assumption. The probabilities of the various processes that would be involved are considered, and the possibility of ultraviolet and infra-red stimulation is mentioned. In the second part, triple collisions are assumed between positive ions and primary and secondary electrons. Langmuir has shown that cathode rays in a highly ionised gas possess Maxwellian distribution of translational velocity over a certain length of their travel. The length of travel for which this is so, and the mean energy of the particles, depend on the current strength in the tube. If there are sufficient triple collisions the primary electrons thereby obtain all possible values of energy, and hence from the laws of probability there is a Maxwellian distribution.
A. J. MEE.

Mean free path of the alkali [metal] ions in different gases. R. B. KENNARD (Physical Rev., 1928, [ii], **31**, 423—430).—With cæsium ions (90 volts) in hydrogen or helium, there is little neutralisation or scattering; there is a loss of velocity of 1·3 volts per collision. Cæsium ions (35 volts) in hydrogen are slowly weakened by neutralisation or scattering. In argon, cæsium ions (90, 35, or 20 volts) are rapidly neutralised. Sodium ions of 455 volts velocity suffer weakening in hydrogen. The free paths are given in terms of those of xenon atoms. A. A. ELDRIDGE.

Mobilities of gaseous ions in hydrogen sulphide–hydrogen mixtures. L. B. LOEB and

L. Du Sault (Proc. Nat. Acad. Sci., 1928, **14**, 192—199; cf. A., 1926, 449).—Mobilities in hydrogen sulphide and hydrogen sulphide–hydrogen mixtures have been measured. At low pressures the inverse pressure law does not appear to hold accurately for the positive ions, whilst it appears to hold for the negative ions. Free electrons were observed in hydrogen sulphide below 50 mm. Thus, hydrogen sulphide is between air and oxygen in its power of attaching electrons to form ions. W. E. Downey.

Cathode sputtering. A. Günther-Schulze (Z. tech. Phys., 1927, **8**, 169—178; Chem. Zentr., 1927, ii, 385).—The effect is ascribed to volatilisation of the cathode by the impinging cations; the greater part of the gaseous atoms returns to the cathode by diffusion, but a small part escapes. This portion is the greater the smaller is the gas pressure, the greater is the partial pressure of the gaseous metal, and the nearer is the collecting plate. Chemical reaction with formation of volatile compounds between the cathode material and the filling gas also increases the sputtering: the formation of a layer of a compound of high heat of volatilisation, *e.g.*, alumina, decreases it.
A. A. Eldridge.

Oscillatory ionisation currents from clouds of cadmium oxide particles. H. P. Walmsley (Phil. Mag., 1928, [vii], **5**, 561—573).—The ionisation currents from cadmium oxide clouds dispersed from an arc have been found to fluctuate rapidly. The magnitude of the effect has been compared with that to be expected from the theory of chance fluctuations, and it is concluded that the fluctuations represent time changes in the ionisation density of the cloud. The currents must arise from the breaking down of unstable complexes produced during the coagulation of the cloud, and it is thus concluded that the fluctuating current arises from the superposition of currents corresponding with successive groups of unstable particles. A. E. Mitchell.

Different magnetic states of the cobaltous ion. A. Chatillon (Ann. Physique, 1928, [x], **9**, 187—260).—The temperature coefficient of magnetisation of the cobaltous ion has been investigated. In aqueous solutions Co^{++} has an atomic magnetic moment of 25 magnetons and a negative Curie point, $-12°$ Abs., independent of concentration and of the nature of the anion. In alcoholic solution the corresponding number is 23. Anhydrous sulphates, if the temperature of calcination does not exceed 400°, generally have a magnetic moment of 25 and a Curie point at $-20°$ to $-30°$ Abs. If the salt is calcined at a red heat the magnetic moment is 26 and the Curie point $-50°$ Abs. This transition is purely a temperature effect. In all, including solutions in aqueous hydrochloric acid, five different magnetic moments of Co^{++} have been found: 22, 23, 24, 25, and 26 magnetons, respectively. Fractional moments, 23·5 and 25·6, are probably due to mixtures. C. W. Gibby.

Colour and magnetism of ions. G. Joos (Ann. Physik, 1928, [iv], **85**, 641—642).—Recent work on the spectra of Ti^{++} and Ti^{+++} (Astrophys. J., 1927, **66**, 13) lends strong support to the conclusion (A., 1927, 94) that the carriers of colour and magnetism for the ions of the transition elements cannot be simple ions and must be complex molecules.
R. A. Morton.

Measurement of the moments of iron and nickel at low temperatures. P. Weiss and R. Forrer (Compt. rend., 1928, **186**, 821—823).—The atomic moments of iron and nickel have been determined from the saturation magnetisation at the absolute zero of temperature, this being derived from the magnetisation measured in a field H, at a temperature T by double extrapolation towards $H=\infty$ and $T=0$. The total error of the measurements was about 0·2% (including that due to impurities) and atomic moments of 11 and 3 magnetons were found for iron and nickel, respectively. The value for the magneton of 1126·6 obtained in the case of iron is in agreement with recent determinations. J. Grant.

Extension of Langevin's theory of atomic magnetism to molecules constituting electronic isomerides. S. S. Bhatnagar and C. L. Dhawan (Phil. Mag., 1928, [vii], **5**, 536—545).—The magnetic susceptibilities of a number of compounds are shown to correspond closely with the expression $\chi_m = -2{\cdot}85\times10^{10}\Sigma(K\bar{r}_1)^2$, where   represents the value of the molecular radius given by $(r_1{}^3+r_2{}^3+\ .\ .\ .\ .)^{1/3}$, where r_1, r_2, etc. are the atomic diameters of the elements forming the molecule and K is an arbitrary constant. K is characteristic of a given group of electronic isomerides, whilst in isomorphous series it is proportional to the atomic numbers.
A. E. Mitchell.

Source of magnetism due to atomic structure. K. Honda (Z. Physik, 1928, **47**, 691—701).—Theoretical. W. E. Downey.

Polarisation of canal-ray light in weak electric fields. I. H_β-Radiation in a transverse field. E. Rupp (Ann. Physik, 1928, [iv], **85**, 515—528).—The polarisation ratio I_p/I_s (I_p being the intensity parallel to, and I_s that at right angles to the ray axis), of the H_β-line from canal-ray light in weak electric fields, has been determined for various fields and velocities. When the polarisation ratios for points along the canal-ray stream are plotted against the distance, the curves exhibit characteristic periodicities, which become more marked with decreasing velocities and increasing fields. The phenomena are qualitatively in accord with the oscillations of a classical anharmonic oscillator showing different phases along the stream. R. A. Morton.

Radioactivity of potassium isotopes. M. Biltz and H. Zeigert (Physikal. Z., 1928, **29**, 197—200).—Hevesy (this vol., 4) has prepared potassium chloride with an enhanced proportion of the isotope of atomic weight 41. The atomic weight of potassium, instead of appearing to be 39·104 as in ordinary potassium chloride, is 39·109 for this material. The mass spectrograph indicates for ordinary potassium chloride, 95% of K^{39} and 5% of K^{41}, so that the new material must contain $4{\cdot}8\pm1\%$ more of the heavier isotope than is present in the ordinary material. The β-activity of both preparations has been determined, using a Hoffmann vacuum electrometer, and since the new material exhibits $4{\cdot}2\pm0{\cdot}8\%$ more activity than the old, it is concluded that the radioactive

constituent of potassium is the isotope of atomic weight 41. R. A. MORTON.

Mechanism of the evolution of radon from radioactive minerals in liquid media. V. SPITZYN (Trav. Radium Minerais radioact., [Russia], 1926, **2**, 264—271; Chem. Zentr., 1927, ii, 2442).—The amount of radon removed from radioactive minerals in unit time by flowing water is independent of the velocity of flow; hence the radioactivity of radioactive springs must fall proportionally to the increase in flow of the spring. The value increases (up to ten-fold) with increase in fineness of division of the mineral, and (except for thorianite) increases with rising temperature. The value (at 20°) increases in the order: samarskite, thorianite, pitchblende, autunite. In dilute sodium chloride solution larger values, and in kerosene, alcohols, carbon tetrachloride, and ethyl acetate, smaller values were obtained. Specimens coated with paraffin or Wood's alloy evolved less radon than uncoated specimens. A. A. ELDRIDGE.

Normal radium solutions. W. BOTHE (Z. Physik, 1928, **46**, 896—898).—Data relating to standard radium solutions are discussed which indicate that the activity of such solutions up to an age of seven years shows no deviations greater than the order of the experimental error. R. W. LUNT.

Half-value period of protoactinium. Quantity in uranium minerals and uranium residues. O. HAHN and E. WALLING (Naturwiss., 1927, **15**, 803; Chem. Zentr., 1927, ii, 2272—2273).—The half-value period of protoactinium is determined as 20,760 years, corresponding with $1{\cdot}29\times10^{-7}$ g. per g. of uranium. The best source of protoactinium is the Joachimsthal radium residues. The "residual residues" contain 185 mg. of protoactinium per ton (1000 kg.). A. A. ELDRIDGE.

Disintegration of radium-*E* from the point of view of wave mechanics. G. P. THOMSON (Nature, 1928, **121**, 615—616).—Ellis and Wooster's result (this vol., 103) that in the disintegration of radium-*E* the single β-particle emitted has an initial energy varying from 40,000 to 1,050,000 volts can be reconciled with the new wave mechanics. A. A. ELDRIDGE.

Synthesis of ammonia by α-rays. S. C. LIND and D. C. BARDWELL (J. Amer. Chem. Soc., 1928, **50**, 745—748).—A stoicheiometric mixture of nitrogen and hydrogen, after passing a thin *X*-ray bulb containing radon, contains ammonia; the yields are higher than those found by Usher in stagnant gas (J.C.S., 1910, **97**, 389). About 0·2—0·3 mol. of ammonia is formed per ion pair produced in the mixture. It is predicted that equilibrium should occur when the mixture contains 9·09% of ammonia by volume. The results agree qualitatively with the observed decrease in velocity coefficient in the decomposition of ammonia by α-rays as a function of the ammonia concentration. S. K. TWEEDY.

Exact determination of the ionisation produced by single α-particles. H. ZEIGERT (Z. Physik, 1928, **46**, 668—715).—The use of a Hoffmann electrometer for photographically recording the ionisation produced by single α-particles is described, together with a statistical analysis of the results obtained with a number of radioactive substances. A new radioactive substance which exists as an impurity in zinc is reported. R. W. LUNT.

Heating effects of thorium and radium products. S. W. WATSON (Proc. Roy. Soc., 1928, **A**, **118**, 318—333).—Measurements have been made of the relative amounts of heat emitted by radon in equilibrium with its products of short life, radium-*B*+*C*, radium-*C*, thorium-*B*+*C*, and thorium-*C*. The method used was similar in principle to that employed by Rutherford and Robinson (Phil. Mag., 1913, [vi], **25**, 312), and consisted in measuring the change of balance of a Wheatstone bridge when two opposite arms were heated by the radioactive substance. The bridge was standardised by a heating coil, made as similar as possible to the radioactive source. The results obtained agree within 1 or 2% with the theoretical values calculated from Hess and Lawson's data for the number of α-particles emitted by 1 g. of radium per sec., viz. $3{\cdot}72\times10^{10}$ (cf. A., 1924, ii, 649); they are as follows (g.-cal. per g.-hr.: radon, observed 101·6, theoretical 102·4; radium-*B*+*C*, observed 43·1, theoretical 43·8; radium-*C*, observed 42·9, theoretical 43·4; thorium-*B*+*C*, observed 50·7, theoretical 49·7; thorium-*C*, observed 47·9, theoretical 47·2. If Geiger and Werner's value, viz., $3{\cdot}4\times10^{10}$ α-particles per sec. per g. (A., 1924, ii, 226), is correct, it follows that 10—12% of the heating must be caused by easily absorbed radiation which has not been taken into account in the calculations. This would require about 40, 70, and 80 quanta per atom for radium, radium-*C*, and thorium-*C*, respectively, if the radiation were of a wave-length of 1 Å., and correspondingly more quanta for softer radiation. If such an additional emission of energy does occur, the proportion which it bears to the total energy must be nearly the same for a large number of radioactive products. L. L. BIRCUMSHAW.

Problem of geological time. I. Evidence from radioactive minerals. A. HOLMES (Scientia, 1927, **42**, 263—272).—The evidence is considered, and the value $1\text{—}1{\cdot}5\times10^{9}$ years is determined. CHEMICAL ABSTRACTS.

Phenomena, similar to those of radioactive bodies, shown by metals. (MLLE.) S. MARACINEANU (Compt. rend., 1928, **186**, 746—748; cf. A., 1927, 807).—A continuation of the experiments on metals from the roof of the Paris Observatory has shown that the activation is not due to radioactive dust or emanations from the atmosphere. It persists for a long period after removal of the metal from the roof and decreases slowly according to an exponential rule in a manner comparable with that of polonium. Since it is most marked with lead, it may be due to reintegration of lead into polonium by solar energy with the formation of radium-*D*. This is supported by observations of the α-radiation of polonium. J. GRANT.

Radioactive radiation. K. W. F. KOHLRAUSCH (Physikal. Z., 1928, **29**, 153—168).—The expression $1/N\,.\,\Sigma\log v$ (N being the atomic number and v a characteristic frequency in the sense of the classical dispersion theory) enters into Bohr's formulæ for the

energy loss and ionisation which occur with the passage of α- and β-particles through matter. Certain assumptions make possible a theoretical treatment which can be tested by means of the data on the energy losses, ranges, and ionisations effected with α- and β-particles of various velocities, penetrating various materials. Agreement of a high order is always obtained, but although some instances of remarkably good verification are observed, it is not in general possible to evaluate atomic constants. This limitation arises from the fact that the theory applies only to particles of high velocity and to atoms of low atomic number. Nevertheless the success achieved by using only the simplest scheme indicates that the Bohr theory has great value as a principle for introducing order. R. A. MORTON.

Liquid stars and atomic volume. A. S. EDDINGTON (Nature, 1928, **121**, 496).

[Liquid stars and atomic volume.] J. H. JEANS (Nature, 1928, **121**, 496—497).

Structure of an atom of nitrogen. VII. H. COLLINS (Chem. News, 1928, **136**, 178—180).—Speculative.

Equipotential surface electrons as an explanation of the packing effect. W. E. DEMING (Physical Rev., 1928, [ii], **31**, 453—465).—Theoretical. With static models of the helium nucleus, packing can be satisfactorily accounted for by postulating that the electrons and protons shall be equipotential surface distributions having the usual total charges and radii, whereas ordinary electrons account for only 10% of the effect. With dynamic models, neither kind offers a solution. A. A. ELDRIDGE.

Statistical method for determining certain properties of the atom. I. E. FERMI (Atti R. Accad. Lincei, 1927, [vi], **6**, 602—607).—Mathematical. A statistical method for calculating the distribution of the electrons round the nucleus of an atom is developed. From the result attained, it is possible to calculate the energy required to ionise the atom completely, that is, to strip it of electrons, and also to determine the variation in potential at different distances from the nucleus and, thus, the electric field in which the electrons of the atom occur.

T. H. POPE.

Quantum theory of the capture of electrons. J. R. OPPENHEIMER (Physical Rev., 1928, [ii], **31**, 349—356).—The mean free path for the capture of electrons from atoms by α-particles is computed to vary approximately with the sixth power of the velocity of the α-particle, a result in accord with experiment. The probability of radiative recombination of electrons and protons is also computed.

A. A. ELDRIDGE.

Interference of light quanta. A. PROCA (J. Phys. Radium, 1928, [vi], **9**, 73—80).—Theoretical. If time is taken as one of the co-ordinates in developing the quantum theory, it is found that quanta must be coherent. W. E. DOWNEY.

Quantum theory of the electron. II. P. A. M. DIRAC (Proc. Roy. Soc., 1928, **A**, **118**, 351—361; cf. this vol., 344).—A continuation of the theory of atoms with single electrons. Proof is given of the conservation theory, which states that the change in the probability of the electron being in a given volume during a given time is equal to the probability of its having crossed the boundary. From a determination of the selection rule for j it is found that from states with $j-2$, transitions can take place to states with j -1, -2, or 3. This is exactly equivalent to the two selection rules for j and k of the usual theory, and is therefore in agreement with experiment. To determine the relative intensities of the lines of a multiplet on the present theory, it is only necessary to consider one Zeeman component of each line. The ratios found are in agreement with those of previous theories based on the spinning electron model.

L. L. BIRCUMSHAW.

Relativistic quantum theory of ideal gases. F. JÜTTNER (Z. Physik, 1928, **47**, 542—566; cf. A., 1911, ii, 579, 972).—An extension of previous work. Mathematical. A. J. MEE.

Central fields and Rydberg formulæ in wave mechanics. J. C. SLATER (Physical Rev., 1928 [ii], **31**, 333—343).—A theoretical discussion.

A. A. ELDRIDGE.

The asymmetric two-centre problem according to the wave-mechanics and its application to crystal theory. Scattering power of atoms. K. F. NIESSEN (Physikal. Z., 1928, **29**, 132—143).—The scattering power of the atom in lattices of the diamond or wurzite type has been calculated using the treatment of the two-centre problem given by the wave mechanics. R. A. MORTON.

Heisenberg's indetermination principle. E. H. KENNARD (Physical Rev., 1928, [ii], **31**, 344—348).—The principle is applied to cases where the position and velocity of an electron are observed by allowing it to pass through shutters opened momentarily at known times. A. A. ELDRIDGE.

Distribution of molecular velocities, excited states, and transition probabilities in degenerated gases. E. PERSICO (Atti R. Accad. Lincei, 1928, [vi], **7**, 137—141).—The analyses of Pauli and Fermi have been extended to derive expressions for the distribution of molecular velocities and for the probabilities of transition from one energy level to another in a degenerated monatomic gas.

R. W. LUNT.

Interpretation of band spectra. R. DE L. KRONIG (Z. Physik, 1928, **46**, 814—825).—Mathematical. R. W. LUNT.

Structure of Fraunhofer lines and quantitative spectrum analysis of the atmosphere of the sun. A. UNSOLD (Z. Physik, 1928, **46**, 765—781).—A modified form of Milne's theory of the radiation equilibria in the atmosphere of the sun has been introduced. Determinations of the intensity distribution in Fraunhofer lines are described which are held to establish the newer form of the theory. From these data it is shown that the electron partial pressure in the chromosphere is of the order of 10^{-6} atm. R. W. LUNT.

Nitrogen after-glow. J. C. MCLENNAN, R. RUEDY, and J. M. ANDERSON (Nature, 1928, **121**, 537—538).—Although the heat of dissociation of

molecular nitrogen is considered to be equivalent to 11 volts from a consideration of the band spectrum, the intensity distribution in the spectra of radiations from mixtures of foreign vapours with active nitrogen does not accord with this value. Experiments on the addition of xenon and krypton with excess of nitrogen afforded no lines of these elements in the spectrum of the after-glow, whereas addition of mercury causes the appearance of strong mercury lines. It is concluded that chemiluminescence plays a part in the phenomena associated with active nitrogen.

A. A. ELDRIDGE.

Influence of containing walls on the after-glow of nitrogen and oxygen. G. HERZBERG (Z. Physik, 1928, **46**, 878—895).—The intensity of the after-glow in oxygen, nitrogen, and oxygen–nitrogen mixtures excited by an electrodeless ring discharge under unspecified conditions has been examined in the pressure ranges 0·05—1·2 mm. It has been shown that the after-glow, particularly in nitrogen, does not occur if the containing vessel of quartz is heated in a vacuum to remove gases condensed on the surface. The experiments are held to establish that a surface-poisoning of the quartz is essential to production of the after-glow. As the fraction of oxygen in the mixture is increased the intensity of the nitrogen after-glow diminishes to a minimum and then passes through a maximum; correspondingly the intensity of the oxygen after-glow passes through a maximum and falls to a minimum at the same composition at which the nitrogen after-glow is a minimum; the intensity then passes through a second maximum and vanishes in pure oxygen. The percentage of oxygen at which the intensity of both after-glows reaches a minimum depends on the total pressure of the gas mixture, and shifts towards higher nitrogen concentrations as the pressure is increased. R. W. LUNT.

Measurement of oxygen bands in the violet and ultra-violet regions of the spectrum. H. FESEFELDT (Z. wiss. Phot., 1927, **25**, 33—60).—Tables are given showing the results of measurements of the oxygen bands discovered by Runge and Grotrian (Physikal. Z., 1914, **15**, 545; Runge, Physica, 1921, **1**, 254) in the region 3140—4450 Å. The line intensities, frequencies, and the mean errors of measurement are also given. W. CLARK.

Interchangeability of zinc oxide and dyes in optical sensitisation. C. NEUWEILER (Z. wiss. Phot., 1928, **25**, 187—224).—In light, zinc oxide acts on aqueous solutions of organic dyes of widely different classes. In pure, air-free aqueous solution the dyes are both oxidised and reduced. In presence n anodic depolariser they are exclusively reduced. With vat dyes, photolysis still occurs even at the highest reduction potentials (safranin, $\varepsilon_h = +0·15$ volt. (ferences of potential (up to about) between the anodic and cathodic photolysis processes can be overcome by light. With azo-dyes the photolytic reduction is not reversible; *i.e.*, the reduction products were not reconverted into dyes by the oxygen of the air. The alkalinity of the zinc oxi e, and heating, play no part in the reactions studied. Under certain conditions, sensitising dyes can exert the same photolytic effect on organic dyes as zinc oxide. The necessary condition is that the absorption region of the sensitiser must coincide with that of the acceptor on the short wave-length side.

W. CLARK.

Absorption spectra of photo-electrically conducting crystals. R. OTTMER (Z. Physik, **46**, 798—813).—The extinction coefficients of the following substances have been determined in the range 2000—9500 Å. after colouring due to exposure to hard X-rays: lithium chloride and fluoride; sodium fluoride, chloride, and bromide; potassium fluoride, chloride, bromide, and iodide; rubidium chloride. The position and value of the maximum in the region 5000—6000 Å. are unaffected by the degree of coloration of the salt. The maximum at 4700 Å. in rock salt is diminished by exposure to blue light; measurements of the conductivity of rock salt during exposure to light of different wave-lengths shows that the absorption in the neighbourhood of 7200 Å. is unconnected with the conductivity. R. W. LUNT.

Alkaline-earth halide spectra and their origin. O. H. WALTERS and S. BARRATT (Proc. Roy. Soc., 1928, **A**, **118**, 120—137).—The bands in the spectra of the alkaline-earth halides can be very conveniently observed in absorption against a continuous background spectrum. The absorption spectra observed were those of a column of vapour about a foot long, at a temperature of 1000—1200°. The continuous background spectrum was provided by a 500 candle-power "Pointolite" lamp, down to 3800, and by the positive crater of a carbon arc down to 2200. For the calcium and magnesium halide spectra, excess of calcium or magnesium turnings was heated with the powdered and dehydrated metal halide salt. The strontium and barium vapours were obtained by heating a mixture of metallic calcium and the strontium or barium halide. Evidence is given in support of the view that the bands originate, not from normal halide molecules, but from subhalide molecules of the type MX. It is highly probable that such molecules exist in the vapour state at 1000° in equilibrium with the metal and normal salts. The ease of preparation of these salts appears to increase with the atomic weight of the halogen, as found by Guntz (A., 1924, ii, 610). All the molecules except those of the magnesium halides have band groups in the visible region. In general, the group of largest wave-length in each spectrum consists of bands degraded to the short wave-length side. The next group—usually in the near ultra-violet—is degraded to the short wave-length side. When other groups were found in absorption, the direction of degradation alternated from one group to the next. New groups of bands have been detected in the ultra-violet, but these do not appear to be arranged according to the Rydberg series law, and it is concluded that the various groups of bands in the spectra do not correspond with successive members of a single atomic line series, but rather with the first members only of several such series. The bands obtained in absorption were compared with the corresponding emission spectra from flames and arcs, and in general no differences in structure or intensity distribution were observed. The structure of the calcium subfluoride band at 5292,

however, is very different in emission and absorption. The fine structure of the absorption band appears only at reduced pressures; it is usually represented by a weak continuous spectrum only.

L. L. BIRCUMSHAW.

Analysis of the absorption spectrum of cobalt chloride in concentrated hydrochloric acid. W. R. BRODE (Proc. Roy. Soc., 1928, A, **118**, 286—295).—A detailed study of the absorption spectrum of cobalt chloride in concentrated hydrochloric acid between wave-length values of 720 and 595 μμ has been made on a new model of the Hilger–Nutting spectrophotometer. The data obtained by this method were confirmed by making photographs with Ilford panchromatic plates on a Judd Lewis photometer and Littrow spectrograph. The principal absorption band consists of seven component bands, and two or more bands were found in the weak portion of the spectrum (575—440 μμ). The seven bands appear to be at 695, 679, 666, 648, 626, 610, and 595 μμ. The observed absorption curve can be resolved into seven similarly-shaped bands of different intensities, which will add together to produce the observed compound curve. There is a constant frequency difference between adjacent bands of 12·28*f* (*f*=vibrations/sec.$\times 10^{12}$), and the frequencies of the component bands are integral multiples of this constant frequency difference. A relation appears to exist between the odd- and even-numbered component bands and their relative intensities.

L. L. BIRCUMSHAW.

Ultra-violet absorption of iodides in solution. G. SCHEIBE (Sitzungsber. phys.-med. Soc. Erlangen, 1927, **58—59**, 2 pp.; Chem. Zentr., 1927, ii, 2151).—In aqueous solution, lithium, sodium, potassium, magnesium, and strontium iodides have an absorption maximum at 225 mμ, a minimum at 209 mμ, and a second maximum at about 192 mμ. In alcoholic solution the positions are 216, 204, and 192 mμ, respectively. Aqueous zinc and cadmium iodides behave similarly, but exhibit differences in alcoholic solution.

A. A. ELDRIDGE.

Resolution of an absorption band regarded as common to praseodymium and neodymium. L. FERNANDES (Z. anorg. Chem., 1928, **169**, 267—271).—By an examination of the absorption spectra of crystals of neodymium sulphate and of a solid solution of praseodymium sulphate in lanthanum sulphate, the absorption band at 469 μ has been resolved, the two compounds proving to have no wave-length in common.

R. CUTHILL.

Influence of electric fields on the absorption spectrum of ruby. A. ARSENJEWA (Z. Physik, 1927, **45**, 851).—Preliminary measurements of the absorption spectrum of ruby when subjected to intense electric fields of the order of 10^6 volts $cm.^{-1}$ show that the lines 6670 and 6910 are shifted to 6930 Å.

R. W. LUNT.

Absorption of ultra-violet glasses. C. WINTHER (Z. wiss. Phot., 1928, **25**, 230—232).—Curves given show the ultra-violet transmission for a number of specimens of ultra-violet glass and of ordinary plate glass. Variation of thickness of the glass specimens was adjusted by altering the exposure time according to the method of Henri.

W. CLARK.

Absorption spectrum of solutions of formaldehyde. S. A. SCHOU (Compt. rend., 1928, **186**, 690—692).—The absorption bands of a solution of formaldehyde vapour absorbed in hexane at —70°, and of the vapour itself, fall between 3542 and 2750 Å., and show maxima at 2940 and 2935 Å., respectively. The latter are in the same region as those of hexane solutions of acetaldehyde and propaldehyde (A., 1926, 556).

J. GRANT.

Spectrographic study of cyanamide. Ultra-violet absorption spectra of cyanamide, dipropylcyanamide, and dipropylcarbodi-imide. A. FRANSSEN (Bull. Soc. chim., 1928, [iv], **43**, 177—193).—From a study of the absorption spectra of cyanamide, dipropylcyanamide, and dipropylcarbodi-imide in hexane, ether, and alcohol solutions, it is concluded that in these solvents an equilibrium exists between the two forms of cyanamide $N{:}C{\cdot}NH_2$ and $NH{:}C{:}NH$, the proportion of the latter increasing with dilution. Beer's law does not hold for cyanamide in ethereal or alcoholic solution. Discontinuities occur when the coefficient of molecular absorption is plotted against the wave-lengths of the light employed.

H. INGLESON.

Near infra-red absorption of benzene and toluene. J. BARNES and W. H. FULWEILER (J. Opt. Soc. Amer., 1927, **15**, 331—336).—The authors' previous work (A., 1927, 918) has been extended by using a concave grating with a dispersion of 9·33 Å./mm. to the determination of the absorption maxima in liquid benzene and toluene. Two maxima for benzene are recorded at 8744 and 7133 and one for toluene at 8767 Å. Further work on hydrocarbons is in progress.

R. W. LUNT.

Infra-red absorption by the N–H linking. II. Aryl-, alkyl-, and aryl-alkyl-amines. J. W. ELLIS (J. Amer. Chem. Soc., 1928, **50**, 685—695).—A continuation of the previous investigation, the values given for the wave-lengths in which are corrected slightly (A., 1927, 291). Bands occur at 1·49—1·55 μ and 1·03—1·06 μ with the primary amines, and, diminished in intensity, with the secondary amines, but do not appear at all with the tertiary amines. They thus appear to originate in the N–H linkings and form a "harmonic" series with the band at 2·80—3·05 μ (cf. Bell, A., 1927, 862). Absorption maxima at 2·01—2·03 μ and at 1·21—1·23 μ, also apparently characteristic of the amino-group, may be "combination" bands arising from the 2·80—3·05 μ and the 1·49—1·55 μ maxima taken with the band at 6·25 μ. The N–H bands are interpreted in a manner analogous to the modified interpretation of the C–H bands (A., 1927, 608).

S. K. TWEEDY.

Composition of the Kundt displacements in an absorption spectrum with several maxima. P. VAILLANT (Compt. rend., 1928, **186**, 755—757).—The absorption coefficients of solutions of erythrosin or malachite-green in water, or in benzene containing 30% of alcohol, have been measured. The absorption band of the former consists of two bands of unequal intensities which are displaced *en bloc* with

the spectrum without deformation, when the solvent is changed. The displacement is greatest on the red side where the more intense band occurs. Malachite-green has two maxima (in the violet and orange), the two bands being displaced simultaneously but independently. These displacements are expected to aid the explanation of certain exceptions to Kundt's law, which are usually supposed to be due to changes in the nature of the absorbing particles accompanying a change in solvent. J. GRANT.

Cholesterol and vitamin-*D*. I. M. HEILBRON, R. A. MORTON, and W. A. SEXTON (Nature, 1928, **121**, 452—453).—The existence of a faint band in the spectrum of ergosterol at 260 $\mu\mu$ is confirmed, but it is suggested that the bands in "cholesterol-*E*" at 315 and 304 (Bills, Honeywell, and MacNair, this vol., 332) are due to the presence of traces of cholesterilene. A. A. ELDRIDGE.

Contact activation of hydrogen by metals. M. POLJAKOV (Naturwiss., 1927, **15**, 539—540; Chem. Zentr., 1927, ii, 2264).—When hydrogen at 3—5 mm. pressure is passed over palladium, nickel, or iron at 400—800°, no luminescence is observed, but if a small stream of oxygen or air is added at a point remote from the metal, a violet, green, or yellow luminescence occurs. The luminescence is not observed with a mixture of hydrogen and oxygen. A. A. ELDRIDGE.

Atomic spectral lines associated with the band fluorescence of alkali metals. J. C. MCLENNAN and R. RUEDY (Nature, 1928, **121**, 500—501).—The band systems of sodium in the red and green, respectively, can be obtained on the spectrograms of the light emitted by the metal vapours which have been rendered fluorescent; moreover, the *D*-lines on the fluorescence spectrograms are very broad even at low temperatures and at moderate pressures. The emission of the atomic resonance lines results from the dissociation of the excited molecules; molecular dissociation can take place when the energy associated with a quantum of the absorbed light is greater than the energy corresponding with the atomic resonance potential plus that representing the heat of dissociation. This consideration accounts for the abnormal width of the *D*-lines and explains why the absorption of red and green spark-line radiation does not effect the emission of the yellow *D*-lines from sodium vapour. A. A. ELDRIDGE.

Resonance in collisions of the second kind. Sensitised fluorescence and chemiluminescence. H. BENTLER and B. JOSEPHY (Naturwiss., 1927, **15**, 540; Chem. Zentr., 1927, ii, 2264).—When mercury and sodium vapours are illuminated in a quartz vessel with a cooled mercury vapour lamp, the red fluorescence radiation of the sodium is visible. The intensity distribution is unexpected, those lines of the subordinate series being most intense for which the higher energy level corresponds with the most complete absorption of the exciting energy. In the inductor discharge in sodium and mercury vapours there is, in comparison with that in sodium vapour, an increase in intensity of the higher members of the subordinate series relatively to the lower members. In the chemiluminescence of the reaction of sodium with mercuric chloride, the lines $5S—2P$, $5D$, $6D—2P$, and $7S—2P$ are strengthened. The energy of an excited atom on collision appears chiefly as exciting energy of the impinged atom; conversion of a part of the exciting energy into energy of translation is much less likely. A. A. ELDRIDGE.

Fluorescence and band spectrum of cadmium vapour. A. JOBLONSKI (Z. Physik, 1927, **45**, 878—891; cf. Kapuścinski, A., 1927, 712).—A new absorption band has been detected in saturated cadmium vapour in the temperature range 500—800°. The band extends from 2150 to 1990 Å. with a maximum at 2114 Å., and absorptive power of the saturated vapour in this region increases rapidly with temperature. At temperatures from 600° to 700° a fluorescence band is observed in the region 2110—2140 with a maximum at 2128 Å.; it is most strongly excited by radiation of wave-length 2110—2126 Å. This band corresponds with the first triplet of the second subordinate series. Above 700°, the emission diminishes, due to the excitation of bands of shorter wave-lengths. R. W. LUNT.

Ultra-violet fluorescence of iodine monobromide vapour. A. FILIPPOV (Naturwiss., 1927, **15**, 682—683; Chem. Zentr., 1927, ii, 2264).—The ultra-violet fluorescence spectrum of iodine monobromide vapour contains bands at 3500, 3400, 3325, 3265, 3205, 3160, 3120, 3050, 3015 Å. A mixture of iodine monobromide vapour with nitrogen at 260 mm. yields bands with maxima at 3860, 3715, 3550, 3425, 3160, and 3045 Å. A. A. ELDRIDGE.

Fluorescence of mercury vapour. R. W. WOOD and V. VOSS (Nature, 1928, **121**, 418—419).—The fact that a double quartz bulb containing mercury vapour exhibits fluorescence in the light of an aluminium spark only when one bulb is cooled by an air blast is ascribed to the presence of traces of water vapour. Otherwise, fluorescence may occur in the absence of distillation. Practically all the brighter arc lines in the violet and ultra-violet were observed; they appear to result from two-stage absorption. Superheating destroys the blue-green band and enhances the ultra-violet band and arc lines. A. A. ELDRIDGE.

Origin of the spectrum of the glow of phosphorus. H. J. EMELÉUS and R. H. PURCELL (J.C.S., 1928, 628—630; cf. A., 1927, 497).—A discussion of the various possibilities. No definite conclusion can be reached. C. W. GIBBY.

Spectrum of calcium-strontium sulphide-samarium mixed phosphors. M. TRAVNICEK (Ann. Physik, 1928, [iv], **85**, 645—646; cf. this vol., 106).—A correction of a mis-statement by Tomaschek (this vol., 219). R. A. MORTON.

Photo-electric limits of the alkali halides. N. GUDRIS and L. KULIKOWA (Z. Physik, 1927, **45**, 801—807).—With a technique previously described (A., 1926, 777), the minimum frequency by which photo-electric emission can be excited has been determined for sodium chloride, bromide, and iodide; potassium chloride, bromide, and iodide; rubidium and cæsium iodides. Except with sodium iodide the limiting wave-length of excitation for these substances is

increased by about 100 Å. after the substances have been exposed to the light of an aluminium spark for several hours. This phenomenon has been examined for sodium chloride by determining the limiting wave-length corresponding with samples treated with various types of radiation. Ultra-violet light, weak X-rays, and γ-rays shift the neighbourhood of the limiting wave-length from 2026—2170 to 1270—2250; for natural blue and electrolytically coloured salt the region is 2250—2300, whilst in salt strongly coloured by X-rays the region of critical excitation is shifted to 4000—5000 Å. R. W. LUNT.

Variation with temperature of the dielectric constants of gases and vapours. I. Carbon dioxide and air. H. A. STUART (Z. Physik, 1928, **47**, 457—478).—A method of finding ε at various temperatures with an accuracy of 1 in 10^6 is described, with the object of settling the electric moments of the molecules in question and, for carbon dioxide, the configuration of the molecule. In the calculations from the results air is assumed to behave as a perfect gas, but for reduction of observations in the case of carbon dioxide Clausius' equation of state is used. The absolute values of $\varepsilon-1$ at *S.T.P.* are: for carbon dioxide, $987\pm12\times10^{-6}$ and for air, $582\pm7\times10^{-6}$. For carbon dioxide the expression $(\varepsilon-1)d_0/d$ is constant within the limits of experimental error, which leads to the conclusion that the carbon dioxide molecule possesses zero electric moment, from which the three atoms in the molecule must lie in a straight line. This result also follows from considerations of electrostriction. With air, the above expression increases slightly in value at the higher temperature, which is to be expected from measurements of variation of refractive index with temperature. The infra-red spectrum of carbon dioxide is considered at some length, and in it a further confirmation of the straight-line configuration is found. A. J. MEE.

Effect of radioactive radiation on the dielectric constant of dielectrics. G. GUEBEN (Compt. rend., 1928, **186**, 861—863).—The irradiation of thin sheets of a number of different dielectrics by means of radium bromide has shown (with a degree of accuracy of 0·1%) that no variation in ε is produced as in the case of gaseous dielectrics. J. GRANT.

Specific weight and volume of ions and their compounds, including metals considered as compounds of metal ions with electrons. J. GEISSLER (Z. Elektrochem., 1928, **34**, 86—91).—Certain additive ionic volumes have been calculated and from these the molecular volumes of a number of actual compounds including certain metals, which are considered as compounds of metal ions with electrons, have been computed. Molecular volumes are given by the sum of the additive ionic volumes involved plus a corrective term, the magnitude of which is determined by the volumes of the ions concerned. Certain ions, notably the electron, hydroxyl, oxygen, and fluoride ions, have negative additive volumes. J. S. CARTER.

Volume chemistry. III. Oxygen compounds. Hydroxyl group. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 251—255, 268—274; Chem. Zentr., 1927, ii, 1534).—"E-values" are determined for hydroxyl oxygen under various conditions of combination in organic compounds. A. A. ELDRIDGE.

Refractivity of normal saturated monobasic aliphatic acids. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1928, **47**, 415—417).—Polemical against Waterman and Bertram (cf. Verkade and Coops, this vol., 220; Waterman and Bertram, A., 1927, 1167; this vol., 220). M. S. BURR.

Vibrational levels and heat of dissociation of Na_2. F. W. LOOMIS (Physical Rev., 1928, [ii], **31**, 323—332).—Most of Wood's magnetic rotation lines in the blue-green region accord with the expression: $\nu=20301{\cdot}7+(124{\cdot}13n'-0{\cdot}84n'^2)-(158{\cdot}5n''-0{\cdot}73n''^2-0{\cdot}0027n''^3)$. The heat of dissociation is then calculated to be $1{\cdot}0\pm0{\cdot}1$ volt. A. A. ELDRIDGE.

Residual rays, natural frequencies, and infra-red dispersion. O. FUCHS and K. W. WOLF (Z. Physik, 1928, **46**, 506—518).—The theories of Ladenburg and of Debye have been extended to derive a relationship between the refractive index, n, and therefore also the dielectric constant, ε, and the natural frequencies of a substance exhibiting line absorption in the ultra-violet and in the infra-red: $(n^2-1)/(n^2+2)=e^2/3\pi m_i\Sigma^i N p_i/(\nu_i^2-\nu^2)$, where e is the electronic charge, the mass of resonators i, p_i the number of such resonators per molecule, N the number of molecules per c.c. Values of n have been calculated by using a four-term formula and are shown to be in good agreement with theory for sodium and potassium chlorides. The values of ν_4, the infra-red frequency, are shown to agree well with the residual ray frequencies of these substances. It is also shown that values of the dielectric constant calculated by extrapolation of the above formula are in satisfactory agreement with experiment. R. W. LUNT.

Dispersion of carbon dioxide from 2300 to 130,000 Å. O. FUCHS (Z. Physik, 1927, **46**, 519—525).—The formula of Fuchs and Wolf (preceding abstract) has been simplified for gases by replacing $(n^2-1)/(n^2+2)$ by $2(n-1)/3$; in this form, using four characteristic frequencies corresponding with 720·41, 1480·0, 43,100, 149,100 Å., the formula leads to values of the refractive index, n, in good agreement with the collected data of a number of workers. The first wave-length corresponds with the ionisation potential 14 volts, 866 Å., the second with the centre of the band observed by Lyman, 1300—1600 Å. The value of the dielectric constant calculated by extrapolation to zero frequency is 1·000975, in good agreement with the recent value of Zahn, 1·000976. R. W. LUNT.

Rotatory dispersion of alkyl aspartates. F. P. MAZZA (Atti R. Accad. Lincei, 1928, [vi], **7**, 148—150).—The results previously published (A., 1927, 500) are discussed and the conclusions confirmed; the work of Pagliarulo (A., 1927, 610) is criticised. O. J. WALKER.

Rotatory dispersion of tartaric acid. F. BURKI (Helv. Chim. Acta, 1928, **11**, 369).—The author's exponential equation (A., 1924, ii, 218) may be expressed in the form $[\alpha]=A/\lambda^2e^{\alpha/\lambda^2}-B/\lambda^2e^{\beta/\lambda^2}$, where A, B, α, and β are constants. The variation of

the molecular rotation of tartaric acid with wave-length (Lowry and Austin, A., 1922, ii, 414) is satisfactorily represented by a formula of this type.

J. S. CARTER.

Effect of temperature on the rotatory powers of [optically] active substances. R. LUCAS (Compt. rend., 1928, **186**, 857—859).—The author explains the rotatory powers of certain compounds by their existence in several unimolecular configurations in equilibrium, passage from one to the other taking place in a discontinuous fashion, subject to the effects of temperature and of the solvent. Boltzmann's law shows that a point of inflexion or a maximum on the rotation–temperature curves indicates the presence of two or three molecular forms, respectively, and since the curves for ethyl and *iso*butyl tartrates and for *iso*butyl diacetyltartrate show maxima, these compounds belong to the latter type.

J. GRANT.

Magnetic rotary dispersion of methyl and propyl alcohols. D. O. JONES and E. J. EVANS (Phil. Mag., 1928, [vii], **5**, 593—608).—The magnetic rotation of methyl alcohol has been measured for the wave-lengths 0·4379—0·2600 μ, and it has been shown that Verdet's constant δ can be represented by the equation $n\delta\lambda^2=1\cdot189[\lambda^2/(\lambda^2-0\cdot1100^2)]^2$, where n is the refractive index of methyl alcohol for the wave-length λ and 0·1100 μ is the wave-length of the absorption band in the extreme ultra-violet. Similar measurements for *n*-propyl alcohol have shown that Verdet's constant for this is given by the expression $n\delta\lambda^2=1\cdot553[\lambda^2/(\lambda^2-0\cdot1138^2)]^2$. The frequencies of the basic bands given above are approximately double those determined by Henri. Methyl and *n*-propyl alcohols have weak absorption bands at 0·2207 and 0·2273 μ, but these do not contribute materially to the magnetic rotation.

A. E. MITCHELL.

Action of a magnetic field on optically active substances. G. CALCAGNI (Notiz. chim.-ind., 1927, **2**, 429; Chem. Zentr., 1927, ii, 2263—2264).—When a current is passed through a solenoid surrounding a polarisation tube containing an optically active or inactive substance, in a clockwise direction (from the observer's point of view), rotation of the plane takes place to the left, and *vice versa*; the effect is independent of the substances and of the concentration of the solution.

A. A. ELDRIDGE.

Theory of light-scattering in liquids. C. V. RAMAN and K. S. KRISHNAN (Phil. Mag., 1928, [vii], **5**, 498—512).—A new theory of light-scattering in liquids is based on the fact that, if a molecule departs in shape appreciably from spherical, the strength of the polarisation field will depend on the orientation of the molecule in the field. The results are supported by existing data.

A. E. MITCHELL.

Scattering of light in dispersed systems of concentration. G. I. POKROVSKI (Z. Physik, 1928, **46**, 753—758).—It is shown that for dispersed systems of high concentration the intensity, I_d, of a beam after scattering by a thin layer is expressed by the equation $I_d=I_0[1-\exp.(-a\psi/\theta)]$, where ψ and θ are quantities that can be calculated from the refractive index of the medium and from the relative refractive index of the dispersed phase, a is a constant, and I_0 the incident intensity. Values calculated in this way agree fairly well with Woronkoff's data for silk fibres dispersed in various media.

R. W. LUNT.

Law of periodicity. II. P. PETRENKO-KRITSCHENKO (J. Russ. Phys. Chem. Soc., 1928, **60**, 149—152).—See A., 1927, 713.

Position of rare-earth elements in the periodic system. J. F. SPENCER (J. Amer. Chem. Soc., 1928, **50**, 264—268).—From a consideration of solubility data and of the magnetic ionic moments as a function of the number of electrons in the tervalent ion, the rare-earth metals are inserted in the periodic table as follows:

Series.	Group III.		Group IV.	
8	La		Ce, Pr, Nd, Il	
9		Sa, Eu, Gd		Tb
10	Dy, Ho, Er, Tu, Yb, Lu		Hf	

S. K. TWEEDY.

Anomalous groups in the periodic system of elements. E. FERMI (Nature, 1928, **121**, 502).—A brief account of work to appear elsewhere.

A. A. ELDRIDGE.

New type of secondary radiation. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, **121**, 501—502).—When light is scattered by molecules in dust-free liquids or gases, the ordinary diffuse radiation having the same wave-length as the incident beam is accompanied by a modified scattered radiation of degraded frequency.

A. A. ELDRIDGE.

Co-ordination and atomic structure. P. RAY (J. Indian Chem. Soc., 1928, **5**, 73—89).—Views concerning the electronic configuration of complex compounds are summarised, and a scheme for electron distribution in complexes is suggested. Complex compounds are differentiated as strong (perfect) or weak (imperfect); the former include most sixfold cobaltic, some sixfold ferrous and ferric, all sixfold and fourfold platinum, and the sixfold chromic, tervalent rhodium, ter- and quadri-valent iridium, and a few ruthenium complexes, whilst the latter are transitional between true complexes and double or associated compounds, *e.g.*, nickel, copper, zinc, cadmium, and cobaltous complexes. Tendency to assume the external electronic configuration of the next higher inert gas by the central ion is the main factor in the formation of perfect complexes. For the weak class it is assumed that the various units share electrons with the central ion at different levels; in the perfect class a more or less inner level of electrons takes part in the sharing. Thus the nature of the electron distribution in the central ion determines the type of co-ordination. The stability of the complex increases with the number of electrons in any sub-group as it gradually becomes filled up; a lone electron tends towards instability.

A. A. ELDRIDGE.

Molecular structures of methane. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 166—171). Two structures of the methane molecule are given, one in which the hydrogen positions are joined to the

carbon atom by a single-electron linking and another in which this link is composed of two "electron positions." Dynamic isomerides of both types are described, their moments of inertia calculated, and a comparison is made with the observed moments.

W. E. DOWNEY.

Symmetry of methane derivatives with four identical groups. K. WEISSENBERG (Naturwiss., 1927, **15**, 662—664; Chem. Zentr., 1927, ii, 2260—2261).—Molecules of the type CX_4 which possess a dipole moment must have a pyramidal configuration. The equivalence of the four substituents can be demonstrated in the amorphous and crystalline states and in some cases in solution (cf. following abstract). If a molecule CX_2Y_2 possesses a pyramidal structure, stereoisomerism of the type CXYXY and CXXYY must be postulated. The probability of pyramidal configuration is limited to compounds CX_4 in which the substituents themselves have the character of dipoles; thus pentaerythritol possesses two enantiomorphic forms. Compounds of the type X:CY·Z may also, according to the new theory, possess pyramidal configuration and exist in enantiomorphic forms.

A. A. ELDRIDGE.

Electric dipole moments of dissolved molecules of the type CX_4. L. EBERT and H. VON HARTEL (Naturwiss., 1927, **15**, 669—670; Chem. Zentr., 1927, ii, 2261).—The following dipole moments ($\times 10^{-18}$) were determined: $C(OMe)_4$ 0·8, $C(OEt)_4$ 1·1, $C(CH_2{\cdot}OAc)_4$ 2·6, $C(CH_2Cl)_4$ $<0{\cdot}2$, CCl_4 $<0{\cdot}1$. Thus among molecules of the type CX_4 are to be found those of regular tetrahedral and those of pyramidal structure.

A. A. ELDRIDGE.

Electric moment of the water molecule. J. W. WILLIAMS (Physikal. Z., 1928, **29**, 204—205).—From the following measurements of dielectric constants: benzene, $2{\cdot}282+0{\cdot}001$; solution of benzene saturated with water at 25°, $2{\cdot}294\pm0{\cdot}001$, and the fact that 100 g. of the solution contain 0·073 g. of water, it is shown that the electric moment of water is $(1{\cdot}70\pm0{\cdot}06)\times10^{-18}$. Since the simple alcohols and phenols show values of $1{\cdot}63$—$1{\cdot}66\times10^{-18}$, it is concluded that the water molecule is typically dipolar.

R. A. MORTON.

Model of the triatomic molecules of water and carbon dioxide. F. J. VON WISNIEWSKI (Z. Physik, 1928, **47**, 567—588).—A model for triatomic molecules is described and applied to water and carbon dioxide. The three positive ions are supposed to lie in a straight line (called the axis of the molecule) equidistant from each other. The electrons rotate in circular orbits in a common plane which is perpendicular to the axis of the molecule, and passes through the middle ion, which is the common centre of the orbits. The distance of the electrons measured radially from the common centre will be 120° as the electrons are distributed symmetrically. The moment of inertia, J, of this model is calculated, assuming that different masses are associated with each ion. The result is then applied to water vapour. There can be two kinds of water molecule. (1) a symmetrical molecule in which the ions are arranged in the order H–O–H along the axis of the molecule, and (2) an unsymmetrical molecule in which the ions are in the order H–H–O. The moments of inertia, J_{HHO} and J_{HOH}, for the two molecules, are calculated using the expression previously obtained, and their ratio $J_{HHO}/J_{HOH}=\omega_{HOH}/\omega_{HHO}$ is found to be 2·25. This agrees very well with the observations of Hettner on the absorption spectrum of water vapour which show the existence of two different angular velocities the ratio of which is 2·3. The absolute values of ω_{HOH}, ω_{HHO}, J_{HOH}, and J_{HHO} are calculated by obtaining d, the length of the axis of the molecule, from an equation for the dielectric constant of the model, which is calculated in a later part of the paper. The values so obtained agree closely with those derived experimentally by Hettner. The diamagnetic susceptibility of the molecule is also calculated using a formula derived in a later part of the paper, and this agrees fairly well with that obtained experimentally by Weiss and Piccard. The symmetrical model has no electric moment, whereas the unsymmetrical model will have some electric moment.

In applying the model to carbon dioxide the distance between the ions at the ends of the axis is first calculated by two methods: (1) from the value of the dielectric constant, (2) from the diamagnetic susceptibility. The values agree well with each other. Two kinds of molecule are considered, the symmetrical (O–C–O) and the unsymmetrical (O–O–C); J is calculated for each. The ratio of the corresponding angular velocities agrees well with the results obtained by Schaefer and Philipps on the absorption bands of carbon dioxide. The rest of the paper is devoted to the calculation of the dielectric constant, ε, and the diamagnetic susceptibility, χ, triatomic molecules assuming the above model. The results obtained are $\varepsilon=1+5{\cdot}06\times10^{10}d^3$, and $\chi=-1{\cdot}70\times10^6d^2$, where d is the distance of the ions lying at the ends of the axis of the molecule from each other.

A. J. MEE.

Fundamental frequencies, interatomic forces, and molecular properties. J. R. BATES and D. H. ANDREWS (Proc. Nat. Acad. Sci., 1928, **14**, 124—130).—Theoretical. Assuming that a non-polar molecule acts as an harmonic oscillator, the displacement at which the potential energy of the oscillator equals the heat of linking is found to have the same value for all non-polar linkings.

W. E. DOWNEY.

Existence of zero-point energy in the rock salt lattice by an X-ray diffraction method. R. W. JAMES, I. WALLER, and D. R. HARTREE (Proc. Roy. Soc., 1928, A, **118**, 334—350).—Within certain limits of frequency, the atomic scattering curve (giving F as a function of $\sin\theta/\lambda$, λ being the wave-length of the radiation employed and 2θ the angle of scattering) of an atom for X-radiation can be calculated by assuming that every element of charge scatters according to the classical laws. The F curves calculated from the Schrödinger distribution of charge for the ions of sodium and chlorine, obtained theoretically by an approximate method, are compared with the experimental values of F obtained from an investigation of the temperature factor of X-ray reflexion from rock salt (this vol., 225). The F-curves so calculated are in very close agreement with the experimental curves, if it is assumed that the crystal

possesses zero-point energy of half a quantum per degree of freedom, as proposed by Planck. For both sodium and chlorine the observed curve is higher than the calculated one for small values of θ. For somewhat higher angles the observed curve falls below the calculated one, but crosses it again and lies slightly above it for values of sin θ/λ greater than 0·9. The difference between the *F*-curves with and without zero-point energy is very considerable, especially for large angles of scattering, since the mean amplitudes of vibration of the atoms at the absolute zero are somewhat greater than the radii of the regions within which the density distributions of the *K*-electrons are concentrated, and for high angles of scattering the form of the *F*-curves depends almost entirely on the *K*-electrons. L. L. BIRCUMSHAW.

Analysis of crystal structure by means of Röntgen rays. N. H. KOLKMEIJER (Chem. Weekblad, 1928, **25**, 175—183).—An account of the standard method of determining cell structure and dimensions from the reflexion angles and intensities, illustrated by reference to the elements lithium and copper and the compounds sodium chloride and iron pyrites. S. I. LEVY.

Crystal structure of beryllium sulphate tetrahydrate. R. FRICKE and L. HAVESTADT (Z. anorg. Chem., 1928, **170**, 35—41).—The salt $BeSO_4,4H_2O$ crystallises in the tetragonal holohedral class. The elementary cell is space-centred, and contains 4 molecules of the hydrate; the lengths of its edges are: $a=b=8{\cdot}083$, $c=10{\cdot}75$ Å. The space-group is probably D_{4h}^{18}. R. CUTHILL.

Study of micas (fluoride-free) by means of X-rays. C. MAUGUIN (Compt. rend., 1928, **186**, 879—881).—*X*-Ray examination of micas has shown them to be made up of elementary leaflets (clinorhombic prisms), 10 Å. thick. In muscovite and margarite the leaflets occur in pairs which are identical, and in biotite the lattice structure is triple that of the elementary micas. Calculations of the weights of the component elements from the density, the percentage composition, and the dimensions of the lattice have shown that 12 atoms of oxygen (the only electronegative element) are always present. They probably always form the same scaffolding in which the atoms of electropositive elements (which occur in varying and often fractional numbers) are distributed at varying intervals. J. GRANT.

Crystal structure of potassium. E. POSNJAK (J. Physical Chem., 1928, **32**, 354—359).—Contrary to the experience of former investigators (Hull, Physical Rev., 1917, [ii], **10**, 661; McKeehan, A., 1922, ii, 709), normal *X*-ray diffraction effects have been obtained from rotating samples of potassium prepared in sealed capillary tubes. Potassium appears to be body-centred cubic, the unit cube containing two atoms, $a=5{\cdot}333\pm0{\cdot}005$ Å.; $d_{calc.}$ is 0·851. In agreement with earlier determination, the lengths of the edges of unit cubes of lithium and sodium were found to be 3·51 and 4·30 Å., respectively. The failure to obtain definite diffraction patterns is attributed to the formation of films of moisture or oxide on the metal, or to the action of the metal on the glass used. L. S. THEOBALD.

Crystal structure of potassium hydroxystannate, $K_2Sn(OH)_6$. R. W. G. WYCKOFF (Amer. J. Sci., 1928, [v], **15**, 297—302).—Potassium hydroxystannate is of the same chemical type as potassium chloroplatinate, but possesses rhombohedral symmetry. The analysis of Laue photographs shows the atomic arrangement of potassium hydroxystannate to be a distortion of that of potassium chloroplatinate. The distortion takes the form of compression along a threefold axis. W. E. DOWNEY.

Space-lattice analysis of potassium sulphate [potassium chromate] and potassium selenate. (FRL.) E. KOCH-HOLM and N. SCHÖNFELDT (Wiss. Veröff. Siemens-Konz., 1927, **6**, 177—187).—The values of *J*, calculated from the measurements made, for the *a*-, *b*-, and *c*-axes, respectively, are: for potassium sulphate, 7·50, 7·45, and 7·60; for potassium chromate, 10·25, 10·30, and 10·40, and for potassium selenate, 5·28, 5·88, and 6·02 Å. The unit cell contains in each case 4 molecules, and the three substances have the same unit structure, probably B_h^{16}. S. I. LEVY.

Arrangements of the micro-crystals in zinc and sodium obtained by sublimation. T. YAMAMOTO (Mem. Coll. Sci. Kyoto, 1928, **11**, 39—41).—When zinc and sodium are sublimed those portions which condense in a region of comparatively high temperature appear to be perfect crystals when examined under the microscope. By *X*-ray examination, however, they have been shown to be composed of irregular aggregates of micro-crystals containing several fragments of a fibrous structure. Those portions condensing in a region of low temperature form a so-called amorphous powder which, on *X*-ray investigation, however, does not appear to be amorphous but to consist of an irregular aggregate of micro-crystals. The crystalline fragments are generally larger in zinc than in cadmium. M. S. BURR.

Structure of artificial ultramarines. III. Silver and alkali silver ultramarines which are derivatives of Guimet's ultramarine-blue with high silica content, and mixed alkali ultramarines and *n*-butyl silver ultramarine. F. M. JAEGER and F. A. VAN MELLE (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 885—904; cf. A., 1927, 715).—When ultramarine is heated with silver nitrate solution in a sealed tube at 120—130°, liberation of silica, alumina, and sulphur accompanies the reaction and the composition of the silver ultramarine obtained is probably best represented by $Ag_6Al_6Si_6O_{30}S_3$, whilst that obtained by heating with ammoniacal silver chloride has the composition $Ag_4Na_2Al_6Si_6O_{30}S_3$. When the fully-substituted silver ultramarine is boiled for 50 hrs. with 20 equivalents of lithium, sodium, potassium, rubidium, or cæsium chloride, or is heated in a sealed tube for 50 hrs. at 130° with sodium, potassium, ammonium, or rubidium chloride or cæsium iodide, the velocity of replacement of the silver is most rapid, and the degree of displacement most complete, in the case of lithium, and decreases in the order given, *i.e.*, with increasing at. wt. Moreover, with equimolecular concentration of salt solutions, other conditions being unchanged, a greater amount of substitution of silver occurs with

the iodides than with the chlorides (with the possible exception of cæsium) and is more nearly complete the greater is the concentration of the salt solution. The compositions of the mixtures obtained under varying conditions have been determined. Thus the yield of $Na_6Al_6Si_6O_{30}S_3$ is increased from 67·5 to 88·5% by doubling the concentration of the sodium iodide solution. These results prove that, contrary to the conclusion of Heumann (A., 1880, 367), there is no upper limit to the degree of substitution of silver by sodium, but an equilibrium, depending on the concentration of the salt solution and other conditions, is established. An examination of the *X*-ray powder spectrograms of the various products shows that the introduction of increasing quantities of lithium in place of silver decreases the value of the grating constant a_0, whilst substitution of lithium by sodium, potassium, ammonium, rubidium, or cæsium causes an increase, the magnitude of which increases in the order given. The relative intensities of the diffraction images are also modified by alkali substitution, but no clear relationship could be established. These conclusions are confirmed by the composition of mixtures obtained when silver ultramarines are fused with 30—40 equivalents of alkali iodides, the amount of silver substitution which occurs depending on the conditions. The colour of the resulting product is always blue, irrespective of the colour of the original silver ultramarine. In a similar manner mixed alkali ultramarines and derivatives of calcium, strontium, barium, zinc, and manganese are also obtained, the colour of the latter series, however, being green, grey, or even white. Similar partial substitution of the silver occurs when the original silver ultramarine is heated with methyl, ethyl, or *n*-butyl iodide. Thus on heating for 50 hrs. at 130° with *n*-butyl iodide, a dull green ultramarine (38·6% Ag) is obtained, which by repetition of the process is converted into greenish-grey *di-n-butyl silver ultramarine*, $Bu_2Ag_4Al_6Si_6O_{30}S_3$. This, if further heated with five times the theoretical quantity of butyl iodide for 50 hrs. at 160°, yields *penta-n-butyl silver ultramarine*, $Bu_5AgAl_6Si_6O_{30}S_3$, without any change in the general structure taking place.

J. W. Baker.

Crystal form and crystallographic and mineralogical properties of the double salt $ZnI_2,KI,2H_2O$. V. Stanicu and O. Voicu (Bul. Soc. Stiinte Cluj, 1927, 3, 244—249; Chem. Zentr., 1927, ii, 2171).—The salt is orthorhombic (prismatic and domatic types), $a:b:c=0·703:1:0·524$; n 1·792, d_{21}^{21} 3·813, hardness $2\frac{1}{2}$. It exhibits strong positive double refraction. A. A. Eldridge.

X-Ray analysis and crystal structure of cadmium–silver alloys. II. G. Natta and M. Freri (Atti R. Accad. Lincei, 1927, [vi], 6, 505—511; cf. this vol., 223).—The β-phase undergoes a second transformation when cooled slowly below 200° and forms a mixture of crystals of the α- and γ-phases. For the γ-phase (54—64·1 at.-% Cd) a cubic structure appears probable with an elementary cell containing one molecule of Ag_2Cd_3 and $a=4·70$ Å. Many lines were obtained which do not agree with this structure and it was not possible to apply the more accurate Laue and rotating crystal methods in this case. It is shown, however, that the silver–cadmium alloys have a great similarity to those of copper and zinc, and from a comparison of the two sets of alloys the silver–cadmium γ-phase probably has a cubic lattice with a unit cell of length 9·99 Å. The δ- and ε-phases (66·1—89·6 at.-% Cd) have a hexagonal lattice with axial ratio $c/a=1·58$, the side of the unit cell varying regularly from 3·04 to 3·09 Å. The η-phase (95% Cd) has the same structure as pure cadmium and consists of solid solutions of silver in the cadmium lattice.

O. J. Walker.

Calculation of the energy and the parameter of a lattice of the corundum type. V. Schmaeling (Z. Physik, 1928, 47, 723—731).—Mathematical.

W. E. Downey.

Form of the carbon atom in crystal structure. I. E. Knaggs (Nature, 1928, 121, 616—617).—The space-group of pentaerythritol tetra-acetate is C_{4}^{4}; the results of Gerstacker, Moller, and Reis (Z. Krist., 1928, 66, 355) are criticised. The following values are recorded: a 11·98 Å.; c 5·47 Å.; d 1·273.

A. A. Eldridge.

Structure analyses in the crystalline carbon series. (Frl.) E. Koch-Holm (Wiss. Veroff. Siemens-Konz., 1927, 6, 188—201).—The structure of various crystalline preparations of carbon, formed by the decomposition of illuminating gas caused to impinge on inert surfaces maintained at definite temperatures ranging from 1200° to 2700°, was examined by *X*-ray spectrum analysis, and in each case the space-lattice of graphite was identified. Measurement of particle size showed an extension in the direction (111) increasing from the value 45 Å. for ordinary carbon to the particle size for graphite; the extension in the direction (001) is less. The hardness throughout the series shows a maximum at the particle size of 9·0 μμ. S. I. Levy.

Influence of carbamide on the crystal habit of sodium chloride. F. Gille and K. Spangenberg (Z. Krist., 1927, 65, 204—250; Chem. Zentr., 1927, ii, 406).—It is considered that the fall in conductivity on addition of carbamide to sodium chloride solution is not due only to increased viscosity, but that double salts must be formed in solution. The velocity of growth of the single faces has now been determined. In glycerol solution the cubic is the final form. The double salt, $NaCl,CO(NH_2)_2,H_2O$, is leafy, with rhombic symmetry and small axial angle; n_α 1·479, n_β 1·485, n_γ 1·543. A. A. Eldridge.

X-Ray spectra of organic substances in the solid and the liquid state. R. O. Herzog and W. Jancke (Z. Physik, 1927, 45, 749).—Acknowledgment is made of the work of Stewart, Morrow, and Skinner which was omitted from the authors' recent paper (A., 1927, 1130). R. W. Lunt.

X-Ray diagrams of liquids, and the shape and arrangement of the molecules in the liquid state. J. R. Katz (Z. angew. Chem., 1928, 41, 329—340; cf. this vol., 222).—To ascertain the origin of the plurality of "amorphous rings" in the *X*-ray diagrams of certain liquids, organic compounds with molecules of a known form—either that of a disc or that of a rod—have been examined. Quinoline, and similar compounds with molecules con-

sisting of two coupled rings, also numerous benzene derivatives, give two, sometimes three, rings, the relative intensity of the second (outer) ring increasing with the introduction of side-chains. The diameter of the innermost ring varies from compound to compound, but with benzene derivatives the value calculated from it for the distance between the centres of adjacent molecules deviates more and more from that calculated from the molecular volume as side-chains are introduced. With every compound, however, the diameter of the outer ring is fairly constant at about $3{\cdot}6_5$ Å., which must therefore be assumed to correspond with some magnitude common to all the molecules. The most probable assumption is that either the thickness of the molecules is involved, or else the distance between the molecules, taken as disc-shaped, measured from centre to centre of the discs in the direction of their thickness. Benzene itself gives only one ring, which is surrounded by a halo with a sharp edge having a diameter of about 3·0 Å., which perhaps indicates that the thickness of the ring is brought up to $3{\cdot}6_5$ with substituents. On complete hydrogenation of the molecules with two coupled rings, the second ring in the diagram disappears. In the reduced rings, the carbon atoms will no longer lie in the one plane, but, particularly with the larger rings, will be arranged in a zigzag, so that the thickness of the disc, in so far as the molecule may still be regarded as disc-shaped, may be expected to show an increase, tending, however, to a limit, with increase in the number of atoms in the ring. The diagram of partly reduced compounds frequently consists of a ring with a halo, this representing the transition between a system of two rings and a single ring. The results here, however, are also in part dependent on the position of the remaining double linkings, and their effect on the rigidity of the molecule. Similar relations prevail in the reduction of benzene derivatives. The cyclic ketones with more than 5 carbon atoms give a two-ring diagram. With increase in the number of carbon atoms, the intensity of the outer ring becomes greater, and with more than 12—13 carbon atoms exceeds that of the inner ring; at the same time, the diameter increases, until, with more than 15—16 carbon atoms, it assumes a stationary value. With aliphatic alcohols, acids, and aldehydes with unbranched chains, on the other hand, the diameter of the outer ring remains constant, corresponding with a period of identity of 4·5 Å., as soon as the number of carbon atoms exceeds 4—6. This quantity is identified with the transverse dimension of the molecule. There is also an inner ring, the diameter of which corresponds with the length of the molecule. In this case, the period of identity is the greater the longer and the less branched is the carbon chain. The thickness of the molecule also increases with branching of the chain. With the normal amines, ketones, and paraffins, no interferences have been detected. In some instances it appears possible that, owing to association, the measured lengths of the molecules may correspond with double molecules. From the well-defined value for the length of the molecule which is in general obtained, it seems certain that the majority of the molecules of these aliphatic compounds must have a rigid form, resembling that of a straight rod. In view of the smallness of the contraction which occurs when the liquids crystallise, it is consequently necessary to suppose that the molecules are in part arranged in small groups even in the liquid state, the axes of the groups, however, not being oriented in any way. This state is closely analogous to that of certain colloidal solutions, in which the particles have the form of discs or rods, and show a pronounced tendency to range themselves parallel to each other in small groups. The fact that for liquids with approximately spherical molecules the distance between the molecules calculated from the amorphous ring of the *X*-ray diagram is in good agreement with the value calculated from the molecular volume may also point to the existence of molecular groups with perhaps a regular or hexagonal lattice in these liquids, or may be only a consequence of the limitations of space in the liquid state. The formation of groups of molecules in this way probably occurs whenever a substance with rigid molecules having the shape of rods or discs is subjected to such conditions that its volume is very small, *e.g.*, in a liquid far below its critical temperature, but what part the forces of crystallisation play in bringing about this state is uncertain. Stewart and Morrow's hypothesis that a special cybotactic state of matter is involved (A., 1927, 1015) is improbable. R. CUTHILL.

X-Ray diffraction in liquid normal paraffins. G. W. STEWART (Physical Rev., 1928, [ii], **31**, 174—179).—The ionisation-diffraction angle curves for pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane, and pentadecane show one peak only, at an angle indicating a lateral spacing of 4·63 Å. Two additional faint peaks are exhibited by pentadecane and tetradecane at angles corresponding with 2·1 and 1·23 Å. A. A. ELDRIDGE.

Crystal structures of β-benzene hexabromide and hexachloride. R. G. DICKINSON and C. BILICKE (J. Amer. Chem. Soc., 1928, **50**, 764—770).—New *X*-ray data are recorded (cf. A., 1927, 98). The data for β-benzene hexabromide are qualitatively accounted for by assigning to the bromine atoms the parameter values $x=0{\cdot}39$, $y=0{\cdot}22$, $z=0{\cdot}085$ in the general positions of the space-group T_h^6. These values are in agreement with a molecule containing a *cyclo*hexane ring of tetrahedral carbon atoms, each bromine atom being surrounded by eight others. The intensity data for the chloride are similar to, but not always identical with, those for the bromide, showing that the parameters for the two compounds cannot be very different. S. K. TWEEDY.

X-Ray examination of highly-polymerised organic substances. E. OTT (Helv. Chim. Acta, 1928, **11**, 300—323).—*X*-Ray examination of paraformaldehyde and the α-, β-, γ-, and δ-polyoxymethylenes shows that the structures are almost identical. The elementary parallelepiped is rhombic, base-centred, pseudohexagonal, and apparently contains eight $CH_2{\cdot}O$ groups. The dimensions are, $a=7{\cdot}79$, $b=4{\cdot}53$, $c=7{\cdot}02$ Å. The corresponding axial ratio is $a:b:c=1{\cdot}72:1:1{\cdot}55$. The grouping $(CH_2{\cdot}O)_4$ is of especial significance in determining the structure. The four carbon atoms are arranged along the c-axis and lie in the same plane (100) as the oxygen atoms. Macroscopic examination shows that the crystal form

is rhombic-holohedral, pseudohexagonal. Examination of the polyoxymethylene diacetates containing 8—19 CH_2·O groups shows that the length of the molecule increases by about 2 Å. with each addition of the group CH_2·O. Mie and Hengstenberg (A., 1927, 647) investigated the polyoxymethylenes and found for the dimension *c* the value 3·54 Å. The present value is held to be correct. J. S. Carter.

X-Ray study of cellulose and cellulose acetates. J. J. Trillat (Compt. rend., 1928, **186**, 859—861).—*X*-Ray crystallograms of cellulose, oxycelluloses, and hydrocelluloses are similar and show evidence of crystal structure. "Hydracelluloses" and alkali-cellulose give crystal diagrams analogous to one another, but differing from those of cellulose. Cellulose acetates show the presence of well-defined crystals in an amorphous phase, the latter increasing at the expense of the former when the more acetylated products are destroyed by hydrolysis. The structure of the haloes is dependent on the amount of acetyl radical present and changes progressively as acetylation proceeds. An hypothesis of the gel structure of the cellulose acetates is outlined, and the above method suggested for control purposes in their manufacture. J. Grant.

X-Ray investigations of rubber and related substances. P. Rosbaud (Z. Elektrochem., 1927, **33**, 511—513).—Photographs of "frozen" rubber in the unstretched state showed marked Debye–Scherrer interference rings which disappeared again on "thawing." Balata and gutta-percha gave Debye–Scherrer diagrams in the unstretched state, and in the stretched condition "fibre diagrams" in which the position of the interference lines was the same within the limits of experimental error. The value c=9·35 found agrees well with the value 9·30 Å. found by Clark with balata. The unit cell is small, and contains 2—8 molecules, although the actual size could not be determined. Raw rubber, stretched in the way described by Feuchter (B., 1926, 204; 1927, 119), showed in its *X*-ray image the most marked parallel orientation of its particles. It shows an exertion curve similar to that of stretched balata and gutta-percha. "Sol-caoutchouc," "gel-caoutchouc," and "total-caoutchouc" (cf. Pummerer, B., 1926, 597) showed marked interference spots when stretched and also when vulcanised cold and stretched. W. Clark.

Hardness of tellurium crystals. E. Schmid and G. Wassermann (Z. Physik, 1928, **46**, 653—667). —The tensile strength of large single crystals of tellurium has been determined for various orientations of the mechanical forces relative to the crystal axes. R. W. Lunt.

Deformation of crystals of β-brass. G. I. Taylor (Proc. Roy. Soc., 1928, A, **118**, 1—24; cf. Taylor and Elam, A., 1926, 997).—Compression and tensile tests have been carried out on large single crystals of β-brass, which has a structure similar to that of α-iron. The results are similar to those obtained with iron crystals in that the direction of slip is a crystal direction of type (111), whilst the plane of slip varies according to the orientation of the crystal axes relative to the direction of the principal stress. Contrary to the case of iron, however, in a certain range of orientations of the crystal axes slip occurs on a definite crystal plane of type (110). The condition determining the type of distortion which will occur in any given case is the variation in resistance to shear which takes place as the plane of slip rotates about the direction of slip. Calculation of this variation from the experimental results shows that resistance to shear is least when the plane of slip coincides with one of type (110). On either side of this position, shear stress increases linearly. This property is also possessed by the "hexagonal rod" model suggested by the author and Elam (*loc. cit.*), and by Hume-Rothery's model (cf. this vol., 111). It is shown that the hypothesis that the conditions of slipping are determined by the geometrical considerations put forward by Hume-Rothery is unsound. It is found that for β-brass, as would be expected from crystallographic symmetry, resistance to shear on a given plane differs according to the sense of the direction of slip. This has not been observed for α-iron. L. L. Bircumshaw.

Resistance change of single crystals of bismuth in a longitudinal magnetic field. G. W. Schneider (Physical Rev., 1928, [ii], **31**, 251—259).—The resistance change as a function of the orientation of the vertical crystallographic axis was investigated. A. A. Eldridge.

Linear compressibility of thirteen natural crystals. P. W. Bridgman (Amer. J. Sci., 1928, [v], **15**, 287—296; cf. *ibid.*, 1925, [v], **10**, 483).—The previously described method of measuring compressibility has been applied to thirteen natural crystals and the results obtained are discussed. W. E. Downey.

Electrical conductivity of silicon. H. J. Seemann (Physikal. Z., 1928, **29**, 94—95; cf. this vol., 226).—It is contended that Koenigsberger's theory of electrical conductivity loses its experimental support in the similar electrical behaviour of the true metals and the semi-conductors. W. E. Downey.

Electrical resistance of bismuth solidified in a magnetic field. L. Tieri and V. Ricca (Nuovo Cim., 1927, **4**, 248—251; Chem. Zentr., 1927, ii, 2267).—The results indicate that the crystals are arranged with the principal axis in the direction of the lines of force. A. A. Eldridge.

Phenomenon of saturation in the current carried by continuously irradiated crystals. W. Flechsig (Z. Physik, 1928, **46**, 788—797).—Experiments on the conductivity of continuously irradiated crystals as a function of the electric force led Gudden and Pohl (*ibid.*, 1923, **17**, 331) to suggest that in such experiments the electrons in the crystal were displaced to a distance depending on the frequency of the light, and that therefore when this distance was equal to the thickness of the crystal saturation currents would be observed. Experiments on potassium chloride crystals irradiated with monochromatic light, 4600 Å., are described which show that for crystals of different thickness the same current values are obtained for the same values of the electric force divided by the thickness of the crystal. It is shown that it follows from this that the displacement of the electrons x is related to the electric force E by x—kE, where k is a constant

which is independent of the particular crystal of potassium chloride examined. R. W. LUNT.

Electrification in gases due to friction with solid surfaces. E. PERUCCA (Z. Physik, 1928, **46**, 747—752).—Experiments are described in which electrification results from the friction between a stream of mercury vapour and an iron electrode; the conditions were chosen so that the vapour was free from droplets. It is therefore concluded that droplets play no part in the observed phenomenon. R. W. LUNT.

Electrical and luminous effects produced by rolling mercury on glass in a vacuum. M. DUFFIEUX (J. Phys. Radium, 1928, [vi], **9**, 61—70).—The effects produced by rolling mercury in an evacuated flask have been studied. A current is found to be set up between the mercury as positive pole and the glass as negative pole. At temperatures below 100° the discharge caused by this current emits the arc spectrum of mercury, but above 100° a phosphorescent vapour above the liquid emits the continuous spectrum of mercury. The mechanism of the electrification is discussed. It is found that the electrical layer which attracts the liquid is on the glass. W. E. DOWNEY.

Tribo-electricity and friction. II. Glass and solid elements. III. Solid elements and textiles. P. E. SHAW and C. S. JEX (Proc. Roy. Soc., 1928, **A**, **118**, 97—108, 108—113; cf. *ibid.*, 1926, **A**, **111**, 339).—II. By means of an arrangement designed to give constant conditions of pressure and surface, measurements have been made of the sign and amount of charge acquired when glass rods and various solid elements are rubbed together. The elements tested were of a high degree of purity, special attention being paid to surface cleanliness. The glass was cleaned by boiling in chromic or nitric acid, followed by exhaustive treatment with boiling water. The following elements never, with any type of glass surface tried, give a negative charge: carbon, cadmium, iron, lead, bismuth, silver, copper, gold, platinum, magnesium, tungsten. The elements zinc, tin, aluminium, antimony, nickel, cobalt, selenium, tellurium, arsenic, chromium, thallium, and sulphur acquire an ultimate negative charge. The initial positive charge shown is attributed to the slight acid effect residual on the glass. In the few cases tested, rubbing in a vacuum gives the same result as in the open air. Little difference in degree is found, and none in sign, between the behaviour of soda and lead glass. Evidence is given of the predominating influence on the charging of residual acid, alkali, or water films on the glass. Mercury, tested in a vacuum by a special method, shows positive charges, but becomes negative if air is introduced. Various theories of frictional electricity are discussed, and an attempt is made to apportion to each recognised source of charge its own weight in the various experiments.

III. The textiles tested were specially purified silk, cotton, and filter-paper. The arrangement of the different elements, according as they charge textiles and glass, is found to correspond closely with their chemical qualities. It is impossible to devise a simple tribo-electric series of one column to include all solids, for it is found that of three solids (A, B, C) A may be positive to B, B to C, and yet C be positive to A. Anomalies are found with the strongly electropositive metals aluminium, magnesium, chromium, nickel, cobalt, zinc, and tin, which appear in two places in the tribo-electric series. L. L. BIRCUMSHAW.

Electronic theory of metals from the point of view of Fermi's statistics. I. General, conduction, and emission phenomena. II. Thermo-electric, galvano-magnetic, and thermo-magnetic phenomena. A. SOMMERFELD (Z. Physik, 1928, **47**, 1—32, 43—60).—I. A simplified and expanded form of statistical theory is developed and applied to the phenomena of thermal and electrical conduction and to the Richardson effect.

II. Statistical theory is applied to the Thomson effect, the Peltier effect, thermo-electric power, and to the general phenomena of magnetic fields, including the Hall and Nernst effects. J. W. SMITH.

Electron emission of cold metals. W. V. HOUSTON (Z. Physik, 1928, **47**, 33—37).—It is shown that the Sommerfeld treatment of the Richardson effect (cf. preceding abstract) can explain the observed electron emission of cold metals, on the assumption that the outer field diminishes the work of splitting off of the electrons. Owing to several difficulties, which are enumerated, exact agreement of the theory with experimental data cannot yet be obtained. J. W. SMITH.

Electronic theory of metals from the point of view of Fermi's statistics, especially concerning the Volta effect. C. ECKART (Z. Physik, 1928, **47**, 38—42).—The Sommerfeld treatment is applied to a mathematical discussion of the Volta effect. J. W. SMITH.

Physical interpretation of thermo-electric emission. A. VON HIPPEL (Z. Physik, 1928, **46**, 716—724).—An attempt is made to give a physical interpretation of thermo-electric emission in terms of the ion–atom collisions taking place due to the thermal ionisation associated with the temperature of the emitting substance. R. W. LUNT.

Measurement of the contact potential between metals in a vacuum. G. MONCH (Z. Physik, 1928, **47**, 522—541).—Two new methods of measuring the contact potential between metals in a vacuum are described. The first employs a valve with a copper grid and a nickel anode; full experimental details are given. The second method makes use of the curve of electron velocity against potential obtained first with a valve with an anode of one metal, and then with an anode of the other metal. Experimental details for the measurement of the potential and anode current and for the construction of the valve are given, and curves are obtained from which the contact potentials can be obtained. The results show that the contact potential varies according as the metal is previously heated or not. In some experiments, hydrogen was led into the valve, when there was a marked difference in the type of curve obtained. The observation of Vieweg that the potential series of the elements is inverted when the metals are heated is confirmed. A. J. MEE.

Kerr and Faraday effects in gases. II. Quadratic effect. R. DE L. KRONIG (Z. Physik, 1928, **47**, 702—711; cf. this vol., 342, 343).—Mathematical. W. E. DOWNEY.

Yellow ferric hydroxide resulting from the controlled oxidation of ferrous sulphide in suspension. (MLLE.) S. VEIL (Compt. rend., 1928, **186**, 753—755; cf. A., 1926, 567).—The oxidation of a suspension of ferrous sulphide in water by a current of air yields a yellow ferric hydroxide having half the magnetisation of the brown hydroxide, but yielding an anhydride considerably more magnetic than that obtained either from the latter or from the ordinary sulphide. The magnetochemical changes during the oxidation of ordinary ferrous sulphide, therefore, are a function of the procedure followed. Warm water modifies the yellow hydroxide, producing a brown type equivalent to iron in magnetic properties and yielding an oxide less magnetic than before, whilst reprecipitation from acid solution increases the magnetism of the hydroxide and of its corresponding oxide. J. GRANT.

Magnetisability of thin films of manganese. H. FREESE (Physikal. Z., 1928, **29**, 191—197).—Manganese appears to exist in two different states; in the normal state it resembles the paramagnetic elements, and in the other state it is more akin to the ferromagnetic elements. The paramagnetic and ferromagnetic modifications show susceptibilities of the order 10×10^{-6} and 2000×10^{-6}, respectively. Weiss (A., 1910, ii, 388) and Kuh (Diss., Zurich, 1911) found that after remelting in hydrogen, manganese became partly ferromagnetic. Kuh's results are largely confirmed, but reproducible conditions for the preparation of the ferromagnetic form have so far eluded determination. In order to test the possibility of a connexion between the adsorption of hydrogen and the ferromagnetic behaviour, manganese was prepared by the methods of cathode sputtering in hydrogen, and electrolysis with simultaneous liberation of hydrogen. Prepared in either of these two ways manganese shows a normal susceptibility of the order 10^{-5}. R. A. MORTON.

Specific heat of hydrogen gas at low temperatures from the velocity of sound; a precision method of measuring the frequency of an oscillating circuit. R. E. CORNISH and E. D. EASTMAN (J. Amer. Chem. Soc., 1928, **50**, 627—652).—The specific heat of hydrogen was measured at 80—373° Abs. by determining the velocity of sound in long, wide tubes of the gas. Elaborate precautions were taken to ensure a high order of accuracy (0·5%). A rapid method of measuring the frequency of any regularly oscillating circuit with an accuracy of 1 in 10^6 is described, as well as the construction of an efficient 6 ft. thermostat suitable for use at low or moderately high temperatures. The theoretical principles involved in the calculation are discussed in detail; the characteristic equation $pv-RT+a/v$, where a is a function of T only, is adopted for hydrogen. Using Lewis' method of calculation, the energy difference between the first two rotational states of the hydrogen molecule is found to be 1060 g.-cal./mol., and the relative probabilities of these states 1 : 1·69. Incorrect application of Kirchhoff and Helmholtz's equation (which, the present authors show, agrees with experiment) for the effect of the walls of the resonating tube on the velocity of sound in the contained gas makes some of the results of Partington and Shilling too low by about 13%. The velocity of sound in dry, carbon dioxide-free air at 24° is 345·66 metres/sec., and in hydrogen at 0°, 1260·9 metres/sec. The thermal expansion of a specimen of brass was investigated between 81·7° and 273·1° Abs. The variation in density of dried air described by Stock and Ritter (A., 1926, 669) is shown to be non-existent. S. K. TWEEDY.

Specific heats of gases as pure temperature functions. A. BATSCHINSKI (Z. Physik, 1927, **45**, 892—894).—The specific heats of a gas for which the equation of state $pv=RT$ is assumed valid are related to the gas constant by the equation $c_p-c_v+p(dc_p/dp)_v-v(dc_v/dv)_p=AR$, where A is a constant. When c_p and c_v are functions of temperature only, the equation of state becomes $T=\alpha pv+\beta p+\gamma v+\delta$, where α, β, γ, and δ are arbitrary constants, and $c_p-c_v=AT/\alpha T+\beta\gamma-\alpha\delta$. By choosing values so that $\alpha\delta=\beta\gamma$, the following relationships are derived: $c_p-c_v=A/\alpha$ and $T/\alpha=(p+\gamma/\alpha)(v+\beta/\alpha)$. The latter expression is identical in form with the equation of state observed by Tammann for a series of liquids at 0—50° and at pressures from 10^3 to 3×10^3 atm., $CT=(p+K)(v-b)$; by identifying α with $1/C$, c_p+c_v should have a constant value of AC. It is shown from Tammann's data that this is roughly true. By extending this analysis a solution has been obtained for the equation of state for which c_p-c_v has a constant value AR. R. W. LUNT.

Specific heats of ferromagnetic substances. L. F. BATES (Proc. Roy. Soc., 1928, **A**, **117**, 680—691).—An investigation has been made of the thermal and magnetic behaviour of the ferromagnetic compound manganese arsenide, which has a critical point at about 45°. The material was prepared by Hilpert and Dieckmann's method (A., 1911, ii, 985, 1090), and found to consist almost exactly of equal parts of manganese and arsenic. To insure an extremely slow supply of heat to the substance in the thermal measurements, a modification of the Nernst–Eucken method was employed, and the specific heat of the compound was found over a series of small temperature intervals. The specific heat rises to a maximum at about 42·2°, then falls rapidly to a slightly defined minimum in the neighbourhood of 46°, after which a slow rise with rising temperature is observed. An examination of the magnetic induction of the substance when placed in a strong magnetic field shows that a marked resemblance exists between the curves giving the variation of the specific heat and magnetic induction, respectively, with temperature. The curves in general have many features in common with those obtained by Sucksmith and Potter for nickel and Heusler's alloy (A., 1926, 893). It is considered that magnetic phenomena in the region of the critical point are evidence of a transformation which in this case appears to be complete at that temperature, but which, in general, may reach only a particular stage at the critical point. L. L. BIRCUMSHAW.

Exact determination of the specific heat of solid substances between 0° and 1625°. I. Method and apparatus. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 905—920).—A detailed description is given of the apparatus used in the exact determination of specific heats between 0° and 1625° to an accuracy of at least 0·1%. The jacket temperature can be maintained at 20°±0·001° over prolonged periods, and the thermo-electric system employed makes it possible to determine the block aluminium calorimeter temperature differences of 0·0001° with absolute certainty. Initial heating of the substance, the specific heat of which is to be determined, is carried out in an electric resistance furnace which is so perfectly insulated that even at 1625° no radiation of heat to the calorimeter occurs. Electrical and mechanical devices are used by means of which the heated metal can be dropped directly from the furnace into the calorimeter within 0·05—0·1 sec., and complete heat interchange with the calorimeter occurs within a few seconds. The cooling constant and the water equivalent of the calorimeter are accurately determined. J. W. BAKER.

Specific heat and molecular pressure of liquids. K. M. STACHORSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 163—170).—Expressions for internal pressure of liquids were derived from Dupre's equation for molecular pressures (Ann. Chim. Physique, 1864, [iv], **2**, 185; 1865, [iv], **6**, 274) and the expression for the difference of molecular specific heat at constant pressure and constant volume. Values for molecular pressures of different liquids as calculated from these formulæ and from surface-tension values agreed fairly well. For associated liquids, with the exception of water, the values of internal pressures were of the same order as for non-associated liquids, being, thus, in disagreement with the existing conception of high internal pressures of associated liquids. A. RATCLIFFE.

Variation of the specific heat of aniline with temperature using the continuous-flow electric method. H. R. LANG (Proc. Roy. Soc., 1928, **A**, **118**, 138—156).—Full experimental details are given of measurements of the specific heat of aniline by the continuous-flow electric method over short ranges of temperature between 5° and 75°. Special precautions were taken to obtain pure, dry aniline, and corrections were applied for the minute water content of the samples. The rate of change of the specific heat with temperature over the range investigated was found to increase with rising temperature. Below 5°, the results are uncertain owing to the high viscosity of aniline at that temperature. Between 5° and 60°, the specific heat is represented in terms of the 20° g.-cal. per 1° by the formula $s=0{\cdot}4951+2{\cdot}87\times10^{-4}(t-20)+2{\cdot}7\times10^{-6}(t-20)^2+6{\cdot}1\times10^{-8}(t-20)^3$. The results are compared with those of previous investigators. L. L. BIRCUMSHAW.

Apparatus for determining rise in b. p. F. RUSCH (Ann. Physik, 1928, [iv], **85**, 647—648).—A simple spraying contrivance is inserted in a test-tube and two streams of boiling liquid are projected against the bulb of a Beckmann thermometer. R. A. MORTON.

M. p. of calomel. O. RUFF and R. SCHNEIDER (Z. anorg. Chem., 1928, **170**, 42—44).—The f. p. of mercurous chloride heated for varying periods at temperatures a little above its m. p. so as to cause a partial decomposition into mercuric chloride and mercury has been determined. By extrapolation of the curve connecting the f. p. with the amount of mercuric chloride present, as determined by subsequent analysis, the m. p. of pure mercurous chloride has then been found to be about 543°. R. CUTHILL.

Two different liquid states of helium. W. H. KEESOM and M. WOLFKE (Compt. rend., 1927, **185**, 1465—1467; cf. A., 1926, 568).—It is concluded from the present and from previous results that liquid helium can exist in two different states. The transformation occurs at 2·3° Abs. under a vapour pressure of 38 mm., heat being absorbed when the form stable at high temperatures is the end-product. This form has the higher density and surface tension and the lower heat of vaporisation. The temperature of the triple point of the gas and the two liquid phases of helium is of the same order as that of the solid, liquid, and vapour phases of most other substances. J. GRANT.

Chemical constant of hydrogen vapour and the failure of Nernst's heat theorem. R. H. FOWLER (Proc. Roy. Soc., 1928, **A**, **118**, 52—60).—Dennison's work on the specific heats of gaseous hydrogen at low temperatures (A., 1927, 817) is applied to a study of the vapour-pressure equation of hydrogen and of its chemical constant as determined by gaseous equilibria. The vapour-pressure equation can be accounted for satisfactorily if both antisymmetrical and symmetrical molecules (*i.e.*, molecules for which the rotational quantum numbers are odd and even, respectively) are present indifferently in the vapour and condensed phases. It follows from this, however, that the weight of the hydrogen molecule in the crystal form cannot be unity, but must be 9 and 1 for the lowest states of the antisymmetrical and symmetrical molecules, respectively. The constant in the vapour-pressure equation is therefore smaller than the chemical constant of gaseous hydrogen by 0·36. This result is in agreement with Eucken's work (A., 1925, ii, 97). It is concluded that Nernst's heat theorem is inapplicable to hydrogen reactions as ordinarily conducted, although it would probably be true of such reactions if they were conducted at extravagantly slow rates, so that the hydrogen, instead of being in a state of metastable equilibrium, was in its true equilibrium state. L. L. BIRCUMSHAW.

Effect of intensive drying on the vapour pressure and vapour density of ammonium chloride. W. H. RODEBUSH and J. C. MICHALEK (Proc. Nat. Acad. Sci., 1928, **14**, 131—132).—Polemical against Smits (A., 1927, 819). W. E. DOWNEY.

Budde effect with a mixture of bromine vapour and air. E. BROWN and D. L. CHAPMAN (J.C.S., 1928, 560—564; cf. Ludlam, A., 1925, ii, 470; Lewis and Rideal, A., 1926, 484).—Almost complete drying (exposure to phosphorus pentoxide for 396 days) of a mixture of bromine vapour and air does not inhibit the Budde effect. C. W. GIBBY.

Validity of gas equations. IV. W. Herz (Z. Elektrochem., 1928, **34**, 68—69).—The saturation pressures p and densities d of the saturated vapours of various substances at the temperatures $2/3T_c$, $9/10T_c$, and T_c, where T_c is the critical temperature, are tabulated. The value of the ratio p/d is least at the critical temperature and about 2—2·5 times as great at $9/10T_c$. The values for $9/10T_c$ and $2/3T_c$ are approximately equal. Values of p, d, and p/d for ether, methyl alcohol, and chlorine at various temperatures up to T_c are tabulated and it is shown that as the temperature falls from T_c the value of p/d increases rapidly, is maximal, and then decreases slowly. Over a considerable range of temperature the value of p/d is approximately constant.

J. S. Carter.

Internal pressure of liquid carbon dioxide from solubility measurements [of naphthalene and iodine]. E. L. Quinn (J. Amer. Chem. Soc., 1928, **50**, 672—681).—A method of determining solubilities of solids in liquids of very high vapour pressures is described and is used to measure the solubility of iodine and of naphthalene in liquid carbon dioxide between 25° and —21°. The densities of the solutions were determined in a special type of pyknometer. The iodine solution is violet, indicating the absence of solvation. The solvent has an internal pressure lower than that of the common solvents.

S. K. Tweedy.

Absolute zero of the externally controllable entropy and internal energy of a substance and a mixture. R. D. Kleeman (Phil. Mag., 1928, [vii], **5**, 668).—An alternative establishment of the theorem previously deduced (A., 1927, 520) that the specific heat of a substance at constant volume is positive.

A. E. Mitchell.

Theory of the liquid state. E. N. Gapon (J. Russ. Phys. Chem. Soc., 1928, **60**, 249—264).—Expressions for the internal pressure of a liquid were derived based on the assumption of proportionality of the total surface energy and internal pressure. From these equations relationships between contraction and expansion and between surface tension and contraction of liquids were established.

A. Ratcliffe.

Viscosity of liquid metals and alloys. II, III. L. Losana (Notiz. chim.-ind., 1927, **2**, 63—66, 121—125; Chem. Zentr., 1927, ii, 367).—The viscosities of the following metals and alloys have been determined: zinc, lead, cadmium, tin, lead (0—100%)-tin, antimony (1—20%)-tin, copper (1—10%)-tin, tin–copper–antimony, tin (5—30%)-zinc, aluminium (5—50%)-zinc, silicon (0·5—35%)-aluminium, iron (0·5—5%)-aluminium, tin (1—8%)-aluminium, zinc (1—5%)-aluminium, copper (1—12%)-aluminium, magnesium (2—80%)-aluminium, aluminium–copper–silicon, aluminium–silicon–magnesium, aluminium–copper–magnesium, aluminium–copper–zinc, copper–tin–lead, copper–tin–zinc, copper–zinc, and copper–zinc–manganese–iron–nickel.

A. A. Eldridge.

Approximate theories of diffusion phenomena. S. Chapman (Phil. Mag., 1928, [vii], **5**, 630—636).—The original diffusion theory of Meyer and its several modifications are discussed and their inability to explain such phenomena as the Soret effect is demonstrated. It is suggested that the correct theory of the various diffusion phenomena depends on the determination of the velocity distribution function for the particles which in non-uniform states deviates slightly from the Maxwellian form. This theory establishes the expectation that a thermal gradient in an otherwise uniform fluid will set up a diffusive flow. No easy approximate theory of thermal diffusion has been deduced.

A. E. Mitchell.

Cryoscopic evidence of compound formation in mixtures of organic liquids. W. M. Madgin, J. B. Peel, and H. V. A. Briscoe (J.C.S., 1928, 707—711).—Evidence is adduced to show that certain binary liquid mixtures contain compounds. Separate solutions of the two liquids in a solvent (benzene, nitrobenzene, or bromoform) are prepared so that they exhibit the same depression of f. p. If, on admixture, the depression of f. p. is less than in the separate solutions, clear evidence, independent of theories or calculations, is obtained that the solutes have combined. In general, a rise of temperature occurs on mixing those liquids where it can be shown that combination has taken place. It has been shown that, even in comparatively dilute solutions, compounds are formed by the following pairs of liquids: *o*-chlorophenol – pyridine; *o*-chlorophenol – aniline; *o*-chlorophenol–ether; chloroform–ether; chloroform–acetone; bromoform–acetone; acetone–carbon disulphide.

E. S. Hedges.

Binary liquid mixtures and so-called molecular compounds. G. Weissenberger (Metallbörse, 1927, **17**, 708; Chem. Zentr., 1927, ii, 2144).—The vapour-pressure curve of a binary liquid mixture shows considerable deviations from linearity. Positive deviations occur if the two kinds of molecules are mutually repellent, and negative deviations when they attract one another.

A. A. Eldridge.

Hydrogen. VII. Density, refractivity, and absorption of light of concentrated aqueous solutions of hydrogen halides. G. F. Hüttig and H. Kükenthal (Z. Elektrochem., 1928, **34**, 14—18; cf. A., 1927, 529).—In continuation of similar work on solutions of lithium halides (A., 1925, ii, 963), densities and refractivities of solutions of hydrochloric acid and hydrobromic acid at various concentrations have been determined, and coefficients of extinction for hydrochloric acid solutions measured in the region λ 2300—2800. Further data for the densities, molecular contractions, and refractivities of solutions of lithium halides are also recorded.

H. J. T. Ellingham.

Solubility of silver in mercury. A. A. Sunier and C. B. Hess (J. Amer. Chem. Soc., 1928, **50**, 662—668).—The solubility of silver in mercury is recorded up to 200°; it is given by $\log N = -1074{\cdot}2/T+0{\cdot}501$, where N represents the number of atoms of silver per 100 total atoms. The results agree with those of Joyner (J.C.S., 1911, 99, 195). A solubility tube is described which permits sampling without removing any of the equilibrium mixture from the thermostat or introducing sampling devices.

S. K. Tweedy.

[Solubility of natural calcium sulphate hemihydrate.] P. P. Budnikov (Z. anorg. Chem., 1928,

170, 111).—It is suggested that Sworykin's "natural hemihydrate" (A., 1927, 820) was really anhydrite partly transformed into the dihydrate.

R. CUTHILL.

[**Solubility of natural calcium sulphate hemihydrate.**] A. SWORYKIN (Z. anorg. Chem., 1928, **170**, 112).—Budnikov's suggestion (cf. preceding abstract) is refuted. R. CUTHILL.

Solubility of chromium anhydride in aqueous solutions of sulphuric acid. A. V. RAKOVSKI and D. TARASENKOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 7—12).—The solubility of chromium anhydride was determined in water and in aqueous solutions of sulphuric acid at temperatures from 0° to 100°. Metastable systems can be readily realised. The smooth solubility curves in the region of high sulphur trioxide content suggest the existence of only one solid phase. A. RATCLIFFE.

Sorption of water vapour by activated charcoals. I. Apparatus, technique, and nature of charcoals used. P. G. T. HAND and D. O. SHIELS (J. Physical Chem., 1928, **32**, 441—455).—The apparatus and technique used for experiments on the sorption and desorption of water vapour by charcoal by a static and a dynamic method are described. Data relating to the charcoals used are given.

L. S. THEOBALD.

Adsorption of iodine by carbon from certain organic solvents. TRIVIDIC (Compt. rend., 1928, **186**, 865—867).—It is shown that carbon activated by zinc chloride adsorbs iodine from methyl, ethyl, and *iso*amyl alcohol, benzene, toluene, *o*-, *m*-, and *p*-xylene, chloroform, carbon tetrachloride, and carbon disulphide, in accordance with Freundlich's rule (cf. Davis, J.C.S., 1907, **91**, 1666). J. GRANT.

Adsorption of vapours by carbon and silica gel. J. TRAUBE and S. BIRUTOWITSCH (Kolloid-Z., 1928, **44**, 233—239).—Measurements have been made of the adsorption of the vapours of a number of organic liquids by "carboraffin" and by silica gel, dry air saturated with the vapour being passed over the adsorbent. The results obtained are in agreement with Langmuir's idea of a unimolecular adsorbed layer. E. S. HEDGES.

Adsorption from concentrated solutions and the adsorption of liquids. R. DEFAY (Bull. Soc. chim. Belg., 1928, **37**, 63—87).—An experimental study of the problem which Ostwald and Izaguirre (A., 1922, ii, 480) have worked out theoretically has been made for charcoal and aqueous solutions of acetic acid. The results obtained are in accord with the theory, but the author criticises the assumption that the solute and solvent are adsorbed independently of each other. He shows that the results may be explained equally well if this assumption is not made and Schmidt's idea of the adsorption maximum is used.

A method has been devised for measuring the adsorption of a liquid on a solid and has been applied to the measurement of the adsorption of water on kieselguhr. F. J. WILKINS.

Adsorption of organic compounds on hydrated oxides and fuller's earth. D. P. GRETTIE and R. J. WILLIAMS (J. Amer. Chem. Soc., 1928, **50**, 668—672).—The adsorption from $0{\cdot}01M$-solution of eighteen organic compounds (alkaloids, amino-compounds, dextrose) by hydrated oxides of silicon, iron, and aluminium and by fuller's earth was investigated. The adsorption by silica is roughly proportional to the basic strengths of the organic compounds, and by alumina, to the acidic strengths of the compounds, although in the latter case piperidine is also adsorbed very appreciably. Fuller's earth behaves somewhat similarly to silica; it adsorbs eight times as much caffeine as the latter. Iron oxide adsorbs irregularly, perhaps because of impurities; strongest adsorption occurs in the case of acidic substances. A second sample of iron oxide, prepared differently, gave entirely different, irregular results.

S. K. TWEEDY.

***X*-Ray method for the investigation of substances adsorbed on charcoals.** O. RUFF, F. EBERT, and F. LUFT (Z. anorg. Chem., 1928, **170**, 49—61).—Attempts to obtain *X*-ray interference diagrams with crystalline substances adsorbed from aqueous solution on to charcoal have in general been unsuccessful, animal charcoal, ordinary wood charcoal, and activated wood charcoals giving qualitatively similar results. It thus appears that in these cases the thickness of the adsorbed layer is not sufficient to produce interference of *X*-rays. Mercuric chloride, silver nitrate, and auric chloride, however, adsorbed on "supranorit" cause interference, but the lines which appear correspond, not with these salts, but with mercurous chloride, metallic silver, and metallic gold, respectively. The same reduction occurs, although in a smaller degree, even when the charcoal is most carefully purified, so that it is to be regarded as a property of the carbon itself. Whether reduction will take place or not actually depends on the electrochemical nature of the metal involved; copper sulphate, or even potassium aurocyanide, is not reduced. If the acidity of the solution from which adsorption takes place exceeds a certain value, none of the salts is reduced. For carbon saturated with adsorbed mercuric chloride, it is calculated that the surface of the carbon, assumed to be uniformly covered with the salt, exceeds 60 sq. metres/g., and each molecule of chloride is held by at least 11 carbon atoms. R. CUTHILL.

Adsorption of dyes in aqueous solution by carbon, silica gel, and earths. S. BIRUTOWITSCH (Kolloid-Z., 1928, **44**, 239—242).—The adsorption of methylene-blue, night-blue, rhodamine, Congo-red, azo-blue, and eosin was studied, using different forms of carbon, silica gel, and earth as adsorbents. For all the dyes the forms of carbon retain the same order, viz., norit 4X, carboraffin, Merck's animal charcoal. The remaining adsorbents vary in adsorptive power with the nature of the dye, the chief factor being the acid or basic character of the dye, and attention is directed to the importance of the polar character of the adsorbent. E. S. HEDGES.

Rôle of phosphates in the taking up of dyes by mordants. C. E. WHITE and N. E. GORDON (J. Physical Chem., 1928, **32**, 380—400).—The effect of potassium dihydrogen phosphate on the adsorption of crystal-violet and orange-II by gels of silica,

alumina, ferric oxide, and chromium oxide has been investigated. The phosphate increases the adsorption of the basic dye, crystal-violet, by the gel, but with the acid dye, adsorption is decreased. Silica gel was inactive towards orange-II with or without phosphate present. When the phosphate was removed from $0{\cdot}01N$-potassium dihydrogen phosphate and $0{\cdot}012N$-phosphoric acid by iron oxide gel and orange-II added, no dye was adsorbed, and when the phosphate was added to iron and aluminium oxide gels which had adsorbed dye at varying p_H values, the dye was liberated and phosphate adsorbed. Grinding of the gels which had attained equilibrium in the phosphate solution allowed further adsorption of phosphate to take place. A comparison of the amounts of orange-II taken up by the gels in the presence of acid showed high adsorption by the aluminium, chromium, and iron oxide gels with hydrochloric or sulphuric acid, but slight or no adsorption with phosphoric acid, the order of decreasing adsorptive power of the gels being that given. The solubility of aluminium phosphate in phosphoric acid solutions of varying p_H value parallels the adsorption of orange-II by aluminium oxide gel in phosphate solutions. Finally, iron and chromium phosphates dissolve at the same p_H as that at which the respective gels adsorb the dye. The above results are explained on the view that a relatively insoluble compound is formed between the gel and the phosphate. Metallic ions are then no longer available to form the metal-dye compound which brings about adsorption. Equations supposed to represent the adsorption of an acid dye by an inorganic gel are given. L. S. THEOBALD.

Adsorption of hydrogen ions and its effect on the swelling and electrical charge of gelatin. B. N. GHOSH (J.C.S., 1928, 711—719).—Simultaneous measurements were undertaken of the swelling, electrical charge, and adsorption of hydrogen ions on the same sample of gelatin in order to decide whether there is any relation between these quantities. The amount of acid adsorbed by gelatin was calculated from measurements of the hydrogen-ion concentration of the acid solution before and after adsorption, by the *E.M.F.* method. The electroendosmotic method was used to measure the variation of electrical charge with hydrogen-ion concentration. At first, with increasing concentration of hydrogen ions the swelling, electrical charge, and adsorption of hydrogen ions all increase. About p_H 2·6, the swelling reaches its maximum value and then begins to diminish, whilst the electrical charge and adsorption of hydrogen ions continue to increase. It is inferred that electrostatic repulsion between the similarly charged particles of the gel cannot be the cause of the swelling, and also that swelling is not due to the increasing hydration of the particles with increasing electrical charge. The amount of hydrogen ions taken up by gelatin can be calculated with fair accuracy from Langmuir's adsorption equation. On this basis an equation for swelling, similar to that of Wilson and Wilson (cf. A., 1918, ii, 260), has been derived. Proportionality between the amount of hydrogen ions adsorbed and the electrical charge has been observed. For hydrochloric, nitric, and trichloroacetic acids, the ratio of the electrical charge to the amount of hydrogen ions adsorbed is nearly constant. For sulphuric acid, the ratio diminishes with increasing hydrogen-ion concentration. E. S. HEDGES.

Adsorption at crystal–solution interfaces. II. Individual macroscopic potassium alum crystals grown in the presence of gelatin and dyes. F. G. KEENEN and W. G. FRANCE (J. Amer. Ceram. Soc., 1927, **10**, 821—827; cf. Eckert and France, this vol., 358).—A carefully selected seed crystal of potassium alum about 0·2 g. in weight was fastened to the end of a platinum wire and suspended in a small glass cell, being placed so that the two most prominent cube faces were in a horizontal position. Fifty c.c. of a saturated alum solution containing a weighed amount of dye were poured into the cell and the crystal was allowed to grow for 24 hrs. at 30°. A photographic record of the growth of the crystal was obtained, and this film, when projected on the screen, gave a magnification of about thirty times. In this way the rates of growth of the cube and octahedral faces could be computed. Bismarck-brown F and diamine-sky-blue F.F. were the only dyes which coloured the crystal and affected its form. Gelatin was also without influence except at those concentrations at which the solution approached the gel state. Bismarck-brown in concentrations of less than 0·1% decreased the rates of growth of the cube faces to a much greater extent than those of the octahedral faces. Diamine-sky-blue in corresponding concentrations stopped the growth of the cube faces, but did not influence the rate of growth of the octahedral. The observed phenomena may have their origin in one or more of three sets of factors, viz., (1) the structure of the crystal face; (2) the characteristics of the dye molecule, *i.e.*, its size and shape, together with the existence and orientation of the polar groups; (3) general environmental conditions such as interfacial energy and viscosity. A. T. GREEN.

Surface tension of liquid mixtures. K. M. STACHORSKY (Z. Elektrochem., 1928, **34**, 111—112).—The surface tension of liquid mixtures cannot be expressed as a linear function of the molecular proportions. For binary mixtures of normal liquids the function is hyperbolic. H. F. GILLBE.

Surface tension at the interfacial layer of two non-miscible liquids. C. BELCOT (Ber., 1928, **61**, [*B*], 355—360).—To explain the Donnan effect Romann and Belcot (Bull. Soc. chim., 1924, [iv], **35**, 685) have assumed that the hydroxyl ions cause the diminution of the surface tension. In alkaline solutions of varying total but identical ion concentration the surface tension must therefore remain constant and the same drop numbers be observed. The author gives an account of the calculations necessary for the preparation of solutions of equal ionic concentration with special reference to ammonium, diethylammonium, and sodium hydroxides. H. WREN.

Variations in surface tensions of solutions. S. L. BIGELOW and E. R. WASHBURN (J. Physical Chem., 1928, **32**, 321—353; cf. Johlin, A., 1925, ii, 1054).—The decrease of surface tension with time,

of solutions of sodium oleate, sodium glycocholate, and glycerol, as observed by earlier workers, has been confirmed and extended to solutions of phenol, resorcinol, pyrogallol, and propionic, succinic, and valeric acids. The capillary-rise method as developed by Richards and Carver (A., 1921, ii, 384) was used. The degree of the agitation which is required for a return to a maximum value after a fall has taken place has a marked effect on the time which elapses before the fall again commences. It is suggested that the fall in surface tension with time is due to adsorption of the organic solute at the glass–solution as well as at the solution–vapour interface. Solutions of certain esters and alcohols in water show an increase in surface tension with time, and in this case, after a rise to a maximum, the fresh surface formed by agitation gives the original minimal value, from which a fresh rise at once commences. In general, the greater the initial lowering of surface tension by the solute the greater and more rapid is the following rise. Coal gas, but not pure gases such as hydrogen, oxygen, carbon and sulphur dioxides, affects the surface tension of water in a similar manner. The increase in surface tension with time is attributed to the evaporation of solute from the surface at a rate greater than that by which it is replaced from the solution by diffusion. Closed capillarimeters must be employed in measuring surface tension in many cases and rubber connexions must be eliminated from the apparatus used. The small quantity of solute necessary to affect surface tension has been measured, and methods for estimating the rates of diffusion at a surface, and the concentration at the surface of a meniscus, are suggested. Further, the degree of hydrolysis of an ester or the rate of any chemical reaction which affects surface tension sufficiently, can be followed by a method now described. For further details, the original paper should be consulted. L. S. THEOBALD.

Explanation of a so-called "intertraction" phenomenon. N. K. ADAM (Proc. Roy. Soc., 1928, A, **118**, 262—263; cf. A., 1927, 16; Wright, A., 1926, 901; 1927, 520).—A slow upward current of water, impinging on a disc of filter-paper soaked in dye solution, drives out the colour in streamers. This confirms the author's previous explanation of the so-called "intertraction" phenomenon.

L. L. BIRCUMSHAW.

Membranometric [surface skin formation] researches on colloidal solutions. WO. OSTWALD and M. MEISSNER (Kolloidchem. Beih., 1928, 26, 1—57).—An improved method of investigation is based on the lag in the movement of the meniscus when a partly immersed capillary tube is moved up and down. By using a small skin area results are obtained which are reproducible within about 10%, according to the nature of the solution. A quantity called the membrane effect is defined in terms of the lag–time curves, and a rapid method of evaluating this is indicated. The membrane effects shown by various solutions are compared with their foaming power and surface-tension lowering, but no general relation is found between these quantities. Within certain groups of chemically related compounds, such as dyes and soaps, these quantities change in the same direction. Soap solutions form more elastic films than solutions of dyes. S. M. NEALE.

Hydration of ions and molecules. E. N. GAPON (J. Russ. Phys. Chem. Soc., 1928, **60**, 237—248).—The degree of hydration of a dissolved substance can be determined by the change in the velocity of diffusion produced by the addition of indifferent substances and by measurements of the velocities of dissolution. The degrees of hydration of alcohols indicated by the two methods are in good agreement. A. RATCLIFFE.

Density and electrostriction of dilute manganese salt solutions. A. N. CAMPBELL (J.C.S., 1928, 653—658).—Measurements have been made of the densities of dilute solutions of manganese chloride, sulphate, and nitrate over the concentration range 0·5—0·01N, using the sinker method of Kohlrausch and Hallwachs. From these figures the electrostriction curve has been plotted, and this is shown not to follow the course predicted by Nernst. The refractivities have been determined over the same range, and the molecular refractivities and dispersions evaluated. From the molecular dispersion, the refractive indices of the anhydrous solid salts have been calculated for the hydrogen C and F lines. It appears that the effect of calculating with the "true molecular volume" is to indicate, in the cases of manganese chloride and nitrate solutions, a negative electrostriction, *i.e.*, an expansion of the solvent.

E. S. HEDGES.

Syntheses of electro-negative sols by the tartaric acid method. A. V. DUMANSKI and A. G. KNIGA (J. Russ. Phys. Chem. Soc., 1928, **60**, 229—236).—Some physico-chemical properties of solutions of tartaro-stannic and tartaro-titanic acids have been studied. The density and viscosity of these solutions are proportional to the concentration of the oxides. With increase in concentration the optical activity and electrical conductivity are found to increase. Schulze's law does not apply to the coagulation of stannic oxide. A. RATCLIFFE.

Production of colloidal gold and platinum in phosphoric acids. A. MÜLLER, F. URBACH, and F. BLANK (Kolloid-Z., 1928, **44**, 185—186).—A solution of pure orthophosphoric acid was evaporated and the temperature subsequently raised to red heat, the operation being carried out in a gold vessel. The viscous mass of metaphosphoric acid obtained on cooling exhibited a bluish-violet coloration, remaining quite clear over a period of 2 years. The preparation gave an intense yellowish-brown Tyndall cone, and ultramicroscopical examination established the colloidal nature of the substance, although no Brownian movement was observable on account of the high viscosity of the medium. If similar operations are carried out with phosphoric acid in a platinum vessel, some of the platinum is dispersed to form a brownish sol. E. S. HEDGES.

Nuclear silver sols free from protective colloids. A. GALECKI (Z. anorg. Chem., 1928, **170**, 45—48; cf. Voigt and Heumann, A., 1927, 932).—Silver sols suitable for use as nuclei have been pre-

pared by reducing an ammoniacal solution of silver nitrate at the b. p. with an ethereal solution of phosphorus. These sols are amicroscopic, free from silver ions, and are precipitated in a gelatinous form by electrolytes; they are sensitive to light. Used as nuclei in the reduction of ammoniacal silver nitrate solution at 80° with formaldehyde, they give rise to sols with particles of a definite size, the particles being smaller and more stable the fresher is the sol used as nucleus. Such sols change only slowly on keeping; they are sensitive to light, but are not so sensitive to electrolytes as the nuclear sols. R. CUTHILL.

Structure of oil and mercury drops examined by Millikan and Mattauch. S. N. RAY (Kolloid-Z., 1928, **44**, 186—188).—Theoretical considerations lead to conclusions which agree with the results obtained experimentally by Mattauch. E. S. HEDGES.

Determination of particle size in sols. H. J. C. TENDELOO (Chem. Weekblad, 1928, **25**, 158—161).—A short account of the methods available. There is no very satisfactory method for lyophile colloids; it is suggested that von Smoluchowski's formula might be applied to the case of colloid particles distributed over a water surface. S. I. LEVY.

Distribution of particle size in reversible polydispersed systems. N. VON RASCHEVSKY and E. VON RASCHEVSKY (Z. Physik, 1927, **46**, 300—304).—By applying Planck's theory of dilute solutions to a polydispersed system considered as a mixture of monodispersed systems, the characteristic function and distribution function have been determined. R. W. LUNT.

Motion of sub-microscopic silver particles in gases. O. TRAUMER (Z. Physik, 1927, **46**, 237—252).—The rate of fall of silver particles, $1{\cdot}16\times10^{-5}$—$4{\cdot}13\times10^{-5}$ cm. in diameter, in nitrogen has been examined by Ehrenhaft's method. The results show that the velocity of fall is normal and that particles produced from silver vapour or from a low-tension silver arc are spherical and of normal density. The electric charge carried by such particles is generally less than the electron charge; the minimum value observed is $1{\cdot}13\times10^{-10}$ e.s.u. R. W. LUNT.

Theory of the spontaneous division of drops of microscopic size. N. VON RASCHEVSKY (Z. Physik, 1927, **46**, 568—593).—The method of Gibbs has been employed in the investigation of the stability of drops of microscopic size. It is shown that, if the velocity of change of the size and constitution of the drops is small due to chemical transformations, and if effects due to electric charges are neglected, the drops are absolutely stable for a positive surface tension in the absence of capillary-active adsorbents. Under the same condition but with negative surface tension, the drops are always labile and tend to disperse. In the presence of dissolved capillary-active adsorbents and with a positive surface tension the drops are stable. A number of other related problems are discussed. R. W. LUNT.

Analysis of dilute salt solutions from the opacity of fine suspensions obtained from them. A. BOUTARIC and (MLLE.) G. PERREAU (Compt. rend., 1928, **186**, 692—694).—Suspensions of precipitated silver chloride and phosphate and magnesium hydroxide are stabilised by the addition of a 10% solution of gum arabic or dextrin, and may then be determined nephelometrically. Barium sulphate is stabilised after an interval of 15 min., but the stability of aluminium phosphate and calcium oxalate is decreased by the gum. In all cases, starch and gelatin, which are also supposed to be stabilising colloids, decreased the stability. J. GRANT.

Viscosity of colloids in presence of electrolytes. N. R. DHAR, D. N. CHAKRAVARTI, and M. N. CHAKRAVARTI (Kolloid-Z., 1928, **44**, 225—233).—Measurements have been made of the viscosity of the following sols, both with and without addition of electrolytes: thorium hydroxide, cerium hydroxide, silicic acid (each prepared by both hot and cold methods), tungstic acid, and benzopurpurin. In every case the first effect on adding small amounts of electrolytes is a fall in the viscosity. In the case of thorium hydroxide, the addition of thorium nitrate produces a greater fall in the viscosity than that produced by potassium iodide because of the increased charge. With increasing quantities of electrolytes, the viscosity of silicic acid sol first falls, then rises to a maximum and falls once more. The viscosity of a 1% solution of gelatin rises on addition of increasing amounts of potassium chloride or barium chloride, whilst with hydrochloric acid and sodium hydroxide the viscosity increases to a maximum and subsequently falls. From theoretical considerations it is concluded that, by increasing the charge of colloid particles, the surface, degree of hydration, and the viscosity are lowered. This is shown to be in accordance with the experiments. E. S. HEDGES.

Viscosity and hydration of emulsoids. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 139—148).—The kinetics of synæresis and the influence of alcohol on the velocity have been studied in experiments with the gel of geranine. The results are in agreement with those calculated by the formula of Gatchek. The concentration of the gel at which synæresis should not occur was calculated from theoretical considerations and found to be in close agreement with the experimental values. An explanation is put forward for the absence of synæresis in concentrated solutions. A. RATCLIFFE.

Properties of "pure" cellulose as a colloid. P. P. VON WEIMARN (Kolloid-Z., 1928, **44**, 212—218).—The dispersion of natural cellulose in concentrated solutions of very soluble salts is inhibited by the waxy coating of the material. A study has therefore been made under these conditions of the dispersion of cotton previously extracted with solvents in a Soxhlet apparatus, and these cellulose preparations are arranged according to the relative ease of dispersion in a hot solution of sodium thiocyanate. Pure cellulose forms a suspensoid colloid in water and has two stability maxima—one in presence of small amounts of electrolytes and another in concentrated salt solutions. Intermediate concentrations of electrolytes precipitate the cellulose. E. S. HEDGES.

Colloid nature of lignic acid and so-called Cassel-brown. E. WEDEKIND and G. GARRE (Kol-

loid-Z., 1928, **44**, 205—212).—Lignic acid is readily peptised by means of small concentrations of hydroxyl ions. The particles of the sol are negatively charged and the sol is coagulated by addition of acid reagents or on adding a positively charged sol. The gel does not adsorb acids (with the exception of sulphuric acid), thus differing from Willstatter's lignin. The moist gel fixes iodine irreversibly to the amount of 63% of the dry weight of the substrate, and it also fixes basic dyes. Both as sol and as gel, lignic acid shows a strong similarity to Cassel-brown, which is easily peptised under the same conditions. Cassel-brown is a typical humic acid of colloidal character, which differs from lignic acid only in auto-oxidation phenomena and the colour deepening connected therewith. E. S. HEDGES.

Reduction of auric chloride in presence of lyophilic colloids. I. TRAUBE and (FRL.) D. JACOBY (Z. anorg. Chem., 1928, **170**, 85—98).—By the action of reducing agents on auric chloride in presence of various lyophilic colloids, it has been found that highly disperse solutions of colloidal gold are obtained and that the degree of dispersity diminishes as the concentration of the colloid falls until ultimately precipitation occurs. In some instances, however, the dispersity decreases with decrease in the amount of colloid only up to a certain point, beyond which it increases again. Frequently, small amounts of the colloid cause precipitation, whereas clear sols result when no colloid is present. The reverse sometimes occurs. These observations point to the necessity for care in the determination of gold, and also in the industrial separation, *e.g.*, with ferrous sulphate, where colloidal ferric hydroxide may readily be formed. Sodium silicate also exerts a marked peptising influence on gold sols. Since the gold in quartz veins was originally in the form of a gel, it seems probable that gold is more widely distributed than is normally supposed, but in such a finely dispersed form that its detection would be extremely difficult. R. CUTHILL.

Colloidal gold in alkali halide crystals. F. BLANK and F. URBACH (Naturwiss., 1927, **15**, 700; Chem. Zentr., 1927, ii, 2269).—Coloured crystals were obtained by melting alkali halides with gold halides; the colour appears after solidification and changes during cooling. The final colour depends on the rate of cooling, and on the chemical nature of the salts. The colour, which is reddish-violet, blue or green, or yellow with potassium chloride, bromide, or iodide, respectively, is due to colloidal gold. On dissolution in water, gold separates. A. A. ELDRIDGE.

Influence of hydrogen and hydroxyl ions on colloidal systems. M. P. VENKATARAMIER (J. Mysore Univ., 1927, **1**, 183—186).—The distinctive properties of hydrogen and hydroxyl ions with respect to the stability of colloids are due to the fact that many substances adsorb water and that the outermost hydration layers are slightly dissociated. The changes in stability are due to the neutralisation of either hydrogen or hydroxyl ions, preferentially adsorbed on the surface. The fact that acid does not reverse the charge on silica indicates that soil acidity cannot be ascribed to the silica acting as an acid in stoicheiometric proportions, but is rather due to the preferential adsorption of hydrogen ions by the hydrated substances. The colloid behaviour of stearic acid illustrates the importance of hydration. R. A. MORTON.

Chemical reactions in presence of lyophilic colloids. T. ITO (Z. anorg. Chem., 1928, **170**, 99—106).—The reduction of silver nitrate and numerous other reactions have been carried out in solutions containing lyophilic colloids. The complex relationships observed in the reduction of auric chloride (see Traube and Jacoby, above) were absent here, however, the rapidity of precipitation diminishing in a normal manner with increasing concentration of colloid. R. CUTHILL.

Method for measuring coagulation. B. JIRGENSONS (Kolloid-Z., 1928, **44**, 202—205).—A method is devised for following the coagulation of sols by means of a spectroscope. With decrease in the dispersity of the sol, a displacement of the diffuse absorption boundary occurs from the violet part of the spectrum towards the red, returning to the violet region when sedimentation occurs. The results of experiments on some typical sols are tabulated. E. S. HEDGES.

Influence of hydrogen-ion concentration on the coagulation value of ferric oxide sol. H. FREUNDLICH and G. LINDEAU (Kolloid-Z., 1928, **44**, 198—202).—The hydrogen-ion concentration of ferric oxide sols prepared by Graham's method was kept constant by means of a buffer solution of sodium acetate and acetic acid, and the minimal concentration of sodium chloride required for precipitation was measured. For a given concentration of buffer solution the coagulation value rises with increasing hydrogen-ion concentration, the relation being nearly linear for small p_H values. When the hydrogen-ion concentration is constant, the coagulation value for sodium chloride is smaller for lower concentrations of the buffer solution. An antagonism between chloride and acetate ions is indicated. E. S. HEDGES.

Effect of ammonia on the flocculation of sols by electrolytes. P. C. L. THORNE, A. R. KENNEDY, and A. H. HOLLOWAY (Kolloid-Z., 1928, **44**, 190—198).—The flocculation of sols of gold, silver, platinum, selenium, mercuric sulphide, cadmium sulphide, stannic hydroxide, silver iodide, and emulsions of olive oil by electrolytes (calcium chloride, sodium chloride, and bromide, potassium chloride, nitrate, and bromide) has been studied in the presence of ammonia. With the exception of a stannic hydroxide sol prepared by peptisation of the precipitated hydroxide with ammonia, all the sols were stabilised by ammonia in small quantities, but higher concentrations of the ammonia assisted the precipitation. The effect of the ammonia depends on its total concentration, and not on its ionic concentration. In general, the more concentrated sols require more ammonia for stabilisation. Experiments on the rate of coagulation of red gold sols by electrolytes in the presence of ammonia showed that increasing amounts of ammonia retard the rate of coagulation progressively. When the coagulation of the sol has once started, however (*e.g.*, by adding the electrolyte before the ammonia), the ammonia is powerless to

protect the sol. The effect of the ammonia is not chemical, but is traced to adsorption on the surface of the colloid particles. Ammonia has a similar effect on coarse suspensions of wood-charcoal, barium sulphate, kaolin, and flowers of sulphur, but not on starch or precipitated silica. It was demonstrated by direct titration that marked adsorption of ammonia occurs. A parallel was observed between adsorption and stability of the suspensions. E. S. HEDGES.

Colloidal platinum. III. Natural acidity and coagulation by acids. S. W. PENNYCUICK and R. J. BEST (J.C.S., 1928, 551—560; cf. A., 1927, 1137).—The hydrogen-ion concentration of platinum sols, prepared by sparking under conductivity water, was measured by means of the quinhydrone electrode. The p_H values obtained from nine different pure platinum sols ranged from 4·60 to 4·28, and the measurements showed that the sols become more acid on keeping or on boiling. The acidity, as determined by the quinhydrone electrode, is somewhat less than that obtained by a conductometric method, but is considered to be a more trustworthy value. In the coagulation of platinum sols by a number of acids, flocculation occurred at a nearly constant hydrogen-ion concentration (p_H 3·44—3·69), and evidence is adduced to show that during this coagulation no acid is removed by the platinum particles, the natural acidity of the sol remaining. These conclusions were confirmed by conductometric measurements. It is suggested that the colloidal platinum particles consist of atoms of platinum together with complex anions of the constitution PtO_4. The corresponding hydrogen ions are considered to be bound as a double layer at the surface, and not free as formerly supposed. The natural acidity of the sols is due to a free acid, probably hexahydroxyplatinic acid, $H_2Pt(OH)_6$, which behaves as a strong acid at these low concentrations. E. S. HEDGES.

Sensitisation of Prussian-blue sols and Odén's sulphur sols by gelatin and tannic acid. S. GHOSH and N. R. DHAR (Kolloid-Z., 1928, 44, 218—224).—Sols of Prussian-blue tend to be coagulated by potassium chloride or barium chloride in presence of small quantities of gelatin, there being an optimum value. Greater amounts of gelatin stabilise the sol. The sensitising effect of gelatin is more marked when hydrochloric acid is the coagulating agent. Small amounts of tannic acid stabilise Prussian-blue when potassium chloride is the precipitating agent, but have a sensitising effect when hydrochloric acid is used. Small quantities of gelatin lower the stability of Odén's sulphur sols towards potassium chloride and barium chloride, an excess of gelatin causing coagulation. Tannic acid stabilises the sulphur sols. In general, the presence of acids favours stability, and alkalis have the opposite effect. The coagulating power of the sodium and potassium salts of weak organic acids on the sulphur sol diminishes with increasing dissociation constant; this effect is traced to removal of the stabilising pentathionic acid by the alkali. The deviations from the Schulze–Hardy rule which are to be observed in the coagulation of sulphur sols with cations of various valencies are attributed to the production of acid by hydrolysis of the salt added. From the experiments it is concluded that the following causes are operative in the sensitisation of sols by means of gelatin, albumin, tannic acid, etc.: (*a*) repression of hydrolysis of the sol by hydrogen ions present in the sensitiser, (*b*) reversal of charge of the sensitiser by hydrogen ions contained in the sol, (*c*) neutralisation of the charge of the sol by the oppositely charged sensitiser. E. S. HEDGES.

Temperature of coagulation of pure copper colloidal solution. B. M. REID and E. F. BURTON (J. Physical Chem., 1928, 32, 425—432).—The temperature of coagulation of a copper sol prepared by Bredig's method varied between 190° for the pure sol and 134° for a sol containing small but increasing amounts of potassium chloride, indicating that the temperature of coagulation falls with an increase in particle size. Coagulation by contamination from glass surfaces was avoided by the use of a copper tube to contain the sol. The possible effects on coagulation of increasing molecular motion, change in dielectric constant, and in the ionic product for water with temperature are discussed. The results suggest that heat alone is sufficient to cause or to accelerate coagulation in a dispersoid system. L. S. THEOBALD.

Fractional precipitation and ultrafiltration of cellulose nitrate. W. KUMICKEL (Kolloidchem. Beih., 1928, 26, 161—198).—Cellulose nitrate may be separated into fractions called *A* and *B* by precipitation of acetone solutions by addition of water, or by ultrafiltration. *A* and *B* differ in several properties, notably in viscosity and in the relation between viscosity and water content. *B* is cellulose nitrate degraded by hydrolysis or oxidation. The fractions show no difference in nitrogen content or in solubility in ether–alcohol. The variation of viscosity with concentration does not follow the Arrhenius formula, and the specific viscosities are not additive. Over a certain concentration range, however, the log. viscosity–concentration graph is linear. When water is added to an acetone solution of cellulose nitrate the viscosity first falls, then rises slowly to a maximum at which further addition of water causes precipitation and a greater fall in viscosity. Reducing the ultrafilter pore size leads to filtrates of lower specific viscosity, and with a very fine filter, pure solvent may be obtained. S. M. NEALE.

Peptisation of ferric hydroxide by arsenious acid. M. A. BOUTARIC and G. PERREAU (Rev. gén. Colloïd., 1928, 6, 1—8).—A quantitative study has been made of the peptisation of ferric hydroxide (freshly precipitated by adding ammonia to ferric chloride solution) by aqueous solutions of arsenious oxide. The amount of ferric hydroxide peptised under various conditions was determined by separating the residue and weighing after calcination. The course of the peptisation can be represented by the equation $dx/dt-K(a-x)$, where x is the amount peptised in the time t, and a is the limiting quantity of substance peptised. In practice, peptisation is somewhat slow, equilibrium being attained only after several hours. For a given quantity of ferric hydroxide, increasing concentrations of arsenious acid

produce a rise in the amount of substance peptised, which afterwards passes through a maximum and then decreases, without peptisation ever being complete. Similarly, with a constant concentration of arsenious acid and progressively increasing amounts of ferric hydroxide, the amount of peptised material passes through a maximum. In each case, measurements were also made by a refractometric method of the amount of arsenious acid adsorbed by the ferric hydroxide. It appears that for peptisation a definite quantity of arsenious acid has to be adsorbed by each particle of the adsorbate. On the other hand, an excess of arsenious acid produces flocculation, not peptisation. Precipitated ferric hydroxide becomes less readily peptisable on ageing. Temperature has little or no influence on the amount peptised.

E. S. HEDGES.

Property of certain silica gels. P. BARY (Compt. rend., 1928, **186**, 863—864).—Silica gels produced by precipitation of sodium silicate with hydrochloric acid, washed, and allowed to dry slowly in air at the ordinary temperature, break into small pieces when heated, or when dropped into water or solutions of salts. In the latter case a loud explosion similar to that produced by breaking glass results, the effect being most marked with $0\cdot001N$-solutions of acids. It is almost or completely absent with benzene, toluene, and carbon tetrachloride. The phenomenon is probably connected with the entry of water into the narrow pores of the gel, and not to hydration.

J. GRANT.

Theory of the colloid reactions of the cerebrospinal fluid. W. SCHMITT (Kolloidchem. Beih., 1928, **26**, 58—160).—The albumin, globulin, and albumin-globulin contained in the fluid were highly purified and separated by electrodialysis, and their reactions with gold sol, gum mastic, and gum benzoin were investigated. Four classes of flocculation reactions are distinguished, viz., adsorption between colloids similarly charged, with and without electrolyte action, flocculation at the isoelectric point, and mutual precipitation of oppositely charged colloids.

S. M. NEALE.

Nitrogen-oxygen-nitrogen oxide equilibria. N. W. KRASE (J. Physical Chem., 1928, **32**, 463—465).—The free energy of formation of nitric oxide from its elements has been re-calculated using the data of Briner and co-workers (A., 1926, 916; 1927, 121), and the new equation connecting heat of formation and temperature is $\Delta F^{\circ}=21{,}600-3\cdot70T$. The re-calculated values of for nitric oxide, nitrogen peroxide, nitrogen tetroxide, and nitric acid are 20,500, 11,570, 21,900, and −18,560 g.-cal. respectively (cf. Lewis and Randall, "Thermodynamics").

L. S. THEOBALD.

Equilibrium constants of the reactions $CO+3H_2 \leftarrow CH_4+H_2O$; $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$; and $2CO+2H_2 \leftarrow CH_4+CO_2$. K. M. CHAKRAVARTY (Z. Elektrochem., 1928, **34**, 22—25).—Constants for above equilibria at temperatures ranging from 800° to 1300° have been calculated (*a*) from the variation with temperature of the equilibrium constants for $C+2H_2 \leftarrow CH_4$; $2CO \rightleftharpoons C+CO_2$; and $CO_2+H_2 \leftarrow CO+H_2O$, and (*b*) from the heats of reaction and the specific heats and chemical constants of reactants and products. The figures obtained are compared and discussed.

H. J. T. ELLINGHAM.

Reversibility of a reaction induced by the electric spark or current. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1928, **186**, 948—950; cf. A., 1927, 1156).—The decomposition, at pressures of the order of 15 mm., of carbon dioxide into oxygen and carbon monoxide by an electric spark or a continuous current is reversible, and takes place progressively to the extent of 74 and 32%, respectively. A continuous spark discharge corresponding with a current of low intensity produces a greater combination of carbon monoxide and oxygen than a spark discharge from a high-capacity condenser representing the same expenditure of energy.

J. GRANT.

Ebullioscopic determination of the molecular state of resorcinol in aqueous solutions of sodium chloride. F. BOURION and E. ROUYER (J. Chim. phys., 1928, **25**, 234—248).—A more detailed account of work already published (this vol., 233).

Refractometric evidence relating to the condition of strong electrolytes in concentrated solutions. K. FAJANS, H. KOHNER, and W. GEFFCKEN (Z. Elektrochem., 1928, **34**, 1—10).—Previous work (cf. Fajans, A., 1927, 1023) is reviewed and discussed. Measurements of the refractivity of sulphuric acid in solutions of concentrations up to 95% have now been made. The refractivity falls slightly with increasing concentration up to 40 mol.%, but rises gradually with further increase in concentration. These effects are attributed respectively to the processes (1) $SO_4''+H_3O^{\cdot}=HSO_4'+H_2O$ and (2) $HSO_4'+H_3O^{\cdot}=H_2SO_4+H_2O$. The conversion of the ion $H_3O^{\cdot}$ into water should increase the refractivity, but this effect is opposed by a larger decrease due to conversion of SO_4'' into HSO_4' in (1) and by a smaller decrease due to conversion of HSO_4' into H_2SO_4 in (2). The actual changes in refractivity are very small. The general conclusion from refractometric evidence is that strong electrolytes are incompletely dissociated in aqueous solutions, and that they differ only in degree from weak electrolytes, so that no sharp line of demarcation can be drawn between the two classes. The essential modification of the classical theory which is necessitated by recent work lies in taking account of interionic forces in the quantitative treatment of the subject. The recent work of Nernst and Naude (this vol., 127, 368) on heats of dilution leads to similar conclusions, but the refractometric data lead to the conclusion that at given concentration the degrees of dissociation of lithium and sodium chlorides are of the same order of magnitude even up to $5N$. The contrary conclusions of Nernst and Naude are discussed. Bjerrum's theory of "ionic association" is also discussed and criticised.

H. J. T. ELLINGHAM.

Dissociation constant of acetic acid and activity coefficients of the ions in certain acetate solutions. E. J. COHN, F. F. HEYROTH, and (Miss) M. F. MENKIN (J. Amer. Chem. Soc., 1928, **50**, 696—714).—An expression is deduced for the apparent

dissociation constant of acetic acid based on the Ostwald dilution law in combination with the Debye–Hückel equation for the activity coefficient of an ion (cf. Cohn, A., 1927, 206). The expression is modified so as to apply to mixtures of acetic acid and sodium acetate, and from *E.M.F.* measurements in such solutions with an ionic strength low enough to eliminate specific ion effects (cf. Walpole, J.C.S., 1914, **105**, 2501, 2521) the true dissociation constant, K, of acetic acid is found by graphical methods to be $1{\cdot}86\times10^{-5}$ (? at 25°), in agreement with Kendall (J.C.S., 1912, **101**, 1275). This value is obtained only if Sørensen's early value (0·3380 volt) for the potential of the $0{\cdot}1N$-calomel electrode is assumed; if Sørensen's revised value (0·3357 volt) is adopted K becomes $1{\cdot}7\times10^{-5}$. It is suggested that *E.M.F.* measurements on mixtures of a weak acid with one of its salts might be used for standardising calomel electrodes, since they can be compared with conductivity measurements corrected for interionic forces. The activity coefficient of the acetate anion is independent of the potential of the $0{\cdot}1N$-calomel electrode. The salting-out constant in the Debye–Hückel equation is constant for sodium acetate–acetic acid mixtures; this may be because in the most dilute acid solutions the ionic strength is proportional to the sodium-ion concentration. Interpolation tables and graphs are given to facilitate the preparation of buffer solutions of the same ionic strength and varying p_H, or *vice versa*. The present results and those in the previous paper enable buffer solutions of known ionic strength and having p_H between 3·6 and 7·6 to be prepared.

S. K. Tweedy.

First dissociation constants of *s*-diphenylguanidine and *p*-phenylenediamine. P. Walden and H. Ulich (Z. Elektrochem., 1928, **34**, 25—28).—The electrical conductivity of very dilute solutions of *s*-diphenylguanidine in water of specific conductivity $0{\cdot}4-1{\cdot}2\times10^{-6}$ ohm^{-1} has been measured in a silica cell. Corrections for carbon dioxide in the water, for the electrostatic forces between the ions, and for the activity coefficients of the ions are shown to be less than the experimental error, and the first dissociation constant of the base is found to be $(8{\cdot}19\pm0{\cdot}65)\times10^{-5}$. It is said that the dissociation constants of bases can be accurately determined by the conductivity method provided that the conductivity of the water is not greater than 5% of that of the solutions employed. Determinations of the hydrogen-ion concentration of the above solutions by electrometric or colorimetric methods gave only approximate values for the dissociation constant, but confirmed the order of its magnitude. From conductivity measurements of more concentrated solutions of *p*-phenylenediamine, its first dissociation constant is found to be $(1{\cdot}30-0{\cdot}10)\times10^{-8}$, in satisfactory agreement with previous determinations by the electrometric method.

H. J. T. Ellingham.

Strong electrolytes. J. A. V. Butler (Nature, 1928, **121**, 500).—Theoretical. A. A. Eldridge.

Method of determining chlorine-ion concentration. Y. Katsu (J. Biophys., 1927, **2**, 123—131).—The author describes the preparation of a silver chloride electrode for the measurement of chlorine-ion concentration of the body fluids which is better suited to this purpose than is the calomel electrode. The normal electrode potential of the $0{\cdot}1N$-calomel electrode against the silver chloride electrode is evaluated with the aid of Ghosh's theory as 0·1064 volt at 18°. H. Ingleson.

Activity of potassium and sodium chlorides in aqueous solution. Y. Katsu (J. Biophys., 1927, **2**, 133—143).—The activity of the chlorine ion in the solutions was measured by using the silver chloride electrode (see above), with the object of ascertaining whether the theories of Ghosh or Debye express the experimental results as was done in the case of hydrochloric acid. At dilutions of 1—500 litres the results obtained were not in agreement with either theory.

H. Ingleson.

Method of measuring the activity of alkali metal ions in a solution. Y. Katsu (J. Biophys., 1927, **2**, 145—149).—A description of the preparation and use of potassium and sodium amalgam electrodes is given. H. Ingleson.

Combination of glycine and chlorine ion. Y. Katsu (J. Biophys., 1927, **2**, 151—164).—With the view of elucidating the mode of combination of proteins with metallic chlorides the diminutions in activity of chlorine ion in solutions of potassium, sodium, and calcium chlorides of concentrations 0·02—$0{\cdot}0025N$ caused by the addition of glycine in a concentration $1N$ have been measured. It is concluded that the reduction in chlorine-ion activity is caused by adsorption. H. Ingleson.

Activity theory of Ghosh and of Debye and Hückel for strong electrolytes. Y. Katsu (J. Biophys., 1927, **2**, 109—122).—The *E.M.F.* of a series of cells composed of a $0{\cdot}1N$-calomel electrode and a hydrogen gas electrode with various concentrations of hydrochloric acid were measured at 13°, 18°, and 25°. Values of the activity coefficient below $0{\cdot}002N$ deduced from the equations of Ghosh and of Debye and Hückel agree with experiment within the limit of experimental error. At higher concentrations there is satisfactory agreement with the former equation, but it is necessary to introduce an empirical correction factor into the latter equation to obtain agreement with experiment. H. Ingleson.

Extension of the idea of entropy. V. Njegovan (J. Chim. phys., 1928, **25**, 65—69).—The usual conception of entropy has no physical meaning because, in its thermodynamic definition, energy originating from the interior of a substance is neglected.

L. F. Gilbert.

Entropy and "entropy constant" of gases and of gaseous mixtures. J. J. van Laar (Z. Physik, 1927, **45**, 635—649).—The author's analysis of the relation between entropy and the vapour pressure of a substance in the solid, liquid, or gaseous state has been extended to a consideration of gaseous mixtures, thereby leading to a resolution of the so-called paradox of Gibbs. R. W. Lunt.

Free energies of some hydrocarbons. A. W. Francis (Ind. Eng. Chem., 1928, **20**, 277—282; cf. Smith, B., 1927, 593).—Equations have been derived for the free energies of formation of methane,

ethane, octane, ethylene, acetylene, benzene, toluene, naphthalene, and *cyclo*hexane as functions of temperature. Within the cracking temperature range 427—727°, the relation is practically linear, and a much-simplified form of equation may be employed. In order to determine the true stability relations between various hydrocarbons the equations are plotted with the ordinates reduced to free energy of formation per carbon atom, since a comparison on any other basis leads to erroneous conclusions. The paraffin hydrocarbon lines are nearly parallel, those of aromatic hydrocarbons have a much lower slope, indicating the smaller decomposing effect of temperature, and whilst that of ethylene is nearly parallel to the aromatic lines, the higher olefine lines have slopes approximating to those of the paraffins. Acetylene is the only hydrocarbon the stability of which is increased by temperature, but it never becomes stable with respect to its elements. Although certain reactions which normally would be accompanied by a slight increase in free energy can be forced to proceed under pressure if there is a decrease in volume, practical pressures will not usually overcome an unfavourable free energy change of more than 5000 g.-cal. According to the equations, the paraffins and the higher olefines are the only hydrocarbons which are thermodynamically stable, and above 260° methane is the only thermodynamically stable hydrocarbon. This, which seems inconsistent with ordinary cracking reactions, is explained by the fact that in all cracking operations true chemical equilibrium is never attained. The polymerisation of olefines should be possible up to about 500°, and would be favoured still more in the liquid phase, or with higher pressures. On the other hand, free energy considerations would indicate that the condensation of methane to higher hydrocarbons is impossible. The polymerisation of methane, ethane, etc. by α-particles is not in contradiction with this conclusion, for in this case the energy is supplied by the α-particle (cf. Lind and Bardwell, A., 1926, 1077). The formation of acetylene from methane could take place only at very high temperatures, when all but a trace of acetylene would be decomposed. No paraffin hydrocarbon should be capable of direct condensation to a higher hydrocarbon, but lower ones may be formed simultaneously with higher ones, since there is then no change in free energy. The direct removal of hydrogen from a paraffin to form an olefine with the same number of carbon atoms is possible only at high temperatures and to a limited extent. The synthesis of motor fuel from water gas can take place only below about 450°. W. J. POWELL.

Free energies of some alcohols. A. W. FRANCIS (Ind. Eng. Chem., 1928, **20**, 283—285; cf. preceding abstract).—Equations for the free energies of formation of methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, *tert.*-butyl, active amyl, and *n*-heptyl alcohols been derived for the temperature range 227—4_7 . The results show that the free energy associated with the dehydration of ethyl alcohol to ethylene becomes zero at about 207°. W. J. POWELL.

Transformation temperature of liquid sulphur into viscous sulphur. P. MONDAIN-MONVAL and P. SCHNEIDER (Compt. rend., 1928, **186**, 751—753).—The temperature at which sulphur undergoes internal transformation (160° for pure sulphur; see A., 1926, 127) has been examined viscosimetrically. The temperature is raised by the addition of foreign substances (triphenylmethane, naphthalene, phenol, or camphor) up to a limit corresponding with the separation of a new phase rich in the added substance. For 2% solutions the rise is proportional to the molecular concentration of the added substance. This explains the absence of a discontinuity at 160° in the solubility curves. J. GRANT.

Equilibrium between alcohols and salts. II. E. LLOYD, C. B. BROWN, D. G. R. BONNELL, and W. J. JONES (J.C.S., 1928, 658—666).—In continuation of previous work (A., 1926, 357), measurements have been made of the solubilities of cobalt chloride and bromide, cadmium chloride, bromide, and iodide, cupric chloride, nickel bromide, magnesium nitrate, calcium nitrate, ferric chloride, and sodium bromide in both methyl and ethyl alcohols, and of the solubilities of lithium chloride, potassium bromide, barium nitrate, calcium iodide, and sodium iodide in methyl alcohol. In addition, the solubilities of cupric chloride in *n*-propyl, *iso*amyl, and benzyl alcohols, and those of calcium chloride and bromide in *n*-propyl, *n*-butyl, *n*-amyl, *iso*amyl, and benzyl alcohols have been measured. The composition of the solid phases and the dissociation pressures of most of the alcoholates were determined. Attention is directed to the decomposing action of certain salts on the alcohols. For example, aluminium chloride when added to methyl or ethyl alcohol gives an immediate violent evolution of hydrogen chloride. A saturated solution of ferric chloride in either methyl or ethyl alcohol at temperatures above 50° yields chloroform and a red ferric precipitate, and on boiling evolves hydrogen chloride. Below 50°, there is evidence of the slow formation of ethyl chloride in the ethyl-alcoholic solution. Traces of chloroform are produced when a saturated solution of cupric chloride in ethyl alcohol is boiled. The calculation of the affinities of salts for alcohols, and of their heats of combination, from the dissociation pressures is indicated. The close agreement between the values of the maximum work, as calculated by the application of the van der Waals and perfect gas equations, is noted, and the full thermodynamic expression for the maximum work is given. E. S. HEDGES.

Molybdenum sulphides. I. Pressure of sulphur vapour from molybdenum trisulphide. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 19—22).—Direct and continuous measurement may be effected by observing the temperatures at which the vapour pressure is equal to that of sulphur kept at a fixed temperature (cf. Ruff and Graf, A., 1907, ii, 947; Matthies, A., 1906, ii, 663). For sulphur at 217°, 237°, and 249°, this equality occurs with cupric sulphide at 423·5°, 431·5°, and 439·5°, respectively (cf. Allen and Lombard, A., 1917, ii, 194). The emission of sulphur vapour from molybdenum trisulphide is a reversible process, the vapour pressure being 4·0 mm. at 355°, 28·8 at 390 , and 178·6 at 418°; the log. of the pressure is a linear function of the temperature. T. H. POPE.

Molybdenum sulphides. II. Equilibrium of reduction of molybdenum disulphide by hydrogen. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 109—112; see preceding abstract).—The equilibrium $MoS_2+2H_2 \rightleftharpoons 2H_2S+Mo$ has been studied between 805° and 1100° starting from the disulphide and hydrogen. A dynamic method is used to measure the ratios p_{H_2S}/p_{H_2} for each temperature (cf. Jellinek and Zakowski, A., 1925, ii, 401). From these ratios and from the dissociation constant of hydrogen sulphide the tension of molybdenum sulphide is calculated. By applying the reaction isochore the heat of the reaction is obtained. The values are −20, −28, and −24 kg.-cal. for the temperature ranges 805—910°, 910—1005°, and 1005—1100°, respectively. O. J. WALKER.

Formation of carbides in the system metal–carbon–oxygen. G. MEYER and F. E. C. SCHEFFER (Rec. trav. chim., 1928, 47, 401—405).—It is shown that the four types of pressure–temperature curves previously described (A., 1927, 220; B., 1927, 546) for the systems metal–carbon–oxygen containing a stable carbide, include all possible equilibria. From a knowledge of the values of the heats of transformation, it is possible to decide to which type a particular system belongs. The system nickel–carbon–oxygen has been studied from this point of view. M. S. BURR.

Alloys of sodium, potassium, cadmium, and mercury. E. JANECKE (Z. Metallk., 1928, 20, 113—117).—In the various binary and ternary systems of the metals sodium, potassium, cadmium, and mercury the following compounds have been isolated: KHg, golden-yellow needles (m. p. 178°); KHg_2 (m. p. 178°); KHg_3 (m. p. 201°); KHg_4 (m. p. 182°); KHg_8, isometric crystals (m. p. 70°); Na_3Hg, glistening silvery scales (m. p. 67°); NaHg, needles with reddish lustre (m. p. 217°); $NaHg_2$, silvery-white crystals (m. p. 349°); $NaHg_4$, small silvery needles (m. p. 155°); Na_2K (decomp. 6·9°); $NaCd_2$ (m. p. 380°), $NaCd_4$ (m. p. 355°), KCd_3, needles (m. p. above 550°) $NaKHg_2$ (m. p. 188°), and NaCdHg (m. p. 325°). No quaternary compound appears to exist. Most of the above compounds form eutectics with adjacent compounds or with one or other of the constituent metals. The equilibrium diagrams for the ternary systems Na–Cd–Hg and Na–K–Hg are discussed. A. R. POWELL.

Production of vitriols. III. System zinc sulphate–sulphuric acid–water. G. AGDE and F. SCHIMMEL (Z. angew. Chem., 1928, 41, 340—341; cf. B., 1927, 388).—The solubility of zinc sulphate in aqueous solutions of sulphuric acid at −10° to 39° has been measured, the results showing that the solubility is considerably depressed by the acid. The temperatures of transition of the heptahydrate into the hexahydrate in presence of varying amounts of sulphuric acid have been determined; some f.-p. data are also recorded. R. CUTHILL.

Systems $Cd(NO_3)_2$–HNO_3–H_2O; $Zn(NO_3)_2$–HNO_3–H_2O; $Mg(NO_3)_2$–HNO_3–H_2O at 20°. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 146—148).—From a study of the solubility curves of the nitrates in solutions containing nitric acid it is shown that the following hydrates can exist in equilibrium with solutions containing nitric acid up to the percentage given in parentheses: $Cd(NO_3)_2,4H_2O$ (52·95%), $Cd(NO_3)_2,2H_2O$ (60·01%), $Zn(NO_3)_2,6H_2O$ (34·45%), $Zn(NO_3)_2,4H_2O$ (59·21%), $Mg(NO_3)_2,6H_2O$ (49·12%). O. J. WALKER.

Equilibrium studies on alumina and ferric oxide, and on combinations of these with magnesia and calcium oxide. W. C. HANSEN and L. T. BROWNMILLER (Amer. J. Sci., 1928, [v], 15, 225—242).—The *X*-ray diagram of aluminium hydroxide prepared by adding ammonia solution to aluminium chloride and drying the precipitate at 110° is the same as that of the hydroxide obtained by the action of air on a solution of sodium aluminate, but is different from the gibbsite diagram. On heating at 200—215°, the precipitated hydroxide becomes amorphous, the dehydration curve having a point of inflexion corresponding with the loss of 2 mols. of water. At 900—950°, however, a new form appears which is probably represented by Ullrich's γ-alumina (Norsk Geol. Tidsskr., 1925, 8, 115), and at 1000° the crystalline form slowly becomes that of corundum. Precipitated ferric hydroxide dried at 110° is amorphous, but at 300° it passes into hæmatite. The *X*-ray diagrams of co-precipitated mixtures of the two hydroxides heated at 1200° show that hæmatite dissolves about 14% of corundum, and corundum also dissolves a little hæmatite. A *compound*, $4CaO,2MgO,Al_2O_3,Fe_2O_3$, has been prepared by heating a mixture of magnesium oxide with the compound $4CaO,Al_2O_3,Fe_2O_3$ (this vol., 367). At 1370°±5°, this is transformed into magnesium oxide and a liquid. The *compound* $2CaO,MgO,Fe_2O_3$, obtained by heating a mixture of calcium carbonate with magnesium oxide and ferric oxide, decomposes in a similar manner at 1410°±5°. The following binary systems form complete series of solid solutions, the refractive indices of which have been determined: $4CaO,2MgO,Al_2O_3,Fe_2O_3$ with $4CaO,Al_2O_3,Fe_2O_3$, or $2CaO,MgO,Fe_2O_3$, or $2CaO,Fe_2O_3$; $2CaO,Fe_2O_3$ with $2CaO,MgO,Fe_2O_3$, or $4CaO,Al_2O_3,Fe_2O_3$. Measurements of the refractive index show that up to 2% of the alumina in the compounds $3CaO,Al_2O_3$ and $5CaO,3Al_2O_3$ may be replaced by ferric oxide, giving homogeneous products. R. CUTHILL.

Equilibria in the ammonia-soda process under pressure. B. NEUMANN and R. DOMKE (Z. Elektrochem., 1928, 34, 136—153).—An apparatus is described for the determination of solubilities at pressures up to 3 atm. Equilibrium diagrams for the system sodium chloride–ammonium hydrogen carbonate–water from 20° to 40° and at various pressures have been obtained; the results are discussed with reference to increased yields in the technical process. H. F. GILLBE.

Phase-rule study of the removal of sugar from molasses. I. Ternary system strontium oxide–sucrose–water. G. GRUBE and M. NUSSBAUM (Z. Elektrochem., 1928, 34, 91—98).—The ternary system strontium oxide–sucrose–water has been examined at eleven temperatures between 0° and 100°. The experimental data seem to show that $SrO,9H_2O$, $2SrO,C_{12}H_{22}O_{11}$, $SrO,C_{12}H_{22}O_{11}$, and

$C_{12}H_{22}O_{11}$ exist as solid phases. Whilst the distrontium compound can exist only within a restricted region above 96°, the remaining solids are deposited from solutions of appropriate composition at all temperatures between 0° and 100°. J. S. CARTER.

Heats of adsorption of certain organic vapours on charcoal at 25°. J N. PEARCE and L. MCKINLEY (J. Physical Chem., 1928, **32**, 360—379; cf. Lamb and Coolidge, A., 1920, ii, 471).—A new calorimetric method, based on that described by Coolidge (B., 1924, 359), has been devised to measure heats of adsorption at various temperatures. Condensation effects are avoided by keeping the calorimeter and vapour to be adsorbed at the same temperature, and the charcoal bulb contains a tungsten spiral by means of which the heat evolved is quickly conducted to the calorimetric liquid. The heats of adsorption of nine vapours on a gas-free, coconut-shell charcoal, activated by steam, have been measured at 25°. The total quantity of heat evolved during adsorption is definite and reproducible, and is independent of the mode of addition of the vapour and of the previous history of the charcoal provided evacuation at 550° has taken place. Contrary to Lamb and Coolidge (*loc. cit.*), carbon tetrachloride and chloroform did not reduce the heat evolved when a given quantity of vapour was adsorbed in a subsequent run on the same sample of charcoal. The results for each vapour can be represented by equations of the form $h - mX^n$, where h is the heat evolved per g. of charcoal by the adsorption of X c.c. (*N.T.P.*), and m and n are constants. The value of n is always less than unity and has a mean value of 0·918 for the vapours named below. The values of m vary more widely and inversely as n, and increase with temperature, whilst n decreases. The molecular heats of adsorption at 25° in kg.-cal. are: ethyl chloride 11·5, carbon disulphide 12·5, methyl alcohol 13·9, acetone 14·4, chloroform 14·5, propyl chloride 15·4, carbon tetrachloride 15·4, benzene 15·7, and ether 15·8, which are in good agreement with the values found at 0° by Lamb and Coolidge (*loc. cit.*). The relation between the heats of adsorption and of compression is discussed. L. S. THEOBALD.

Electrochemical behaviour of acetylene. R. MÜLLER and H. KUMPFMILLER (Z. Elektrochem., 1928, **34**, 70—74).—The saturated solutions of acetylene in acetone at 18° and 25° are about 0·82 and 0·60*M*, respectively. Solutions of acetylene in acetone contain small quantities of hydrogen ions produced in accordance with $C_2H_2 \rightarrow H^{\cdot} + C_2H'$ and $C_2H_2 \rightarrow 2H^{\cdot} + C_2''$. It is probable, however, that the ions, especially C_2'', form complexes with the solvent or with undissociated acetylene. Measurements of the electrical conductivities at 25° show that the molecular conductivity is minimal at about $v=7$. The electrode $Ag|AgNO_3$ in acetone shows a fairly constant potential, but measurements of the *E.M.F.* of $Pt|$quinhydrone$(0{\cdot}005M)C_2H_2|AgNO_3|Ag$, and $Pt|C_2H_2|AgNO_3|Ag$ showed no simple variation with the acetylene concentration. The *E.M.F.* of the cells $C|C_2H_2|AgNO_3|Ag$, however, were in qualitative agreement with the Nernst formula, suggesting an equilibrium between carbon and carbon ions. Electrolysis of acetone solutions of acetylene under various conditions yielded results which are difficult to interpret, but which suggest the re-dissolution of some of the products of electrolysis or their participation in secondary processes. On prolonged electrolysis hydrogen is evolved at the cathode, whilst the anode becomes coated with a yellowish-brown deposit. The solution gradually becomes yellow and on evaporation a brown, viscid liquid of unknown composition is obtained. J. S. CARTER.

Theoretical [electrode] potential of the alkaline-earth metals. G. DEVOTO (Z. Elektrochem., 1928, **34**, 19—22).—From data for the decrease of free energy accompanying certain reactions and from values of solubility products, the following values for normal electrode potentials at 25° have been calculated: $Ca|Ca^{\cdot\cdot}$, $2{\cdot}90 \pm 0{\cdot}02$; $Sr|Sr^{\cdot\cdot}$, $2{\cdot}945 \pm 0{\cdot}05$; $Ba|Ba^{\cdot\cdot}$, $2{\cdot}96 \pm 0{\cdot}05$; $Mg|Mg^{\cdot\cdot}$, $2{\cdot}35 \pm 0{\cdot}05$. These values are all higher than those obtained from measurements of the decomposition voltage of fused salts. The probable sequence of elements in the electrochemical series now becomes Ba, Li, Sr, Rb, K, Ca, Na, Mg. H. J. T. ELLINGHAM.

Theoretical potentials of sodium, potassium, and calcium. P. DROSSBACH (Z. Elektrochem., 1928, **34**, 205—211; cf. A., 1927, 421).—Theoretical. The potentials of sodium, potassium, and calcium are calculated as $-2{\cdot}52 \pm 0{\cdot}02$, $-2{\cdot}73 \pm 0{\cdot}02$, and approximately $-3{\cdot}03$ volt, respectively. The method of calculation is fully described. H. INGLESON.

Temperature coefficient of the electrode potential of 0·1*N*-calomel electrode. Y. KATSU (J. Biophys., 1927, **2**, 95—107; see this vol., 478).—Measurements were made between 13° and 43° of the *P.D.* (E_0) of the 0·1*N*-calomel electrode against the normal hydrogen electrode, by an indirect method involving the cell $Pt|H_2$(1 atm.)|butyric acid $(0{\cdot}1M)||KCl(0{\cdot}1M)HgCl|Hg$, using Bjerrum's method for the elimination of the diffusion potential. The p_H value of the acid solution was obtained from the dissociation constant and the value of E_0 derived from the relation $p_H - (E - E_0)0{\cdot}0001983T$, E being the *E.M.F.* of the cell. The temperature coefficient of E_0 is given by the empirical equation $(E_0)_t = (E_0)_{18} - 0{\cdot}000001(t^2 + 54t - 1296)$. The author's results are in good agreement with the values given by Sørensen, Lewis, and Clark. H. INGLESON.

Physical interpretation of electrolytic solution potentials. A. VON HIPPEL (Z. Physik, 1927, **45**, 471—475).—From the consideration of a thermodynamic cycle involving quantities associated with the electrolytic transfer of metals in a solution from anode to cathode the following expression has been derived for the potential, E, of a normal calomel electrode: $E = H' - S' - I - \phi_{Hg}$. In this expression H' is the work corresponding with the hydration of the metal ions, S' is connected with the heat of sublimation, S, of the metal by the relation $S' = S + D + \frac{3}{2}RT$, where D is a work term due to the diffusion of ions, I is the ionisation potential of the metal, and ϕ_{Hg} is the work of removing an electron from the metal. R. W. LUNT.

Potential difference between two solutions. M. PLANCK (Sitzungsber. Preuss. Akad. Wiss. Berlin,

1927, 285—288).—The author's formula (A., 1890, ii, 1355) for the diffusion potential between two dilute solutions of different electrolytes has been compared by reference to the data of Büchi (A., 1924, ii, 744) with that derived by Henderson (A., 1907, ii, 426; 1908, ii, 655), and the result is in favour of the latter. The difference may be due to the fact that, in Büchi's experiments, no attempt was made to prevent convection and the potential was not measured immediately after contact of the two solutions, but some time later. The possibility of investigating experimentally the difference between the two formulæ is discussed. M. S. BURR.

Theory of galvanic cells. N. ISGARISCHEV (Z. Elektrochem., 1928, 34, 128—129).—An attempt has been made to determine the individual factors which cause the production of electric energy in a galvanic cell; the views put forward are substantially supported by data in the literature, but the need for accurate *E.M.F.* determinations is emphasised. H. F. GILLBE.

Transition cells of the sixth class. E. COHEN and E. J. JOSS (J. Amer. Chem. Soc., 1928, 50, 727—733).—The *E.M.F.* of the cell $Ag(s),AgI(s)|AgI(c_1),PbI_2(c_2),CaCl_2,6H_2O(l)|Pb(s)$ is measured between 120° and 170°. This is a transition cell of the sixth class, the depolariser having a transition point. The graph of *E.M.F.* against t consists of the two straight lines $E=0{\cdot}1870+0{\cdot}000566t$ and $E=0{\cdot}2062+0{\cdot}000435t$, which intersect at the transition temperature of the silver iodide, viz., 146·6°. From the gradients of these lines the heat liberated in the reaction $AgI(\beta)\longrightarrow AgI(\alpha)$ is 1270 g.-cal. S. K. TWEEDY.

Reduction potential of selenium and the energy of aqueous selenous acid. H. F. SCHOTT, E. H. SWIFT, and D. M. YOST (J. Amer. Chem. Soc., 1928, 50, 721—727).—The equilibrium $Se(s)+2I_2(s)+3H_2O(l)=H_2SeO_3(aq.)+4H^{\cdot}+4I'$ is investigated at 25°. The constant $[H_2SeO_3]a_{H^{\cdot}}^4\times a_{I'}^4$, where a represents activity and $[H_2SeO_3]$ the molality of the undecomposed selenous acid, is $1{\cdot}46\times10^{-14}$, whence the reduction potential of the reaction $Se(black)+3H_2O(l)=H_2SeO_3+4H^{\cdot}+4\ominus$ is $-0{\cdot}740$ volt. The standard free energies at 25° of H_2SeO_3, $HSeO_3'$, and SeO_3'' at 1*M* are −101,360, −97,850, and −87,890 g.-cal., respectively. S. K. TWEEDY.

Reduction potentials of maleic and fumaric acids by the dropping mercury electrode. P. HERASYMENKO [with Z. TYVONUK] (Z. Elektrochem., 1928, 34, 74—78).—Using the polarograph described by Heyrovsky and Shikata (A., 1925, ii, 674), reduction potentials can be determined with considerable accuracy. On electrolysis of solutions of maleic and fumaric acids the undissociated acid only is reduced. The normal reduction potentials of the two acids are identical within the limits of experimental error ($\varepsilon_c=-0{\cdot}425$ volt against the normal calomel electrode). The polarisation curves for maleic acid show a maximum, repressed in presence of indifferent salts. J. S. CARTER.

Potentiometric analysis of electrolytes. L. DE BROUCKERE (Bull. Soc. chim. Belg., 1928, 37, 103—110).—A cell of the type $M|cMA(I)|KB(III)|xMA(II)|M$ is used, II containing the solution x to be studied. In I is placed a solution of known concentration $c>x$. This solution is gradually diluted and the *E.M.F.* of the cell for each concentration measured. By extrapolation of the values so obtained, it is possible to determine the concentration of I at which the cell gives no *E.M.F.*, *i.e.*, $c=x$. Solutions of cupric chloride, cadmium sulphate, and sodium chloride of concentrations from 10^{-1} to 10^{-4} g.-equiv. per litre have been analysed with an accuracy of 1—2%. At higher dilutions the results are less trustworthy. A more convenient although less accurate method is to measure the point of zero *E.M.F.* directly. The results obtained are consistent to within 5%. F. J. WILKINS.

Hydrogen overvoltage and the reduction of oxalic acid at mercury cathodes. P. HERASYMENKO (Z. Elektrochem., 1928, 34, 129—136).—The relationship between the mercury cathode potential ε necessary for hydrogen evolution and the hydrogen-ion concentration, expressed by the equation $2RT\log[H^{\cdot}]/F$, has been confirmed experimentally, and is explained on the basis of Heyrovsky's theory of overvoltage by assuming a three-stage mechanism at the cathode, viz., $H^{\cdot}+\varepsilon\longrightarrow H$; $H+\varepsilon\longrightarrow H'$; and $H^{\cdot}+H'\longrightarrow H_2$. The evolution of hydrogen is thus catalysed by hydrogen ions, and the relatively great influence of temperature on the cathode potential is probably due to an increase of this catalytic activity. The mechanism of the cathodic reduction of oxalic acid is bound up with the question of hydrogen overvoltage. The assumptions are made that undissociated oxalic acid forms with the hydrogen ion the complex $H^{\cdot},4(CO_2H)_2$, and that the velocity of reduction is proportional to the surface concentration of this complex and of negatively-charged hydrogen ions. The normal reduction potential of oxalic acid at a mercury cathode is $-0{\cdot}606\pm0{\cdot}007$ volt. H. F. GILLBE.

Relation between the chemical behaviour and overvoltage of metals. E. LIEBREICH (Korrosion u. Metallschutz, 1927, 3, 79—82; Chem. Zentr., 1927, ii, 386—387).—With current intensities not great enough to effect the permanent decomposition of water there is a domain of potential in which the metals tend to pass into solution. Experiments with aluminium, nickel, copper, silver, gold, platinum, and palladium in 0·1% sulphuric acid show that even with the noble metals there is a brief period of oxide formation with weak cathodic polarisation. The retardation of hydrogen production depends on the ease with which oxide is formed at the surface. Overvoltage values provide a measure of the ease of superficial oxidation of the metals. A. A. ELDRIDGE.

Effect of pressure on the voltage required for the electrolytic decomposition of water at constant temperature. C. F. HOLMBOE (Z. Elektrochem., 1928, 34, 67—68).—An apparatus is described for investigating the effect of pressure on the relation between voltage and current density in electrolysis. Experiments with sodium hydroxide solution (d^{18} 1·16) at 19·1° and at pressures of about 1, 50, and 100 atm. indicate that the voltage required to produce a given current density (between 1·25 and 8 amp./dm.^{2})

is independent of the pressure within the limits of experimental error. H. J. T. ELLINGHAM.

Contact electricity, thermo-electricity, and cohesion pressure. R. VON DALLWITZ-WEGNER (Z. Elektrochem., 1928, **34**, 42—49).—Values of the cohesion pressure, K, of various substances at 0° and 100° are calculated from the relation, $K=84\cdot1d[(1+at)/a]/M$, where d=density, M=mol. wt., t=temperature, and a—coefficient of cubical expansion. For solids, the values of K range from 13×10^6 for diamond to $56\cdot5\times10^3$ for lead at 0°, the sequence of the various substances corresponding with the order of hardness. For mercury at 0°, K—31×10^3. The relation of the cohesion pressure to contact electricity and thermo-electricity is discussed, and an equation is developed whereby the $E.M.F.$ of a thermo-element with a temperature difference of 100° between the hot and cold junctions can be calculated from the cohesion pressure data. For a platinum–silver element satisfactory agreement is obtained with the observed value, but for many thermo-elements there are notable discrepancies. These discrepancies are attributed to the fact that small amounts of impurities in the metals can have a large effect on the $E.M.F.$ and on K, so that agreement can be expected only if K is determined for the particular samples of metal used in the thermo-element. H. J. T. ELLINGHAM.

Cathodic overvoltage. E. LIEBREICH and W. WIEDERHOLT (Z. Elektrochem., 1928, **34**, 28—41).—In continuation of previous work (A., 1925, ii, 44, 404), the course of current–potential curves has been determined for the cathodic and anodic polarisation of electrodes of copper, silver, gold, platinum, palladium, graphite, and amorphous carbon in $0\cdot02N$-sulphuric acid and for copper and silver electrodes in $0\cdot02N$-sodium hydroxide. With increasing cathodic polarisation, all the metals exhibit an " activation period " before hydrogen evolution begins. During this period, the metal becomes coated with a thin film of hydroxide or basic salt which hinders the evolution of hydrogen, either mechanically, or by consuming it in reduction processes. The hydrogen overvoltage of the metals is regarded as being essentially determined by this film formation. The formation of the film itself is attributed to the reaction of the metal with the hydroxyl ions liberated in its immediate neighbourhood by the initial discharge of hydrogen ions to form hydrogen which is occluded in or adsorbed by the metal. Amorphous carbon exhibits no activation period and graphite scarcely any. In these cases the hydrogen overvoltage is attributed to the formation of gaseous hydrocarbons and the occlusion of these gases and of hydrogen in the electrode. It is suggested that the hydrogen overvoltage of metals is intimately connected with their capacity for becoming coated with a more or less adherent film of the type which is associated with passivity phenomena. H. J. T. ELLINGHAM.

Valency of chromium in its deposition from aqueous solutions of chromic acid. E. LIEBREICH (Z. Elektrochem., 1928, **34**, 41—42).—Whereas the data obtained by Stscherbakov and Essin (A., 1927, 839) for current efficiencies in the electrolysis of chromic acid solutions containing a high concentration of sulphuric acid correspond with the formation of chromium by discharge of chromic ions, the data for solutions weaker in sulphuric acid are in better agreement with the view that the metal is formed by discharge of chromous ions. H. J. T. ELLINGHAM.

Quantum theory of quasi-unimolecular gas reactions. O. K. RICE (Proc. Nat. Acad. Sci., 1928, **14**, 113—118; cf. A., 1927, 833).—Theoretical. The way in which the reaction rate falls with pressure in the case of gas reactions which are unimolecular and the motions of the molecules are quantised, is investigated. W. E. DOWNEY.

Influence of temperature on the formation of the explosion wave. P. LAFFITTE (Compt. rend., 1928, **186**, 951—953).—The author's method (A., 1926, 913) has shown that for atmospheric pressure, and temperatures up to 350°, a rise of the temperature at which the gas mixtures ($2H_2+O_2$) and (CH_4+2O_2) are exploded by an electric spark produces the same effect as dilution of the initial mixture by an inert gas, *i.e.*, the formation of the explosion wave is retarded, and the luminosity, noise, and intensity of the explosion are decreased. In both cases, an increase in pressure (*loc. cit.*) or of density facilitates the formation of the explosion wave. J. GRANT.

Kinetics of the combination of hydrogen and oxygen. C. N. HINSHELWOOD and H. W. THOMPSON (Proc. Roy. Soc., 1928, **A**, **118**, 170—183).—The whole course of the gaseous reaction between hydrogen and oxygen has been examined by a static method at constant temperature and volume over a range of temperature from the region where the reaction is undoubtedly a heterogeneous surface reaction to near the point at which the combination ceases to be isothermal and passes into explosion. The apparatus was essentially the same as that previously described (cf. A., 1924, ii, 251). At temperatures below or not much above 500°, the reaction is approximately of the first order, in agreement with the results of Bone and Wheeler (Phil. Trans., 1906, **A**, **206**, 1). It is greatly accelerated by the presence of powdered silica in the bulb, and somewhat retarded by the presence of steam. From about 520° to 530° a reaction comes into prominence which is quite different from the low-temperature reaction. A definite order cannot be assigned to the reaction, for the apparent order tends to increase with pressure and with rise of temperature, but on the average, the influence of pressure between 540° and 560° is roughly characteristic of a fourth-order reaction. It is strongly auto-catalysed by steam and has a high temperature coefficient. At high temperatures the normal positive catalytic effect of the walls of the reaction chamber is replaced by a negative effect, which may be due to the catalytic destruction of an autocatalyst for the principal reaction (cf. Egerton and Gates, B., 1927, 738), or to the interruption of "reaction-chains" (cf. Christiansen, A., 1924, ii, 242), or to a combination of both causes. It is suggested that the high-order reaction is the true gas reaction between hydrogen and oxygen. L. L. BIRCUMSHAW.

Oxidation of phosphorus vapour at low pressures. N. SEMENOV (Z. Physik, 1927, **46**, 109

131).—The oxidation of phosphorus vapour at low pressures has been re-examined in the light of Bodenstein's criticisms (A., 1927, 326) on the work of Chariton and Walta (*ibid.*, 122). Whilst the comments on technique are admitted, the conclusions of Bodenstein are held to be false. It has been established that there is a critical oxygen pressure below which the oxidation of phosphorus vapour is immeasurably slow; this critical pressure depends on the partial pressure of phosphorus vapour, the partial pressure of admixed argon, the diameter of the reaction vessel, and on the temperature. It is held that a chain reaction takes place and that the walls of the containing vessel de-activate active molecules which come in contact with the walls.

R. W. LUNT.

Theories of unimolecular gas reactions at low pressures. II. O. K. RICE and H. C. RAMSPERGER (J. Amer. Chem. Soc., 1928, **50**, 617—620).—The thermal decomposition of azomethane occurs in accordance with the second reaction-rate theory outlined previously (A., 1927, 833). A brief discussion is given. The thermal decomposition of ethyl ether (Hinshelwood, A., 1927, 212) fits the second theory better than the first.

S. K. TWEEDY.

Decomposition of azo*iso*propane. A homogeneous unimolecular reaction. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1928, **50**, 714—721).—The thermal decomposition of azo*iso*propane between the initial pressures of 4·6 and 0·025 cm. and at temperatures between 250° and 290° is a homogeneous unimolecular reaction (cf. A., 1927, 425). The velocity coefficient (in terms of pressure) is $5{\cdot}6\times10^{13}\times e^{-40,900/RT}$, even at low pressures; the second theory of Rice and Ramsperger (A., 1927, 833) requires this coefficient to become smaller below 0·025 cm. if the azo*iso*propane molecule has 45—50 " degrees of freedom," and the specific heat of the gas is probably large enough to permit this high number. The results are discussed in relation to collision theories of reaction rate.

S. K. TWEEDY.

Phenomena of inertia and chemical reactions. E. PUXEDDU (Gazzetta, 1928, **58**, 95—103).—Previous work on chemical reactions in aqueous solution which show a period of induction is discussed, viz., the action of sulphurous acid on iodic acid and of mercuric chloride on sodium hydrogen carbonate. It is concluded that such phenomena can be explained only by assuming that in all chemical processes there is an initial period of retardation, which under ordinary conditions is generally very short. In order to show the existence of induction periods in simpler systems the precipitation of the sulphates of the alkaline-earth metals and of sulphur from sodium thiosulphate by means of sulphuric acid has been studied under varying conditions of temperature and of concentration. The induction period shown by these reactions decreases with a rise of temperature or an increase of concentration.

O. J. WALKER.

Kinetics of the reaction between iodine and potassium nitrite in light and darkness. A. BERTHOUD and W. BERGER (Helv. Chim. Acta, 1928, **11**, 354—363).—Since iodine in presence of potassium nitrite cannot be directly titrated with sodium thiosulphate (cf. this vol., 486) the data of Dhar and co-workers (A., 1924, ii, 466; 1926, 252) regarding the kinetics of the reaction $KNO_2+I_2+H_2O\longrightarrow KNO_3+2HI$ are without value. The kinetics of the thermal and photochemical reactions have now been investigated under conditions precluding the development of acidity during the course of the reaction. Iodine was determined by titration with sodium arsenite. The experimental numbers obtained in a study of the photochemical reaction suggest for the predominating scheme: (i) $I_2+h\nu\longrightarrow 2I$; (ii) $2I+H_2O\longrightarrow HIO+I'+H^{\cdot}$; (iii) $HIO+I'\longrightarrow I_2+OH'$; (iv) $HIO+NO_2'\longrightarrow NO_3'+H^{\cdot}+I'$; (v) $I_2+I'\rightleftharpoons I_3'$. The photochemical reaction follows the Grotthus–Draper law. When the absorption of light is small the reaction rates observed under the experimental conditions are fairly satisfactorily represented by the relation $-d[I_2]/dt=kI_0[KI_3][KNO_2]/[KI]([KI]+b[KNO_2])$, where k and b are constants and I_0 is the light intensity. A similar scheme holds for the thermal reaction save that reactions (i) and (ii) are replaced by the process $I_2+H_2O\longrightarrow HIO+I'+H^{\cdot}$. The rate of disappearance of iodine is then represented by an expression differing from the preceding only by the absence of the quantity I_0.

J. S. CARTER.

Velocity of ionic reactions. III. R. N. J. SAAL (Rec. trav. chim., 1928, **47**, 385—396).—By the oxidation potential method previously described (this vol., 248, 373), the velocity coefficient of the bimolecular reaction between ferrous and persulphate ions has been determined in different concentrations of potassium chloride, magnesium chloride, and magnesium sulphate. Practically the same values were obtained with equivalent concentrations of excess of neutral salt. This is not in accordance with theory and might be ascribed to the accelerating influence of the magnesium ion. It is shown that the catalytic influence of iron salts on the reaction between persulphate and iodine, observed by von Kiss and von Zombory (A., 1927, 632), cannot be wholly explained by the reactions $2Fe^{\cdot\cdot}+S_2O_8''\longrightarrow 2Fe^{\cdot\cdot\cdot}+2SO_4$ and $2Fe^{\cdot\cdot\cdot}+2I'\longrightarrow 2Fe^{\cdot\cdot}+I_2$. The amount of iodine formed by catalysis, as calculated from the coefficients of these reactions, is much smaller than that found by experiment. The velocity coefficient of the bimolecular reaction $I_2+Fe(CN)_6''''$ has been determined in the presence of 0·1 and $1N$-potassium chloride, and the latter is found to have a strong retarding action which is not in accordance with Bronsted's theory.

M. S. BURR.

Action of bromine on formaldehyde. F. E. C. SCHEFFER and N. B. VAN WENT (Rec. trav. chim., 1928, **47**, 406—414).—The rate of reaction of bromine with formaldehyde can best be explained by supposing that formic acid is obtained as an intermediate product and that only the dissociated fraction of this acid reacts with bromine (cf. Bognar, A., 1910, ii, 282). If k_1 is the velocity coefficient at 25° of the reaction $HCHO+Br_2+H_2O\rightarrow HCO_2H+2H^{\cdot}+2Br'$ and k_2 that of the reaction $HCO_2'+Br_2\rightarrow CO_2+H^{\cdot}+2Br'$, it has been shown that, on the assumption that the ionic dissociation constant of formic acid at 25° is $2{\cdot}14\times10^{-4}$, $k_2=1{\cdot}0\times10^4k_1$. The simultaneous reactions can only

be studied quantitatively provided that the quantity of formaldehyde which reacts is small compared with the total quantity present, and also that a certain amount of hydrobromic acid is present at the beginning. M. S. BURR.

Decomposition of *p*-phenetylcarbamide when heated in aqueous solution. K. TAUFEL, C. WAGNER, and H. DUNWALD (Z. Elektrochem., 1928, **34**, 115—127).—When heated in aqueous solution at 100° *p*-phenetylcarbamide breaks down primarily into *p*-phenetidine and cyanic acid and into *p*-phenetylcarbimide and ammonia. The cyanic acid and *p*-phenetylcarbimide undergo hydrolysis to ammonia, carbon dioxide, and *p*-phenetidine. In acetic acid solution, at a certain concentration of *p*-phenetidine, di-*p*-phenetylcarbamide is formed. The velocity of the primary decomposition is considerably reduced by the presence of ammonia. The acid dissociation constant of the cyanic acid, determined by colorimetric measurements, is $2{\cdot}2\times10^{-4}$, whilst the basic dissociation constant of *p*-phenetidine, determined conductimetrically, is about 8×10^{-9}. The hydrolysis of the cyanate ion in alkaline solution is approximately unimolecular, being scarcely influenced by the hydroxyl-ion concentration; the velocity coefficient at 100°, time being expressed in minutes, is 0·0028. The indophenol reaction cannot be applied for the detection of *p*-aminophenol in urine if *p*-phenetidine or its derivatives be present, since secondary *p*-aminophenols are then produced on heating with concentrated sulphuric acid. H. F. GILLBE.

Decomposition of diacetone alcohol by weaker bases. G. ÅKERLÖF (J. Amer. Chem. Soc., 1928, **50**, 733—744).—The decomposition velocity at 25° of diacetone alcohol in sodium chloride and sodium sulphate solutions of weak bases is recorded. The following dissociation constants are calculated ($\times10^5$): ammonia, 1·85 (reference value); methylamine, 350; dimethylamine, 97; trimethylamine, 6·5; ethylamine and diethylamine, 130; triethylamine, 63. It is considered that the values for the stronger bases are more accurate than those previously recorded. The above decomposition velocity seems to be proportional to the mean activity of the hydroxides and not to the activity of the hydroxyl ion; for this reason the activity coefficients of the weaker bases as electrolytes in salt solutions, unlike those of weak acids, cannot be calculated on the assumption that the proportionality factor between the activity and the reaction velocity is the same for weak and strong bases. The corrected mean activity coefficients are recorded; they decrease in dilute salt solutions by amounts comparable with those observed by Harned and Hawkins for weak acids in the same salt solutions (this vol., 251). S. K. TWEEDY.

Potentiometric indication in the formation of azo dyes. F. MULLER (Z. Elektrochem., 1928, **34**, 63—66).—By the use of a platinum electrode and a standard calomel electrode, the formation of azo dyes from diazonium salts may be followed potentiometrically. J. S. CARTER.

Foundations of theory of binding forces. F. EBEL and E. BRETSCHER (Helv. Chim. Acta, 1928, **11**, 281—300).—The stabilities of atom linkings are discussed and it is shown that under appropriate conditions a measure of the magnitude of the binding forces may be determined from a study of the rates of chemical reactions. A suitable reaction for the purpose appears to be that between *p*-toluenesulphonyl halides and aromatic primary amines (A., 1927, 1177). A study of the dynamics in the systems *p*-toluenesulphonyl chloride (bromide)–aniline, and *p*-toluenesulphonyl chloride (bromide)–aniline–dimethylaniline shows that the ratio of the velocity coefficients for the reactions between aniline and dimethylaniline and the reaction complex $C_7H_7{\cdot}SO_2Cl(Br),3NH_2Ph$ is independent of the halogen. J. S. CARTER.

Kinetics of the oxidation of hydriodic acid by free oxygen. A. BERTHOUD and G. NICOLET (J. Chim. phys., 1928, **25**, 163—181).—See A., 1927, 736.

Dynamics of reduction of oxides by carbon. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1928, **170**, 62—70).—The reduction of oxides when heated with carbon has been investigated with the aid of heating curves. With cupric oxide and manganese dioxide, the reduction ultimately becomes very vigorous, as the reactions are here exothermic. This stage starts at the temperature at which combustion of the particular kind of carbon employed commences, provided that the pressure of oxygen produced by dissociation of the oxide is, as is the case with manganese dioxide, sufficient to permit of such rapid oxidation of the carbon that inflammation actually occurs. With cupric oxide, however, the pressures are so small that rapid reduction does not start until the temperature is nearly 200° above the ignition point of the carbon. In the reduction of ferric oxide, the action of a magnet shows that considerable action has taken place before the first sign of it appears on the heating curve in the form of a slight decrease in the rate of rise in temperature, the temperature beyond this point successively passing through a maximum, then through a minimum, and rising again. The maximum, which is reminiscent of the boiling of a superheated liquid, cannot correspond with the commencement of the endothermic reduction to the metal of ferrosoferric oxide formed in a previous stage of the reaction, since it does not appear on the heating curve of a mixture of ferrosoferric oxide and carbon, which scarcely affords indication of any reaction whatever; it probably denotes the commencement of the reaction $3Fe+2CO \longrightarrow Fe_3C+CO_2$. Cadmium oxide and cobaltous oxide also give curves with either maxima or arrest points. For all three oxides, the temperature at which reduction begins apparently rises with decrease in the amount of carbon and with increase in the rate of heating. The endothermic reductions of nickel monoxide and sesquioxide, lead oxide, and stannic oxide occur slowly over such a wide temperature interval that the heat of reaction does not visibly affect the heating curves. R. CUTHILL.

Connexion between reactivity and electrical conductivity in the solid state. J. A. HEDVALL (Z. anorg. Chem., 1928, **170**, 71—79).—Heating curves of binary solid mixtures of barium oxide with cuprous chloride, bromide, and iodide show that the intensity of the reaction $BaO+2CuX=BaX_2+Cu_2O$

decreases in this order, whereas the temperature at which rapid reaction sets in rises. Analysis of the products of reaction by extracting unchanged cuprous halide with pyridine confirms these results. The reaction temperatures approximate to the temperatures at which the conductivities of the solid cuprous halides begin to increase rapidly (Tubandt, Rindtorff, and Jost, A., 1927, 919), from which it may be concluded that the action of rise in temperature in loosening the lattice affects both reactivity and conductivity similarly. Since slow reaction occurs even at temperatures at which cuprous chloride and iodide are purely electronic conductors, and since the alkaline-earth oxides are electronic conductors at all the temperatures involved in the present investigation (Horton, A., 1906, ii, 260), it appears that atomic or molecular lattices, as well as ionic lattices, are able to take part in reactions. Examination of the data previously obtained for the reactions between sulphates and alkaline-earth oxides (A., 1923, ii, 860) shows that the highest reaction temperatures are those of the sulphates of calcium, strontium, and magnesium, the cations of which have the inert gas structure, and cause, therefore, very little deformation, and consequently a minimum loosening of the lattice.

R. Cuthill.

Determination of reaction temperatures in mixtures of powders by means of heating curves. J. A. Hedvall and E. Gustafsson (Z. anorg. Chem., 1928, **170**, 80—84).—Determination of the temperature of commencement of rapid reaction between barium oxide and cuprous chloride or bromide from the appearance of the colour of cuprous oxide gives results which agree well with those obtained from heating curves (cf. preceding abstract). The transition from the white of the mixture of reactants to the red of the resultants is not, however, perfectly sharp, since a certain amount of reaction occurs before the rapid phase begins. A repetition of the experiments on the reaction between barium oxide and cupric sulphate (A., 1923, ii, 860), in which the formation of cupric oxide imparts a black colour to the reacting mixture, has given similar results.

R. Cuthill.

Dissolution of aluminium and its alloys in presence of different electrolytes. N. A. Isgarischev and V. M. Iordanski (J. Russ. Phys. Chem. Soc., 1928, **60**, 113—126).—The dissolution of aluminium and its alloys with copper, nickel, and magnesium in hydrochloric acid and potassium hydroxide solution was studied. The velocity of dissolution increased with increasing copper content of the alloy; the presence of magnesium had no definite influence and that of nickel only a very slight one. Pure aluminium dissolved more rapidly in N-hydrochloric acid than in $2N$-sulphuric acid. The presence of chlorine and fluorine ions, potassium bromate, iodate, or chlorate increased considerably the velocity of dissolution of aluminium in $2N$-sulphuric acid; other oxidising agents had a less marked influence.

A. Ratcliffe.

Investigation of the corrosion of metals [iron] with a thermobalance. K. Inamura.—See B., 1928, 233.

Action of water, air, oxygen, and carbon dioxide on the corrosion of iron. K. Inamura.—See B., 1928, 233.

Corrosion of copper and brass. K. Inamura.—See B., 1928, 233.

Dislocation theory of catalytic action. J. Boeseken (Chem. Weekblad, 1928, **25**, 135—140).—Consideration of several cases of the Friedel–Crafts reaction leads to the conclusion that the catalyst acts, not by virtue of, but in spite of the formation of intermediate compounds. The catalyst acts by activating the reacting material, and different catalysts may activate the same substance in different ways, producing specific "dislocations" or temporary polarities by a kind of induction. In physical catalysis the effect is produced rather by alterations in the entropy of the system than by considerable changes in the energy of activation; in chemical catalysis the energy factor is the more important.

S. I. Levy.

Synthesis of ammonia; argon as catalyst. E. Goldstein (Z. Physik, 1928, **47**, 274—279).—In a discharge tube containing argon and nitrogen and fitted with an aluminium cathode, the passage of current causes the nitrogen spectrum to disappear if the cathode is cooled in liquid air. Aluminium in an atmosphere of argon melts very readily to give fresh surfaces which are reactive towards nitrogen. A method of introducing small amounts of nitrogen into the discharge has been devised, and it is found that the catalytic process can go on indefinitely.

Helium, contaminated with hydrogen and nitrogen in traces, was used to fill a discharge tube which was cooled in liquid air. After the discharge had been passing for a short time, the spectrum corresponded with relatively pure helium. If now the tube was allowed to return to the ordinary temperature, the yellowish-green ammonia spectrum was observed. In about 2 hrs. the composition of the gas in the discharge tube is almost the same as that at the beginning.

R. A. Morton.

Acid and salt effects in catalysed reactions. XII. The water catenary ($H^{\cdot}$–H_2O–OH') in the iodination of acetone. H. M. Dawson and A. Key (J.C.S., 1928, 543—551).—The rates of reaction of acetone with iodine in isohydric series of buffer solutions have been measured with an acetone concentration of 20·0 c.c. per litre, iodine initially about $0{\cdot}001M$, and hydrogen-ion concentrations between $18{\cdot}5\times10^{-5}$ and $0{\cdot}065\times10^{-5}$. The velocities due to the catalytic constituents of water are calculated from the equation $v_0=k_h[H^+]+k_{OH}[OH^-]+k_w[H_2O]$. Water molecules accelerate the reaction, but k_w is small. The ratio k_{OH}/k_w is about 5×10^{10}. The velocity due to the joint action of hydrogen and hydroxyl ions agrees well with the values calculated from the generalised catalytic formula $r=\cosh\log_e n$, where r is the reduced ionic velocity and n is the reduced hydrogen-ion concentration.

C. W. Gibby.

New induced reaction. Oxidation of potassium nitrite by iodine induced by sodium thiosulphate. A. Berthoud and W. Berger (Helv. Chim. Acta, 1928, **11**, 364—368).—Titration of solu-

tions of iodine containing potassium nitrite with solutions of sodium thiosulphate yields incorrect results. With increasing concentration of nitrite the quantity of iodine as determined by titration tends towards a value which is about half that actually present. Solutions of thiosulphate containing nitrite may, however, be titrated with solutions of iodine. Correct results are obtained when titration of the iodine-nitrite mixture is effected with a solution of sodium arsenite. It is suggested that the observed behaviour is due to a reaction between iodine and potassium nitrite induced by sodium thiosulphate.

J. S. CARTER.

Effect of neutral salts on certain catalytic decompositions. C. C. FRENCH (J. Physical Chem., 1928, **32**, 401—414; cf. Harned, A., 1918, ii, 436; Kilpatrick, A., 1926, 919).—The velocity of decomposition of hydrogen peroxide by neutral potassium iodide and of nitrosotriacetonamine by potassium hydroxide in various salt solutions has been measured at $25\pm0{\cdot}01°$ with constant catalyst and varying salt concentrations. Decomposition of the hydrogen peroxide by the apparatus or filter-paper was negligible, but concentrated (1·5—3*N*) solutions of sodium and potassium bromides, or of the chlorides of calcium, barium, strontium, and magnesium, brought about a slow decomposition in the absence of the iodide catalyst. The sulphates of lithium, sodium, potassium, and magnesium showed no effect. In the presence of the catalyst, all the salts mentioned showed an increased velocity of decomposition except potassium sulphate, in which case, in agreement with Walton (A., 1904, ii, 319), a slight decrease was obtained. The results are in general agreement with those of Harned (*loc. cit.*). The velocity of decomposition of nitrosotriacetonamine in presence of potassium hydroxide decreases with increasing concentration of added salt in the order (decreasing velocity) potassium chloride, sodium chloride, potassium bromide, lithium chloride, and potassium iodide. In common with Clibbens and Francis (J.C.S., 1912, **101**, 2358), irregular results were repeatedly obtained with the alkali sulphates in this decomposition. The nature of the neutral salt effect is discussed.

L. S. THEOBALD.

Insulin and amino-acid catalysis [of the oxidation of dextrose and lævulose by hydrogen peroxide]. J. M. ORT (J. Amer. Chem. Soc., 1928, **50**, 420—425).—The accelerating influence of certain amino-acids on the oxidation by very dilute hydrogen peroxide of dextrose (cf. Ort and Bollman, A., 1927, 450) at p_H 10 and 30° has been investigated more fully and similar investigations have been made with lævulose and with both sugars in the presence of insulin. A more rapid current of nitrogen has been used, and the oxidation potential curves of mixtures of hydrogen peroxide with dextrose alone or dextrose plus amino-acid show that there is a general parallelism between the catalytic action of the amino-acids and the grouping of these acids according to specific dynamic action, tyrosine being an exception; with lævulose the relationship is less marked, whilst insulin decreases still further this agreement. Insulin retards the oxidation of dextrose or lævulose by hydrogen peroxide, but has no marked influence on this oxidation in the presence of amino-acids. In all the experiments, the maximum rate of recovery to reducing conditions occurs in the region between 0·5 and —0·15 volt, and below —0·20 volt the rate of decrease of oxidation potential falls abruptly. A. WORMALL.

Catalytic chlorination of acetic acid to chloroacetic acid. H. BRÜCKNER.—See B., 1928, 254.

Gaseous catalysis by means of metals of the platinum group. L. DUPARC, P. WENGER, and C. URFER (Helv. Chim. Acta, 1928, **11**, 337—348; cf. A., 1925, ii, 1177).—The relative efficiencies of metals of the platinum group in promoting the oxidation of ammonia and the reduction of oxides of nitrogen were measured. Catalysts were obtained by the deposition of the metal on asbestos. The actual numbers presented illustrate the dependence of the reaction yield on the metal content of the catalyst, temperature, and the rate of passage of the reacting gas mixture.

[With P. CHARVOZ.]—Oxidation of ammonia by air (1 vol. of ammonia+10 vols. of air) in presence of rhodium is maximal (93%) at about 600—620° for a catalyst containing 0·1% of rhodium at a gas velocity equivalent to the passage of 1 litre of ammonia/hr.

[With C. LEMPERT and HEFTI.]—Oxidation of ammonia by oxygen (1 vol. of ammonia+2 vols. of oxygen) in presence of a palladium catalyst is remarkable in that two maxima are observed, one at 400° and one at 700°. Maximal oxidation (96%) is obtained at 700° with a catalyst containing 2% of palladium at a gas velocity equivalent to the passage of 5 litres of ammonia/hr. Oxidation by air is also characterised by the occurrence of two maxima at the same temperatures. The oxidation is maximal (68%) at 700°, the catalyst concentration being 1%, and the gas velocity (litres of ammonia/hr.) unity.

[With G. ROSSIER.]—Oxidation of ammonia by air is only partial in presence of iridium catalysts, the maximal yield (51%) being obtained with a 2% catalyst at 700° and a gas velocity of 2 litres of ammonia/hr.

[With HEFTI.]—Measurements were made with the gas mixtures, N_2O+4H_2 and $NO+2{\cdot}5H_2$. Using palladium catalysts no reduction of nitrous oxide to ammonia occurs. With nitric oxide two maxima are observed at 400° and 700°, respectively. The measurements were made with a gas velocity (litres of nitric oxide/hr.) unity. Under these conditions the yield of ammonia is maximal (98%) at 700° with a catalyst containing 5% of palladium. Reduction of nitrous oxide in presence of an iridium catalyst is effected in accordance with the equation $N_2O+H_2=N_2+H_2O$, the catalyst becoming incandescent at about 350° when the total gas velocity is 10 litres/hr. Nitric oxide is, however, reduced to ammonia, the yield with a 2% catalyst at temperatures between 400° and 700° being about 54%. Above 330° the catalyst becomes incandescent, the rate of reaction increasing with the rate of passage of the gaseous mixture.

The present data are in entire agreement with theory suggested in the earlier paper. The catalytic efficiencies of the platinum metals are determined by chemical, rather than by physical, factors.

J. S. CARTER.

Catalytic oxidation of ammonia. VIII. L. Andrussov.—See B., 1928, 261.

Catalytic hydrogenation of carbon oxides. V. N. Morris and L. H. Reyerson (Proc. Indiana Acad. Sci., 1927, **36**, 203—206).—In attempts to synthesise formaldehyde and methyl alcohol at atmospheric pressure, the most favourable results for the former were obtained by using a platinised gel as catalyst with mixtures of hydrogen and carbon dioxide. Hydrogen and carbon monoxide, with a copper catalyst, afforded a mixture of products. The results at 8—27 atm. were no better.

Chemical Abstracts.

Catalytic decomposition of methyl alcohol. D. F. Smith and C. O. Hawk (J. Physical Chem., 1928, **32**, 415—424).—The decomposition of methyl alcohol vapour into carbon monoxide and hydrogen by various catalysts, chiefly oxides and mixtures of oxides prepared in various ways, has been investigated at temperatures near 300°. Zinc oxide prepared by igniting the carbonate, mixtures of zinc oxide and chromic or vanadic acid, and of cadmium oxide and chromic acid show marked catalytic activity. The activity of the zinc oxide–chromium oxide catalysts is optimal with atomic proportions of 4 of zinc to 1 of chromium, and is largely dependent on the previous history of the sample of catalyst used. The small percentage of carbon dioxide almost invariably obtained with all catalysts is regarded, not as an impurity, but as a by-product of the decomposition.

L. S. Theobald.

Positive and negative catalysis of the setting of plaster of Paris. P. P. Budnikov (Kolloid-Z., 1928, **44**, 242—249).—The course of the setting of plaster of Paris was followed by a thermometric method. Rapid rise of temperature first occurs, with the formation of a colloidal gel of gypsum, after which hydration becomes slower and the temperature gradually falls. After a definite induction period a rapid crystallisation of the dihydrate from the gel takes place with further rise of temperature. The duration of this induction period depends on the presence of foreign substances, some of which shorten the period whilst others lengthen it. A study has been made of the effect of addition of a number of salts, acids, bases, double and complex salts on the velocity of setting. The phenomenon is ascribed to various causes, such as the alteration in the solubility of gypsum in presence of other substances, the change in the velocity of coagulation of the gypsum gel, and in some cases the formation of compounds by addition, or double decomposition between the calcium sulphate and the substance added.

E. S. Hedges.

Decomposition of potassium chlorate. III. Effect of pressure on the decomposition of potassium chlorate–manganese dioxide mixtures. H. M. McLaughlin and F. E. Brown (J. Amer. Chem. Soc., 1928, **50**, 782—789).—For each temperature between 70° and 350° there is a pressure above which the catalytic decomposition of potassium chlorate in presence of manganese dioxide, which is an irreversible reaction, is very slow or absent. Decomposition occurs at 68° under 0·03 cm. pressure, and at pressures from 200 to 500 atm. undecomposed potassium chlorate remains even after heating for hours at about 300°. Water seems to promote the catalyst.

S. K. Tweedy.

Catalytic decomposition and oxidation of formic acid. E. Müller and K. Schwabe (Z. Elektrochem., 1928, **34**, 170—185).—The catalysts, finely-divided palladium, platinum, rhodium, iridium, ruthenium, and osmium, were prepared by the method of Paal and Poethke (A., 1926, 936). The catalytic decomposition of the acid was followed by observing the amount of hydrogen and carbon dioxide produced and the oxidation by oxygen was determined in a similar manner. Measurements of the potentials of the catalysts were made while these reactions were taking place. Palladium is by far the most active metal in decomposing the acid; platinum is much less so, whilst the other metals are inactive. The oxidation is strongly catalysed by palladium, platinum, and rhodium but not by the other metals. Only those metals which are able to raise the pressure of the adsorbed hydrogen on their surfaces to atmospheric pressure can assist the decomposition of formic acid. Those metals which are unable to do this are suitable as catalysts for the oxidation. Such metals, during the oxidation process, have a potential which indicates that $c_{H_2}/c_{O_2}>1$ and leads to the conclusion that the oxidation is dependent on an activation of the hydrogen, and not of the oxygen.

H. Ingleson.

Catalytic activity of thallium. O. W. Brown, C. Brothers, and G. Etzel (J. Physical Chem., 1928, **32**, 456—458; cf. A., 1922, ii, 833).—Thallium supported on asbestos is a good catalyst for the production of azobenzene from nitrobenzene. The optimum temperature is 260° with a rate of flow of 14 litres of hydrogen per hr. Activity is retained for a considerable time. Aluminium hydroxide, pumice, and "nonpareil" brick supported the thallium in good physical condition, but the yields of azobenzene in these cases were negligible. Finely-divided metallic thallium without supports lost activity through incipient fusion.

L. S. Theobald.

Catalysis with copper in the Ullmann reaction. P. E. Weston and H. Adkins (J. Amer. Chem. Soc., 1928, **50**, 859—866).—Samples of metallic copper prepared by different methods, or even copper compounds, may be used to catalyse the reaction between acet-*p*-toluidide and bromobenzene (cf. A., 1903, i, 692). The yields (8—43%) depend on the sample of copper used, the reaction temperature and duration of heating, and the amount and nature of the solvent. The best yields were obtained when no solvent was employed. The low yields in some solvents suggest that concentration of the active catalyst has been reduced, as is illustrated by the action of water. The true catalyst is apparently an alcohol-soluble compound formed between copper and the acylated amine in the presence of air. If copper washed with ether and heated in a stream of hydrogen be employed, the catalytic action is destroyed. A certain amount of copper must be used to give maximum yields. If carbonates other than those of sodium or potassium are used to take up the halogen acid formed during the reaction or if organic bases are employed, no reaction occurs. Metallic silver, silver iodide, or

silver oxide cannot be used in place of copper. In the reaction between potassium phenoxide and bromobenzene to give diphenyl ether, the true catalyst seems to be a combination of phenol and copper produced in dry air. J. D. FULTON.

Electrolysis of water with alternating current. CANAUD (Compt. rend., 1928, **186**, 688—690).—The electrolysis of water by an alternating current (50 cycles) of 120 volts at 5 amp. between electrolytic iron electrodes is accompanied by the evolution of the gases dissolved in the water from those portions of the liquid which become heated. After preliminary boiling or at 80—90° the gas evolution is small, but increases considerably when the boiling solution is electrolysed, and the amount of hydrogen is then proportional to the duration of electrolysis. To obtain comparable results, the preliminary period in which oxidation of the electrodes to ferrous oxide occurs should be eliminated, and comparison made only of the volumes of hydrogen liberated. J. GRANT.

Electrolytic formation of dithionate. O. ESSIN (Z. Elektrochem., 1928, **34**, 78—84).—Friessner (A., 1904, ii, 480) has already shown that electrolysis of solutions of sulphites affords sulphate and dithionate. The dependence of the yield of dithionate on various factors has now been investigated. Addition of ammonium fluoride has an appreciable effect, maximal at a concentration 0·1%, in increasing the yield. The yield is also increased by heating the anode (electrodes were of smooth platinum) for some time immediately prior to the electrolysis. When anodes so treated are used, addition of ammonium fluoride depresses the yield. Previous anode polarisation favours the formation of dithionate. Combination of the three factors, pre-heating, polarisation, and addition of fluoride, leads to yields of dithionate which never exceed 45%. Theoretical considerations show that the maximum possible yield is 50%. J. S. CARTER.

Electrochemically prepared perphosphates. F. FICHTER and E. GUTZWILLER (Helv. Chim. Acta, 1928, **11**, 323—337; cf. A., 1918, ii, 439).—Improvements in the method for the preparation of potassium perphosphate are described. The influence of current density, duration of electrolysis, and composition of the electrolysed solution on the yields of perphosphate and permonophosphate obtained by the electrolysis of solutions of rubidium and ammonium phosphates in presence of small amounts of the corresponding chromates and fluorides has been investigated. Solutions of ammonium perphosphate are unstable and undergo fairly rapid decomposition. The oxidations produced by solutions of perphosphates are accelerated in presence of small quantities of manganous, ferrous, nickel, lead, and especially silver salts. The following *perphosphates* have been obtained: rubidium, $Rb_4P_2O_8$; silver (?), $Ag_4P_2O_8$; $Ba_2P_2O_8,4H_2O$; zinc, $Zn_2P_2O_8,4H_2O$; lead, $Pb_2P_2O_8$. J. S. CARTER.

Theory of electro-deposition of chromium from aqueous solutions of chromic acid. V. SCHISCHKIN and H. GERNET (Z. Elektrochem., 1928, 57—62).—The electro-deposition of chromium from aqueous solutions of chromic acid containing small quantities of sulphates has been investigated in its dependence on temperature and current density, and the deposits obtained under various conditions have been examined microscopically. The yield of metal–temperature curves are characteristic. At constant current density the yield at low temperatures is considerable, the deposit being brown and contaminated with oxide. With rise of temperature deposits of dull appearance are obtained, and the yield falls rapidly. Further rise of temperature produces a lustrous deposit and a further reduced yield. At still higher temperatures the deposit again becomes dull, with a fine, matt surface, and the yield is again reduced. Microscopical examination shows the lustrous deposit to be covered with fissures and to contain occasional cavities. The duller deposits obtained at lower temperatures or higher current densities show an irregular granular structure, whilst the fine, matt deposits obtained at higher temperatures show no crystalline structure whatever. Rotation of the cathode, dilution of the chromic acid solution, and increase in the concentration of sulphate favour the formation of the lustrous deposit. The results are briefly discussed. J. S. CARTER.

Electrochemical preparation of Berlin-blue. B. ORMONT (Z. Elektrochem., 1928, **34**, 106—111).—Berlin-blue is deposited at the anode when a solution of potassium ferrocyanide is electrolysed with iron electrodes, the current efficiency being nearly 100% if sodium chloride is present in the solution; the energy required is 1 kw.-hr./kg. Oxidation of the anode deposit, which is at first white, to the pigment is accelerated by blowing air through the slightly acid solution. In presence of sodium sulphate or nitrate, oxygen is evolved as a consequence of the passivity of the anode, and a dark-blue deposit is obtained; the energy required in these circumstances is between 1·5 and 4 kw.-hrs./kg., but decreases as the temperature rises, or on the addition of a trace of sodium chloride. A current density of 100 amp./dm.² may be employed. H. F. GILLBE.

Electrolytic detinning of scrap copper. W. W. STENDER and A. A. IVANOV.—See B., 1928, 268.

Electrolysis of anhydrous formic acid. E. BAUR [with F. SOMLO and H. W. MACKINNEY] (Helv. Chim. Acta, 1928, **11**, 372—375).—When anhydrous formic acid containing sodium formate is electrolysed between platinum electrodes the probable primary cathodic and anodic products are formaldehyde and formyl peroxide, respectively. J. S. CARTER.

Dependence of electrochemical processes on pressure. H. ERLENMEYER (Helv. Chim. Acta, 1928, **11**, 348—354).—Various electrochemical processes have been effected in presence of nitrogen at pressures ranging up to 1000 atm. On electrolysis of a solution of potassium fumarate under a pressure of 1000 atm. the current strength first increases and then falls to zero. The anode becomes coated with fumaric acid. A number of electrolytic oxidations and reductions are considerably restricted at high pressures. The restriction is apparently due to the diminished gas evolution and consequent less efficient agitation

of the solution in the immediate vicinity of the electrode. When the periodicity exhibited by certain electrochemical processes is dependent on electrodic evolution of gas, periodicity is repressed by working at high pressures; otherwise the periodicity is independent of the pressure. Conductivity, potential, and passivity effects are independent of pressure.

J. S. CARTER.

Electrolysis of benzoic acid. E. BAUR and E. MÜLLER (Z. Elektrochem., 1928, 34, 98—103).—An investigation of the electrolytic reduction of an aqueous-alcoholic solution of benzoic acid containing sulphuric acid using a lead cathode shows that the cathode gas contains benzene, carbon dioxide, and traces of carbon monoxide and formaldehyde. The predominating product in the cathode liquor is an oil possessing the empirical formula C_6H_8O, which is probably *cyclo*hexenone. Carbon is usually deposited on the cathode. Electrolytic oxidation yields an anode gas containing benzene, carbon dioxide, and some carbon monoxide, indicating the formation and decomposition of benzoyl peroxide.: $C_6H_5\cdot CO_2\cdot OBz+H_2O=C_6H_5\cdot CO_2H+C_6H_5\cdot CO_2\cdot OH$; $C_6H_5\cdot CO_2\cdot OH=C_6H_6+CO+O_2$.

J. S. CARTER.

Electrochemical production of graphitic oxide. B. K. BROWN and O. W. STOREY.—See B., 1928, 271.

General theory of photochemical reactions of halogens. J. CATHALA (J. Chim. phys., 1928, 25, 182—215).—Since the threshold frequency for the photochemical reaction between hydrogen and chlorine is nearly equal to the frequency corresponding with the beginning of continuous absorption in the absorption spectrum of chlorine, it may be affirmed that the first stage of the photochemical reactions of the halogens is the dissociation into neutral atoms, this process taking place strictly in accordance with the Stark–Einstein law. Theories involving the formation of active molecules and exchanges of activation between molecules by impacts are therefore to be discarded. Since the free atoms are formed in amounts which are proportional to the time, yet their concentration remains extremely small, it is necessary to postulate the existence of some process whereby they are destroyed. The hypothesis is therefore advanced that Cl_3 molecules are formed by the reaction $Cl+Cl_2=Cl_3$. These collide with free atoms, and at the moment of impact there is regrouping of the electronic orbits, forming "quasi-molecules," according to the equation $Cl_3+Cl=2Cl_2$, which then pass out among the other molecules of the gas, and there lose their surplus energy. A similar process occurs with both bromine and iodine. The application of this theory to several of the investigated photochemical reactions is now considered. Assuming that the synthesis of carbonyl chloride is effected through the reaction $Cl_3+CO=COCl_2+Cl$, the rate of formation is proportional to the quantity $[CO][Cl_2]^{3/2}$, which is in excellent agreement with the experimental results. The anticatalytic effect of oxygen may be attributed to its combining with free chlorine atoms to form chlorine peroxide, and so causing a decreased formation of Cl_3; the reaction $Cl_3+O_2=ClO_2+Cl_2$ also occurs. In the reaction of hydrogen with chlorine, it is probably the reaction $Cl_3+H_2=2HCl+Cl$ which is important. Assuming that the mechanism of the action of oxygen is the same as that for carbonyl chloride, a formula substantially the same as that found experimentally by Thon (A., 1927, 323) results. Oxides of chlorine also seem to be involved in the sensitisation of photochemical reactions by chlorine. In the period of induction which occurs when hydrogen and chlorine react in presence of traces of ammonia, the reaction $NH_3+Cl_3=3HCl+N$ is probably taking place. Hydrogen bromide is formed by a series of reactions analogous to those enumerated for hydrogen chloride; the retarding effect of iodine arises from the formation of bromine iodide. The hypothesis of the formation and reaction of triatomic halogen molecules is also capable of rendering an explanation of the photochemical reactions of iodine and bromine in solution. A satisfactory general explanation of the effect of water on the reactions of the halogens may be obtained by supposing that the intense electric field in the vicinity of the water molecules increases the activities of the reacting molecules.

R. CUTHILL.

Photolysis of solutions of hydriodic acid in hexane and in water. E. WARBURG and W. RUMP (Z. Physik, 1928, 47, 305—322).—The photolysis of hydriodic acid has been investigated in terms of Einstein's law. Hydriodic acid, carefully freed from iodine, was distilled in a stream of carbon dioxide. The photolysis was carried out in a special vessel, fitted with quartz windows, and so arranged that the solution scoured the window through which the light entered. The source of light was an electric spark, and the intensities before and after absorption were measured bolometrically. Hydriodic acid in hexane (0·08—1·16*M*-solution) follows Einstein's law. The specific photochemical action, φ (molecules of hydriodic acid decomposed per g.-cal. absorbed), decreases for aqueous solutions, contrary to the equivalence law, for increasing wave-lengths of the light source and, strongly, for decreasing normality of the solution. This behaviour is general to aqueous solutions. For 0·01*M*-hexane solutions φ is only slightly below equivalence, but disappears for corresponding aqueous solutions; in the latter case the acid is dissociated. For higher concentrations two factors have to be considered: part of the acid is dissociated and only the undissociated part is truly photochemically decomposed; part of the absorbed light is absorbed by the dissociated molecules and has no photochemical action. The anomaly of the wave-length of the source is explained as due to the formation by hydriodic acid of hydrates in water solution, but not in hexane solution.

W. E. DOWNEY.

Photosensitisation. II. Source of cadmium resonance radiation. J. R. BATES and H. S. TAYLOR (J. Amer. Chem. Soc., 1928, 50, 771—773; cf. A., 1927, 1153).—A cadmium lamp is described similar to the quartz mercury arc, but containing a 50% cadmium–tin alloy. Ammonia, and probably hydrogen, are unaffected by the action of cadmium atoms in the 2^3P_1 state at 255°, but ethylene is polymerised, in complete agreement with theoretical considerations.

S. K. TWEEDY.

Quantum yield in the photochemical decomposition of nitrogen dioxide. R. G. Dickinson and W. P. Baxter (J. Amer. Chem. Soc., 1928, **50**, 774—782).—Light decomposes gaseous nitrogen dioxide into nitric oxide and oxygen, as suggested by Norrish (A., 1927, 528); by carrying out the experiment at sufficiently low partial pressures the number of molecules of oxygen produced for each quantum absorbed is found to be : λ 4350 Å., 0·0046; λ 4050 Å., 0·36; λ 3660 Å., 0·77, these values being almost independent of pressure in the range investigated (3—40 mm.). S. K. Tweedy.

"Highly attenuated" flames. I. H. Beutler and M. Pólanyi (Z. Physik, 1928, **47**, 379—406).—A "highly attenuated" flame is defined as the reaction zone where the counter-flowing streams of two reacting gases, each at a pressure of about 10^{-3} mm., meet. The light emitted by such a flame is a chemiluminescence. The reactions studied were those between sodium and chlorine and sodium and iodine. Sodium vapour, produced by heating the metal at one end of a tube (100 cm. × 3 cm.), streamed down the tube and met a stream of halogen gas issuing from a container at the other end of the tube. The two elements reacted over 10—20 cm. of the tube length and deposited sodium halide, which was collected on a series of adjacent glass rings. By keeping the flame steady and subsequently analysing the amounts of halide on the rings the distribution of halide in the reaction zone was determined. At the low pressures used each molecular encounter resulted in reaction, so the reaction velocity could be calculated from the precipitate distribution. The corresponding light distribution along the reaction zone was determined photographically and the efficiency calculated from this distribution and the reaction rate distribution. It is concluded that the reactions take place in the gaseous state. The previous conclusions of Haber and Zisch (A., 1922, ii, 461) that free atoms react with molecules according to the scheme $A+BC \longrightarrow AB+C$ has been confirmed for sodium and potassium when they react with halogens, liquid halides, and hydrochloric acid. The primary reaction between sodium and chlorine is $Na+Cl_2 \longrightarrow NaCl+Cl$ and is non-luminescent. The light emission arises from the secondary reaction, $Na_2+Cl \longrightarrow NaCl+Na$, in which the NaCl molecule retains the reaction energy and by collision transmits this energy to a free sodium atom. The reaction $Na+Cl \longrightarrow NaCl$ proceeds at a thousandth of the speed of the reaction $Na_2+Cl \longrightarrow NaCl+Na$. W. E. Downey.

Influence of adsorbed ions on the absorption of light by silver bromide. K. Fajans, H. Fromherz, and G. Karagunis (Z. Elektrochem., 1927, —554).—In explanation of the previous work of the authors (cf. A., 1927, 529), there is the possibility that long wave-lengths are absorbed by a bromide body to the same extent as by a silver body, but that the red rays are active only in the latter case because reaction with the excess of silver salt binds the bromine and prevents back reaction. To test this, the influence of adsorbed ions on the light absorption of silver bromide was studied. Sols containing about 1 millimol. of silver bromide per litre were prepared, with excess of silver nitrate or of potassium bromide varying from 0 to 1 millimol. per litre. The degree of coagulation of these sols became stationary after about 12 hrs.; during the next 2 hrs., which was the time necessary to carry out a measurement of absorption, it did not vary more than 1—2%. With increase of concentration of the excess salt the degree of coagulation decreases, but to a different extent for the two salts. The coagulation tends to a constant value with increase in the concentration of the salts, because the surface of the silver bromide becomes saturated with the ions. This constant value is obtained with 60% excess of silver nitrate (0·6 millimol. per litre), and with 40% excess of potassium bromide. The ratio of the degree of coagulation in the two cases is 1 : 0·35. The dispersity of a sol containing 100% excess of silver nitrate was the same as that of a sol containing 5% excess of potassium bromide. These two sols were used for the purpose of absorption measurement. Silver bromide–gelatin emulsions were also studied, various "bodies" being produced by bathing in solutions of the perchlorates of silver, thallium, and sodium, and potassium bromide. Curves were obtained by plotting the log. of wave-length against the log. of the extinction coefficient. With aqueous sols, the extinction coefficient, k, is practically the same for both sols in the region λ 3800—4470 Å., and the curves are approximately linear. The slope of the curves is slightly greater than that deduced from Rayleigh's formula. For the silver bromide–gelatin plates, plotting log. of wave-length against log. of extinction (*i.e.*, log kcd), the curves are again straight lines in the spectral region λ 3800—4700 Å., both for the pure silver bromide and for plates bathed in silver or sodium perchlorate, and potassium bromide. The curve for pure silver bromide lies slightly above those of the other three, which practically coincide, and remain nearly straight lines into regions of long wave-length. The slope is again slightly higher than that demanded by Rayleigh's formula. This shows that in this case, and also in the case of the aqueous sol, scattering is largely responsible for the extinction. There is a large difference between the extinction of the silver body and that of the bromide body and the pure silver bromide, which is not due to coagulation by the salts in which the plates were bathed. The extinction of the silver body, even in the near ultra-violet, is greater than that of the bromide body; *i.e.*, the absorption of the silver bromide is influenced by adsorbed ions. The difference between the extinctions of the silver body and the bromide body increases on passing from the ultra-violet to the yellow, with both plates and sols. This indicates an extension of the light absorption into the longer wave-lengths by the absorbed silver ions. It is assumed that the size of the absorbed light quantum depends only on the absorption of energy in the first phase of the process of transfer of an electron from a bromide to a silver ion, *i.e.*, the separation of an electron from a bromide ion. It will therefore depend on the condition of the bromide ions in the silver bromide space-lattice. It is so markedly different in the case of sodium bromide from that of silver bromide, owing to the deforming action of the silver ions on the bromide ions

in the surface of silver bromide. The shift of absorption due to adsorbed silver ions is due to their distorting effect on the neighbouring bromide ions in the silver bromide lattice. W. CLARK.

Photo-sensitivity of silver bromide and the corpuscular theory of light. A. MARCH (Z. Physik, 1928, **46**, 759—763).—The evidence relating to the photo-sensitivity of silver bromide in weak light is used to sustain an argument for the corpuscular nature of light. R. W. LUNT.

Theory of photographic exposures. L. SILBERSTEIN (Phil. Mag., 1928, [vii], **5**, 464—489).—Attempts to modify the quantum theory of photographic exposures previously stated by the author (*ibid.*, 1922, [vi], **44**, 257; 1923, [vi], **45**, 1062; B., 1922, 960) have led to unsatisfactory results. Similarly, the mathematical statement of the assumption of Toy (B., 1923, 426) that prior to the exposure there are a certain number of nuclei distributed haphazardly among the grains of the emulsion such that the energy required to convert them into development centres is a Maxwell distribution function, does not represent the experimental data. Arising from the "concentration speck" theory of Sheppard, Trivelli, and Loveland (B., 1925, 785) a further theory is developed in which the rate of increase of area of a nucleus is considered as proportional to its original area and no quantum relationships are assumed. The number of grains k made developable by an exposure E is then given by the expression $k/N=[\phi(g-\alpha)-\phi(ge^{-cE}-\alpha)]/[\phi(g-\alpha)+\phi(\alpha)]$, where ϕ is an error function, g and α are constants for a given emulsion, c is a coefficient depending on the grain size and the nature of the grains, and N is the total number of grains with nuclei originally of areas between zero and the minimum developable area. Values calculated from this expression are in good agreement with observed results for several emulsions. A. E. MITCHELL.

Optical and photographic properties of a series of typical cyanine dyes. O. BLOCH and F. M. HAMER.—See B., 1928, 285.

Photochemical reactions. III. Influence of polarised radiations on certain photochemical reactions. S. S. BHATNAGAR, H. L. ANAND, and A. W. GUPTA (J. Indian Chem. Soc., 1928, **5**, 49—57).—Polarised and heterogeneous light of equal intensities have the same effect on the photochemical reactions occurring between diammonium oxalate and mercuric chloride and on the decomposition of alkaline hydrogen peroxide. From previous results (A., 1925, i, 1179; ii, 811) it is concluded that polarised light possesses a selective effect only in heterogeneous systems. G. A. C. GOUGH.

Photochemical action of bromine on maleic and fumaric esters. J. EGGERT [with F. WACHHOLTZ and R. SCHMIDT] (Z. Elektrochem., 1927, **33**, 542—545).—The effect of changes in the experimental conditions on the values of ϕ and α was studied, where ϕ is the ratio of the number of molecules converted to the number of quanta absorbed, and α is the ratio of bromine molecules added to the number of quanta absorbed. For the ethyl ester, ϕ and α are independent of variation of the ester concentration and of the radiation intensity; with the methyl ester and free maleic acid, there is no dependence at high concentrations, but at low concentrations ϕ decreases with decreasing ester concentration, and with increasing intensity. Both ϕ and α are markedly dependent on temperature in all cases. ϕ is independent of the bromine concentration and α is proportional to this concentration in all three cases. The effect of change of wave-length of the active light (blue, 4360 Å.; green, 5470 Å.; ultra-violet, 3650 Å.) is as follows: ethyl ester, $\phi_{bl}/\phi_{gr}=1\cdot9$; $\alpha_{bl}/\alpha_{gr}=2$; methyl ester, $\phi_{bl}/\phi_{gr}=2\cdot3$; $\alpha_{bl}/\alpha_{gr}=1\cdot9$; free maleic acid $\phi_{uv}:{}_{1}:\phi_{gr}=5:4:1$. A reaction mechanism is pictured in which the bromine atoms combine with the unsaturated ester molecules, E, to form relatively stable compounds of the type EBr, before they are able to recombine to form molecules. In the conversion of maleic into fumaric ester, the collision of bromine atoms with the maleic ester molecules is supposed to favour the change from the maleinoid to the fumaroid form, until the bromine atom is eventually fixed to form the radical EBr. In the additive reaction it is assumed that at the moment of collision between the bromine atom and the ester molecule, a bromine molecule which may collide simultaneously will be taken up to form dibromosuccinic ester, with re-liberation of the bromine atom. W. CLARK.

Conversion of maleic into fumaric acid by bromine atoms. F. WACHHOLTZ (Z. Elektrochem., 1927, **33**, 545—547).—In the system maleic acid–sulphuric acid–bromine, at high concentrations of maleic acid the quantum yield, molecules of fumaric acid/$h\nu=\phi=430$ at 21°. At lower concentrations of maleic acid ϕ is less and becomes dependent on the concentration of maleic acid and on the light intensity. The light reaction may be imitated by the reduction of bromic acid, hypobromous acid, and bromine in presence of maleic acid. Reduction of bromine by ferrous sulphate gives a yield of 10,000 molecules of fumaric acid per atom of bromine (*i.e.*, per ferrous ion). The yield is practically independent of the concentration of the reactants as long as the concentration of ferrous ion is small ($[Fe^{\cdot\cdot}]<10^{-5}$), but at higher concentrations it becomes dependent on the ferrous-ion concentration. The temperature coefficient is 2. These facts, together with those given in the paper of Eggert (preceding abstract), lead to the view that bromine atoms are responsible for the conversion of maleic into fumaric acid. In the reaction $Br_2+h\nu=2Br$, every fiftieth absorbed quantum is effective. W. CLARK.

Photochemical reactions. I. Effect of the dielectric constant of the medium on the velocity coefficient. K. G. MATHUR, R. S. GUPTA, and S. S. BHATNAGAR (Indian J. Physics, 1928, **2**, 243—255).—The velocity coefficients for the photobromination of cinnamic acid have been determined in carbon tetrachloride, carbon disulphide, ethyl ether, chloroform, ethyl formate, ethyl bromide, and ethyl acetate. Curves have been plotted showing rates of transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone, ether, methyl ethyl ketone, chloro-

form, and benzene. Contrary to the suggestion made by Winther (A., 1925, ii, 1082), no direct relationship can be observed between the velocity coefficients of the photochemical reaction considered and the dielectric constants of the solvents employed. M. S. BURR.

Action of light on diazo-derivatives. A. SEYEWETZ and D. MOUNIER (Compt. rend., 1928, **186**, 953—955).—The decomposition of diazo-compounds by ultra-violet light, and the influence of substituents, the value of the medium, and temperature, are investigated. The decomposition of a 0·4% solution of diazosulphanilic acid is proportional to the period of irradiation until 90% of the original diazo-compound is decomposed, the remainder condensing with the phenol produced by the decomposition. In the presence of acids ($p_H<7$), the diazo-solution is very sensitive to light, but relatively stable to heat, whilst in alkaline solution (sodium diazonaphthol-sulphonate, $p_H>7$), the reverse is true. Similar results are obtained at 35°, 56°, 80°, and 100°, but as the temperature approaches that at which thermal decomposition of the diazo-compound occurs, this action then preponderates. Substitution of negative radicals in the benzene nucleus, which increases the stability of the diazo-compound to heat, decreases its stability towards light, the order of increasing stability being *p*-OH(anhydride) < *p*-SO_3H(anhydride) < *p*-CO_2H(anhydride) < *p*-Cl (chloride) < *p*-NO_2 (chloride) < benzenediazonium chloride, decomposition being complete only in the first two cases. The effect of the nitro-group is the same in the *o*-, *m*-, and *p*-positions. Decomposition by light of the diazo-compounds derived from sulphanilic acid, *p*-aminophenol, and aniline yields the corresponding phenol as in thermal decomposition; the derivative of *p*-aminobenzoic acid yields *p*-hydroxy- and *p*-chloro-benzoic acids, whilst from the brown precipitate obtained by decomposition of nitrobenzenediazonium chlorides is isolated a substance which is probably dinitrodiphenyl ether. J. W. BAKER.

Attempt to prepare triatomic hydrogen. H. M. SMALLWOOD and H. C. UREY (J. Amer. Chem. Soc., 1928, **50**, 620—626).—Unsuccessful attempts to prepare triatomic hydrogen by means of corona discharge and "ozonisation," combustion of oxygen in hydrogen, vacuum discharge, and passage of hydrogen over hot metallic wires are described. If a discharge is passed through hydrogen at 9 cm. pressure and at liquid air temperatures, a considerable pressure decrease occurs only if the electrodes are immersed in the liquid air. Previous work is criticised and it is concluded that the existence of triatomic hydrogen has not yet been established. A very delicate test for hydrogen sulphide is described. S. K. TWEEDY.

[Silver subfluoride.] A. HETTICH (Z. anorg. Chem., 1928, **170**, 107—108).—Brody and Millner's thermochemical calculations in connexion with the determination of the structure of silver subfluoride (this vol., 223) are defective, but in any case the two alternative structures are fundamentally the same, both involving simply an intermingling of silver atoms, ions, and fluoride ions. If silver fluoride or subfluoride is heated at 200—300° with mercury, it appears largely to dissolve. When the product after cooling is treated with water, it gives up considerable amounts of silver ions. R. CUTHILL.

Existence of silver oxide, Ag_4O_3. A. P. ROLLET (Compt. rend., 1928, **186**, 748—750).—Silver sesquioxide, Ag_4O_3, the existence of which has been disputed, was formed by the anodic oxidation of a silver electrode in an alkaline solution containing potassium, with a mercury cathode. The concentrations used were 1—12*N*, the temperatures 0—30°, and the anodic current densities 1—70 milliamp./dm.^{2} Its formation, together with that of Ag_2O, was confirmed from the curves relating the intensity of the current discharge and the time. J. GRANT.

Displacement of metals from solutions of their salts by less electropositive elements. IV. Potassium and sodium ammonoberyllates. F. W. BERGSTROM (J. Amer. Chem. Soc., 1928, **50**, 652—656).—*Potassium ammonoberyllate*, $Be(NH_2)NHK,NH_3$, $Be(NH_2)_2,KNH_2$, or $K[Be(NH_2)_3]$, is obtained as a colourless solid by the action on excess of beryllium of a liquid ammonia solution of potassium. It is vigorously hydrolysed by water and resembles the corresponding aluminate in properties rather than the magnesiate. The *sodium* salt is obtained similarly; it will not react with magnesium (cf. A., 1927, 30), but when added to a solution of magnesium thiocyanate a precipitate of composition $Mg(NH_2)_2,Be(NH_2)_2$ is obtained. Beryllium cleansed by a liquid ammonia solution of ammonium chloride is insoluble in pure liquid ammonia (cf. Cottrell, A., 1914, i, 373), but dissolves slowly in a liquid ammonia solution of sulphur, forming a yellow precipitate, soluble in excess, of ammoniated beryllium mono- or poly-sulphide. All attempts to prepare beryllium amide were unsuccessful. S. K. TWEEDY.

Action of liquid ammonia solutions of ammonium salts on metallic beryllium. Ammoniated beryllium halides and ammonobasic beryllium salts. F. W. BERGSTROM (J. Amer. Chem. Soc., 1928, **50**, 657—662).—The colourless beryllium halide di- or tetra-ammoniates, $BeCl_2,4NH_3$, $BeCl_2,2NH_3$, and $BeBr_2,4NH_3$, are obtained on dissolving beryllium in liquid ammonia solutions containing excess of ammonium halide. The first salt passes into the second when heated in a vacuum at 210—255° (cf. Biltz and Messerknecht, A., 1925, ii, 1183). The *salts* $3Be(NH_2)_2,BeI_2,4NH_3$, $3Be(NH_2)_2,BeBr_2,4NH_3$, $3Be(NH_2)_2,BeBr_2,8NH_3$, and $5Be(NH_2)_2,BeI_2,4NH_3$ were prepared by the action of liquid ammonia solutions of normal beryllium halides on metallic beryllium. The compound $2BeBr_2,Be(NH_2)_2,8NH_3$ also probably exists. S. K. TWEEDY.

Complex compounds of beryllium. VI. R. FRICKE and F. ROBKE (Z. anorg. Chem., 1928, **170**, 25—34; cf. A., 1927, 829).—By interaction of beryllium chloride with *n*-butylamine, diethylamine, or 4-methylquinoline in ethereal solution, with cinnamaldehyde in benzene solution, and with benzophenone or *p*-toluidine in the molten state there result crystalline *compounds* which are usually white or colourless, and consist of 2 mols. of the organic compound combined with 1 mol. of the chloride. Anisole apparently forms a compound, but it has not been

possible to prepare it in a pure state. The following m. p. have been determined: $BeCl_2,2C_5H_5N$ (A., 1925, ii, 886), 152°; $BeCl_2,2Et_2O$ (*ibid.*, ii, 886), 33°; $BeCl_2,2CH_2Ph\cdot CN$ (A., 1926, 694), 151·5°. Thermal analysis of the system $BeCl_2,2CH_2Ph\cdot CN$–phenylacetonitrile has not yielded any evidence of compound formation. Beryllium aminoacetate in aqueous solution does not manifest any tendency to form an internal complex. R. CUTHILL.

Reactions of activated magnesium. A. P. TERENTIEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 85—89).—For the activation of magnesium iodine, bromine, or ammonium chloride was used. Activated magnesium reacted readily with alcohols, giving alkoxides at 100°. In the synthesis of butyric acid from ethyl malonate, ethyl sulphate was used instead of ethyl iodide when the reaction was carried out with activated magnesium. A. RATCLIFFE.

Reactions of activated magnesium. A. P. TERENTIEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 91—93).—When magnesium is activated with iodine the reaction with ammonia starts at 300°. After heating for 5 hrs. at 350—400°, a substance is obtained which is supposed to be $Mg(NH_2)_2$. Attempts to isolate it in a pure state failed. Activated magnesium also reacts with aromatic amines more readily and at lower temperatures than ordinary magnesium. Experiments were carried out with aniline, methylaniline, diphenylamine, *o*-anisidine, α- and β-naphthylamine, and acetanilide. The reactions commenced at temperatures slightly above 130—150°. A. RATCLIFFE.

Ammines of double salts. XI. G. SPACU and C. CREARGA (Bul. Soc. Stiinte Cluj, 1927, **3**, 160—170; Chem. Zentr., 1927, ii, 2170; cf. Spacu and Caton, Bul. Soc. Stiinte Cluj, 1927, **3**, 105).—The following *ammines* of double salts are described: $[Cd(C_5H_5N)_6]Br_2,NH_4Br$; $[Cd(C_5H_5N)_2]Br_2,NH_4Br$; $[Cd(NH_3)_6]Br_2,NH_4Br$; $[Cd(NH_3)_2]Br_2,NH_4Br$; $[Zn(C_5H_5N)_2Br_3]K$; $[Zn(NH_3)_6]Br_2,KBr$; $[Zn(NH_3)_2]Br_2,KBr$. The original double salts, $CdBr_2,NH_4Br$ and $ZnBr_2,KBr,2H_2O$, are considered to be formulated $NH_4[CdBr_3]$ and $K[Zn(H_2O)_2Br_2]$, respectively. A. A. ELDRIDGE.

Constitution of double salts. XIV. Double ammines of iodides. G. SPACU and O. VOICU (Bul. Soc. Stiinte Cluj, 1927, **3**, 321—352; Chem. Zentr., 1927, ii, 2170—2171; cf. preceding abstract).—Double iodides of heavy metals with alkali metals, when exposed to a current of dry ammonia at the ordinary temperature, yield hexammines, $[M''(NH_3)_6]I_2,nM'I$ (n=1 or 2). Potassium cadmium iodide affords compounds, $[M''X_6]I_2n,M'I$ (n=1 or 2), with piperidine or aniline, whilst potassium zinc iodide gives compounds $[M''X_2]I_2,nM'I$ or $[M''X_2I_{n+2}]M'_n$ (n=1 or 2). It is concluded that the original double salts are formulated $[M''(H_2O)_n]M'_x$ (x=1 or 2, n=1 or 2) or $[M''(H_2O)_n]I_2,(x+1)M'I$ (x=0 or 1, n=1, 2, or 6).

Potassium zinc iodide, $KI,ZnI_2,2H_2O$, obtained by evaporation of a solution of the constituent salts over sulphuric acid, forms transparent rhombic prisms, is hygroscopic and sensitive to light; it loses 1 mol. of water at 70° and the remainder at 95°. The following *ammines* are described: $[Cd(NH_3)_6]I_2,KI$; $[Cd(C_5H_5N)_6]I_2,KI$; $[Cd(C_5H_5N)_2]I_2,KI$; $[Cd(NH_3)_6]I_2,2KI$; $[Cd(C_5H_5N)_6]I_2,2KI$; $[Cd(C_5H_5N)_2]I_2,2KI$; $[Cd(H_2O)_4(PhNH_2)_2]I_2,2NaI$; $[Zn(NH_3)_6]I_2,2KI$; $[ZnI_4(C_5H_5N)_2]K_2$; $[ZnI_4(PhNH_2)_2]K_2$; $[Zn(NH_3)_6]I_2,KI$; $[Zn(C_5H_5N)_2]I_2,KI$; $[Zn(PhNH_2)_2]I,KI$. A. A. ELDRIDGE.

Ammonous nitrides. I. Ammonous cobaltous nitride, ammonous aluminium nitride, and stannous imide. F. W. BERGSTROM (J. Physical Chem., 1928, **32**, 433—440).—The precipitate obtained by pouring a liquid ammonia solution of ammonium bromide into a solution of sodium or potassium aminoaluminate, $Al(NH_2)_2NHK$, has a composition varying from 40·7 to 55·6% Al to 38·8 to 52·0% N, with little alkali metal or bromine as impurity. It is best regarded as an "ammonous aluminium nitride," AlN,xNH_3, analogous to hydrous oxides. Similarly, cobaltous amide (A., 1925, ii, 231) should be regarded as ammoniated cobaltous nitride, Co_3N_2,xNH_3, since it loses ammonia slowly and irreversibly under liquid ammonia even at low temperatures. *Stannous imide* was prepared as a brown precipitate by the slow addition of a dilute, liquid ammonia solution of ammonium bromide to a solution of potassium amminostannite. It is hydrolysed by water, and is amphoteric. Stannous imide when heated at 340° in a vacuum yielded *stannous nitride*. L. S. THEOBALD.

Rare earths. E. WILKE-DORFURT and O. SCHLIEPHAKE (Z. anorg. Chem., 1928, **170**, 129—144).—Lanthanum nitrate may be separated relatively rapidly from admixed praseodymium nitrate by dissolving the mixed oxides in perchloric acid, and subjecting the solution, preferably at a concentration of 60%, to fractional precipitation with ammonia in the cold, the mixture being heated at 50—70° previous to filtration. Similarly, the separation of neodymium from accompanying praseodymium and lanthanum with the aid of an ammonium and a cadmium salt according to Prandtl's method (A., 1924, ii, 615) is more advantageously carried out in perchloric acid solution than in nitric acid solution. From a solution of neodymium oxide in perchloric acid, the *perchlorate* may be obtained as the hexahydrate, or as red crystals of the anhydrous salt. By adding a solution of ammonium perchlorate to a mixed solution of antipyrine and a nitrate of one of the following metals, or, in the case of neodymium, by adding antipyrine to a solution of the perchlorate, *hexa-antipyrineperchlorates* have been obtained, these containing 6 mols. of antipyrine per mol. of metallic perchlorate, and having the colour, m. p., and solubility at 20° (in g./100 c.c. of solution), respectively, as follows: lanthanum, colourless, 290—295° (decomp.), 1·48; neodymium, red, 285—289° (decomp.), 0·98; cerium (cerous), white, 295—300° (decomp.), 1·07; praseodymium, green, 286—291° (decomp.); yttrium, colourless, 293—296° (decomp.), 0·55. Analogous *hexa-antipyrineiodides* have been obtained by mixing solutions of the corresponding simple iodides and of antipyrine; the data for these are: lanthanum, yellow, 268—269°, 29·5; neodym-

ium, red, 270—272°, 11·3; cerium (cerous), yellow, 268—270°, 13·12; yttrium, colourless, 280—282°, 4·44. Cerous iodide is conveniently prepared by passing hydrogen sulphide into a suspension of iodine and an excess of cerium dioxide. R. CUTHILL.

Di- and tetra-substituted siloxens. H. KAUTSKY and A. HIRSCH (Z. anorg. Chem., 1928, **170**, 1—17; cf. A., 1925, ii, 698).—Acetic acid, acetic anhydride, and their homologues slowly react with siloxen on warming, but no definite compounds can be isolated, and it seems that at most only one hydrogen atom is replaced by an acid radical. Well-defined substitution products, *monoacetatomonoiodosiloxen*, $Si_6O_3H_4I(OAc)$, and *diacetatodibromosiloxen*, $Si_6O_3H_2Br_2(OAc)_2$, have, however, been prepared by adding to siloxen successive small amounts of a solution of the halogen in acetic anhydride, and removing the liquid phase from the solids in the reacting system before each new addition of halogen; otherwise with bromine only the *monoacetatodibromosiloxen*, $Si_6O_3H_3Br_2(OAc)$, is formed, the hydrogen bromide produced by the reaction preventing further substitution. By brominating with a solution of bromine in carbon disulphide and removing the hydrogen bromide from the system from time to time, a *tetrabromosiloxen*, $Si_6O_3H_2Br_4$, results, and with high concentrations of bromine, *hexabromosiloxen*, $Si_6O_3Br_6$. All these new compounds are yellowish solids; their constitutions have not been ascertained. With water they are hydrolysed to *hydroxy-compounds*, and with ammonia or amines *amino-compounds* are formed. R. CUTHILL.

Composition of titanium peroxide. M. BILLY (Compt. rend., 1928, **186**, 760—762).—The pertitanic salt studied (the double sulphate of potassium and titanium) always contained a proportion of oxygen corresponding with the ratio Ti/O_3 whether it was prepared at 0° or 15°, but lost its active oxygen in a vacuum. Hydrolysis by an excess of water at 10—20° and at 0° (cf. A., 1921, ii, 553) produced hydrates giving the ratios Ti_2/O_5 and $Ti_2/O_{5\cdot27}$, respectively. The fixation of active oxygen by Ti_2O_5 or TiO_2 tends to an equilibrium dependent on the temperature and concentration. J. GRANT.

Selenium oxyfluoride. E. B. R. PRIDEAUX and C. B. COX (J.C.S., 1928, 738—745; cf. A., 1927, 532).—Selenium oxyfluoride, $SeOF_2$, has been prepared by heating selenium oxychloride with silver fluoride at 140°. It is a colourless, fuming liquid, d 2·67, b. p. 121—129°, m. p. 4·6°. It attacks glass rapidly, forming chiefly selenium dioxide. Silica reacts violently in accordance with the equation $2SeOF_2 + SiO_2 = 2SeO_2 + SiF_4$. Crystalline silicon gives silicon tetrafluoride, red selenium, and selenium dioxide. It also attacks red phosphorus and sulphur. The properties of selenium oxyfluoride are compared with those of a solution of selenium dioxide in hydrofluoric acid. C. W. GIBBY.

Introduction of bromine and of iodine into ...tes. A. DUBOIN (Compt. rend., 1928, **186**, 762—764).—Compounds of the type $KX,K_2O,CoO,4SiO_2$, where X is Cl, Br, or I, have been obtained by a method analogous to that originally described for the chlorine compounds (A., 1921, ii, 403). They are easily decomposed by hydrochloric acid and form isomorphous crystals (probably orthorhombic), n^{15} (mean) 1·505, 1·540, and 1·572 ($\pm$0·003 in each case), respectively, and d^0 2·8—2·95. J. GRANT.

Landolt reaction. A. THIEL (Z. Elektrochem., 1928, **34**, 113—114).—A discussion. The mechanism of the Landolt reaction cannot yet be considered as fully elucidated. H. F. GILLBE.

Hydrate of cobaltic fluoride. G. A. BARBIERI and F. CALZOLARI (Z. anorg. Chem., 1928, **170**, 109—110).—It is denied that, as Birk has implied (A., 1927, 1157), the authors have stated that cobaltic fluoride prepared by their method is anhydrous; no determinations of the water content were made. R. CUTHILL.

Dehydration of barium platinocyanide by X-rays. A. TRAPESNIKOV (Z. Physik, 1928, **47**, 732—744).—By repeated dehydration and hydration of barium platinocyanide, $BaPt(CN)_4,4H_2O$, evidence has been obtained, using a microbalance, of crystal hydrates containing 3·75, 3·5, and 3·25 mols. of water. The original hydrate is green, that containing 3·75 mols. of water is brick-red or brown. Prolonged irradiation of the green salt by X-rays produces an orange-coloured substance, but loss of water could not be established. The irradiated salt recovered its original colour when left unilluminated. W. E. DOWNEY.

Preparation of hydrazine by Raschig's method. O. MAGIDSON [with J. FRANKEL] (Trans. sci. chem.-pharm. inst., Moscow, 1923, **6**, 21—28; Chem. Zentr., 1927, ii, 2542).—Ammonia solution (d 0·9, 3 litres) and 5% gelatin solution (300 c.c.) are stirred during the addition of $2N$-hypochlorite solution (1·5 litres); the evaporated mixture is filtered and, when cold, is treated with dilute sulphuric acid, hydrazine sulphate crystallising out. The presence of a small quantity of sulphuric or nitric acid is very unfavourable. A. A. ELDRIDGE.

Preparation of radium from Russian sources. W. CHLOPIN (Trav. Radium Min. radioact., 1924, **1**, 1—176; Chem. Zentr., 1927, ii, 2499).—A monograph. The separation of radium and barium may be achieved by fractional precipitation of the bromides with hydrogen bromide. A. A. ELDRIDGE.

Concentration and isolation of element 91. A. VON GROSSE (Naturwiss., 1927, **15**, 766—767; Chem. Zentr., 1927, ii, 2272).—About 2 mg. of protoactinium pentoxide, practically free from other elements, and having an α-activity about 23×10^4 as great as that of an equal mass of uranium-I, has been prepared by employing the following properties: (i) it is precipitated, together with zirconium and hafnium, by addition of phosphoric acid to a solution containing mineral acid and hydrogen peroxide, (ii) it is separated from phosphoric acid by fusion with alkali carbonate, (iii) it is separated from zirconium and hafnium either by fractional crystallisation of the oxychlorides in concentrated hydrochloric acid (protoactinium accumulating in the mother-liquors) or by precipitation as oxalate in company with added

thorium, from which it is separated by precipitation with hydrofluoric acid. A. A. ELDRIDGE.

Preparation of chemically pure chromic anhydride. A. V. RAKOVSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 13—17).—Chemically pure chromic anhydride can be obtained by treating potassium or sodium dichromate with sulphuric acid, *d* 1·84. The technical product is conveniently obtained by treating technical sodium dichromate with lime water and calcium chloride, the calcium chromate thus obtained being decomposed with sulphuric acid.

A. RATCLIFFE.

Theory of sampling. J. MIKA (Z. anal. Chem., 1928, **73**, 257—264).—Mathematical. The relation between the minimum weight of the sample taken for analysis and the degree of fineness of a heterogeneous mixture is deduced from the theory of probability, and it is shown that, when the material has been ground as finely as possible in an agate mortar, a few mg. will give an average sample with an error much below the usual permissible analytical errors. In the usual method of sampling large quantities of coarse material by grinding portions in stages, the usually accepted ratio of sample weight to total weight at most stages is shown to be far too small.

A. R. POWELL.

Nephelometric analysis using a spectrophotometer. K. JABŁCZYNSKI and W. STANKIEWICZ (Rocz. Chem., 1927, **7**, 534—548).—The application of a polarisation spectrophotometer to the nephelometric analysis of crystalline and amorphous precipitates indicates that results obtained by previous nephelometric methods are unacceptable, since the degree of opacity found depends on various factors, such as the relative concentrations of the reagents used, the order in which they are added, the velocity of stirring, the presence or absence of protective colloids, etc. Of these factors, stirring has no perceptible influence on results obtained for amorphous precipitates and little influence on a crystalloid system containing a protective colloid. Spectrophotometric nephelometry may give results accurate to within 1·5% under standardised conditions.

R. TRUSZKOWSKI.

Colorimetric analysis using a spectrophotometer. K. JABŁCZYNSKI and W. STANKIEWICZ (Rocz. Chem., 1927, **7**, 549—558; cf. preceding abstract).—Measurements by means of a polarisation spectrophotometer of the intensity of unit coloration produced by the addition of ammonium thiocyanate to acid ferric chloride show that this is not constant, but increases with concentrations of iron and excess of ammonium thiocyanate. The intensity of coloration produced by the addition of ammonia to cupric salts is almost independent of the concentration of the latter, and changes little with that of the former; if sodium hydroxide solution be used in place of ammonia, the intensity of coloration increases rapidly with concentration, whilst if Fehling's solution be added, it is also dependent on the concentration of copper. Using nickelous salts and ammonia, the intensity of coloration falls with increasing concentration of ammonia, and with decreasing concentrations of nickel. In those cases where the concentration of the substrate does not affect the accuracy of the determination, colorimetric determination may be applied under standardised conditions; in other cases, to which Beer's law does not apply, the following law is followed: $(c_1/c_2)^x = d_2/d_1$, where c is the concentration and d the intensity of coloration. Colorimetry is not therefore applicable to the determination of metals of the second type.

R. TRUSZKOWSKI.

Exact determination of the equivalence point in potentiometric titrations. I. M. KOLTHOFF (Rec. trav. chim., 1928, **47**, 397—400).—A reply to Hahn and Weiler (A., 1927, 124) and Hahn and Frommer (A., 1927, 743). A simple and accurate method is given for finding the point of equivalence when the potential curve has only a slight slope near the end-point, or is unsymmetrical. From the experimental data obtained during titration it is possible to calculate the equilibrium constant of the reaction involved and, from this, the magnitude of the inflexion potential. The point on the potential curve corresponding with this potential gives the position of the point of equivalence. If the titration is carried to the correct equivalence potential exact results may be expected even in cases where the classical method, *i.e.*, finding the point at which $\Delta E/\Delta c$ is a maximum, does not give satisfactory results. M. S. BURR.

New indicator papers for determination of hydrogen-ion concentration. W. U. BEHRENS (Z. anal. Chem., 1928, **73**, 129—137).—The preparation of a series of indicator papers by the use of two or three colouring substances, one of which is an indicator, so that each paper is grey at a definite p_H value, but assumes positive colours of p_H values above or below the "grey" value, is described. The grey colour changes in one direction for increasing acidity and in another for diminishing acidity, but the shades so produced change only in intensity and not in colour on either side of the "grey" point. Formulæ are given for a series of papers covering the p_H range from 1·5 to 8·0. S. I. LEVY.

Membrane hydrolysis at indicator papers. H. KROEPLIN (Kolloid-Z., 1928, **44**, 188—190).—A study has been made of Wulff's method of measuring the hydrogen-ion concentration of turbid solutions by means of indicator papers. Wulff's Paper I has an alkali error. Papers II and III gave an error on the acid side in solutions poor in salts, due to membrane hydrolysis of the colouring matter contained in the paper. This difficulty can be obviated by the addition of neutral salts (*e.g.*, 35 millimols. of potassium chloride). E. S. HEDGES.

Standardisation of silver nitrate solutions used in chemical studies of sea-waters. T. G. THOMPSON (J. Amer. Chem. Soc., 1928, **50**, 681—685).—Silver nitrate solutions for oceanographic purposes may be standardised against pure sodium chloride instead of standard sea-water. If sea-water at 20° contains x grams of chlorine per litre and y g. of chlorine per kg., then $y = 0·008 + 0·99980x - 0·001228x^2$. S. K. TWEEDY.

o-Tolidine method for determining chlorine in water. F. R. MCCRUMB.—See B., 1928, 246.

Determination of hypochlorous and chlorous acids, especially by potentiometric methods. E. Muller and H. Dietmann (Z. anal. Chem., 1928, **73**, 138—145).—Existing methods are based on titration of the hypochlorite by standard arsenite solution, and subsequent addition of excess of iodide, the iodine liberated by the chloric acid being titrated by means of thiosulphate. Difficulties have arisen from the necessity of avoiding excess of arsenite in the reduction of the hypochlorite. In carrying out the determination potentiometrically, abnormal potential curves are frequently obtained; the abnormalities are shown to arise from insufficient alkali, since four equivalents of alkali are necessary to neutralise the acids arising from the oxidation of 1 mol. of arsenious oxide. When sufficient alkali is present, the curves are smooth and normal. Satisfactory curves are also obtained if the reduction of the hypochlorite is effected by means of sulphite; in this titration the acidity of the solution is not increased. S. I. Levy.

Detection of traces of soluble bromides. H. Baines.—See B., 1928, 261.

Colorimetric determination of iodine in artificial light. L. S. van der Vlugt (Chem. Weekblad, 1928, **25**, 196—197).—The difficulties of comparing the solutions in Fellenberg's method (Biochem. Z., 1923, **139**, 396) are minimised by using artificial light from a metal-filament lamp passing through cobalt glass. A suitable apparatus is described. S. I. Levy.

Titration of dilute sulphite solutions with standard iodine solutions. H. M. Mason and G. Walsh (Analyst, 1928, **53**, 144—149).—When iodine solution is run into sulphite solution the volume of iodine required for oxidation of a given volume of sulphite is less than when the sulphite solution is run into the iodine. The hydriodic acid set free during the titration of iodine into sulphite does not reduce sulphur dioxide, but by increasing the acidity of the solution makes loss by volatilisation easier. Agitation of the solution during titration may cause loss of sulphur dioxide, and it is advisable, unless extreme accuracy is necessary (in which case the iodine should be titrated with sulphite), to run the bulk of the iodine solution into the sulphite solution, mix gently, and complete titration with the few necessary drops of iodine solution. Volatilisation is regarded as the main cause of loss of sulphur dioxide, with oxidation as a secondary cause. D. G. Hewer.

Oxidation of sulphites by air. H. M. Mason and G. Walsh (Analyst, 1928, **53**, 142—144).—Neutral sulphite solutions are rapidly oxidised by air at temperatures approaching 100°; with acid solutions oxidation is slower at the ordinary temperature and probably also at higher temperatures. The distillation process is fairly accurate when the sulphite solution is added to boiling acid solution, and oxidation of some of the sulphur dioxide, increasing with time, occurs in the distilling flask during the time taken to start boiling. If carbon dioxide is used in a sulphite distillation which lasts for more than a few minutes, it must be free from oxygen, but in the case of foodstuffs losses are nearly certain to occur owing to the presence of absorbed air; removal of air by use of a vacuum, or extremely rapid heating and distillation is recommended. D. G. Hewer.

Stability of solutions of potassium metabisulphite. R. J. Phillips (Analyst, 1928, **53**, 150).—Fifty c.c. were pipetted after each 24 hrs. from a 0·1% solution of potassium metabisulphite in a stoppered litre flask and titrated directly with 0·05N-iodine solution, the contents of the flask being maintained at 15·6°. The relative sulphur dioxide content was found to be 100·0, 98·2, 94·6, 93·5, 92·2, and after 144 hrs. 91·3%. D. G. Hewer.

Quantitative precipitations in highly concentrated solutions. I. [Determination of sulphuric acid.] V. Njegovan and V. Marjanovic (Z. anal. Chem., 1928, **73**, 271—279).—By precipitating concentrated solutions of sulphates with concentrated barium chloride solution, diluting and heating for some time, the barium sulphate is obtained in a coarsely granular form which does not adsorb other salts from the solution. The analysis is conducted as follows: The solution, containing not more than 0·3 g. of sulphate ion, is evaporated to dryness on the water-bath and the residue is stirred with 5 c.c. of 10% hydrochloric acid and 1 c.c. of saturated barium chloride solution. After addition of 100 c.c. of hot water, the solution is left for 30 min. on the water-bath, and the clear liquid decanted through a Gooch crucible. The precipitate is stirred with 1 c.c. of concentrated hydrochloric acid and 50 c.c. of water, heated for 10 min., collected on the Gooch crucible, washed with cold water, dried at 100°, ignited, and weighed. The results are unaffected by the presence of alkali chlorides or nitrates, or of salts of magnesium, copper, or iron; calcium salts and phosphates, however, interfere. A. R. Powell.

Barium sulphate losses in gravimetric determinations. H. R. Jensen (Analyst, 1928, **53**, 136—138).—A series of tests was made with three independent standards to check the solubility of barium sulphate at and below acid concentrations used in gravimetric analysis. A slight invariable loss of sulphate was found averaging 0·0009 g. for nine determinations with free hydrochloric acid up to 0·02N (350 c.c.). With higher acid concentration and volumes of 350 c.c. significant losses (averaging 0·007 g.) were frequent but not invariable, and were highest when the precipitates were collected within 18 hrs. A similar solvent action was found for the mixed acids present under the conditions obtaining in typical sulphur dioxide determinations. A systematic investigation of all the conditions for the determination of very small amounts of barium sulphate is considered desirable. D. G. Hewer.

Iodometric determination of persulphate. L. von Zombory (Z. anal. Chem., 1928, **73**, 217—219).—The persulphate solution (10 c.c.) is treated with 25 c.c. of a 10% solution of potassium chloride and with 1—1·5 g. of potassium iodide in a stoppered flask. After 1 hr. the liberated iodine is titrated with thiosulphate. The potassium chloride acts as an accelerator of the action between iodide and persulphate. A. R. Powell.

Determinative mineralogy. II. P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (Amer. J. Sci., 1928, [v], 15, 253—261; cf. this vol., 267).—The following microchemical tests, suitable for use in mineral analysis, are described. To detect 1 μg. of tellurium, the mineral grain is dissolved in 1 drop of concentrated nitric acid, then the solution is evaporated, and the residue warmed with 1 drop of $5N$-sulphuric acid, then after addition of a second drop of acid the clear liquid is removed from the precipitate and evaporated almost to dryness, when thin plates, probably of $2TeO_2,SO_3$, separate on cooling. Addition of a saturated solution of quinol in concentrated sulphuric acid at this stage will cause a separation of black needles or rods of elementary tellurium, visible under the microscope even when only 0·1 μg. is present. The quinol reagent may also be used in the same way to detect selenium, the limit of the sensitivity being 0·08 μg. To detect manganese, the solution is first evaporated twice with nitric acid to remove chlorine, and then solid silver nitrate and ammonium persulphate are added, when the purple colour of permanganate is visible if as little as 0·005 μg. of manganese is present.

R. CUTHILL.

Hydrogen peroxide as an oxidising agent in the Kjeldahl method for determining nitrogen. E. GUBAREV (Zhur. exp. Biol. Med., 1927, 6, 261—265).—"Perhydrol" (1 c.c.) is added after preliminary heating of the material for 10 min. with sulphuric acid.

CHEMICAL ABSTRACTS.

Volumetric determination of ammonia with hypobromite by the ordinary and by a potentiometric method. I. M. KOLTHOFF and A. LAUR (Z. anal. Chem., 1928, 73, 177—195).—The hypobromite method for the determination of ammonia has been thoroughly examined. In all cases high results were obtained due to the oxidation of part of the ammonia to nitrite. In the iodometric determination of the excess of hypobromite the blue colour returns repeatedly and the results are therefore very erratic. The greater the alkalinity of the solution to which the hypobromite is added the nearer the results approach to the theoretical; under favourable conditions the error may be kept within $+1\%$.

A. R. POWELL.

Stable colour standards for the determination of nitrites in water. R. DANET.—See B., 1928, 246.

Determination of nitrates. L. SZEBELLÉDY (Z. anal. Chem., 1928, 73, 145—153).—The reduction of nitrates to nitrites by ferrous sulphate in concentrated sulphuric acid solution may be used, with suitable precautions, for the determination, the end-point being indicated by the colour due to the compound of ferrous sulphate with nitrous oxide when excess of nitrate is present. Dissolved oxygen is removed from the solutions by addition of potassium hydrogen carbonate immediately before the titration; the ferrous sulphate solution must be frequently standardised by titration against pure potassium nitrate. Chlorides and bromides interfere, and must be precipitated by treatment with silver sulphate. The precautions necessary to obtain accurate results are described.

S. I. LEVY.

Production of uniform stains in the Gutzeit test for arsenic. A. S. DODD (Analyst, 1928, 53, 152).—A metal band encircles the top of the glass exit tube and is fixed by a small screw nail serving to tighten the band and also acting as a hinge for the top, which is a flat disc with a circular hole the same size as the bore of the exit tube, with projections at opposite sides as a hinge and spring fastener. The spring has a small hole to hold the catch pin. Strips of mercuric chloride paper are slipped under the top and clipped down, and the stains are uniform and sharp to the edge.

D. G. HEWER.

Quantitative separation of arsenic, antimony, and tin. A. THURMER (Z. anal. Chem., 1928, 73, 196—200).—The alkaline solution of the thio-salts obtained in the usual course of analysis is treated with nitric acid until it is just neutral to litmus, then boiled with 10 g. of ammonium chloride and an excess of hydrogen peroxide until oxygen ceases to be evolved. After cooling to 30°, 1—2 c.c. of hydrochloric acid are added and the solution is treated for 30—40 min. with hydrogen sulphide, whereby antimony and stannic sulphides are precipitated whilst the arsenic remains in solution as arsenate and thioarsenate. The precipitate is collected, washed with ammonium chloride, and dissolved in 40 c.c. of concentrated hydrochloric acid. The solution is diluted to 300 c.c., 17 g. of ammonium chloride are added, and the mixture is treated with hydrogen sulphide at 95—98° for 1 hr. to precipitate antimony sulphide. Tin is recovered from the filtrate by boiling off the excess of hydrogen sulphide, neutralising with ammonia, and boiling with ammonium nitrate. Arsenic is recovered from the first filtrate as ammonium magnesium arsenate after reoxidising with hydrogen peroxide.

A. R. POWELL.

Colorimetric field determination of the carbon dioxide tension and free carbon dioxide, hydrogen carbonates, and carbonates in solution in natural waters. II. Critical mathematical analysis of theory and data. E. B. POWERS and J. D. BOND (Ecology, 1927, 8, 471—479).—It is assumed that all active substances of homogeneous and heterogeneous equilibria attain equilibrium provided time is afforded, that the equilibrium points are determined by the carbon dioxide tension of the system (provided that this is the only modifying factor), and that the hydrogen-ion concentration, unless entirely stabilised by a strong acid, increases or decreases with increase or decrease of carbon dioxide tension; hence $C_H=(Kk_{g18}P)^n$, where $k_{g18}P$ is the solubility product of carbonic acid, and n is the exponent of the rate of increase in C_H.

CHEMICAL ABSTRACTS.

Detection and determination of calcium, barium, and strontium. O. MACCHIA (Chem.-Ztg., 1928, 52, 281—282).—The carbonate precipitate obtained in the ordinary group analysis is dissolved in hydrochloric acid and the solution is neutralised with ammonia and treated with 4—5 times its volume of a hot saturated solution of potassium ferrocyanide; calcium produces a white, crystalline precipitate of $CaK_2Fe(CN)_6,3H_2O$. The cold solution is filtered, rendered ammoniacal, and treated hot with potassium

chromate, and finally the filtrate from the barium chromate is treated with sodium carbonate to precipitate strontium. An alternative procedure is to dissolve the original carbonate precipitate in malonic acid and add a slight excess of ammonia; a white precipitate indicates barium. The filtrate is treated with 4—5 times its volume of methyl alcohol, warmed for 20 min., filtered, and treated with potassium cyanate; in the presence of calcium a white, flocculent precipitate is obtained. The first method may be used for the quantitative separation of the metals, the calcium precipitate being washed with a cold saturated solution of potassium ferrocyanide and dissolved in hydrochloric acid for the usual oxalate precipitation. The barium chromate precipitate is converted into sulphate and the strontium carbonate into oxide for weighing. A. R. POWELL.

Electrolytic determination of zinc. M. GIORDANI (Annali Chim. Appl., 1928, **18**, 63—65).—The separate preparation of a lead peroxide anode and a coppered cathode involved in Belasio and Mellana's method for the electrolytic determination of zinc in solutions containing sulphuric acid (A., 1927, 953) may be obviated by the addition to the electrolyte of a reducing substance such as alcohol or, better, dextrose (cf. Oettel, Chem.-Ztg., 1893, **17**, 543, 577) which effects the destruction of any persulphuric acid formed. The solutions tested were prepared by dissolving about 0·6 g. of pure zinc in sulphuric acid, neutralising with ammonia, adding 20 c.c. of 0·5N-sulphuric acid, 5 g. of sodium sulphate, and 12 g. of dextrose and diluting to 250 c.c. The current, 0·3 amp., corresponded with the cathode density $ND=$ 0·6 (Winkler's coppered gauze). The spiral anode of lead wire 2 mm. in diameter and 18 cm. in length was paraffined at its intersection with the liquid surface. The results were virtually theoretical.

T. H. POPE.

Determination of cadmium. G. SPACU and J. DICK (Z. anal. Chem., 1928, **73**, 279—283).—The neutral cadmium solution (50—100 c.c.) is heated to boiling, treated with 0·5—1 g. of ammonium thiocyanate and 1 c.c. of pyridine, cooled, and filtered through a porous filtering crucible. The precipitate of $Cd(CNS)_2,2C_5H_5N$ is washed successively with cold water containing 3 g. of ammonium thiocyanate and 5 c.c. of pyridine per litre, 25% alcohol containing 1 g. of ammonium thiocyanate and 20 c.c. of pyridine per litre, a 10% solution of pyridine in absolute alcohol, and finally ether containing a few drops of pyridine. After drying for 10 min. in a vacuum desiccator the compound is weighed; it contains 29·07% of cadmium. A. R. POWELL.

Potentiometric determination of copper with ferrocyanide. E. MULLER and S. TAKEGAMI (Z. anal. Chem., 1928, **73**, 284—288).—Copper cannot satisfactorily be titrated in aqueous solution with either potassium or lithium ferrocyanide, as the precipitate obtained is of somewhat uncertain composition. In 30—50% alcohol fairly good results are obtained with the lithium salt if the second maximum is taken as end-point. During the course of the titration the potential gradually rises and passes through a maximum, then falls rather abruptly to a minimum, and rises sharply to the second maximum. A. R. POWELL.

Activated form of oxalic acid. [Determination of mercury.] F. OBERHAUSER and W. HENSINGER.—See this vol., 505.

Applications of ceric sulphate in volumetric analysis. I. Preparation and stability of solutions of ceric sulphate containing free sulphuric acid. II. Potentiometric study of the reactions between ceric and ferrous or oxalate ion. Application to the standardisation of ceric solutions. III. Potentiometric determination of cerium. N. H. FURMAN (J. Amer. Chem. Soc., 1928, **50**, 755—764).—Ceric sulphate solutions in dilute sulphuric acid, prepared by the method of Meyer and Aufrecht (A., 1904, ii, 175), are stable; they should be protected from direct sunlight. The solutions may be used for the potentiometric titration of ferrous sulphate, platinum or gold-amalgam-platinum electrodes being used (cf. this vol., 383). The reverse titration may also be carried out. Ceric sulphate solutions may conveniently be standardised by titrating with standard sodium oxalate solution at 50°, either volumetrically or potentiometrically. The bismuthate, persulphate, and ferricyanide methods of determining cerium are in substantial agreement, although the first two are more convenient. Someya's work is confirmed (this vol., 146), but some of the results of Lindeman and Hafstad (A., 1927, 536) could not be repeated. S. K. TWEEDY.

Metal cyanates. I. Ammines with pyridine of simple cyanates. II. Detection, separation, and gravimetric determination of aluminium. R. RIPAN (Bul. Soc. Stiinte Cluj, 1927, **3**, 176—192, 311—320: Chem. Zentr., 1927, ii, 2388—2389).—I. The following *pyridinecyanates* have been prepared: $[AgC_5H_5N]CNO$, $[Mn(C_5H_5N)_4](CNO)_2$, $[Mn(C_5H_5N)_6](CNO)_2$, $[Fe(H_2O)(C_5H_5N)_3](CNO)_2$, $[Fe(C_5H_5N)_6](CNO)_2$, $[Co(C_5H_5N)_4](CNO)_2$, $[Ni(C_5H_5N)_4](CNO)_2$, $[Ni(C_5H_5N)_6](CNO)_2$, $[Zn(C_5H_5N)_2](CNO)_2$, $[Cd(C_5H_5N)_2](CNO)_2$, $[Cd(C_5H_5N)_6](CNO)_2$, $[Cu(C_5H_5N)_2](CNO)_2$, $[Cu(C_5H_5N)_6](CNO)_2$; they are more stable than the simple cyanates. Similar compounds containing magnesium, beryllium, ferric iron, aluminium, or tervalent chromium were not obtained.

II. When an aluminium salt is warmed in solution with potassium cyanate, carbon dioxide is evolved and aluminium hydroxide is precipitated in a less gelatinous condition than usual, even granular; 0·0005 g. of aluminium is thus discernible. The reaction is applicable to the separation of aluminium from zinc or manganese, these metals not giving an insoluble precipitate with alkali cyanate; the aluminium hydroxide is collected, zinc is precipitated from the filtrate with pyridine or ammonium thiocyanate, or manganese with ammonia solution. Organic acids prevent the precipitation of aluminium hydroxide by potassium cyanate; silica is not precipitated from a solution more dilute than 4%. For the gravimetric determination of aluminium, a solution containing 0·2 g. of potassium cyanate for every 0·017—0·02 g. of aluminium and a few c.c. of 2N-ammonium chloride solution is gently heated, and finally boiled

for a few minutes until the precipitate is granular; after partial cooling the precipitate is collected (being washed with water by decantation and on the filter) and ignited wet. A. A. Eldridge.

Reaction of sodium alizarinmonosulphonate with aluminium under different experimental conditions with reference to its use in colorimetry. J. H. Yoe and W. L. Hill (J. Amer. Chem. Soc., 1928, **50**, 748—755).—Atack's method for the colorimetric determination of aluminium (A., 1915, ii, 842) is investigated. Increasing excess of acetic acid increases the rate of change of colour intensity during the first 20 min. only. The intensity is proportional to the aluminium content provided excess of dye is present, and it increases with the time of lake formation; it is very sensitive to slight variations in the ammonia concentration. Temperature has only a slight effect. The dye solution must not be more concentrated than 0·4%. Iron, chromium, cobalt, and manganese must be removed if more than traces are present. S. K. Tweedy.

Determination of aluminium as phosphate. A. Lejeune (Bull. Soc. chim. Belg. 1928, **37**, 110—114).—The determination of aluminium as phosphate according to the procedures of Meurice, Campredon, and Besombe gives in all cases high results owing to the occlusion of phosphoric acid by the aluminium phosphate. The greater the excess of precipitant the higher are the results. Sodium phosphate solutions gave rise to greater occlusion of phosphoric acid than those of ammonium phosphate. This method therefore should be used only when rapid and approximate analyses are required. F. J. Wilkins.

Manganese in steel and pig iron. Volumetric determination by the vanadate method. L. E. Stout and G. C. Whitaker.—See B., 1928, 233.

Determination of manganese in iron and steel by the silver nitrate-persulphate method. S. W. Lipin.—See B., 1928, 267.

Micro-analysis. Micro-burette with stopcock at its upper end. Oxidimetric determination of iron by Knop's method. Potentiometric titrations with small volumes of liquid. A. Benedetti-Pichler (Z. anal. Chem., 1928, **73**, 200—216).—A burette for micro-volumetric analysis consists of a tube 6 mm. in internal diameter with a capillary tube 12 cm. long at its lower end, and a rubber stopper provided with a glass tube and a rubber tube 30 cm. long at its upper end. The rubber tube is provided with an ordinary pinchcock about 5—8 cm. from the stopper, and the lower end of the capillary is coated outside with paraffin wax so that it delivers very small drops. The burette is filled by opening the pinchcock and drawing liquid in through the capillary by applying suction at the end of the rubber tube. A vessel for carrying out potentiometric titrations with small volumes of liquid comprises a thick-walled test-tube with a platinum spiral sealed in at its lower end, and the usual capillary tube filled with N-potassium chloride solution connecting with the N-calomel electrode; a second capillary serves for passing bubbles of air through the liquid to keep it thoroughly stirred during a titration. The titration of small volumes of ferrous sulphate or chloride solutions with dichromate using diphenylamine as internal indicator gives results which are reproducible to within $\pm 0·002$ mg. of iron, using $0·004N$-dichromate solution. The colour change of the indicator takes place simultaneously with the potential change observed in electrometric titration. A. R. Powell.

Potentiometric determination of iron. J. Mika (Z. Elektrochem., 1928, **34**, 84—86).—By the use of a platinum electrode the titration of ferric salts with a solution of sodium thiosulphate may be followed potentiometrically with considerable accuracy when the faintly acid medium (about 0·01% HCl) contains small quantities of copper salts. The customary calomel electrode may conveniently be replaced by a quinhydrone electrode in a solution of p_H 2·8 (16·83 c.c. of $0·1M$-citric acid + 3·17 c.c. of $0·2M$-disodium hydrogen phosphate). J. S. Carter.

Colorimetric determination of small amounts of iron in zinc. W. J. Agnew.—See B., 1928, 234.

Determination of minute amounts of cobalt in steel. W. J. Agnew.—See B., 1928, 233.

[Reactions of cobalt and lead.] A. S. Komarovsky (Z. anal. Chem., 1928, 73, 288—289).—Polemical; a reply to Tananaev. A. R. Powell.

Detection of chromium, manganese, mercury, silver, and copper by spot tests. N. A. Tananaev and I. Tananaev (Z. anorg. Chem., 1928, **170**, 113—127).—Spot tests, to be carried out on filter-paper as previously described (A., 1924, ii, 571; 1925, ii, 324; cf. also Feigl, this vol., 382), and depending on the reduction of silver, mercuric, or cupric ions in presence of ammonia or sodium hydroxide, have been devised for the detection of the above metals. Chromic salts are oxidised by warming with silver nitrate and sodium hydroxide, and after the addition of ammonium nitrate to dissolve silver oxide and convert sodium hydroxide into sodium nitrate the chromate is detected either with silver nitrate, or with an acetic acid solution of benzidine, this latter producing a blue colour. Cobalt, nickel, and lead are oxidised by silver nitrate in presence of sodium hydroxide, the black stain produced on the paper not being removed by ammonium nitrate. Ammoniacal silver nitrate solution reveals manganese by giving rise to an intense black colour, but does not react with cobalt, nickel, lead, or chromium. The same reaction may be applied to the detection of silver. Mercurous ions are precipitated with hydrochloric acid, and the washed precipitate is treated with ammonia. To detect mercuric ions in absence of silver or mercurous ions, manganous nitrate and sodium hydroxide are added, when a black colour shows the presence of a mercuric salt. Cupric salts are reduced to the cuprous state with potassium iodide, or, if the amount of copper is very small, with a solution of silver iodide in potassium iodide solution, and the cuprous ions oxidised again with silver nitrate, after the removal of free iodine with arsenite. Ferric salts interfere with this test, but this difficulty may be overcome by washing away the

ferrous salts, produced by the reducing action of the iodide, before silver nitrate is added to the cuprous iodide. In a mixture of mercurous and silver ions, the presence of the latter is demonstrated by the re-appearance of a black colour when the black colour resulting from the action of ammonia on the mixed chlorides is removed with bromine water, and manganese nitrate and ammonia are added. If manganese and silver are present together, but mercurous ions are absent, a black colour appears on the addition of ammonia only; this test is, however, conclusive only if it gives a positive result. The presence of chromium and either silver or mercuric ions is proved by the formation of chromate when the solution is treated with sodium hydroxide, R. CUTHILL.

Artificial daylight. J. W. T. WALSH (J. Sci. Instr., 1928, **5**, 81—88).—The uses of artificial daylight and means for its production are discussed. Artificial daylight having the same spectral distribution as true daylight is distinguished from "sensation" daylight in which the same visual effect is produced by means of a different spectral distribution. The former only can be used for matching colours, whilst the latter is permissible for general illumination. The only practical method of producing artificial daylight is the subtractive method, in which the excess of red and yellow light is removed by an absorbing screen, or by reflexion from a coloured surface. Its production is therefore less efficient than that of ordinary artificial light. C. J. SMITHELLS.

Nomography. O. LIESCHE (Chem. Fabr., 1928, 161—164).—Methods of constructing charts for the elimination of calculation in supplying analytical results are discussed, and two types of chart for reading percentage of sulphur from the weight of substance taken and of barium sulphate obtained are given. S. I. LEVY.

Technique of spectrum analysis. T. NEGRESCO (J. Chim. phys., 1928, **25**, 216—233).—The apparatus and methods employed in the laboratory of the Sorbonne are described. It is pointed out that the frequent absence of agreement between the results of different authors for the intensities of spectral lines is apparently due to the effect on the relative intensities of the lines of variations in the apparatus, in the sensitivity of the photographic plates, and in the mode of reading the spectrogram. Further, it would appear that the spectrum of a particular element is not always independent of any elements which may be combined with it; *e.g.*, in the spectrum of an alloy of copper with 14% of silicon the line 3086, corresponding with the $Si^{\cdot\cdot}$ ion, is relatively more intense than it is in the spectrum of pure silicon. R. CUTHILL.

Production and application of high voltages in the laboratory. G. BREIT and M. A. TUVE (Nature, 1928, **121**, 535—536).—A method of producing and measuring voltages up to 5×10^6 volts is described; high voltages are applied to vacua by the use of external electrodes. A. A. ELDRIDGE.

Capillary electrometer. G. F. KOMOVSKY (Z. Elektrochem., 1928, **34**, 204—205).—A capillary electrometer, made in the form of a ring, is described. H. INGLESON.

Apparatus for the determination of viscosity under different conditions, and the errors induced by changes of velocity of the moving liquid, surface tension, and displacement caused by the air. E. MASTERS and A. E. GODDARD (Ber., 1928, **61**, [*B*], 586—591).—An apparatus for the determination of comparative and relative viscosities is figured and described. It is best adapted for Scarpa's method, whereby the errors caused by air displacement and surface tension and the necessity for determining the density and mean height of the liquid column are eliminated. The advantages claimed are (1) the capillary and bulb are easily separated from one another and therefore easily cleaned; (2) the length of the capillary can be determined with great exactness; (3) small vessels are used, and hence only small volumes of liquid are required, since the time of flow can be varied at will by alteration of the pressure; (4) a correction for kinetic energy is unnecessary. H. WREN.

Combined capillarimeter–viscosimeter. S. T. BOWDEN (J. Physical Chem., 1928, **32**, 459—462).—The apparatus enables density, viscosity, and surface tension to be determined on the same sample of liquid in one vessel. The principle developed in the Richards capillarimeter is utilised together with the relative viscosimeter principle, and the whole is a modified arrangement of the well-known Ostwald apparatus. L. S. THEOBALD.

Apparatus for the determination, in small volumes of fluid, of the osmotic pressure of colloids. E. B. VERNEY (J. Sci. Instr., 1928, **5**, 97—100).—Apparatus is described by means of which the osmotic pressure of the colloids in blood-plasma may be determined at various temperatures, under aseptic conditions, and in volumes of fluid as small as 1 c.c. C. J. SMITHELLS.

Pipette. H. N. RIDYARD (J.C.S., 1928, 748—750).—A pipette suitable for the accurate delivery of small volumes of liquid is described. Errors do not exceed $\pm0.02\%$ with water and $\pm0.1\%$ with benzene. C. W. GIBBY.

Non-spattering semi-automatic wash bottle. N. S. SERINIS (Chemist-Analyst, 1928, **17**, 15—16). CHEMICAL ABSTRACTS.

Spot plate for outside indications. C. A. THOMAS (Chemist-Analyst, 1928, **17**, 18).—The plate is coated with paraffin. CHEMICAL ABSTRACTS.

Burette-reading device. M. HYMAN (J.S.C.I., 1928, **47**, 100T).—A piece of white celluloid has about two thirds of its area blackened. Over this area is placed a strip of transparent celluloid affixed by means of eyelets near the ends, thus allowing the burette to be slipped in between the strips. The device gives good meniscus illumination; parallax error is eliminated by viewing the upper margins of the black area and the transparent celluloid as a coincident line, and the burette reading is obtained by noting the position of the edge of the transparent celluloid in contact with the graduations independently of the meniscus observation.

Rapid method of drying laboratory preparations. M. HYMAN (J.S.C.I., 1928, **47**, 86T).—

Warm, dry air is aspirated through the Buchner funnel in which the substance is collected by fitting a filter funnel with a short stem and side tube over the Buchner funnel and connecting the side tube to a suitable air heater. A thermometer registers the temperature of the air current just above the substance.

Electrically heated Abderhalden drier. E. P. CLARK (Ind. Eng. Chem., 1928, **20**, 306).—The usual jacket filled with the vapour of a boiling liquid was replaced by a Pyrex mantle and "chromel" heating-coil laced to a strip of asbestos board and lying on the bottom of the mantle. Temperatures up to 125° could be maintained at a given point in the tube within 1° throughout the day. C. IRWIN.

Hot-wire manometer. M. KNUDSEN (K. Danske Vidensk. Selsk., 1927, **7**; Mat.-fys. Medd. 15, 3—18; Chem. Zentr., 1927, ii, 2769).—The apparatus employs Wollaston wire of diameter 0·0002 cm. Its function depends on the fact that the current necessary to maintain a particular temperature depends on the pressure of the surrounding gas. A. A. ELDRIDGE.

Apparatus for demonstrating thermal conductivity of hydrogen. (MLLE.) E. SOKOLOVA (Z. anorg. Chem., 1928, **170**, 128).—The apparatus consists of a carbon-filament electric lamp, to the bulb of which are fused tubes for the inlet and outlet of gases. If the lamp is filled with carbon dioxide, the filament glows brightly when the current passes, but if hydrogen is substituted the glow fades. R. CUTHILL.

Modified thermo-regulator. A. LEHRMAN (Ind. Eng. Chem., 1928, **20**, 290).—An electrical thermostat usually consists of two separate heating elements, one constant and one intermittent. The author discards one and replaces it by a variable resistance in the main circuit which is switched in or out by the mercury toluene regulator. C. IRWIN.

Applications of a new ebullioscope. W. SWIENTOSLAWSKI (Rocz. Chem., 1927, **7**, 516—523).—A number of modifications of Cottrell's ebullioscope (A., 1919, ii, 447) are described, giving values accurate to 0·0015—0·002°. These may be used, apart from the determination of b. p., for very delicate barometric and tonometric measurements, for the calibration of thermometers, for the determination of latent heats of vaporisation, and for the determination of equilibrium and velocity coefficients of certain reactions. R. TRUSZKOWSKI.

Rapid extraction apparatus. L. METZ (Z. anal. Chem., 1928, **73**, 219—220).—The apparatus comprises a boiling flask for the solvent provided with a rubber stopper carrying a short, wide cylinder into the rubber stopper at the top of which is fixed a Liebig condenser. The lower part of the cylinder has three glass beads fused inside to support a glass filtering funnel or crucible in which the material to be extracted is placed. A. R. POWELL.

Lecture experiments on the hydrogen-ion concentration changes in the rusting of iron. W. R. G. ATKINS (Nature, 1928, **121**, 615).—An indicator method is used for demonstrating the development of acidity (p_H 3·2) by the addition of hydrogen peroxide solution (p_H 5·6) to ferrous sulphate solution (p_H 4·8), or by atmospheric oxidation of the ferrous salt. The indicator (bromothymol-blue) is also employed to show the change in p_H of water (6·6—8·4) in contact with iron, due to the absorption of carbon dioxide; when carbon dioxide absorbed from the air is liberated by addition of hydrogen peroxide, a solution of p_H originally 5·6—6·0 has p_H 4·6. The experiments are in conflict with the view that oxidation of the iron is the first stage in rusting. A. A. ELDRIDGE.

Geochemistry.

Composition of the air of the streets of Paris. R. CAMBIER and F. MARCY (Compt. rend., 1928, **186**, 918—921).—Under traffic-block conditions the carbon monoxide content of the air at ground-level in Paris streets may commonly rise to 10^{-4} ($0·5\times10^{-3}$ is recorded in an exceptional case), although at 1·6 m. above the ground it never exceeds 6×10^{-5} and falls to about 10^{-5} when traffic circulation is resumed. The authors' figures, which confirm those of Florentin (A., 1927, 1177), show that the mean concentrations of the oxides of carbon are of the same order as in 1877. J. GRANT.

Analysis of the water of Lakes Ursul and Negru. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1927, **3**, 200—209; Chem. Zentr., 1927, ii, 2173).—The density, conductivity, salt content, and composition of the dissolved gas are recorded for samples taken at 2 m. depth. A. A. ELDRIDGE.

Analysis of water from the "Balint" thermal spring. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1927, **3**, 240—243; Chem. Zentr., 1927, ii, 2173).—The density, conductivity, salt content, and composition of the dissolved gas are recorded. A. A. ELDRIDGE.

Radioactivity of some springs of the Pyrenean region. J. ALOY and J. AVERSENQ (Compt. rend., 1928, **186**, 775—777).—The radioactivities of sulphur and other springs in the Pyrenees, and of the gases they evolve, are low in absolute value, although their hororadioactivities are relatively high (maximum recorded, 130·7 millicuries). Springs analogous in composition have similar radioactivities, and cold springs are more active than warm springs. J. GRANT.

Variation in radioactivity and mineralisation of springs. V. SPITZYN (Trav. Radium Minerais radioact., [Russia], 1926, **2**, 272—276; cf. this vol., 455).—A consideration of the relation between radioactivity and salt content of the water of radioactive springs. A. A. ELDRIDGE.

Inner crystal structure of some native metals. H. C. H. CARPENTER and S. TAMURA (Bull. Inst. Min. Met., 1928, No. 282, 22 pp.).—Specimens of native copper, silver, and gold were found on examination to contain twinned crystals. It is highly probable that these did not represent primary structures, but were the outcome of recrystallisation subsequent to the metal having been in some way internally strained. A specimen of meteoric iron, however, appeared largely to have preserved its original crystal structure, and on etching exhibited the characteristic Widmanstatten figures, and also a large number of Neumann bands, showing that the metal had been overstrained.
R. CUTHILL.

Relation between hardness and coefficient of expansion of minerals. M. I. LIPOVSKI (Ann. Inst. Polyt. Oural, 1926, **5**, 123—128).—Data are discussed showing that the hardness of minerals diminishes with increasing coefficient of expansion. A rational scale of hardness is suggested, based on exact measurements of coefficients of expansion.
C. W. GIBBY.

Carbon compounds of the magma. HELLMERS (Z. angew. Chem., 1928, **41**, 342—343).—From the fact that carbides are not capable of existence in the solid crust of the earth yet probably exist in the magma, it may appear conceivable that the methane which is present in the gases from fumaroles is a product of the action of water on carbides. The temperature of its formation under these conditions would be so high, however, that the gas would be very largely dissociated into its elements, so that it is much more probable that it owes its origin to the reactions $CO+3H_2=CH_4+H_2O$ and $2CO+2H_2=CH_4+CO_2$. Carbon monoxide may well arise in the main from the action of carbon on carbon dioxide, but the reaction of carbon with steam must also be taken into account. Examination of three specimens of igneous rocks containing bitumen showed that this latter was a late introduction into the rock, and could not have been formed *in situ*, *e.g.*, by polymerisation. No perfectly definite example of the formation of mineral oil deposits directly from the magma has, in fact, ever been observed. R. CUTHILL.

Weathering of Cheviot granite under the peat. S. J. TOMKEIEFF (Proc. Univ. Durham Phil. Soc., 1927, **7**, 233—243).—The residual products of the weathering of Cheviot granite consist essentially of quartz grains and white mica. Microscopical and chemical analysis shows an absence of kaolinite. It is concluded that the process of weathering consists of a progressive hydration with the resulting splitting of the felspar molecule and subsequent removal of alkalis and silicic acid. Under post-glacial peat deposits, the hydration has proceeded only far enough to produce muscovite, as in the case of Cheviot granite. Under older deposits such as tertiary brown coal, the hydration has gone further, producing kaolinite. W. E. DOWNEY.

Thermomagnetic study of some iron minerals. J. HUGGETT and G. CHAUDRON (Compt. rend., 1928, **186**, 694—696).—Comparison of the magnitudes of the anomalies (at about 570°) shown on the magnetisation–temperature curves of magnetite and other iron minerals heated in a vacuum (cf. A., 1927, 207) shows that the former occurs in small amounts in goethite (previously dehydrated at 600° in a vacuum), ilvaite (after heating at 800°), oligist (Fe_2O_3), martite, lepidocrocite, and ilmenite. The iron sesquioxide point (675°) is also shown, except for ilmenite and ilvaite. Magnetite heated in air shows an anomaly corresponding with superficial oxidation. J. GRANT.

Arrojadite, a new mineral of the wagnerite group. D. GUIMARAES (Publ. Inspect. Obras Contra as Seccas, 1925, No. 58; Chem. Zentr., 1927, ii, 2172).—Arrojadite, $4R'_3PO_4,9R''_3(PO_4)_2$, contains P_2O_5 34·32, Fe_2O_3 12·39, FeO 19·84, MnO 12·33, CaO 5·69, MgO 1·85, Na_2O 4·67, K_2O 1·45, Li_2O trace, H_2O ($<110°$) 0·44, H_2O ($>110°$) 4·96, SiO_2 0·66, SnO_2 1·52. It is monoclinic, dark green, with colourless to light green pleochroism; biaxial negative, γ 1·70, $\gamma—\alpha$ 0·007; hardness >5. A. A. ELDRIDGE.

Eschwegite. D. GUIMARAES (Bol. Inst. Sci. Brazil, 1926, **2**, 1—2; Chem. Zentr., 1927, ii, 2172).—Eschwegite, a new mineral from Minas Geraes, contains Ta_2O_5 21·58, Nb_2O_5 25·17, TiO_2 18·75, $(Y,Er)_2O_3$ 27·28, ThO_2 0·57, UO_2 1·96, Fe_2O_3 2·05, H_2O 3·09, corresponding with the formula $5Y_2O_3,6(TaNb)_2O_5,10TiO_2,7H_2O$. The mineral is reddish-grey, *d* 5·87, hardness 5·5, refraction 2·15—2·20, isotropic. A. A. ELDRIDGE.

Composition of chlorites. J. ORCEL (Bull. Soc. Franç. Min., 1927, **50**, 75—456; Chem. Zentr., 1927, ii, 2172).—A discussion, with some new analyses. According to their composition, chlorites are classed as follows: prochlorite, prochlorite-clinochlor, clinochlor, clinochlor-pennine, pennine, chlorite poor in aluminium, chlorite containing chromium.
A. A. ELDRIDGE.

Microscopical study of some metallic minerals from Peru. J. ORCEL and G. R. PLAZA (Compt. rend., 1928, **186**, 769—772).—The principal minerals examined are enargite, erubescite, chalcopyrite, panabase, blende, pyrargyrite, proustite, and nickel minerals, the predominating elements being copper, lead, zinc, and silver. The minerals may be classified as (1) cupriferous, from which lead is almost absent; (2) cupriferous and plumbiferous, rich in silver; (3) silver minerals. Pyrites was detectable in all the veins. In addition to the customary oxidation products (malachite, azurite, cuprite, etc.) cinnabar was also observed in association with azurite.
J. GRANT.

Cassiterite and topaz from the tin mines of Northern Nigeria. A. SCHOEP (Natuurwetens. Tijds., 1928, **10**, 3—6).—The properties and forms of some crystals of unusual habit are described. The fluorine content of topaz calculated by the method of Penfield and Minor from the inclination of the optic axes is about 20%. S. I. LEVY.

Greenish satinspar (calcite) from Kipushi, Katanga. A. L. HACQUAERT (Natuurwetens. Tijds., 1928, **10**, 7—9).—A spherical agglomeration of massive calcite with elongated crystals of satinspar having a pale green colour was found to contain 0·075% of copper. S. I. LEVY.

Organic Chemistry.

Addition of gaseous hydrogen chloride and bromide to ethylene and propylene under the influence of catalysts. J. P. WIBAUT, J. J. DIEKMANN, and A. J. RUTGERS (Rec. trav. chim., 1928, **47**, 477—495).—The formation of ethyl chloride from ethylene and hydrogen chloride in presence of an asbestos–bismuth chloride catalyst at 15° and 120—200° has been studied. At the ordinary temperature reaction takes place slowly, whilst at the higher temperatures 73—82·4% of ethyl chloride is formed. Aluminium trichloride and vanadium chloride on asbestos have low catalytic activities (cf. Berl and Bitter, A., 1924, i, 256), whilst antimony trichloride and barium chloride are inactive. When ferric chloride is used the results are irregular (7·2—74% of ethyl chloride), and some *s*-dichloroethane is produced at the same time. Using the bismuth chloride catalyst, good yields of ethyl chloride can be obtained from mixtures of ethylene with coal gas or water gas, even if the concentration of ethylene is only 1—2%.

The reaction between propylene and hydrogen chloride is more rapid than with ethylene. Bismuth and antimony chlorides catalyse the reaction, the yields of *iso*propyl chloride being 80% and 68%, respectively, at an initial temperature of 18—20°. Pure asbestos and asbestos–barium chloride at 150° give approximately the same yields of *iso*propyl chloride.

Hydrogen bromide reacts more readily with ethylene and propylene than hydrogen chloride. Bismuth bromide on asbestos catalyses both reactions; at an initial temperature of 20° there are formed 84% of ethyl bromide and 89% of *iso*propyl bromide.

Ethylene or propylene, containing a small amount of hydrogen, can be conveniently prepared by passing ethyl or propyl alcohol vapour over an asbestos–aluminium sulphate catalyst. H. BURTON.

Conjugated compounds. IV. Formation of isomeric additive dibromides from butadiene. E. H. FARMER, C. D. LAWRENCE, and J. F. THORPE (J.C.S., 1928, 729—739).—The addition of bromine (1 mol.) to $\Delta^{\alpha\gamma}$-butadiene has been examined in presence of various solvents (cf. Griner, A., 1893, i, 450; 1894, i, 62; Thiele, A., 1900, i, 2). In all the cases studied varying mixtures of the oily 1 : 2-dibromide ($\alpha\beta$-dibromo-Δ^{γ}-butylene) (ozonolysis products, $\alpha\beta$-dibromopropaldehyde and formaldehyde) and the solid 1 : 4-dibromide ($\alpha\delta$-dibromo-Δ^{β}-butylene), m. p. 53°, are produced. In chloroform, hexane, and carbon disulphide at −15°, the percentages of the 1 : 4-isomeride formed are 63, 38·4, and 65·9, respectively, whilst in acetic acid at 4°, 70% is produced. If quinoline dibromide hydrobromide is used as the brominating agent no 1 : 4-dibromide is produced. When either the pure 1 : 2- or 1 : 4-dibromide is heated at 100° for a few minutes, the resulting product is an equilibrium mixture of the 1 : 2 (20%) and 1 : 4 (80%) compounds. The mechanism of the addition of bromine and the rearrangement phenomena are discussed. H. BURTON.

Competitive interaction of alkyl and aryl halides with magnesium. H. W. RUDD and E. E. TURNER (J.C.S., 1928, 686—691).—Equimolecular proportions of two alkyl or aryl halides are allowed to react with magnesium (1 atom) in presence of ether and the resulting mixture is analysed. It is found that in alkyl bromide–chloride pairs the bromide is more reactive throughout the series and increases thus: $Et<Pr^{a}<Bu^{a}$. For alkyl iodide–chloride the iodide is more reactive initially and then decreases: $Me>Et>Pr^{a}>Bu^{a}$, whilst in the system alkyl bromide–iodide there is an alternating effect. The introduction of a methyl group into any position in bromobenzene increases the reactivity of the bromine atom as compared with the corresponding iodo-compounds. H. BURTON.

Catalytic dehydration of ethyl alcohol by alumina. A. M. ALVARADO (J. Amer. Chem. Soc., 1928, **50**, 790—792).—Pease and Yung (A., 1924, i, 363) and Clark, Graham, and Winter (A., 1926, 45) obtained 62 and 80% of ether respectively by dehydration of ethyl alcohol with alumina. Curves plotted for this reaction show that the maximum yields of ether are 82·2% at 269°, 73·5% at 300°, and 55·0% at 354°, and that the relative amounts of ether and ethylene produced depend on the temperature and the time of contact. The stages in the dehydration appear to be (i) ether, (ii) ethylene. A. McGOOKIN.

Colour reactions of ethyl alcohol. L. EKKERT (Pharm. Zentr., 1928, **69**, 198).—The colorations obtained when alcohol containing a trace of aldehyde is treated with resorcinol and excess of sulphuric acid under various conditions are described. S. I. LEVY.

Preparation of partly acylated chloronitrotrimethylene glycols. E. SCHMIDT, G. RUTZ, and M. TRENEL (Ber., 1928, **61**, [*B*], 472—477).—The following β-chloro-β-nitroethyl esters are prepared by the action of the requisite acid chloride on β-chloro-β-nitroethyl alcohol in chloroform: acetate, b. p. 89—90°/9 mm., d_4^{20} 1·3580, n_D^{20} 1·4429; *propionate*, b. p. 95—96°/8 mm., d_4^{20} 1·2941, n_D^{20} 1·4428; n-*butyrate*, b. p. 107°/9 mm., d_4^{20} 1·2379, n_D^{20} 1·4418; iso*valerate*, b. p. 111—113°/11 mm., d_4^{20} 1·1891, n_D^{20} 1·4414. The esters dissolved in ether when shaken with a large excess of formaldehyde solution containing the sodium salt of the acid from which the ester is derived give the following β-*chloro*-β-*nitro*-γ-*hydroxy*-n-*propyl* esters: *acetate*, b. p. 107—108°/0·02 mm., 146—147°/10 mm., d_4^{20} 1·4066, n_D^{20} 1·4650; *propionate*, b. p. 118—119°/0·2 mm., d_4^{20} 1·3436, n_D^{20} 1·4613; n-*butyrate*, b. p. 117—118°/0·2 mm., d_4^{20} 1·2921, 1·4611; iso*valerate*, b. p. 117—118°/0·15 mm., d_4^{20} 1·2448, n_D^{20} 1·4600. The hydroxypropyl esters with the appropriate acid chloride yield the following mixed esters: β-*chloro*-β-*nitro*-n-*propyl* αγ-*diacetate*, b. p. 139—140°/10 mm., d_4^{20} 1·3400, n_D^{20} 1·4513; α-*acetate* γ-*propionate*, b. p. 98—99°/0·12 mm., d_4^{20} 1·2898, n_D^{20} 1·4492; α-*acetate* γ-n-*butyrate*, b. p. 106—107°/0·05 mm., d_4^{20} 1·2499, n_D^{20} 1·4490; α-*acetate* γ-iso*valerate*, b. p. 117—118°/0·07 mm., d_4^{20} 1·2129, n_D^{20} 1·4476. H. WREN.

Chemical constitution of pentaerythritol. H. BINCER and K. HESS (Ber., 1928, **61**, [*B*], 537—

542).—The constitution $C(CH_2·OH)_4$ is established for pentaerythritol in the following manner. It is converted by boiling hydriodic acid (*d* 1·7) into ββ-di-iodomethylpropane-αγ-diol, m. p. 129·5—130·5°, in 46% yield, which with silver acetate and glacial acetic acid affords pentaerythritol tetra-acetate, m. p. 82—83°, thus showing that change in the skeleton has not occurred during formation of the iodohydrin. The latter compound is converted by hydrogen in the presence of palladised barium sulphate, magnesium oxide, and pyridine into ββ-dimethylpropane-αγ-diol, m. p. 128°, identical with the product derived from *iso*butaldehyde and formaldehyde (cf. Franke, A., 1905, i, 111); the corresponding *dibenzoate*, m. p. 52—54°, is described. Contrary to Zelinsky (A., 1913, i, 254), γ-bromo-ββ-dibromomethyl-*n*-propyl alcohol, m. p. 70—71°, is obtained during the preparation of the dibromohydrin from pentaerythritol and hydrobromic acid at 125°, but is more conveniently made from the reactants at 140°; the tetrabromohydrin, m. p. 148—151°, is simultaneously produced.
H. WREN.

Double sulphates of the copper-magnesium group and the sulphonium bases. II. P. C. RAY and N. RÂY (J. Indian Chem. Soc., 1928, 5, 69—72).—Double *sulphates* of the general formula $M''SO_4,(Me_3S)_2SO_4,8H_2O$, where $M''=Fe''$, Zn, Cd, Mg, Cu, Mn, Ni, and Co, are obtained under similar conditions to those used in the preparation of the corresponding ethyl compounds (A., 1927, 740). By addition of alcohol to concentrated aqueous solutions of these salts, similar *compounds* ($+7H_2O$) are obtained in the first six cases; the cobalt salt affords a compound with $6H_2O$. The anhydrous salts cannot be obtained since dissociation takes place on heating.
G. A. C. GOUGH.

Oxidation of sulphides by perbenzoic acid. I. L. N. LEWIN (J. pr. Chem., 1928, [ii], 118, 282—286). —The organic sulphides are treated at the ordinary temperature in the dark with a 0·2*N*-solution of perbenzoic acid (cf. Prileschaeff, A., 1911, i, 255) in chloroform. Under these conditions, αα'-dichlorodimethyl sulphide is quantitatively converted into the sulphone in 20 hrs., ββ'-dichlorodiethyl sulphide in 4 hrs., and phenyl and benzyl sulphides in 1 hr. They may, therefore, be conveniently analysed in this way by determining iodometrically the excess of perbenzoic acid. H. E. F. NOTTON.

Lead subacetate solution (Goulard's extract) and its reaction with phenols. C. S. GIBSON and E. MATTHEWS (J.C.S., 1928, 596—601).—Goulard's extract (Brit. Pharmacopœia, 1914, 229) is shown to be a solution of the basic lead acetate, $Pb(OH)_2,Pb(OAc)_2$. When mixed with aqueous solutions of phenols precipitates of the composition $Pb(OR)_2,Pb(OH)·OAc$ are formed. These complexes are appreciably soluble in organic media when first precipitated, but when dry are only sparingly soluble.

A solution of the basic lead acetate, $2Pb(OH)_2,Pb(OAc)_2$, is obtained by shaking excess of lead oxide with aqueous lead acetate at the ordinary temperature. H. BURTON.

Acetoacetic ester condensation. M. C. FRANKLIN and W. F. SHORT (J.C.S., 1928, 591—595).—The dry "final product" prepared by the action of sodamide on ethyl acetate (cf. Scheibler and Ziegner, A., 1922, i, 426) contains sodium acetate and sodium acetamide, since it reacts with excess of benzyl chloride, yielding benzyl acetate, acetamide, acetbenzylamide, and ethyl αα-dibenzylacetoacetate.

When sodium is used as the condensing agent the dry "final product" also contains sodium acetate, since treatment with ethyl iodide gives ethyl acetate and ethyl ethylacetoacetate. Benzyl chloride reacts, yielding benzyl acetate, ethyl α-benzylacetoacetate, and ethyl αα-dibenzylacetoacetate.

The structure assigned to the final product by Scheibler and Ziegner is criticised. H. BURTON.

Action of bromine water on certain olefinic acids. J. READ and W. G. REID (J.C.S., 1928, 745—749).—When aqueous solutions of maleic acid (0·05—0·33*N*) are treated with bromine water, 89·3% of the bromine is utilised in bromohydrin formation at the former concentration and 62·5% at the latter. With sodium maleate reaction proceeds several hundred times faster and an increased amount of bromohydrin is produced (95·6—75·6%). Sodium fumarate and itaconic acid react to give 96—97% of bromohydrin at concentrations of 0·05—0 0655*N*, and the decrease at higher concentrations is less marked than for maleic acid. Oleic acid and bromine water react to give 51·5% of bromohydrin at the ordinary temperature and 57·5% at 90°. When the product of the reaction at 90° is heated successively with alcoholic potassium hydroxide and dilute sulphuric acid there is formed a *dihydroxystearic acid*, m. p. 92—93°. Coumarin yields 5-bromocoumarin and an unrecognisable viscous oil. H. BURTON.

Activated form of oxalic acid. F. OBERHAUSER and W. HENSINGER (Ber., 1928, 61, [*B*], 521—533). —If a solution of oxalic acid at about 60° is treated with a deficiency of potassium permanganate in an atmosphere of carbon dioxide or nitrogen it does not, after becoming colourless, liberate iodine from potassium iodide or give a yellow colour with titanic acid reagent. When air is drawn through the solution, hydrogen peroxide is produced in the proportion of 1 mol. for each mol. of oxalic acid which has suffered auto-oxidation. If oxygen is substituted for air, the yield of hydrogen peroxide is increased, the rate of absorption of the gas increasing rapidly to a well-defined maximum and subsequently diminishing quickly. Since oxalic acid, alone or in the presence of manganese sulphate corresponding with the permanganate used, does not yield hydrogen peroxide under these conditions, the presence of an activated form of it must be assumed. This hypothesis is confirmed by the observation that in nearly neutral solution chromic acid, bromine, bromate, iodine, etc. are instantaneously reduced, whilst, under definite conditions, quantitative reduction of silver, platinum, and mercuric salts and distinct reduction of nitrates can be effected. For the determination of mercury as mercurous chloride approximately 0·1*N*-solutions of permanganate and oxalic acid in the ratio 1 : 10 are mixed with potassium chloride and heated on the boiling water-bath. The colour of the perman-

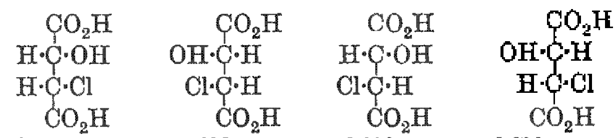
ganate slowly disappears and as soon as the solution begins to become colourless, reduction to mercurous chloride commences. Oxalic acid (1 mol.) reduces exactly 2 mols. of mercuric chloride. The change does not appear to occur between the undissociated molecules of oxalic acid and mercuric chloride, since all addenda which favour dissociation increase the speed of the reaction, and conversely. Increase in the mercury or oxalate ions facilitates the production of mercurous chloride. Reaction is therefore considered to consist in reduction of dissociated mercuric oxalate. Carbon dioxide has an appreciable accelerating effect. Slowly at the atmospheric temperature, more rapidly when heated, the activated oxalic acid regains its normal properties; a period of at least 24 hrs. is necessary to produce this effect under the former conditions. Addition of calcium chloride causes immediate, quantitative precipitation of calcium oxalate without unusual properties.

In the determination of mercury, permanganate may be replaced by manganous sulphate if sodium hydroxide is gradually added to the solution at 60—70°; the intermediate production of manganic oxalate is postulated, which decomposes with evolution of carbon dioxide and production of activated oxalic acid. Potassium manganioxalate may also be used. (The preparation of the salt from potassium permanganate, oxalic acid, and potassium oxalate is described in detail.) Active oxalic acid is produced to a less marked extent by the action of nickelic hydroxide or potassium cobaltioxalate on oxalic acid, but not by chromic acid or gold salts. Attempts to isolate activated oxalic acid yielded only the ordinary acid. In the volumetric determination of mercury, the residual oxalic acid corresponded exactly with that not required by the mercuric chloride.

H. Wren.

Stereochemistry of the tetrahedral carbon atom. VII. Number of the isomeric chloromalic acids. VIII. Configuration of the chloromalic acids. IX. In what phase of the reaction does re-arrangement of the substituents occur during the Walden inversion? R. Kuhn and T. Wagner-Jauregg (Ber., 1928, 61, [B], 481—483, 483—504, 504—521; cf. A., 1927, 852).—VII. The work of Kuhn and Zell (A., 1927, 41) and of Sonn and Rosinsky (A., 1925, i, 1237) has led to the description of two racemic and six optically active chloromalic acids. Resolution of chloromalic acid I by brucine under the conditions of the latter authors leads to the isolation from the more sparingly soluble brucine salt of a dextrorotatory chloromalic acid which is the antipode of the lævorotatory chloromalic acid of Kuhn and Zell. In accordance with theory, therefore, only four active chloromalic acids exist.

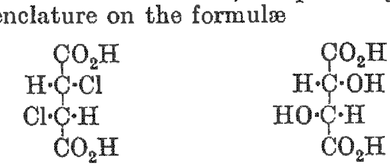
VIII. A solution of the problem is sought in the comparison of as large a number as possible of the physical properties of the two *dl*-chloromalic acids and their ethyl esters with those of the *r*- and *meso*-forms of the dichloro- and dihydroxy-succinic acids. The *meso*-structure is attributed to the chloromalic acid of which the properties fall into line most readily between those of *meso*dichloro- and *meso*dihydroxy-succinic acids, provided that the behaviour of the second chloromalic acid is equally reconcilable with that of *r*-dichloro- and *r*-dihydroxy-succinic acids. Chloromalic acid I is placed with *meso*tartaric and *meso*dichlorosuccinic acids according to the m. p. of the acids, b. p. of the ethyl esters, refractive indices of the esters, and dissociation constants of the acids. In the case of molecular volume the phenomena are complicated by association, due to the presence of the hydroxyl groups, and the data are not a simple function of the molecular structure. Association in benzene solution is shown only by hydroxylated compounds and the differences between the chloromalic esters are too small to be useful in assigning steric configuration. Solubility gives no help, since the isomeric chloromalic acids are equally soluble in water at 0°. For a similar reason observations on the adsorption of the acids from aqueous solution by charcoal and measurements of the dipolar moments of the esters are of no service. The following configurations are assigned:



l-Chloro-*d*-hydroxy- *d*-Chloro-*l*-hydroxy- *d*-Chloro-*d*-hydroxy- *l*-Chloro-*l*-hydroxy-

Chloromalic acid I. Chloromalic acid II.

Chloromalic acids I and II are designated *dl-meso* and *dl-rac*-chloromalic acid, respectively. Basing the nomenclature on the formulæ



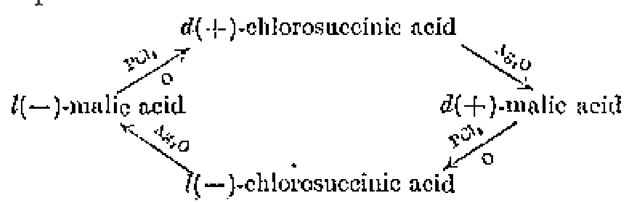
d-Dichlorosuccinic acid. *d*-Tartaric acid.

(cf. Wohl and Freudenberg, A., 1923, i, 182), dextrorotatory chloromalic acid I is regarded as composed of a half molecule of *l*-tartaric and a half molecule of *d*-dichlorosuccinic acid and is therefore termed *d*-chloro-*l*-hydroxysuccinic acid. Since *d*-dichlorosuccinic acid is dextrorotatory (cf. later, p. 507), the sign of rotation of the chloromalic acids is governed by the position of the chlorine atom, thus confirming the conclusion of Kuhn and Zell (*loc. cit.*), based on the principle of optical superposition. The following data are recorded: *r*- and *meso*-dihydroxysuccinic acid, m. p. 205° and 140° respectively; chloromalic acids I and II, m. p. 145° and 157°; *r*- and *meso*-dichlorosuccinic acids, m. p. 173° and 215°: ethyl *r*-tartrate, b. p. 158°/14 mm., d_4^{99} 1·1246, $n^{64·5}$ 1·4246; ethyl *meso*tartrate, b. p. 157·5°/14 mm., d_4^{99} 1·1350, $n^{64·5}$ 1·4315; *ethyl chloromalate* II, b. p. 153·5°/14 mm., d_4^{99} 1·1496, $n^{64·5}$ 1·4305; *ethyl chloromalate* I, b. p. 151·5°/14 mm., d_4^{99} 1·1560, $n^{64·5}$ 1·4321; *ethyl r-dichlorosuccinate*, b. p. 129·5°/12·5 mm., d_4^{99} 1·1636, $n^{64·5}$ 1·4296; ethyl *meso*dichlorosuccinate, b. p. 125·5°/12·5 mm., d_4^{99} 1·1490, $n^{64·5}$ 1·4266. The preparation of *r*-dichlorosuccinic acid, m. p. 170—172° (corr. decomp.), is effected by addition of a slight excess of chlorine to maleic anhydride in strong sunlight, whereas *meso*dichlorosuccinic acid, m. p. 220° (corr.

decomp.), results from the action of chlorine on sodium maleate in saturated sodium chloride solution (cf. Terry and Eichelberger, A., 1925, i, 631). Maleic anhydride with chlorine and bromine or bromine in sunlight affords *dl*-chlorobromosuccinic acid, m. p. 162° (corr. decomp.), and *r*-dibromosuccinic acid, m. p. 169—170° (corr.), respectively. Chlorofumaric acid and hydrogen bromide in glacial acetic acid yield *dl-meso*chlorobromosuccinic acid, decomp. 214·5° (corr.). *Methyl* dl-meso*chloromalate*, b. p. 140·5—141·5°/12 mm., is described.

IX. A method is proposed for the elucidation of the configuration of organic substances which does not depend on comparison of optical activities. A second, asymmetric carbon atom is combined with the compound of unknown configuration so that two antipodes do not result which differ from one another in a large number of physical properties. The added, asymmetric carbon atom is finally removed. The relationship of chlorosuccinic acid to *d*(+)-malic acid to which all space formulæ are referred is established as follows. In the two chlorosuccinic acids, *D'* and the hydroxyl group of *d*(+)-malic acid *D* is considered to be introduced. The chloromalic acids $\left\{\begin{matrix} D' \\ D \end{matrix}\right\}$ and $\left\{\begin{matrix} L' \\ D \end{matrix}\right\}$ are distinguished from one another by m. p., b. p. of ester, etc. Uniformity of position of the hydroxyl groups in the acids is established by their reduction by nascent hydrogen to the same *d*(+)-malic acid (the letters *D*, *D'*, *L*, *L'* denote the position of the substituents, OH and Cl). Of the two chloromalic acids, one in totality of physical properties must be between *d*-tartaric acid $\left(\frac{D}{D}\right)$ and *d*-dichlorosuccinic acid $\left(\frac{D_1}{D_1}\right)$, the other between *meso*-tartaric acid $\left(\frac{L}{L_1}\right)$ and *meso*dichlorosuccinic acid $\left(\frac{L_1}{L_1}\right)$. The observations can be made with the racemic forms of the chloromalic acids (cf. this vol., 506). The inactive chloromalic acids, the configuration of which is elucidated) are converted by replacement of OH by Cl into dichlorosuccinic acids. Since the structure of the latter is known by the accomplished fission of the racemic form, the incidence of a Walden inversion is immediately detected. *d*(+)-Tartaric acid is converted in two stages, through a chloromalic acid of known configuration, into dichlorosuccinic acid. Since the course of the second phase of the change is established, that of the transformation of tartaric into chloromalic acid is elucidated and therefore also the structure of the dichlorosuccinic acid is obtained. The active tartaric and dichlorosuccinic acids are linked with the active malic and monochlorosuccinic acids (reduction, optical superposition, optical comparison of the esters, etc.).

Experimentally the configuration of the inactive chloromalic acids has been established (see this vol., 506) and the position of the hydroxyl groups in the active chloromalic acids is known from their conversion into the malic acids. Direct conversion of ethyl *d*-tartrate into ethyl *l*-chloro-*d*-hydroxysuccinate is effected by thionyl chloride (1 mol.) in presence of pyridine. Methyl *dl-meso*chloromalate is converted by thionyl chloride into methyl *r*-dichlorosuccinate. Methyl *d*(+)-tartrate is transformed by thionyl chloride (2 mols.) into methyl (—)-dichlorosuccinate. It follows therefore that double inversion occurs during the passage of *d*(+)-tartaric acid into (—)-dichlorosuccinic acid. Lævorotatory dichlorosuccinic acid has the chlorine atoms in positions corresponding with those of the hydroxyl groups in *l*(—)-tartaric acid, and should be designated *l*(—)-dichlorosuccinic acid. Direct conversion of an active dichloro- into a monochloro-succinic acid could not be effected, since partial catalytic hydrogenation of the methyl ester affords a mixture of unchanged initial material and methyl succinate. Comparison of the specific rotations of the acids, their methyl and ethyl esters in different solvents and at different temperatures leads to the conclusion, supported by application of the principle of optical superposition, that (—)-dichloro- and (—)-monochloro-succinic acids are configuratively related and that the monochloro-compound is therefore *l*(—)-chlorosuccinic acid. The classical cycle of the malic acids may therefore be expressed :



Inversion occurs therefore during the action of phosphorus pentachloride, whereas silver oxide does not cause configurational change. With respect to the configuration of dextrorotatory chlorosuccinic acid, the authors' results do not agree with those of Clough (J.C.S., 1915, **107**, 1509; 1918, **113**, 526), whose fundamental postulate is considered not to be established theoretically or deducible from physical considerations of the cause of optical activity.

Addition of hypochlorous acid to maleic acid giving exclusively *dl-meso*chloromalic acid (chloromalic acid I) is an example of *cis*-addition. Fumaric acid adds hypochlorous acid mainly in the *trans*-position, only about 20% of it passing by *cis*-addition into *dl-rac*-chloromalic acid (chloromalic acid II). Formation of chloromaleic acid from *meso*chloromalic acid appears as a *trans*-elimination of water, the process being accompanied by molecular transformation and not, as expected, from the tetrahedral model. Hydrolysis of *rac*-chloromalic acid to *meso*tartaric acid proceeds quantitatively, that of *meso*chloromalic acid with inversion to the extent of about 90%.

The following data appear new : methyl *l*(—)-dichlorosuccinate, b. p. 117—118°/13 mm., m. p. 62—63°, $[\alpha]_D^{21}$ —114·1° in carbon disulphide, $[\alpha]_D^{22}$ —69·5° in chloroform, $[\alpha]_D^{21}$ —63·07° in ethyl acetate, $[\alpha]_D^{21}$ —42·97° in methyl alcohol; *ethyl* l(—)-*dichlorosuccinate*, b. p. 127—130°/11 mm., d_4^{20} 1·2784, $[\alpha]_D^{20}$ —53·6°, $[\alpha]_D^{2}$ —104·8° in carbon disulphide, $[\alpha]_D^{5}$ —61·0° in chloroform, $[\alpha]_D^{25}$ —49·40° in ethyl alcohol (90%).

Addition of chlorine to sodium maleate in the presence of sodium chloride yields almost exclusively *meso*dichlorosuccinic acid, whereas, contrary to Terry and Eichelberger (A., 1925, i, 631), sodium fumarate under similar conditions gives, at most, 18% of

r-dichlorosuccinic and more than 80% of *meso*dichlorosuccinic acid. Similar results are obtained with the free acids, but, in this case, addition occurs only in sunlight. H. Wren.

Michael condensation. P. C. Mitter and A. C. Roy (J. Indian Chem. Soc., 1928, **5**, 33—48).—The condensation of ethyl citraconate and ethyl acetoacetate in the presence of sodium and ether or pure sodium ethoxide affords normally *ethyl γ-aceto-β-methylpropane-αβγ-tricarboxylate*, b. p. 182°/6 mm. (hydrolysed with loss of carbon dioxide to *γ-aceto-β-methylpropane-αγ-dicarboxylic acid*, m. p. 119—120°), and a viscous oil which yields the *semicarbazone* of *ethyl 2-methyl*-4 : 6-cyclo*hexadione*-1 : 2-*dicarboxylate*, m. p. 235°. Condensation in the presence of alcoholic sodium ethoxide results in the partial conversion of ethyl citraconate into ethyl itaconate (Hope, J.C.S., 1912, **101**, 892), and hence, under these conditions, ethyl δ-acetobutane-αβδ-tricarboxylate, b. p. 166°/8 mm. (corresponding acid, m. p. 119—120°, not identical with that obtained from the isomeric ester), and *ethyl 1-carbethoxy*-4 : 6-cyclo*hexadione-3-acetate* (*monosemicarbazone*, m. p. 251°) are obtained. The first-named compound, which may also be produced by the condensation of ethyl itaconate and ethyl acetoacetate, was considered by Michael to be the normal condensation product. Similar results are given by the use of ethyl citraconate and ethyl acetopropionate; normal products: *ethyl γ-aceto-β-methylbutane-αβγ-tricarboxylate*, b. p. 185°/9 mm., and *ethyl* 1 : 2-*dimethyl*-4 : 6-cyclo*hexadione*-1 : 2-*dicarboxylate* (*monosemicarbazone*, m. p. 235°); products obtained in the presence of alcoholic sodium ethoxide: *δ-acetopentane-αβδ-tricarboxylate*, b. p. 175°/9 mm., and *ethyl* 1-*carbethoxy*-1-*methyl*-4 : 6-cyclo*hexadione*-3-*acetate* (*monosemicarbazone*, m. p. 247°). Ethyl fumarate and ethyl α-acetopropionate yield *ethyl γ-acetobutane-αβδ-tricarboxylate*, b. p. 149°/5 mm., and *ethyl 1-methyl*-4 : 6-cyclo*hexadione*-1 : 2-*dicarboxylate* (*monosemicarbazone*, m. p. 240°). Ethyl citraconate and ethyl cyanoacetate condense (through the intermediate formation of ethyl itaconate) in the presence of alcoholic sodium ethoxide to give *ethyl δ-cyanobutane-αβ-dicarboxylate*, b. p. 170°/5 mm., and in the presence of a suspension of sodium in benzene to afford *ethyl γ-cyano-β-methylpropane-αβγ-tricarboxylate*, b. p. 190°/6 mm. (corresponding acid, m. p. 164°; cf. Perkin and Thorpe, J.C.S., 1899, **75**, 52). Ethyl fumarate and ethyl cyanoacetate condense under the latter conditions to yield *ethyl γ-cyanopropane-αβγ-tricarboxylate*, b. p. 167°/7 mm., and γ-cyano-αβ-carbethoxypropane-γ-carboxylic acid (decomp. to ethyl γ-cyanopropane-αβ-dicarboxylate, b. p. 282°, on heating; cf. Thorpe, J.C.S., 1900, **77**, 923). G. A. C. Gough.

Mechanism underlying the reaction between aldehydes or ketones and tautomeric substances of the keto-enol type. II. Condensation of mesoxalic ester with cyanoacetic and malonic esters. B. B. Corson, R. K. Hazen, and J. S. Thomas (J. Amer. Chem. Soc., 1928, **50**, 913—918).—Mesoxalic esters react with 2 mols. of cyanoacetic ester in presence of piperidine, giving, according to the ester used, *tetramethyl αγ-dicyanopropane-αββγ-tetracarboxylate*, m. p. 118—120°, and *dimethyl diethyl αγ-dicyanopropane-αββγ-tetracarboxylate*, m. p. 114—115°. The constitution of the former was determined by conversion into tricarballylic acid, whilst its hexamethyl ester could not be obtained by hydrolysing the cyano-groups. The additive compound, *tetramethyl α-hydroxyethane-ααββ-tetracarboxylate*, m. p. 87·5—88·5°, was obtained from methyl mesoxalate and methyl malonate, using piperidine as catalyst. Dehydration of the latter with sulphuric acid or condensation of the reagents with zinc chloride in acetic anhydride gave *tetramethyl ethylenetetracarboxylate*, m. p. 119—120°. Tetraethyl ethylenetetracarboxylate, prepared in an analogous way, has m. p. 54·5—56·5°. The constitution of the esters was proved by reduction to the saturated compound, followed by hydrolysis and removal of carbon dioxide to give succinic acid. Since mesoxalic ester is incapable of enolisation but readily undergoes condensation, it is concluded that enolisation does not necessarily precede reaction. J. D. Fulton.

Resolution of bromosulphoacetic acid. H. J. Backer and H. W. Mook (Rec. trav. chim., 1928, **47**, 464—470).—Bromosulphoacetic acid is resolved through its *strychnine* salt ($+4H_2O$) by the "cold crystallisation" method (A., 1925, i, 359) into d-*bromosulphoacetic acid*, $[M]_{589}$ +32·5° (other rotation values for the acid and its ammonium salt for different wave-lengths are given). l-*Bromosulphoacetic acid*, −30°, is obtained from the *brucine* salt ($+4H_2O$), although evaporation of this salt at 110° yields the *d*-acid. The optically active acids and salts do not racemise rapidly at the ordinary temperature, but do so in presence of alkalis. H. Burton.

Synthesis and polymerisation of formaldehyde. H. Vogel (Helv. Chim. Acta, 1928, **11**, 370—371).—When a mixture of equal volumes of carbon monoxide and hydrogen was passed at 150—180° over a mixture of pumice and zinc dust with 2% of magnesium oxide and 1% of lead oxide, formaldehyde was formed, together with caramel-like polymerisation products. When the resultant gases were passed into lime water containing a little magnesium oxide, only polymerisation products were obtained. These contained formose and α-acrose, but, contrary to the statement of K. and W. F. Short (A., 1925, i, 232), no dextrose. R. K. Callow.

Action of amines on bromoheptaldehyde. A. Kirrmann (Compt. rend., 1928, **186**, 701—702).—Diethylamine reacts with α-bromoheptaldehyde in ethereal solution to yield *α-diethylaminoheptaldehyde*, b. p. 106—107°/11 mm., d^{22} 0·853, n_D^{22} 1·4352 (*hydrochloride*, m. p. 73°). Oxidation with ammoniacal silver oxide in the presence of an excess of potassium hydroxide yields, instead of the corresponding acid, a mixture of *α-hydroxyheptoic acid*, m. p. 65° (*barium* salt $+0·5H_2O$) and hexoic acid. Triethylamine reacts with bromoheptaldehyde much more slowly and less completely to yield the *quaternary ammonium bromide*, $C_6H_{11}·CH(CHO)·NEt_3Br$, m. p. 126°. J. W. Baker.

Reaction between acetone and ammonia. H. Hock and H. Stuhlmann (Ber., 1928, **61**, [*B*], 470—

472; cf. Patterson and McMillan, J.C.S., 1921, **119**, 269).—The action of ammonia and acetone in equimolecular proportions at −65° affords a crystalline *compound*, $COMe_2,NH_3$, m. p. about −41°. It is resolved into its components when heated slightly above its m. p. H. Wren.

Syntheses with phenyl *iso*propyl ketone. J. Blondeau (Bull. Soc. chim., 1928, [iv], **43**, 343—346).—Phenyl *iso*propyl ketone with sodamide and butyl iodide in benzene give in 81% of the theoretical yield of phenyl αα-dimethylamyl ketone, b. p. 160°/33 mm., 268°/760 mm., converted by sodamide (2 mols.) in toluene, on decomposition with water, into *αα-dimethylvaleramide*, m. p. 92° (yield 72%). Reduction of the amide with sodium and alcohol affords 31% of *ββ-dimethylhexan-α-ol*, b. p. 95°/29 mm. (*acetate*, liquid; *phenylurethane*, m. p. 52°), and 15% of *α-amino-ββ-dimethylhexane*, m. p. 65—65°/24 mm. (*chloroplatinate*). *αα-Dimethyldecoamide*, m. p. 92°, b. p. 205°/16 mm., analogously prepared (yield 50%) from β-benzoyl-β-methyldecane, on hydrolysis yields a very small amount of an *acid*, m. p. 118°, and on reduction 30% of *ββ-dimethyldecan-α-ol*, b. p. 134°/19 mm. (*phenylurethane*), together with traces of the corresponding amine. R. Brightman.

Separation of unsaturated stereoisomeric ketones. R. Locquin and R. Heilmann (Compt. rend., 1928, **186**, 705—707).—Methyl α-ethyl-Δ^α-propenyl ketone, b. p. 151—153°, yields a mixture of *semicarbazones* which can be separated into two isomeric forms, m. p. 201° and 161°, respectively. From these, by treatment with oxalic acid, the two *stereoisomeric forms* of the original ketone, b. p. 150—152°/747 mm., $d_4^{1\cdot}$ 0·8718, and b. p. 153—154°/747 mm., d_4^{11} 0·8789, respectively, are obtained. These two forms of the ketone each yield only the corresponding semicarbazone, but by the action of hydrazine hydrate they both give the same *pyrazoline*, b. p. 72—73°/10 mm. [*benzenesulphonate*, m. p. 129—130°: two p-*bromobenzenesulphonates*, m. p. 119° (125° on remelting) and 90—91°, respectively]. Similarly methyl α-*n*-propyl-Δ^α-butenyl ketone, b. p. 70—72°/9 mm., yields two *semicarbazones*, m. p. 141—142° and 110° (121° on remelting), from which the two *stereoisomeric forms* of the ketone, b. p. 71°/11 mm., d_4^{15} 0·8620, and b. p. 74°/11 mm., d_4^{11} 0·8668, are obtained, and which both yield 3-*methyl-5-ethyl-4-*n*-propylpyrazoline* (*benzenesulphonate*, m. p. 107—108°; two p-*bromobenzenesulphonates*, m. p. 155° and 119—121°, respectively) by treatment with hydrazine hydrate. The two stereoisomeric forms could not be interconverted. J. W. Baker.

Trimethylplatinum acetylacetone, a volatile platinum compound. R. C. Menzies (J.C.S., 1928, 565—566).—Thallous acetylacetone reacts with trimethylplatinic iodide in benzene solution to form *trimethylplatinum acetylacetone*, $Me_3Pt\langle{}^{O\cdot CMe}_{O\dot{:}CMe}\rangle CH$, which when heated in a capillary tube decomposes without melting. When heated in a dry tube the compound sublimes, but the vapour is decomposed by the hot glass, giving metallic platinum. Ferric acetylacetone is prepared from thallous acetylacetone and anhydrous ferric chloride. H. Burton.

Variation in rotation and conductivity of sugars in aqueous solution with and without boric acid. II. R. Verschuur (Rec. trav. chim., 1928, **47**, 423—457; cf. this vol., 233).—Numerous measurements of the rotatory powers and conductivities of solutions of maltose, lævulose, α- and β-glucose, α- and β-galactose, and inulin, both in absence and presence of boric acid, have been made. The conductivity of maltose+boric acid shows a maximum at equimolecular concentrations (0·5*M*) and diminishes slightly with either increase or decrease of sugar. Lævulose is the only sugar for which the constants of mutarotation and conductivity are proportional to the concentration of boric acid, and it is found that even traces of the acid causes a large increase in the conductivity. Dextrose shows a greater increase in conductivity than does galactose, if comparison is made between the equilibrium mixtures.

In view of the above results and those previously obtained (*loc. cit.*), the structural formulæ of xylose, arabinose, dextrose, galactose, and mannose are discussed. H. Burton.

Derivatives of γ-xylose. Xylose-monoacetone and its conversion into 2:3:5-trimethyl-γ-xylonolactone. W. N. Haworth and C. R. Porter (J.C.S., 1928, 611—618).—Methylation of xylose *iso*propylidene ether with methyl sulphate and sodium hydroxide yields dimethylxylose *iso*propylidene ether, n_D^{15} 1·4455, $[\alpha]_{5780}$ −46·6°, which is hydrolysed and oxidised by dilute hydrobromic acid at 85° and bromine at 75° to *dimethyl-γ-xylonolactone*, b. p. 105—106°/0·08 mm., n_D^{15} 1·4643, $[\alpha]_{5780}^{21\cdot5}$ +81·5° (after 3 min.) ⟶ 85·1° (1 day) ⟶ 39° (49 days). Treatment of this with phenylhydrazine yields a *phenylhydrazide*, $C_{13}H_{20}O_5N_2$, m. p. 94—95°. Methylation of the lactone by Purdie's reagents affords crude trimethyl-γ-xylonolactone, which yields a *phenylhydrazide*, $C_{14}H_{22}O_5N_2$, m. p. 89—90°, also obtained from the trimethyl-γ-xylonolactone from trimethyl-γ-xylose (Haworth and Westgarth, A., 1926, 600). Pure trimethyl-γ-xylonolactone regenerated from the phenylhydrazide has b. p. 82°/0·06 mm., n_D^{17} 1·4464, and is oxidised by nitric acid, yielding *d*-dimethoxysuccinic acid as the only recognisable product.

The rates of hydrolysis of the lactone to the corresponding acid and of conversion of the acid into the lactone have been studied polarimetrically and are compared with the corresponding results for trimethyl-δ-xylonolactone. The structural formulæ of xylose mono- and di-*iso*propylidene ethers are discussed fully, and it is concluded that these compounds contain the butylene-oxide ring. H. Burton.

Reactivity of methylated sugars. II. Action of dilute alkali on tetramethylglucose. M. L. Wolfrom and W. L. Lewis (J. Amer. Chem. Soc., 1928, **50**, 837—854; cf. A., 1927, 751).—The interconversion of hexose sugars by the action of alkali is not accounted for in methylated sugars by hydration and dehydration (Nef, A., 1908, i, 5), but by simple keto-enolic tautomerism. In tetramethylglucose the following changes occur: HC(:O)·HC(OMe)· — HC(OH):C(OMe)· [I] ⇌ HC(:O)·(MeO)CH·. With

dilute alkali, dextrose gives 2·5% of mannose, 63·5% of lævulose, 31% of unchanged dextrose, and 3% of non-sugar compounds. Tetramethylglucose and tetramethylmannose, with dilute alkali, give the same equilibrium mixture of equal parts of each compound. Evidence for the presence of the dienolic form [I] is obtained by the high iodine value of the alkaline solution and the normal value in acid solution. An accurate iodometric method for determining aldohexoses is described, alone or in presence of ketohexoses. *Tetramethylglucoseanilide*, m. p. 138°, $[\alpha]_D$ +226°, and *tetramethylmannoseanilide*, α −0·38° (0·943 dm.), were prepared. The interconversion of tetramethyl-*d*-glucose and tetramethyl-*d*-mannose indicates the same ring structure in these compounds.

A. McGookin.

Structure of tetramethyl-γ-methylmannoside. P. A. Levene and G. M. Meyer (J. Biol. Chem., 1928, **76**, 809—812).—Tetramethyl-γ-mannose, on oxidation with barium hypoiodite, gave a lactone, m. p. 101—108°, $[\alpha]_D^{15}$ +64·8° in water, identical with that obtained by methylation of mannonolactone (A., 1924, i, 944); tetramethyl-γ-methylmannoside therefore possesses the αδ-lactone structure.

C. R. Harington.

Dynamic isomerism. XXVI. Consecutive changes in the mutarotation of galactose. G. F. Smith and T. M. Lowry (J.C.S., 1928, 666—685; cf. Riiber and Minsaas, A., 1926, 1228).—The mutarotation curves for α-galactose, $[\alpha]_{5461}$ +172·5°, do not obey the unimolecular law, since the velocity coefficient falls progressively from k_e = 0·025 at 7 min. to a limiting value of 0·019. The early stages of mutarotation are rapid (cf. Riiber and Minsaas, *loc. cit.*). With β-galactose, $[\alpha]_{5461}$ +63·5°, there is no change of rotation during 4 min. The rotation then increases rapidly, giving an inflected mutarotation curve with a maximum at about 10 min. The velocity coefficient increases progressively from 0 to 0·019. Assuming that the mutarotation of galactose is represented α ⇌ μ (open-chain) ⇌ β, the rotatory power of μ (58°) must be of the same order as for β-galactose, since no change of rotation occurs during the initial stage of β ⟶ μ.

From a mathematical analysis of the data for mutarotation and the velocity coefficients, assuming that only three isomerides are present in solution, it is deduced that the equilibrium mixture consists of α (28·5%), μ (12%), and β (59·5%).

H. Burton.

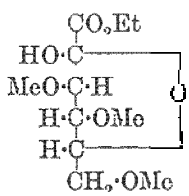
Preparation by the sorbose bacteria of a new reducing sugar with seven carbon atoms. G. Bertrand and G. Nitzberg (Compt. rend., 1928, **186**, 925—928).—The action of the sorbose bacteria on a 3% solution of α-glucoheptitol, m. p. 129—130° (Fischer, A., 1892, 1164, gives 127—128°), in brewer's yeast extract for 6 weeks to 2 months, and repeated precipitation of the product with alcohol, yields a new reducing sugar, *α-glucoheptulose*, $C_7H_{14}O_7$, m. p. 173·5°, $[\alpha]_D^{22}$ −67·8° (in 10% aqueous solution), which does not exhibit mutarotation and is not fermentable. It yields an osazone, m. p. 209—210°, identical with that of α-glucoheptose, and probably has the composition $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CO\cdot CH_2\cdot OH$. The following solubility data are recorded: α-glucoheptitol, 1·70 g./100 c.c. of 80% alcohol at 18°; α-glucoheptulose, 12·07 g./100 c.c. of 60% alcohol, 3·35 g./100 c.c. of 80% alcohol, and 0·37 g./100 c.c. of 95% alcohol at 21°.

J. W. Baker.

Synthesis of sucrose. A. Pictet and H. Vogel (Compt. rend., 1928, **186**, 724—727).—*Tetra-acetyl-γ-fructose*, formed to the extent of 3% in the preparation of the normal derivative (Hudson and Brauns, A., 1915, i, 502), reacts with tetra-acetylglucose in a chloroform suspension of phosphorus pentoxide to afford octa-acetylsucrose. This, when hydrolysed, yields sucrose identical in m. p. and optical properties with the natural product.

G. A. C. Gough.

Polysaccharides. I. Structure of inulin. W. N. Haworth and A. Learner (J.C.S., 1928, 619—625).—Methylation of inulin affords trimethylinulin, m. p. 138—140°, $[\alpha]_D^{20}$ −50·2° in chloroform (cf. Irvine and others, J.C.S., 1920, **117**, 1474; 1922, **121**, 1060), which is hydrolysed by aqueous–alcoholic oxalic acid to a mixture of trimethylfructose and its ethylfructoside. Further treatment with dilute hydrochloric acid gives 3 : 4 : 6-trimethyl-γ-fructose, b. p. about 115°/0·02 mm., n_D^{14} 1·4675, $[\alpha]_D^{20}$ +27·7° in chloroform [*osazone* +H_2O, m. p. 80—82°, (anhydrous) 137—138° (cf. Irvine and others, *loc. cit.*)]. Oxidation of the trimethyl-γ-fructose with nitric acid and subsequent esterification yields (I), which when methylated and then treated with ammonia gives an amide, m. p. 100—101°, identical with that obtained from tetramethyl-γ-fructose (Avery, Haworth, and Hirst, A., 1927, 1057). When (I) is oxidised with acid potassium permanganate there is formed *d*-2 : 3 : 5-trimethyl-γ-arabonolactone, m. p. 31—32°. A structural formula is suggested for inulin in which positions 1 and 2 of a γ-fructose residue are linked to other fructose residues.



(I.)

H. Burton.

Action of organo-magnesium compounds on aliphatic dialkylamides. M. Montagne (Compt. rend., 1928, **186**, 874—877).—Magnesium methyl iodide reacts with butyrdiethylamide to give the normal product, β-diethylamino-β-methylpentane (A., 1926, 942), and also *γ-diethylamino-γ-methylhexane*, b. p. 81°/16 mm. (*picrate*, m. p. 78°; *perchlorate*, m. p. 154°; *chloroaurate*, m. p. 84°; *chloroplatinate*, m. p. 199°), the hydrochloride of which decomposes at 170—180° into diethylamine and γ-methyl-Δ^{β}-hexene, identical with that obtained by the dehydration of γ-methylhexan-β-ol. The new base may be synthesised from αα-methylethyl-*n*-valeramide by the Hoffmann rearrangement followed by diethylation of the product. Since no trace of γ-methylethylamino-γ-methylhexane is formed in the reaction, the interchange of radicals is improbable; it is suggested that the abnormal product occurs through the presence of free methyl iodide in the reaction mixture. This view is supported by the exclusive production of the base when methyl iodide (1 mol.) is added at the beginning of the reaction.

G. A. C. Gough.

Relationships between ring closure and "specific affinity." Ethylenediamine compounds of thallic halides. W. Hieber and F.

SONNEKALB (Ber., 1928, **61**, [*B*], 555—557).—The theoretical considerations of Biltz and Grimm (A., 1925, ii, 842) predict the possibility of the preparation of ethylenediamine compounds with a five-membered subsidiary valency ring from metallic salts the ammoniates of which cannot exist under similar conditions, for example, in aqueous solution. The possibility is realised with thallic chloride, from which the *compounds*, $TlCl_3,3\,en,3H_2O$, $TlCl_3,2\,en,H_2O$ and $TlCl_3,en,H_2O$ are directly derived. The *substances*, $TlBr_3,3\,en,3H_2O$, $TlBr_3,2\,en$, and TlI_3,en are obtained by double decomposition with potassium bromide or iodide. H. WREN.

Reactions and derivatives of iron carbonyl. W. HIEBER and F. SONNEKALB (Ber., 1928, **61**, [*B*], 558—565).—Vigorous action occurs between iron pentacarbonyl and anhydrous hydrazine with formation of a dark red syrup and evolution of 4 mols. of carbon monoxide per mol. of hydrazine when excess of the carbonyl is used. Except for a small amount of semicarbazide, a homogeneous product of the reaction could not be isolated. The viscous mass evolves carbon monoxide and hydrogen when treated with acids and gives a blood-red solution which contains ferrous salt. Ethylenediamine and iron pentacarbonyl in anhydrous pyridine give the *compound* $Fe_2\,en_2(CO)_5$, monoclinic crystals, stable towards air, with evolution of 5 mols. of carbon monoxide for 2 mols. of ethylenediamine. The substance appears to be an additive compound of iron pentacarbonyl and "iron ethylenediamine," since, when decomposed by dilute weak acids it affords iron pentacarbonyl and ferrous salt, exactly one half of the total iron being obtained in the latter form: $Fe(CO)_5,Fe\,en_2+6HX=FeX_2+Fe(CO)_5+2\,en(HX)_2+H_2$. With acetic acid a transitory red coloration of the solution is observed which frequently passes into the green colour of iron tetracarbonyl. The red *compound*, $Fe(CO)_5,Fe\,en$ or $Fe(CO)_4,Fe\,en(CO)$, which is very unstable when moist, can be extracted with ether: $Fe_2\,en_2(CO)_5+2HX=Fe_2\,en(CO)_5+en(HX)_2 \longrightarrow FeX_2+Fe(CO)_4+en(HX)_2+CO+H_2$. The amount of hydrogen evolved is much less than that expected theoretically, but reduction products of the pentacarbonyl could not be isolated.

Decomposition of the compound from indigotin and iron pentacarbonyl in anhydrous pyridine (cf. Kunz and Kress, A., 1927, 366) leads to quantitative regeneration of indigotin; evolution of gas is not observed and the filtrate contains all the iron in the ferrous condition. H. WREN.

Spermine. VII. F. WREDE, E. STRACK, and O. HETTCHE (Z. physiol. Chem., 1928, **173**, 61—68).—An alcoholic solution of spermine reacts quantitatively with the hydriodide of methyl-ψ-thiocarbamide giving the *diguanido*-derivative $[CH_2]_4{:}[NH\cdot[CH_2]_3\cdot NH\cdot C({:}NH)\cdot NH_2,HI]_2$, m. p. about [illegible] (corresponding *hydrochloride* and *chloroaurate*), m. p. about 226° (decomp. after softening at 218°). The free base is converted by carbon disulphide in alcoholic solution at 100° into the *compound*, $C_{14}H_{30}N_8S_4$, m. p. 160—165°. Under similar conditions spermine affords a *substance*, $C_{12}H_{22}N_4S_3$, m. p. 285°, converted by hydrogen peroxide into the *compound*, $C_{11}H_{22}O_5N_4S_2$, m. p. about 305° after darkening at 250°. J. STEWART.

Guanidine derivatives, from the action on guanidine of the esters of amino-acids. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1928, **173**, 51—60).—*Guanidoacetic anhydride* (glycocyamidine), $\begin{matrix}CO\cdot NH\\CH_2\cdot NH\end{matrix}>C{:}NH$, decomp. about 200°, results from the interaction at 0° of guanidine and the ethyl aminoacetate.

dl-α-*Guanidoisohexoic anhydride*, m. p. 248° (*picrate*, m. p. 167—169°), and *guanidonium* d-*anhydro-α-guanidonoglutarate*, m. p. 202°, $[\alpha]_D^{16}$ −16·2°, are similarly prepared.

Contrary to expectations, the reaction was not applicable to the detection and isolation of polypeptide esters. The authors regard the reaction as involving complete loss of ammonia from the guanidine molecule, followed by union of the nascent cyanamide and the α-amino-acid. Using cyanamide, however, the yields of glycocyamidine are small. Traces of guanidine accelerate the reaction; ammonia prevents it completely. J. STEWART.

Constitution of *C*-methylasparagine (homoasparagine). D. MIGLIACCI and M. FURIA (Gazzetta, 1928, **58**, 103—110).—*C*-Methylasparagine (homoasparagine) when heated with carbamide gives the *monoamide*, $C_6H_9O_3N_3$, m. p. 266—267° (in closed tube, decomp.), of *anhydroureidohomoaspartic acid*, $C_6H_8O_4N_2$, m. p. 264—265° (in closed tube, decomp.), which is obtained by hydrolysis, or by the action of carbamide on homoaspartic acid. It is suggested that the new acid is $\begin{matrix}CO\\CO\cdot NH\end{matrix}>CMe\cdot CH_2\cdot CO_2H$, and *C*-methylasparagine $CO_2H\cdot CMe(NH_2)\cdot CH_2\cdot CO\cdot NH_2$. By heating citraconic anhydride in a sealed tube with anhydrous ammonia at 70°, *C*-methylasparagine is not obtained, but only ammonium citraconate. E. W. WIGNALL.

Crystallisation of arginine and histidine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **76**, 701—705).—A technique for the crystallisation of the above two amino-acids is described. Arginine crystallises from water in prisms with $2H_2O$, and from 66% alcohol in anhydrous plates, m. p. 238° (decomp.); histidine forms plates, from water, m. p. 277—278° (decomp.). C. R. HARINGTON.

Modified determination of basic amino-acids. Bases of edestin. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **76**, 707—722).—The protein is hydrolysed with hydrochloric acid and the latter removed by evaporation, the residue is dissolved in water and treated with silver oxide and sulphuric acid to remove chlorides, and the filtrate is treated with excess of silver oxide and barium hydroxide until alkaline to phenolphthalein; the filtrate containing lysine is set aside, and the precipitate reconverted into free amino-acids and precipitated fractionally with silver oxide and barium hydroxide, the precipitate at p_H 7·0 containing histidine, and that at a reaction alkaline to phenol-

phthalein, arginine. The histidine is purified by precipitation with mercuric sulphate and is weighed as dinitronaphtholsulphonate, as is also the arginine; the lysine is purified by precipitation as phosphotungstate, and weighed as picrate. The method can be carried out with 50 g. of protein, a positive correction of 1/9 being applied for losses on the small scale of working. Edestin contains histidine 2·08%, arginine 15·8%, and lysine 2·19%.

C. R. HARINGTON.

Synthesis of glycocyamine from arginine and glycine. M. BERGMANN and L. ZERVAS (Z. physiol. Chem., 1927, **172**, 277—288).—The ethyl ester of diacetylglycocyamine is formed in 50% yield when triacetylanhydroarginine (A., 1926, 1235) is shaken with carefully dried glycine ester in dry ether at the ordinary temperature for 5 hrs. The diacetyl ester, when heated in a sealed tube with concentrated hydrochloric acid to 100°, yields *glycocyamidine hydrochloride* [decomp. 210° (corr.); *picrate*, decomp. 210—215° (corr.)]. This substance has also been prepared by heating glycocyamine hydrochloride in a sealed tube with fuming hydrochloric acid to 140°. Monoacetylglycocyamidine (prisms, decomp. 220—250°) is sparingly soluble in the usual solvents, but dissolves readily in acids; when boiled in acid solution it loses the acetyl group.

A convenient and simple method is given for the preparation of arginine from gelatin, by which 60% of the quantity theoretically possible may be obtained.

H. D. KAY.

Synthesis of creatine from sarcosine and arginine. Synthesis of methylguanidine. M. BERGMANN and L. ZERVAS (Z. physiol. Chem., 1928, **173**, 80—83).—Triacetylanhydroarginine and methylamine are allowed to react in ethereal solution at 20°; the product, m. p. 125—130°, when boiled with sodium hydroxide, gives methylamine, and contains β-acetamido-α-piperidone, m. p. 187°, and *diacetylmethylguanidine* m. p. 88°; the latter is hydrolysed to methylguanidine. A similar reaction between triacetylanhydroarginine and sarcosine (as ethyl ester) gives β-acetamido-α-piperidone and *diacetylcreatine* (*ethyl* ester), m. p. 117° (corr.). The latter is hydrolysed to creatinine hydrochloride, m. p. 261° (corr.); and finally reconverted by alkali into creatine.

J. STEWART.

Hydrogen cyanide. I. Mercuric methyl cyanide and the alleged isomerides of hydrogen cyanide. J. E. COATES, L. E. HINKEL, and T. H. ANGEL (J.C.S., 1928, 540—543).—When mercuric methyl hydroxide is treated with hydrogen cyanide obtained from different sources, or when mercuric methyl iodide is acted on by silver cyanide in presence of various solvents, mercuric methyl cyanide, m. p. 93°, is formed as the sole product (cf Enklaar, A., 1923, ii, 811; 1925, i, 1394; 1926, 718). Contrary to Enklaar's statements, mercuric methyl cyanide is not changed after 9 months at the ordinary temperature, but is decomposed by dilute sulphuric acid, liberating hydrogen cyanide. Treatment of the cyanide with hydrochloric acid gives mercuric methyl chloride; with methyl iodide, a double compound is first produced which decomposes on heating, yielding methylcarbylamine; with silver nitrate silver cyanide is precipitated, and mercuric methyl sulphide is obtained by the action of hydrogen sulphide.

H. BURTON.

Ferrous-ferric cyanides. L. CAMBI and A. CLERICI (Gazzetta, 1928, **58**, 57—64).—The preparation and properties of a number of complex metallic cyanides are described, and the structure of the chromophore group they contain is discussed. Investigation of the blue salts corresponding with Prussian-blue and Turnbull's blue, obtained by precipitating ferrous and ferric salts with the alkali ferro- and ferri-pentacyanides, shows that the complex $[Fe(CN)_5X]$ can give rise to chromophore groups analogous to those obtained from the ions $[Fe(CN)_6]$. The complex groups contained in the ferrous-ferric cyanides can retain the co-ordination arrangement of the complex ions of the alkali ferro- or ferri-cyanides from which they are derived; the presence of ferrous and ferric atoms does not suffice to give the blue cyanides, as is shown in the case of the pink ferrous nitroprussiate. This salt and ferrous cobalticyanide can be represented by the usual co-ordination structure, but the coloured ferrous chromi-, mangani-, and ferri-cyanides have a complex polynuclear structure (cf. Reihlen and Zimmermann, A., 1927, 233). In the last of these compounds, for example, the linkings between the CN groups and the atoms of ferrous and ferric iron are considered to be of the same nature.

O. J. WALKER.

Qualitative analysis of mixtures containing complex cyanogen compounds. M. COPPOLA (Annali Chim. Appl., 1928, **18**, 65—67).—When a mixture of substances is boiled with a concentrated solution of sodium carbonate and hydroxide and the liquid is filtered, the presence of a complex metallic cyanide is indicated by the appearance of a blue coloration on the edge of the filter. Further, addition of a few drops of concentrated nitric acid to a few c.c. of this liquid will yield a greenish-blue coloration. The inconveniences attending treatment of the substance with concentrated sulphuric acid may be avoided as follows: the original insoluble or slightly soluble substance is treated with boiling, dilute hydrochloric acid, and the insoluble residue (*a*) separated from the solution, which is treated with hydrogen sulphide to give a precipitate (*b*) containing all the mercury as sulphide and also the sulphides of arsenic and other metals not present as metallo-cyanides insoluble in hydrochloric acid. The liquid separated from (*b*) is evaporated to dryness on an asbestos gauze, and the dry residue mixed with (*a*) and with the fourfold quantity of ammonium nitrate. The mass is gradually deflagrated in a covered porcelain crucible and then treated, in the cold, with a few drops of concentrated nitric acid and dissolved in hot dilute hydrochloric acid. The complex metallo-cyanides are thus destroyed and their metals converted into oxides, with the exception of silver, which remains as metal; organic compounds are also destroyed and hence do not hinder precipitation of the metals of Group III. Any insoluble part of the deflagrated residue consists of barium sulphate, silver chloride, lead sulphate and chloride, and silica. The hydrochloric acid solution is treated with hydrogen sulphide and the precipitate

collected on the filter already containing *b*, the mixed sulphides being analysed as usual. The filtrate is tested for the other cations. T. H. POPE.

Reaction between ethylenic linking and organomagnesium halides. H. GILMAN and J. H. MCGLUMPHY (Rec. trav. chim., 1928, **47**, 418—422; cf. A., 1923, i, 285; 1927, 874).—The action of several organomagnesium halides towards different ethylenic and acetylenic hydrocarbons has been studied, and it is shown that addition to the double or triple linking does not take place (cf. Rupe and Bürgin, A., 1910, i, 161). H. BURTON.

Absorption spectra of benzene and toluene in alcoholic solution. Detection of benzene as impurity in organic compounds. W. R. ORNDORFF, R. C. GIBBS, (MISS) S. A. MCNULTY, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, **50**, 831—837).—The absorption spectra of benzene and toluene in the vapour state and in absolute-alcoholic solution are plotted and new bands are recorded (cf. Henri, A., 1922, ii, 679; Klingstedt, A., 1923, ii, 48). The bands can be arranged in series (cf. Kronenberger and Pringsheim, A., 1927, 90), which are represented for benzene, in any phase, by Henri's equation. The similarity of the curves for ether, methyl *n*-amyl ether, *cyclo*hexene, and ethylene chlorohydrin to the benzene spectrum observed by Smith, Adams, and Pease (A., 1927, 608) is shown to be due to the presence of benzene as impurity (cf. this vol., 152). The amount is determined approximately by an expression based on spectrographic measurements. A. MCGOOKIN.

Nitration of mixed *m*-dihalogenobenzenes. H. A. MAYES and E. E. TURNER (J.C.S., 1928, 691—697).—Mononitration of (*a*) *m*-chlorobromobenzene, (*b*) *m*-chloroiodobenzene, and (*c*) *m*-bromoiodobenzene with nitric acid at —5°, with subsequent thermal analysis of the mixed mononitro-derivatives formed, gives the following results: (*a*) 1-chloro-3-bromo-4-nitrobenzene (62%) and 1-chloro-3-bromo-6-nitrobenzene (37%); (*b*) 1-chloro-3-iodo-4-nitrobenzene (63%) and 1-*chloro*-3-*iodo*-6-*nitrobenzene*, m. p. 63° (35%); (*c*) 1-bromo-3-iodo-4-nitrobenzene (46%) and 1-*bromo*-3-*iodo*-6-*nitrobenzene*, m. p. 76—76·5° (52%). Small amounts (1—3%) of the *vic.*-substituted derivatives are formed at the same time.

The compound described by Korner (Gazzetta, 1874, **4**, 379) as 1-bromo-3-iodo-6-nitrobenzene, m. p. 126·8°, is 1-*bromo*-3-*iodo*-4 : 6-*dinitrobenzene*, m. p. 125—127°. H. BURTON.

Alkaline hydrolysis of ω-bromo- and ω-chloronitrostyrenes. A. T. DANN, A. HOWARD, and W. DAVIES (J.C.S., 1928, 605—611).—When αβ-dibromo-β-nitrophenylpropionic acids are heated with 30% aqueous sodium acetate a mixture of the *cis*- (lower m. p.) and *trans*-ω-bromonitrostyrenes is obtained. The former are converted into the latter by the action of ultra-violet light. The following constants are recorded for the ω-bromonitrostyrenes: *cis*-*o*-nitro-, liquid at 0°; *trans*-*o*-nitro-, b. p. 165—167°/21 mm., m. p. 39° (lit. 70°); *trans*-*m*-nitro-, b. p. 150°/18 mm., m. p. 77° (lit. 59° and 78—79°); *trans*-*p*-nitro-, b. p. 182°/21 mm., m. p. 160° (lit. 123°). The *cis*-*p*-nitro-compound, b. p. 168—170°/21 mm., m. p. 49°, is obtained by the action of alcoholic sodium acetate on αβ-dibromo-β-*p*-nitrophenylpropionic acid. ω-Chloronitrostyrenes are prepared by the action of hypochlorous acid on the corresponding nitrocinnamic acids. ω-*Chloro*-m-*nitrostyrene* and ω-*chloro*-p-*nitrostyrene* have m. p. 83° and 128° respectively.

Hydrolysis of ω-bromostyrene and the *trans*-ω-bromonitrostyrenes with aqueous-alcoholic potassium hydroxide shows that the order of reactivity of the halogen atom is $o>p>$ unsubstituted $>m$ at 17°. *cis*-ω-Bromo-*p*-nitrostyrene is hydrolysed much more readily than the *trans*-form. For the chloro-compounds the order of reactivity at 41° is $p>o>m>$ unsubstituted. It is concluded that the effect of the nitro-group is transmitted through the unsaturated side-chain. H. BURTON.

Action of magnesium on some ethylenic derivatives of *p*-bromobenzene. R. QUELET (Compt. rend., 1928, **186**, 764—767; cf. this vol., 280).—The products of the interaction of magnesium and *p*-bromopropenylbenzene are the normal compound (about 60%), the additive *compound*, $MgBr\cdot C_6H_4\cdot CH(C_6H_4\cdot CH:CHMe)\cdot CHMe\cdot MgBr$ (see also Rupe and Bürgin, A., 1910, i, 161), and *p*-dipropenylbenzene, m. p. 185—186°. Similar results are obtained with *p*-bromoallyl- and *p*-bromo-Δ^{α}-butenylbenzenes. G. A. C. GOUGH.

Arylsulphonyl magnesium chlorides and their reactions with ethyl sulphate. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1928, **50**, 802—805; cf. A., 1923, i, 26; 1924, i, 382; 1926, 1239).—Arylsulphonyl halides react with magnesium giving compounds $RSO_2\cdot MgX$; hydrolysis of the products yields sulphinic acids. Ethyl sulphate does not replace the group —MgX by ethyl, which seems to indicate that $RS(:O)_2\cdot MgX$ is stable although the structure may be $RS(:O)\cdot OMgX$. Benzene- and *p*-toluene-sulphonyl chlorides were used; the latter reacts only in presence of activated magnesium to give a yellow *solid*, $C_6H_4Me\cdot SO_2\cdot MgCl,Et_2O$. A. MCGOOKIN.

Properties and reactions of β-chloroethyl, β-cyanoethyl, and β-carbethoxyethyl toluene-*p*-sulphonates, including an extension of the Friedel–Crafts reaction. G. R. CLEMO and E. WALTON (J.C.S., 1928, 723—729).—Toluene-*p*-sulphonyl chloride reacts with ethylene cyanohydrin in boiling xylene yielding *ammonium toluene*-p-*sulphonate*, m. p. 325—330°, and β-*cyanoethyl toluene*-p-*sulphonate* (I), b. p. 187—189°/0·5 mm., m. p. 64°. When this is treated with alcoholic hydrogen chloride there is formed the *hydrochloride*, m. p. 101°, of γ-*imino*-γ-*ethoxypropyl toluene*-p-*sulphonate*, which is readily hydrolysed by water yielding β-*carbethoxyethyl toluene*-p-*sulphonate* (II), b. p. 167—169°/0·2 mm. Alkylation of phenols (cf. J.C.S., 1922, **121**, 642) is not possible with either (I) or (II), since they are readily hydrolysed by alkalis forming acrylonitrile and ethyl acrylate respectively. Condensation of (I) with resorcinol in presence of zinc chloride and ethereal hydrogen chloride affords 7-hydroxy-3 : 4-dihydrocoumarin, m. p. 133°.

Ethyl, β-chloroethyl, β-cyanoethyl, and β-carbethoxyethyl toluene-*p*-sulphonates react with benzene

in presence of aluminium chloride to form ethylbenzene (64%), dibenzyl, β-phenylpropionitrile (72%), and ethyl β-phenylpropionate (74%), respectively. β-Choroethyl toluene-*p*-sulphonate reacts with potassium phthalimide at 200° yielding phthal-β-chloroethylimide.

β-Phenylpropionitrile is converted by alcoholic hydrogen chloride into *γ-imino-γ-ethoxy-α-phenylpropane hydrochloride*, $CH_2Ph\cdot CH_2\cdot C(OEt){:}NH,HCl$, m. p. 130°, which is hydrolysed by water to ethyl β-phenylpropionate. Similarly, acrylonitrile furnishes *α-chloro-γ-imino-γ-ethoxypropane hydrochloride*, m. p. 109°, addition of hydrogen chloride taking place. The imino-compound on hydrolysis yields ethyl β-chloropropionate. H. BURTON.

Relations between some physical properties and the constitution of certain naphthalene derivatives. H. DE LASZLO (J. Amer. Chem. Soc., 1928, **50**, 892—904; cf. A., 1925, ii, 179).—The absorption spectra in the vapour phase and in hexane solution of the ten isomeric dichloronaphthalenes can be divided into two parts, the first part consisting of narrow bands the origin of which is attributed to the quantised vibration of certain atoms or groups of atoms in the molecule, whilst the second part consists of wider bands of unknown origin. The vapour-phase bands are similar to those in solution, except that the latter are shifted a constant amount for each part of the spectrum of every isomeride. The molecular absorption coefficient for each part is also widely different. A striking regularity in frequency intervals has been found in all the isomerides, the larger approximating to that for naphthalene, whilst the smaller varies with the position of the substituents. The curves of the solution spectra point to three definite types, the members of each group αα, αβ, and ββ being of the same general type. It is noted that part of the spectrum of the 1 : 4- and 1 : 5-isomerides closely resembles the other, and as the chlorine atoms in the second case are in different rings, the two halves of the naphthalene molecule are regarded as being symmetrical, or at least the α-positions are regarded as optically as well as chemically equivalent. From the similarity of spectra of αβ-isomerides the symmetrical nature of the molecule is again deduced as well as the optical equivalence of the β-positions. In the αα- and ββ-groups the smaller frequency interval increases when the substituent atoms are in different rings. The two pairs of β-positions 2 : 6 and 2 : 7 are not equivalent. The specific exaltations of refractivity are in the order ββ>αβ>αα. Whilst the four α- and four β-positions respectively are optically and chemically equivalent, the α- and β-positions are themselves widely different in character. The m. p. of the ten dichloro- and dibromo-naphthalenes can be ordered into the groups ββ>αα>αβ, where the $\beta_2\beta_6$ compound has always the highest m. p. The latter statement, as far as investigation goes, is valid for the diamino-, hydroxy-, cyano-, nitro-, and methyl derivatives. J. D. FULTON.

2-Iodofluorene. A. KORCZYNSKI (Bull. Soc. chim., 1928, [iv], **43**, 346).—A reply to Chanussot (this vol., 163; cf. A., 1927, 347, 348, 654). R. BRIGHTMAN.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. III. E. DE B. BARNETT and J. W. COOK (J.C.S., 1928, 566—572).—Magnesium benzyl chloride reacts with 1 : 5-dichloro-9-benzylanthrone forming 1 : 5-*dichloro*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthranol*, m. p. 197°, whilst magnesium phenyl bromide gives 1 : 5-*dichloro*-10-*phenyl*-9-*benzyl*-9 : 10-*dihydroanthranol*, m. p. 167°. When these anthranols are dehydrated by hot acetic acid containing a little hydrochloric or sulphuric acid the former yields 1 : 5-*dichloro*-9-*benzyl*-10-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 158°, whilst the latter gives 1 : 5-dichloro-10-phenyl-9-benzylanthracene, m. p. 213°. 1 : 5-*Dichloro*-9-*benzyl*-10-*methylene*-9 : 10-*dihydroanthracene*, m. p. 123°, and 1 : 5-*dichloro*-9-*benzyl*-10-iso*propylanthracene*, m. p. 138°, are obtained similarly from the corresponding crude anthranols. The following 9 : 10-*dihydroanthranols* were obtained from 9 : 9-diphenyl- and 9 : 9-dibenzyl-anthrones and the requisite Grignard reagent: 9 : 9-*diphenyl*-10-*benzyl*-, m. p. 228—230°; 9 : 9-*dibenzyl*-10-*methyl*-, m. p. 175°; 10-*phenyl*-9 : 9-*dibenzyl*-, m. p. 189°, and 9 : 9 : 10-*tribenzyl*-, m. p. 140°. The last compound when treated with hot acetic and hydrochloric acids furnishes 9 : 10-dibenzylanthracene, m. p. 245°. 9 : 9-*Diphenyl*-10-*methylene*- and 9 : 9-*diphenyl*-10-*benzylidene*-9 : 10-*dihydroanthracenes* have m. p. 192° and 254—255°, respectively.

Treatment of 1 : 5-dichloroanthrone with benzyl chloride and aqueous potassium hydroxide affords 1 : 5-dichloro-9-benzylanthrone, m. p. 169°, reduced by zinc dust and alcoholic ammonia to 1 : 5-*dichloro*-9-*benzyl*-9 : 10-*dihydroanthranol*, m. p. 179°, which is dehydrated to 1 : 5 - dichloro - 9 - benzylanthracene. 1-Chloro-9-anthrone with benzyl chloride and potassium hydroxide solution gives 1-*chloro*-10 : 10-*dibenzylanthrone*, m. p. 223°, which with magnesium phenyl bromide yields 1-*chloro*-9-*phenyl*-10 : 10-*dibenzyl*-9 : 10-*dihydroanthranol*-9, m. p. 260°. H. BURTON.

Nitration of benzylaniline. J. REILLY, J. J. MOORE, and P. J. DRUMM (J.C.S., 1928, 563—564).—Whereas dibenzylaniline on nitration in acetic acid solution yields 4-nitrophenyldibenzylamine (Matzudaira, A., 1887, 812), benzylaniline is not nitrated until a mixture of nitric and sulphuric acids is employed, when (at 0°) phenyl-3-nitrobenzylamine and some phenyl-4-nitrobenzylamine are obtained. Acetphenyl-3-nitrobenzylamide, prepared by use of acetic anhydride and sodium acetate, has m. p. 66—67° (Purgotti and Monti, A., 1901, i, 21, give 48°); benzphenyl-3-nitrobenzylamide has m. p. 103°. E. W. WIGNALL.

Catalysis with copper in the Ullmann reaction. P. E. WESTON and H. ADKINS.—See this vol., 488.

Odour and constitution among the mustard oils [thiocarbimides]. II. Effect of halogen substituents. G. M. DYSON (Perf. Ess. Oil. Rec., 1928, **19**, 88—91; cf. this vol., 283).—The *p*-chloro-, *p*-bromo-, and *p*-iodo-phenylthiocarbimides each have a powerful anise odour which is also characteristic of the *o*-iodo-compound, but the *o*- and *m*-chloro-derivatives are very pungent, whilst the corresponding *o*- and *m*-bromo- and *m*-iodo-compounds are only faintly pungent. A theory of the mechanism of odour

is discussed and the odours of a series of dihalogen-substituted phenylthiocarbimides are successfully predicted. The 3 : 4-*dichloro*- (b. p. 262°) and 2 : 4-*dichloro*- (m. p. 42°, b. p. 260°) derivatives have an anise-like odour, that of the 3 : 4-compound being more pungent. The 2 : 5-*dichloro*- (b. p. 265°), 2 : 3-*dichloro*- (b. p. 256—258°), and 3 : 5-*dichloro*- (m. p. 48°, b. p. 274°) *phenylthiocarbimides* are pungent, as also is the 2 : 5-*dibromo*-compound (m. p. 46°). 3 : 4 : 5-*Trichlorophenylthiocarbimide* (b. p. 280°) has a pungent odour with a faint anise character; 2 : 4-*dibromophenylthiocarbimide* (m. p. 64°) has a delicate anise odour. E. H. SHARPLES.

Optically active derivatives of phenylamino-acetic acid. A. MCKENZIE and (MISS) N. WALKER (J.C.S., 1928, 646—652).—Attempted resolution of *r*-desylamine, CHPhBz·NH_2, by sodium hydrogen *d*-tartrate, *d*-camphor-10-sulphonic acid, or *d*-α-bromocamphorsulphonic acid were unsuccessful. Synthesis from optically active materials was attempted. The action of phthalic anhydride on *l*-phenylaminoacetic acid gives, however, *r*-α-phthal-imidophenylacetic acid, m. p. 170·5—171·5° (cf. *d*-β-amino-β-phenylpropionic acid, McKenzie and Tudhope, A., 1924, i, 650, which is not racemised by phthalic anhydride). This is resolved by morphine, yielding l-α-*phthalimidophenylacetic acid*, m. p. 192—193°, $[\alpha]_D^{14·5}$ −51·9° in acetone, $[\alpha]_D^{17·5}$ −20·3° in methyl alcohol; this gives a l-*acid chloride*, but the latter with benzene and aluminium chloride yields only *r*-desylphthalimide. The *l*-acid on treatment with potassium hydroxide solution gives on acidification a dextrorotatory *acid*, m. p. 177—179°, $[\alpha]_D$ +101·8° in acetone, regarded as

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHPh\cdot CO_2H.$$

The resolution of *r*-desylphthalamic acid was next effected, by morphine; l-*desylphthalamic acid* has m. p. 155—157° (decomp.), $[\alpha]_D^{1}$ −159·1°, but when dehydrated on the water-bath it gives only *r*-desyl-phthalimide. On hydrolysis of *l*-desylphthalamic acid by concentrated hydrochloric acid partial racemisation occurs.

Finally, *r*-desylamine hydrochloride was resolved by treatment with *l*-mandelic acid, or with *l*-γγγ-tri-chloro-β-hydroxybutyric acid; d-*desylamine* l-*mandelate* has m. p. 149—150° (decomp.), $[\alpha]_D$ −57·5° in acetone, and the *hydrochloride*, decomp. 230°, has $[\alpha]_D^{16}$ +223·2°; l-*desylamine hydrochloride*, isolated by the use of *d*-γγγ-trichloro-β-hydroxybutyric acid, has similar properties.

The action of nitrous acid on *d*-desylamine hydrochloride yields a product, m. p. 127—131°, $[\alpha]_D$ +30·1° in alcohol, which is partly racemised *d*-benzoin, since *l*-benzoin has $[\alpha]_D^{16}$ −132·5° in alcohol.

d-*Desylamine*, m. p. 82—86° when liberated by sodium carbonate, 87—89° when liberated by sodium hydroxide, is, like *r*-desylamine, unstable; in ethyl alcohol it has $[\alpha]_D$ +200·5°, which rapidly falls, approaching zero; this is, however, attributed to racemisation and not to decomposition, since from the product *r*-desylamine hydrochloride can be obtained. E. W. WIGNALL.

Chlorinated *m*-4-xylidines. I. G. FARBENIND. A.-G.—See B., 1928, 225.

Stilbene derivatives. H. RYAN and N. CULLINANE (Proc. Roy. Irish Acad., 1924, 36, [*B*], 155—163).—Reduction of 2 : 4-dinitrostilbene with alcoholic ammonium sulphide yields 2-nitro-4-aminostilbene, m. p. 110° (sulphate, m. p. 205°; *diazonium chloride*, decomp. 144°), whilst reduction with stannous chloride and acetic and hydrochloric acids gives 4-nitro-2-aminostilbene, m. p. 142—143°. When 2-*nitro-stilbene-4-diazonium sulphate*, decomp. 165°, is treated with boiling absolute alcohol and a little sulphuric acid there is formed 2-nitrostilbene, m. p. 76°. 2-Aminostilbene, m. p. 106°, when diazotised and treated with copper bronze yields stilbene. Similarly, 4-nitro-2-aminostilbene furnishes 4-nitrostilbene, reduced to 4-aminostilbene, m. p. 151°. 2 : 4-Di-aminostilbene has m. p. 119°. Reduction of 2 : 4-di-nitro-4′-methoxystilbene with stannous chloride gives 4-*nitro-2-amino-4′-methoxystilbene*, m. p. 184° (*sulphate*; *hydrochloride*; *acetyl* derivative, m. p. 184—185°), and 2 : 4 : 6-trinitrostilbene yields 4 : 6-*dinitro-2-aminostilbene*, m. p. 216° (*benzoyl* derivative, m. p. 193°; *acetyl* derivative, m. p. 172—173°; *diazonium sulphate*, decomp. 230°). H. BURTON.

Structure of benzidine. Benzidine ammines. II. G. SPACU (Bul. Soc. Stiinte Cluj, 1927, 3, 285—307; cf. *ibid.*, 1924, 2, 187; Chem. Zentr., 1927, ii, 2391).—The following *compounds* containing benzidine are described: $[ZnC_{12}H_{12}N_2]Cl_2$, $[Zn(C_{12}H_{12}N_2)_2]Br_2$, $[Mn(H_2O)_2(C_{12}H_{12}N_2)_2]Cl_2$, $[Mn(C_{12}H_{12}N_2)_2]Br_2$, $[Mn(C_{12}H_{12}N_2)_3](NO_3)_2,4H_2O$, $[Co(C_{12}H_{12}N_2)](SCN)_2$, $[Co(H_2O)_2(C_{12}H_{12}N_2)_2](SCN)_2$ (also $+2H_2O$), $[Co(C_{12}H_{12}N_2)_3]Br_2,4H_2O$, $[Mg(C_{12}H_{12}N_2)_3]Br_2,6H_2O$, $[Mg(C_{12}H_{12}N_2)_3]I_2,6H_2O$, $[Mg(C_{12}H_{12}N_2)_3](ClO_3)_2,4H_2O$, $[CuC_{12}H_{12}N_2]SO_4$, $[Cu(H_2O)_2(C_{12}H_{12}N_2)](OAc)_2$, $[Fe(H_2O)_2C_{12}H_{12}N_2)](NO_3)_3$, $[Fe(C_{12}H_{12}N_2)](NO_3)_3$. The results are regarded as supporting Kaufler's formula for benzidine. A. A. ELDRIDGE.

Potentiometric indication in the formation of azo dyes. F. MULLER.—See this vol., 485.

Acyl derivatives of hydrazine. F. J. WILSON, W. BAIRD, A. C. BROWN, and E. C. PICKERING (J. Roy. Tech. Coll. Glasgow, 1927, [iv], 60—62; cf. A., 1927, 232).—The thermal decomposition of acetone-, pinacolin-, and benzylidene-δ-anilinosemicarbazones follows the normal course:

$$2CRR'{:}N\cdot NH\cdot CONH\cdot NHPh \longrightarrow CO(NH\cdot N{:}CRR')_2 + CO(NH\cdot NHPh)_2 \longrightarrow 2CRR'{:}N\cdot NHPh + CO{<}\begin{smallmatrix}NH\cdot NH\\ N(NH_2)\end{smallmatrix}{>}CO$$

(cf. A., 1926, 1141). The thermal decomposition of acetone-δ-diphenylaminosemicarbazone conforms to the same general scheme, and the intermediate product, tetraphenylcarbohydrazide, was isolated. When acetone-, acetophenone-, and dibenzyl ketone-thiosemicarbazones are heated with phenylhydrazine in toluene solution or suspension, the ketone-phenylhydrazone and -thiosemicarbazide are produced: $CRR'{:}N\cdot NH\cdot CS\cdot NH_2 + NH_2\cdot NHPh \longrightarrow CRR'{:}N\cdot NHPh + NH_2\cdot NH\cdot CS\cdot NH_2$. No δ-anilino-thiosemicarbazone is obtained. L. M. CLARK.

δ-Substituted semicarbazides. I. V. HOPPER (J. Roy. Tech. Coll. Glasgow, 1927, [iv], 48—57).—For the preparation on a large scale of the hydro-

chlorides of δ-phenyl-, δ-benzyl-, and *r*- and *d*-δ-α-phenylethyl-semicarbazides (J.C.S., 1922, **121**, 866), the appropriate amine is heated with acetonesemicarbazone at 125—135° until ammonia ceases to be evolved, the crude acetone-δ-substituted semicarbazone is hydrolysed with 5% hydrochloric acid, and the semicarbazide hydrochloride is isolated by concentration of the aqueous solution. The hydrochlorides react with nitrous acid, giving azides, and with copper chloride, giving sparingly soluble copper derivatives. The free bases, obtained by treatment of the hydrochlorides with aqueous sodium carbonate, yield on heating, or by interaction with iodine, substituted carbamylhydrazines. Benzylcarbamazide reacts with water or alcohol in a sealed tube at 100°, giving *s*-dibenzylcarbamide. No urethane derivative is obtained. α-Phenylethylcarbamazide gave a tarry product only. Neither azide formed a bromo-derivative (cf. Curtius and Burkhard, A., 1899, i, 137). The following are described: *semicarbazide oxalate*, m. p. 146°; δ-*phenylsemicarbazide oxalate*, decomp. above 165°, m. p. 220°; δ-*phenylsemicarbazide hydrochloride copper chloride*, $NHPh\cdot CO\cdot N(CuCl)\cdot NH_2,HCl,10H_2O$; δ-benzylsemicarbazide [*acetyl* derivative, m. p. 145°; *oxalate*, m. p. 160° (decomp.)]; δ-*benzylsemicarbazide hydrochloride copper chloride*, $CH_2Ph\cdot NH\cdot CO\cdot N(CuCl)\cdot NH_2,HCl,4\frac{1}{2}H_2O$ (unstable *hydrate*), decomposed by ammonia, giving a *compound*, m. p. 245°; *benzylcarbamazide*, m. p. 84°; and s-*dibenzylcarbamylhydrazine*, m. p. 237°; r-δ-α-*phenylethylsemicarbazide*, m. p. 92° (decomp.), δ-α-*phenylethylsemicarbazide hydrochloride copper chloride*, r-δ-α-*phenylethylcarbamazide*, m. p. 87°, and a *by-product*, m. p. 157°, probably di-α-phenylethylcarbamide; d-δ-α-*phenylethylsemicarbazide*; d-*di*-α-*phenylethylcarbamide* (?), m. p. 208°, $[\alpha]_D^{17}$ +84·8° in alcohol, and internally compensated s-*di*-α-*phenylethylcarbamylhydrazine* (?), m. p. 220°, occurring as by-products in the preparation of the carbazide hydrochloride; d-δ-α-*phenylethylcarbamazide*, m. p. 73°, $[\alpha]_D^{15}$ +243·7° in alcohol, and s-*di*-α-*phenylethylcarbamylhydrazine*, m. p. 187°; *benzaldehyde*-d-δ-α-*phenylethylsemicarbazone*, m. p. 102°, $[\alpha]_D^{18}$ −296·9° in alcohol.

L. M. Clark.

Behaviour of β-phenylsemicarbazones on oxidation. G. T. Whyburn and J. R. Bailey (J. Amer. Chem. Soc., 1928, **50**, 905—912).—Acetone-β-phenylsemicarbazone (cf. A., 1925, i, 318) on oxidation with permanganate in acetone gives rise to a compound, m. p. 162° (decomp.), regarded as β-*phenyl*-α-*benzeneazomethyl*-α-iso*propylsemicarbazide*, $CHMe_2\cdot N(CH_2\cdot N{:}NPh)\cdot NPh\cdot CO\cdot NH_2$. The analogous *compound* from methyl ethyl ketone has m. p. 144° (decomp.). The product of m. p. 162°, on treatment with 0·5*N*-hydrochloric acid gives rise to acetone, benzene, β-phenylsemicarbazide, diphenyl, and nitrogen. *Pyruvic acid* β-*phenylsemicarbazone* has m. p. 168° (decomp.) (*ethyl* ester, m. p. 149°). The latter is stable to permanganate in acetone. *Diphenyldipropylidenedihydrotetrazone*, $CMe_2{:}N\cdot NPh\cdot NPh\cdot N{:}CMe_2$, m. p. 89°, is obtained by oxidation of acetonephenylhydrazone with permanganate in acetone. Refluxing with alcohol reconverts it into acetonephenylhydrazone, whilst acids hydrolyse it to its original constituents. With pyruvic acid it gives the phenylhydrazone of the latter. Oxidation by ferric chloride of benzaldehyde-β-phenylsemicarbazone gives 3-*hydroxy*-2 : 5-*diphenyltriazole*, m. p. 233°. From acetonephenylhydrazone and phenylcarbimide in molecular proportions at 100° is obtained *acetone*-βδ-*diphenylsemicarbazone*, m. p. 191°.

J. D. Fulton.

Action of light on diazo-derivatives. A. Seyewitz and D. Mounier.—See this vol., 493.

2-*cyclo*Hexyl*cyclo*hexanol. Vavon and V. M. Mitchovitch (Compt. rend., 1928, **186**, 702—705).—In view of the discrepancy between the physical constants of numerous substances described in the literature as 2-*cyclo*hexyl*cyclo*hexanol and those of the *cis*-, m. p. 60°, and *trans*-, m. p. 53—54°, forms of this compound prepared by Vavon, Anziani, and Herynk (A., 1926, 1033) investigation of the following methods of preparation has been made. Catalytic reduction of *o*-hydroxydiphenyl with platinum-black yields only the *cis*-form, m. p. 60°. The action of magnesium *cyclo*hexyl chloride on 2-chloro*cyclo*hexanol and on *cyclo*hexene oxide, however, yields 2-cyclo*pentyl*cyclo*hexylcarbinol*, m. p. 34° (*phenylurethane*, m. p. 122°; *hydrogen phthalate*, m. p. 92—93°; *dinitrobenzoate*, m. p. 102°; p-*nitrobenzoate*, m. p. 49—50°), identical in all respects with the product obtained by the action of magnesium *cyclo*pentyl chloride on hexahydrobenzaldehyde. Rupture of the six-ring to a five occurs in a similar manner to that observed by Godchot and Cauquil (this vol., 410) in the case of 2-chloro*cyclo*heptanol. Thus, in agreement with the Baeyer theory, it has been possible to prepare only two forms of 2-*cyclo*hexyl*cyclo*hexanol.

J. W. Baker.

Rearrangement of phenyl benzyl ether. W. F. Short (J.C.S., 1928, 528).—When phenyl benzyl ether is heated at 225° in presence of anhydrous zinc chloride, or at 180° in a stream of hydrogen chloride, rearrangement occurs. The product, on distillation under reduced pressure, yields phenol, *o*-hydroxydiphenylmethane, *p*-hydroxydiphenylmethane, and products of high b. p. Intermediate formation of benzyl chloride is suggested.

M. Clark.

Action of sodium peroxide on phenol. Preparation of pyrocatechol and quinol. O. Magidson [with E. Posorovskaja and N. Seligsohn] (Trans. sci. chem.-pharm. inst., Moscow, 1923, **6**, 21—28; Chem. Zentr., 1927, ii, 2542).—Sodium peroxide is added in small quantities, with cooling and stirring, to a solution of phenol in sulphuric acid; the mixture is kept for 12 hrs. and then heated at 50—60°. After separation of resinous substances, pyrocatechol (25% of the total yield) and quinol (25%) remain.

A. A. Eldridge.

Introduction of the triphenylmethyl group into phenols. D. R. Boyd and D. V. N. Hardy (J.C.S., 1928, 630—638).—By heating triphenylcarbinol with phenol alone, 4-hydroxytetraphenylmethane (I) is directly obtained, and similarly, using methyl salicylate and hydrolysing the product with hydriodic and acetic acids, 4-*hydroxytetraphenylmethane*-3-*carboxylic acid* (II), m. p. 232°, which is converted into (I) on

heating. Condensation in this manner is not effected with *o*- or *m*-cresol, anisole, or *o*-chlorophenol. From (II), by the action of acetic anhydride and sodium acetate, the 4-*acetoxy*-, m. p. 210°, by that of bromine and acetic acid the 5-*bromo*-4-*hydroxy*-, m. p. 239°, and by that of nitric and acetic acids the *o*-*nitro*-4-*hydroxy*-, m. p. 226°, derivatives of tetraphenylmethane-3-carboxylic acid are obtained.

By the action of triphenylmethoxyphosphorus dichloride (Boyd and Chignell, J.C.S., 1923, **123**, 813; Boyd and Smith, A., 1924, i, 1121) on phenol, (I) is obtained; similarly *m*-cresol yields 4(or 2)-hydroxy-2(or 4)-methyltetraphenylmethane, but *p*-cresol gives triphenylmethane and (?) *di*-p-*tolyl triphenylmethylphosphite*, m. p. 179—180°.

The action of triphenylcarbinol on phenols in presence of acetic and sulphuric acids (Baeyer–Villiger reaction) is re-investigated, using a smaller proportion of sulphuric acid; with *o*-cresol the product is identical with the ααα-triphenyl-β-2-hydroxyphenylethane of Schorigin (III) (A., 1927, 54; this vol., 59). This and the corresponding formulation for the product from *p*-cresol (IV) were based on the formation of triphenylcarbinol from these two products, but not from the *m*-cresol derivative (regarded as 2-*hydroxy*-4-*methyltetraphenylmethane*—now prepared from triphenylcarbinol and *m*-cresol), or from 4-hydroxytetraphenylmethane, by the action of chromic acid. It is now found that, by the action of sulphuric acid, triphenylcarbinol can be obtained from each of the four compounds, each of which gives triphenylmethane on distillation with soda-lime; with a mixture of hydriodic and acetic acids the *o*- and *m*-cresol compounds yield triphenylmethane, whilst the others are stable. Accordingly for Schorigin's compounds (III) and (IV) the constitutions 4-*hydroxy*-*o*-*methyl*- and 2-*hydroxy*-*o*-*methyl*-*tetraphenylmethane* are preferred. Correspondingly, the α-*o*-aminophenyl-βββ-triphenylethane of van Alphen (A., 1927, 867) is renamed 4-*amino*-3-*methyltetraphenylmethane*.

The Baeyer–Villiger reaction is found to be reversible. The mechanism is discussed: the brown colour produced on adding a phenol to the orange-red solution of triphenylcarbinol in acetic and sulphuric acids is considered to be due to the formation of a quinonoid substance, $CPh_3{\cdot}CH{<}{}^{CH.\ H}_{CH{\cdot}CH}{>}C(OH){\cdot}O{\cdot}SO_3H$, by the addition of the CPh_3^+ and HSO_4^- ions to the phenol. The complex then loses sulphuric acid, forming the tetraphenylmethane derivative, or the reverse reaction occurs; with *p*-cresol, sulphuric acid cannot be lost in the above way, and thus triphenylmethane and, probably, a polymerised *p*-quinomethane are formed.

The comparative stabilities of various tetraphenylmethane derivatives towards sulphuric acid are tabulated.

From the compound (III), 4-*acetoxy*-3-*methyltetraphenylmethane*, m. p. 150°, is prepared, and the 4-*methoxy*-compound, m. p. 165°, which is also obtained by the interaction of *o*-tolyl methyl ether and triphenylcarbinol in an acetic and sulphuric acid mixture, and with bromine gives 3-*bromo*-4-*methoxy*-5-*methyltetraphenylmethane*, m. p. 180°.

E. W. Wignall.

Acyl derivatives of *o*-aminophenol. IV. R. E. Nelson, J. R. Matchett, and J. B. Tindall (J. Amer. Chem. Soc., 1928, **50**, 919—923).—The effect of halogen-substituted acyl groups on the molecular rearrangement of diacyl derivatives of *o*-aminophenol on hydrolysis has been studied. It appears that the weight and acidity of any substituent group are not the chief factors in deciding whether it shall be attached to the oxygen or nitrogen atom. *Ethyl* o-*chloroacetoxycarbanilate* from ethyl *o*-hydroxycarbanilate and chloroacetyl chloride or from *o*-chloroacetamidophenol and ethyl chlorocarbonate by the Schotten–Baumann reaction had m. p. 114—115°. Hydrolysis yielded ethyl *o*-hydroxycarbanilate, showing that migration of a chloroacetyl group had taken place in one case from the nitrogen to the oxygen atom. o-*Chloroacetamidophenyl acetate*, m. p. 113—114°, and o-*acetamidophenyl chloroacetate*, m. p. 128—130°, yielded on hydrolysis *o*-acetamidophenol, rearrangement having taken place. *o*-Benzamidophenyl trichloroacetate, m. p. 104°, is hydrolysed to *o*-benzamidophenol. Attempts to acylate β-chloroethyl *o*-hydroxycarbanilate with ethyl chloroformate, or ethyl *o*-hydroxycarbanilate with β-chloroethyl chloroformate, led to the formation of carbethoxycarbonyl-*o*-aminophenol.

J. D. Fulton.

Action of aminosulphonic acid on unsaturated compounds. A. Quilico (Atti R. Accad. Lincei, 1928, [vi], **7**, 141—146).—By the action of aminosulphonic acid on anethole an *ammonium* salt of an unsaturated sulphonic acid is obtained having the composition $(C_{10}H_{11}O)SO_3NH_4$, m. p. 235—240° (decomp.). The sulphonic group is in the side-chain, and the acid is considered to have the structure $MeO{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}SO_3H$. The preparation and properties of the free *acid*, m. p. 70°, and also of the *potassium* and *barium* salts, *chloride*, m. p. 63·5°, and *amide*, m. p. 156°, are described. In the formation of the ammonium salt the aminosulphonic acid probably adds on to the side-chain double linking of anethole, giving the amide of a hydroxysulphonic acid, which by successive elimination of water and hydration is transformed into the ammonium salt of anetholesulphonic acid. This is fundamentally the same kind of action as takes place with simple phenolic ethers such as anisole (cf. this vol., 407).

O. J. Walker.

Direct introduction of substituents in aromatic mercaptans. T. van Hove (Bull. Soc. chim. Belg., 1928, **37**, 88—102).—See A., 1927, 1065.

4-Nitro-2-aminophenyl β-hydroxyethyl or βγ-dihydroxypropyl ether. Chem. Works formerly Sandoz.—See B., 1928, 255.

Preparation of trinitroresorcinol and its salts. A. Majrich (Chem. Obzor., 1927, **2**, 225—227; Chem. Zentr., 1927, ii, 2286).—Optimal conditions, affording a yield 95% of the theoretical, are recorded. The following *styphnates* are described: $Hg_2C_6HO_8N_3,9H_2O$, orange-yellow; $Hg(C_6H_2O_8N_3)_2,18H_2O$, yellow, also $+5H_2O$, silky; $CdC_6HO_8N_3,25H_2O$, yellow; $ZnC_6HO_8N_3,18H_2O$, yellow; $FeC_6HO_8N_3,20H_2O$, olive-green; $NiC_6HO_8N_3,20H_2O$, green; $MgC_6HO_8N_3,4H_2O$, orange.

A. A. Eldridge.

Stereoisomerides of quinite (1 : 4-*cyclo*hexanediol). L. Palfray and L. Rothstein (Compt. rend., 1928, **186**, 872—874).—The stereoisomerides are best separated by crystallisation from acetone, in which the *trans* form is sparingly soluble, followed by centrifuging (cf. Willstätter and Lessing, A., 1901, i, 265). Further purification may be effected by sublimation at 150—200°; under these conditions polymorphous forms of the *cis*-compound are observed. G. A. C. Gough.

Calcium salt of *p*-iodoguaiacol and *p*-iodoguaiacol carbonate. F. R. Greenbaum (Amer. J. Pharm., 1928, **100**, 112—115).—The *calcium* salt of guaiacol is obtained by boiling an ethereal solution of guaiacol with milk of lime, evaporating the mixture to dryness, and extracting the product with methyl alcohol and ether. The *calcium* salt of *p*-iodoguaiacol, a greyish-pink, insoluble powder, obtained in a similar manner, has a low toxicity (maximum tolerated dose in a rabbit 700 mg. per kg. body weight). When administered orally *p*-iodoguaiacol is eliminated unchanged to the extent of 90% in 24 hrs., whilst the calcium salt is excreted more slowly and incompletely (60·6% in 24 hrs.). The calcium is excreted after the iodine. p-*Iodoguaiacol carbonate*, m. p. 167°, is obtained by treating *p*-iodoguaiacol dissolved in dilute sodium hydroxide solution with carbonyl chloride. S. Coffey.

Sulphur derivatives of aromatic methyl ethers. H. H. Hodgson and F. W. Handley (J.C.S., 1928, 625—628).—By reducing the corresponding dinitro-compounds (A., 1926, 516) by sodium sulphide and oxidising the resultant aminomercaptan by exposure to air, 2 : 2′-*diamino*-5 : *di-sul* , m. p. 76° (*diacetyl* derivative, m. p. 202—203°; *hydrochloride*, yielding with nitrous acid *o-methoxybenzene-2 : 1-diazosulphide*, m. p. 80°), and 4 : 4 : 5′ *disulphide*, m. p. 88° (*diacetyl* derivative, m. p. 136°; *hydrochloride*, which diazotises normally), are obtained.

By treatment of the same dinitro-compounds with sodium ethoxide and the corresponding chloronitroanisole, or, less satisfactorily, by the reaction between the latter and sodium monosulphide (Nietzki and Bothof, A., 1895, i, 132), 2 : 2 - and 4 : 4′-*dinitro-o : 5′-dimethoxydiphenyl sulphides*, m. p. 151° and 154°, respectively, which are oxidised by peracetic acid to the corresponding *o* : 5 *phenylsulphones*, m. p. 182° and 245—246°, respectively, are obtained. 2- and 4-Nitro-5-methoxythioanisoles (*loc. cit.*) are similarly oxidised to 2- and 4-*n* *m* *syl-* m. p. 122° and 130°, respectively, and the methoxythioanisidines are converted by the Sandmeyer reaction into 2- and 4-*chloro-5-methoxy-* m. p. 41° and 36°, respectively. No trisulphide is formed when sodium trisulphide reacts with 3-chloro-4- or -6-nitroanisole, the disulphide alone being produced in each case (cf. Blanksma, A., 1901, i, 462; Hodgson and Wilson, A., 1925, i, 532). The characteristic colour reactions given by the above compounds with concentrated and fuming sulphuric acid and chlorosulphonic acid are described.

E. W. Wignall.

Wandering of the acyl group in 2 : 6-dimethoxyphenyl acetate. F. Mauthner (J. pr. Chem., 1928, [ii], **118**, 314—320).—2 : 6-Dimethoxyphenyl acetate is isomerised and demethylated by zinc chloride at 120°, or slowly at the ordinary temperature, to 2 : 3-dihydroxy-4-methoxyacetophenone (Perkin and Wilson, J.C.S., 1903, **83**, 132) [*semicarbazone*, m. p. 229° (decomp.); p-*nitrophenylhydrazone*, decomp. 260°] and a little pyrogallol 1 : 3-dimethyl ether. The ketone is identified by methylation to 2-hydroxy-3 : 4-dimethoxyacetophenone and demethylation to gallacetophenone (cf. A., 1927, 566). Similarly, 2 : 6-*dimethoxyphenyl chloroacetate*, m. p. 65—66°, b. p. 182—183°, is isomerised and demethylated by aluminium chloride at 100° to ω-chloro-2 : : 4-hydroxyacetophenone. H. E. F. Notton.

***cyclo*Propane derivatives.** P. Bruylants and A. Dewael (Bull. Acad. roy. Belg., 1928, [v], **14**, 140—153).—When *cyclo*propyldimethylcarbinol is treated with hydrochloric acid and the product distilled several times there is obtained α-chloro-δ-methyl-Δ^{γ}-pentene, b. p. 132—133°, d_4^{20} 0·92653, n_D^{20} 1·44193, which is converted by prolonged treatment with potassium acetate and a small amount of acetic acid into the corresponding acetate, b. p. 170—171°, d_4^{20} 0·9108, n_D^{20} 1·43107. Hydrolysis of this gives δ-methyl-Δ^{γ}-penten-α-ol, b. p. 157°/744 mm., d_4^{20} 0·85765, n_D^{20} 1·44564, identical with the methylpentenol prepared by Van Aerde (A., 1909, i, 79). The product of the reaction of hydrobromic acid and *cyclo*propyldimethylcarbinol (cf. A., 1909, i, 226), when treated with sodium ethoxide, gives α-ethoxy-δ-methyl-Δ^{γ}-pentene, b. p. 142—143°, d_4^{20} 0·7989, n^{20} 1·41948, also obtained from the above chloro-compound. Hydrochloric acid converts the ethoxypentene into δ-chloro-α-ethoxy-δ-methylpentane, b. p. 172—173°/737 mm., d^{20} 0·9094, which is decomposed by boiling water in presence of calcium carbonate, yielding α-ethoxy-δ-methylpentan-δ-ol, b. p. 182—183° (A., 1926, 1225).

Prolonged treatment of α-chloro-δ-methyl-Δ^{γ}-pentene with boiling water in presence of calcium carbonate and further treatment with alcoholic potassium acetate and a little sodium iodide regenerates mainly *cyclo*propyldimethylcarbinol. An explanation of the change is suggested. H. Burton.

Cholesterol. IV. Different methods of oxidation. E. Montignie (Bull. Soc. chim., 1928, [iv], **43**, 360—364).—Oxidation of cholesterol in acetic acid at 70° with an equal weight of chromic acid (cf. Mauthner and Suida, A., 1896, i, 425) affords a ketone and two ill-defined acids; with excess of chromic acid complete oxidation to carbon dioxide and water takes place, whilst with smaller amounts of chromic oxide oxycholestenone, m. p. 122—123°, is obtained. Iodic acid, alone or in presence of potassium hydroxide, potassium ferricyanide, alone or in presence of alkali, and sodium persulphate, alone or in presence of silver nitrate, are without action on cholesterol. Potassium chlorate and hydrochloric acid afford a mixture of chlorinated compounds containing a ketonic compound, since the product reacts with semicarbazide, giving a semicarbazone, and with phosphorus pentachloride in chloroform, giving an

uncrystallisable compound from which chlorine is eliminated on oxidation. In view of these and earlier results (A., 1927, 556, 969: Windaus, A., 1913, i, 615, 969; 1914, i, 682; 1915, i, 677) it is concluded that cholesterol contains a ring system composed of hydrogenated benzene rings and that oxidation is unlikely to yield further positive information as to its constitution. R. BRIGHTMAN.

Electrolysis of benzoic acid. E. BAUR and E. MÜLLER.—See this vol., 490.

Synthesis and fission of amino-acids. F. KNOOP and H. OESTERLIN (Z. physiol. Chem., 1927, **170**, 186—211).—Some miscellaneous observations are recorded. In the preparation of α-amino-acids from keto-acids, ammonia, and hydrogen, 2 mols. of ammonia give the optimum yield. In place of hydrogen and palladium-black, ferrous salts, or physiological hydrogen donors such as cysteine, may be used. Under conditions similar to the usual amino-acid synthesis, benzaldehyde gives 75% of dibenzylamine, cinnamaldehyde 20% of di-(γ-phenylpropyl)-amine (hydrochloride, m. p. 198—200°), benzophenone only 5% of benzhydrylamine, m. p. 270°, whilst acetophenone, acetone, methyl ethyl ketone, and aldehyde-ammonia are not reduced.

Phenyl-N-dimethylalanine, m. p. 235°, fed to dogs, is recovered unoxidised from the urine; the monomethyl compound gives appreciable amounts of benzoic and hippuric acids. α-Methylamino-γ-phenylbutyric acid, subliming at 282° (hydrochloride, m. p. 190°; p-toluenesulphonyl derivative, m. p. 115—116°), obtained from α-p-toluenesulphonamido-γ-phenylbutyric acid, m. p. 124—125°, or from α-bromo-γ-phenylbutyric acid and methylamine, is partly recovered unchanged, partly converted into d-α-hydroxy-γ-phenylbutyric acid, m. p. 114°, $[\alpha]_D$ $-12.38°$; acetylation to *α-acetmethylamido-γ-phenylbutyric acid* completely prevents this oxidation. Acetylation of phenyl-N-methylalanine (*acetyl* derivative, m. p. 149°) similarly prevents attack.

α-Dimethylamino-γ-phenylbutyric acid, decomp. 178—180° (*copper* salt), *α-acetmethylamido-α-phenylacetic acid*, m. p. 126—128°; *phenyl-N-dimethylglycine*, m. p. 260—262°; ethyl d-glutamate hydrochloride, m. p. 107—108°, $[\alpha]_D$ $+22.8°$; N-acetylglutamic acid, m. p. 195—197°, $[\alpha]_D$ $-22.7°$; p-toluenesulphonylglutamic acid, m. p. 135° (lit., 115°), $[\alpha]_D$ $-16.7°$ (ethyl ester, m. p. 77—78°), and *methylglutamic acid*, m. p. 200° (decomp.), $[\alpha]_D$ -14.2 (*hydrochloride*, m. p. 210—213°; *acetyl* derivative, decomp. 203°; p-*tol ulphonyl* derivative, m. p. 131—132°), are described.

Methylaminomalonic acid, decomp. 137—142°, prepared from bromomalonic acid and methyl-alcoholic methylamine, is decarboxylated by acylating agents, giving, *e.g.*, toluenesulphonylsarcosine. Sarcosine and methylglutamic acid are consumed almost completely in the body, but *o-nitrobenzoylglutamic acid*, m. p. 151°, $[\alpha]_D$ $-74.5°$, is recovered unchanged when fed to dogs. *o-Nitrobenzoylglycine*, m. p. 191°, is described. C. HOLLINS.

5-Nitro-4-hydroxy-o-benzoylbenzoic acid, 3-amino-4-hydroxy-o-benzoylbenzoic acid and 4-hydroxy-o-benzoylbenzoic acid. I. GUBELMANN, H. J. WEILAND, and O. STALLMANN, Assrs. to NEWPORT Co.—See B., 1928, 224.

Bromination of m-methoxycinnamic acid. H. DAVIES and W. DAVIES (J.C.S., 1928, 602—605).—The product of the action of 1 mol. of bromine on m-methoxycinnamic acid, regarded by Bauer and Vogel (A., 1913, i, 1063) as β-bromo-m-methoxycinnamic acid, m. p. 186°, is actually *6-bromo-3-methoxycinnamic acid*, m. p. 189°, as is shown by oxidation to 6-bromo-3-methoxybenzoic acid, m. p. 162°; the bromination residue, m. p. 108—140°, contains a cinnamic acid dibromide derivative. Ethyl m-methoxybenzylidenemalonate with 1 mol. of bromine yields a product regarded by Bauer and Vogel as ethyl α-bromo-3-methoxybenzylidenemalonate, which, however, hydrolyses to an acid, m. p. 173—183°, decomp. to 6-bromo-3-methoxycinnamic acid, and thus contains the bromine atom in the 6-position. The action of 2 mols. of bromine on m-methoxycinnamic acid yields a product, m. p. 130—163° (cf. Bauer and Vogel, *loc. cit.*); this after ozonisation has m. p. 157—165°, and contains some 4(or 2) : 6-dibromo-3-methoxybenzoic acid, identified by preparation from 4(or 2) : 6-dibromo-3-methoxybenzaldehyde (Hodgson and Beard, A., 1925, i, 675), from which 4(or 2) : *6-dibromo-3-methoxycinnamic acid*, m. p. 234°, is also synthesised. E. W. WIGNALL.

β-Phenylethylmaleic acid and the isomeric β-phenylethylfumaric acid. P. CORDIER (Compt. rend., 1928, **186**, 869—872).—α-Hydroxy-α-acetonyl-γ-phenylbutyric acid (Bougault, A., 1912, i, 771) is dehydrated by hydrochloric acid to give α-(β-ketopropylidene)-γ-phenyl-n-butyric acid, m. p. 95°. An aqueous sodium hydroxide solution of the mixture of dibasic acids obtained by oxidation of the latter with alkaline sodium hypochlorite yields *sodium hydrogen β-phenylethylmaleate* (the corresponding *acid*, m. p. 104°, affords the *anhydride*, m. p. 74°, on treatment with acetic anhydride or with dilute hydrochloric acid) on acidification with acetic acid. *β-Phenylethylfumaric acid*, m. p. 202°, obtained from the mother-liquors, does not yield an anhydride under the former conditions. Both acids are reduced to β-phenylethylsuccinic acid by sodium amalgam and the substituted fumaric acid is partly converted into its isomeride on treatment with sodium hydrogen sulphite. G. A. C. GOUGH.

Action of mixed organo-magnesium derivatives on aromatic diethylamides and tetraethylphthalamides. N. MAXIM (Ann. Chim., 1928, [x], 9, 55—111).—Magnesium aryl, aralkyl, and alkyl halides react with aromatic diethylamides either thus $R\cdot CO\cdot NEt_2 + R'MgHal \longrightarrow R\cdot CO\cdot R' + NHEt_2$, or not at all. Magnesium ethyl bromide and benzdiethylamide give in ether or toluene solution phenyl ethyl ketone (31 and 60%). With magnesium benzyl chloride in ether or toluene, deoxybenzoin (21 and 33%) is formed together with a small amount of a ketone, probably $CH_2Ph\cdot CPh:CPhBz$ (*semicarbazone*, m. p. 158—159°), formed by elimination of water from 2 mols. of deoxybenzoin. Benzdiethylamide does not react with magnesium phenyl bromide, but phenylacetdiethylamide yields deoxybenzoin (37%), whilst with magnesium ethyl bromide there is formed benzyl

ethyl ketone (39%). From β-*phenylpropiondiethylamide*, b. p. 170°/11 mm., there are produced β-phenylethyl ethyl ketone (50%) (*semicarbazone*, m. p. 131—132°) and phenyl β-phenylethyl ketone (69%) (*semicarbazone*, m. p. 140°). Magnesium ethyl bromide reacts with diphenylacetamide and dibenzylacetamide to form *benzhydryl ethyl ketone*, b. p. 186°/14 mm. (*semicarbazone*, m. p. 189—190°; *oxime*, m. p. 110°), and *dibenzylmethyl ethyl ketone*, b. p. 205°/17 mm. (*semicarbazone*, m. p. 160—161°), respectively, whilst from the former amide and magnesium phenyl bromide there is produced phenyl benzhydryl ketone. *Diphenylacetdiethylamide*, m. p. 64—65°, and *dibenzylacetdiethylamide*, b. p. 225°/13 mm., m. p. 56°, do not react. Diethylamine and phthalic anhydride react in benzene solution to form o-*NN-diethylphthalamic acid*, b. p. 177°/14 mm., m. p. 153°, which with magnesium ethyl bromide gives diethylphthalide (80%). Similarly, from *tetraethyl*-o-*phthalamide*, b. p. 204°/16 mm., m. p. 36°, *tetraethyl*iso*phthalamide*, b. p. 242°/12 mm., m. p. 85°, and *tetraethylterephthalamide*, m. p. 127°, there are produced diethylphthalide (15%) and o-*propionylbenzdiethylamide*, b. p. 186°/15 mm. (10%) (*semicarbazone*, m. p. 195°; *oxime*, m. p. 110°), m-*dipropionylbenzene*, b. p. 182°/10 mm., m. p. 34° (25%) (*disemicarbazone*, m. p. 222°), and m-*propionylbenzdiethylamide*, b. p. 205°/10 mm. (20%) (*semicarbazone*, m. p. 145°), and p-*dipropionylbenzene*, m. p. 100° (30%) (*disemicarbazone*, m. p. 260°; *dioxime*, m. p. 226°), and p-*propionylbenzdiethylamide*, m. p. 82° (25%) (*semicarbazone*, m. p. 175°; *oxime*, m. p. 105°), respectively. The ketonic amides are unaffected by aqueous potassium hydroxide and hydrobromic acid. Magnesium phenyl bromide has no action on the three tetraethylphthalamides.

Magnesium ethyl and phenyl bromides react with cinnamdiethylamide to form β-*phenylvalerdiethylamide*, b. p. 174°/12 mm., and ββ-*diphenylpropiondiethylamide*, b. p. 225°/10 mm., m. p. 76°, respectively. These amides are produced by the addition of the magnesium derivative to the double linking, and they do not react with the Grignard reagent.

H. BURTON.

Isomerism of the oximes. XXXIII. Oximes of opianic acid and of phthalic anhydride. O. L. BRADY, L. C. BAKER, R. F. GOLDSTEIN, and S. HARRIS (J.C.S., 1928, 529—539).—Opianic acid oxime (I) (Perkin, J.C.S., 1890, 57, 1070) resembles in preparation (in alkaline solution) and in properties the α-aldoximes; it cannot be characterised by its reaction with acetic anhydride, since it then gives its anhydride, but its sodium salt with 4-chloro-*m*-dinitrobenzene gives 2 : 4-*dinitrophenylopianic acid oxime*, m. p. 146°, a resemblance to α-benzaldoxime. It is therefore formulated $\begin{array}{c}C_6H_2(OMe)_2(CO_2H){\cdot}C{=}N\\ \quad\quad\quad\quad\quad\quad\quad H \quad\; OH\end{array}$ the new configuration for α-aldoximes (cf. Brady and Bishop, A., 1925, i, 930). The oxime anhydride (II) (Liebermann, A., 1887, 47) is unaffected by acetic anhydride, and is therefore held to be neither an iminophthalide nor an *iso*indolone-*N*-oxide. Since 2-cyano-5 : 6-dimethoxybenzoic acid, (III) (Hoogewerff and van Dorp, A., 1896, i, 313) has different properties, and is indeed produced by the action of alkali on the anhydride, the latter is best represented $\left[C_6H_2(OMe)_2\left|\begin{array}{l}-CO{\cdot}O\\ -CH{:}N\end{array}\right.\right]$. This, the (new) structure of a β-aldoxime, is in harmony with the action of alkali, which yielded no opianic oxime (to detect which methyl sulphate or 4-chloro-*m*-dinitrobenzene had been added); hemipinimide alone could be isolated. Anhydride formation with change of configuration can be represented (by intermediate formation of the structure $C_6H_2(OMe)_2\left|\begin{array}{l}-CO—O\\ \;\; C{=}—N\\ \;\; H\;HO\wedge H\end{array}\right.$; Meisenheimer, A., 1924, i, 432) easily only by the new configurations for aldoximes, which are thus supported.

The ready inversion of (I) or (II) to hemipinimide (Perkin; Liebermann, *loc. cit.*) could be considered to take place through the cyano-acid (III) or through a *trans*-Beckmann change and the iminophthalide configuration. The second mechanism receives some support from the inversion of N-*methylopianic acid oxime*, m. p. 180·5° (obtained by the interaction of *N*-methylhydroxylamine hydrochloride and opianic acid, which yield no anhydride, even when alcohol is the solvent, in which case ψ-opianic ester is obtained). This inverts on boiling with water to give *N*-methylhemipinimide (also prepared by the action of methyl iodide on potassium hemipinimide); here the cyano-acid mechanism is impossible. It is, however, preferred for opianic oxime, since the cyano-acid (III) readily yields hemipinimide, since opianic oxime anhydride does not contain a quinquevalent nitrogen atom, and since acetophenone-*o*-carboxylic acid oxime anhydride, which by the Beckmann change should give *N*-methylphthalimide, can be distilled unchanged.

By the action of *O*-methylhydroxylamine hydrochloride, or of hydroxylamine hydrochloride in the presence of methyl sulphate, on opianic acid, O-*methylopianic oxime*, m. p. 112°, is obtained.

The absorption spectra of all the above compounds are shown graphically; that of opianic oxime anhydride differs widely from that of the acylated aldoximes, resembling rather that of hemipinimide; no constitutional deductions are made from the spectra.

N-Benzylhydroxylamine hydrochloride and opianic acid yield *N*-benzylhemipinimide.

The white and yellow phthaloximes and their *O*-methyl derivatives (Orndorff and Pratt, A., 1912, i, 190) are re-investigated, and absorption spectra (Pratt and Gibbs, A., 1914, i, 415) are redetermined. Published results are confirmed, but the two forms are not regarded as *cis–trans* isomerides, but rather as examples of a new (unexplained) type of isomerism ("xanthoisomerism"). That the ethers are actually *O*-methyl ethers is shown by methoxyl determination and by hydrolysis to *O*-methylhydroxylamine. By methylating the sodium salts in methyl alcohol by methyl iodide or sulphate, only the *O*-ether is obtained; a white N-*methylphthaloxime*, m. p. 121—122°, is obtained by using *N*-methylhydroxylamine, but no yellow form is obtained. By the action of amyl-alcoholic potassium hydroxide on the white phthaloxime, some anthranilic acid is obtained: this is regarded as a Hofmann reaction.

No trace of 4-nitrosaccharin is obtained from hydroxylamine and 4-nitrobenzaldehyde-*o*-sulphonic acid, even by heating at 160°. E. W. WIGNALL.

Synthesis of a truxinic acid. F. BACHÉR (Ber., 1928, **61**, [*B*], 543—547).—Reduction of methyl benzylidenemalonate by aluminium amalgam and moist ether gives mainly methyl benzylmalonate, but also 5—15% of the two *forms* of methyl βγ-diphenylbutane-ααδδ-tetracarboxylate, m. p. 163—164° and 167—168°, respectively, which are separated from one another by boiling ether. The variety of lower m. p. is converted by sodium methoxide in the presence of well-cooled xylene and toluene into the corresponding *sodio*-derivative, which is transformed by bromine into *methyl* 3 : 4-*diphenyl*cyclo*butane*-1 : 1 : 2 : 2-*tetracarboxylate*, m. p. 148°. The ester can be completely hydrolysed only with great difficulty. The regulated action of alkali hydroxides converts it into the corresponding *dimethyl dihydrogen* ester, m. p. 203—205° (decomp.), which loses carbon dioxide above its m. p. and yields methyl ζ-truxinate, m. p. 238°. Formation of diphenyl*cyclo*butanedicarboxylic acids by combination of two molecules (from benzylidene chloride and β-phenylpropane-ααγγ-tetracarboxylic ester or stilbene dibromide and disodioethanetetracarboxylic ester with subsequent hydrolysis and elimination of carbon dioxide) does not appear possible. H. WREN.

Catalysis at reduced pressures. M. GRIGNARD (Bull. Soc. chim. Belg., 1928, **37**, 41—62).—A series of catalytic hydrogenations of organic substances at low pressures is described, using nickel, copper, platinum-black, and platinum oxide as catalysts, with pumice as a supporting material. It is possible, by adjusting the pressure and temperature, to stop catalytic hydrogenations at the first stage, and to eliminate all secondary changes. In this way ethylenic alcohols such as the methylheptenols are quantitatively converted into the corresponding saturated hydrocarbons. Phenol is reduced to *cyclo*hexenol, acid chlorides to the corresponding aldehydes, and benzaldehyde to benzyl alcohol. The reduction of nitriles can be stopped at the aldimine stage. Benzonitrile gave benzaldimine, b. p. 64°/10 mm., d^{13} 1·009, n_D^{2} 1·5275; hydrochloride, m. p. 203—204°. The hydrochloride on exposure to air hydrolyses to benzaldehyde. Phenylacetonitrile is completely reduced at 200°/220 mm. to *phenylacetaldimine*, b. p. 213—214°/750 mm., n_D^{14} 1·5402 (*hydrochloride*, m. p. 180°). Under certain conditions, phenylacetonitrile is partly hydrogenated to a crystalline solid of m. p. 128—130°, which appears to have the constitution $CH_2Ph\cdot CH(N{:}CH\cdot CH_2Ph)_2$. F. J. WILKINS.

Electrolytic reduction of aldehydes. II. *m*-Nitrobenzaldehyde. G. SHIMA (Mem. Coll. Sci. Kyoto, **11**, [*A*], 1—10).—The effect of variations in current density, temperature, and acidity on the reduction of *m*-nitrobenzaldehyde to *m*-aminobenzyl alcohol has been studied. In aqueous alcohol containing 10% of sulphuric acid a yield of more than 90% is obtained using 5 amp./dm.², with a lead cathode at 25—35°. With a copper cathode, reduction soon ceases and the product contains mainly the hydrobenzoin, $[NH_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CH(OH)\cdot]_2$, with small quantities of *m*-azoxybenzaldehyde and *m*-aminobenzyl alcohol (cf. Gattermann, A., 1897, i, 189; Lob, A., 1898, i, 654). H. E. F. NOTTON.

New general synthetic method for the preparation of arylaliphatic aldehydes. L. BERT (Compt. rend., 1928, **186**, 699—700).—Magnesium aralkyl chlorides (cf. this vol., 279) readily condense with methyl or ethyl orthoformate by the method of Bodroux (A., 1904, i, 250) to yield the acetals of the aldehydes of the type $R\cdot C_6H_4\cdot[CH_2]_n\cdot CHO$, the free aldehydes being readily obtained by hydrolysis of the acetals with boiling dilute hydrochloric acid for 10—15 min. Numerous aldehydes have thus been prepared, the following of which are new: p-*ethyl*-, b. p. 198°/13 mm., d_4^{5} 1·009, n_D^{5} 1·537 (*semicarbazone*, m. p. 175°); 1 : 3-*dimethyl*-, b. p. 136°/35 mm., d_4^{15} 0·996, n_D^{15} 1·529 (*semicarbazone*, m. p. 164°); and 1 : 4-*dimethyl*-, b. p. 105—106°/12 mm., d_4^{5} 1·004, n_D^{5} 1·531 (*semicarbazone*, m .p. 183°), *-phenylacetaldehydes*; β-o-*tolyl*-, b. p. 120°/13 mm., $d_4^{19.5}$ 0·998, $n_D^{19.5}$ 1·522 (*semicarbazone*, m. p. 153°); β-p-*tolyl*-, b. p. 122°/15 mm., d_4^{14} 0·999, n_D^{14} 1·525 (*semicarbazone*, m. p. 174°); β-m-*xylyl*-4-, b. p. 135—136°/14 mm., d_4^{16} 0·994, n_D^{16} 1·525 (*semicarbazone*, m. p. 188°); β-p-*xylyl*-2-, b. p. 133—134°/13 mm., $d_4^{18.5}$ 0·985, $n^{18.5}$ 1·523 (*semicarbazone*, m. p. 182°); p-iso*propylphenyl*-, b. p. 136°/16 mm. (*semicarbazone*, m. p. 158°); 2-*methyl*-5-iso*propylphenyl*-, b.p. 150°/17 mm., d_4^{17} 0·974, $^{17}_{D}$ 1·518 (*semicarbazone*, m. p. 149°), *-propaldehydes*: δ-p-*tolyl*-, b. p. 124°/16 mm., d^{11} 1·011, n^{11} 1·527 (*semicarbazone*, m. p. 124°); δ-m-*xylyl*-4-, b. p. 137—138°/13 mm., d_4^{10} 1·001, n_D^{10} 1·529 (*semicarbazone*, m. p. 135°); δ-p-*xylyl*-2-, b. p. 139°/16 mm., d_4^{12} 0·987, n_D^{12} 1·532 (*semicarbazone*, m. p. 184°); δ-p-iso*propylphenyl*-, b. p. 132°/12 mm. (*semicarbazone*, m. p. 144°), *-butaldehydes*. J. W. BAKER.

Dehydration of *cyclo*heptanone pinacol. M. GODCHOT and G. CAUQUIL (Compt. rend., 1928, **186**, 767—769).—*cyclo*Heptanone pinacol, when heated at 125° in the presence of 50% aqueous oxalic acid or 20% sulphuric acid, is converted into cyclo*heptane*-spirocyclo-*octan-2-one*, m. p. 72° [corresponding *alcohol*, m. p. 41° (*phenylcarbamate*, m. p. 156°)], and $\Delta^{1:1'}$-*di*cyclo*heptene*, b. p. 149—150°/19 mm., d^{19} 0·9736, n_D^{19} 1·526, which may be oxidised to pimelic acid with potassium permanganate. The *spiro*-ketone, which does not yield an oxime or a semicarbazone, is oxidised by nitric acid (*d* 1·40) to 1-*carboxy*cyclo*hexyl*-ε-n-*hexoic acid*, m. p. 116° (chief product; *disilver* salt described), and *cyclo*heptane-1 : 1-dicarboxylic acid (Haworth and Perkin, J.C.S., 1894, **65**, 599). G. A. C. GOUGH.

2-Aminofluorenone. A. ECKERT and E. LANGECKER (J. pr. Chem., 1928, [ii], **118**, 263—281).—The substance regarded by Diels (A., 1902, i, 758) as 1-nitro-2-aminofluorene is shown to be the 3-nitro-derivative as follows: the crude nitration product of 2-acetamidofluorene is oxidised by sodium dichromate and acetic acid to a mixture of nitroacetamido-fluorenones from which is obtained, by hydrolysis and extraction with dilute hydrochloric acid, 7-*nitro*-2-*aminofluorenone* (I), m. p. 279° (indef.) (*acetyl* derivative, m. p. above 300°), whilst the less basic residue contains 3-*nitro*-2-*aminofluorenone* (II), m. p. 269° (*acetyl* derivative, m. p. 245—246°). This yields on deamination 3-nitrofluorenone (Schmidt, A., 1908,

i, 996), reduced by sodium sulphide to 3-*amino-fluorenone*, m. p. 158—159° (*acetyl* derivative, m. p. 215°), from which 3-hydroxyfluorenone is obtained by diazotisation and boiling. The nitroamine (II) is reduced by sodium sulphide to 2 : 3-*diaminofluorenone*, m. p. 186—187°, which yields with butane-βγ-dione a *quinoxaline*, $C_{17}H_{12}ON_2$, m. p. 209°. 2-Acetamido-fluorenone yields on nitration a mixture of the acetyl derivatives of (I) and (II); 2-*urethanofluorenone*, m. p. 167—168°, yields 3-*nitro*-2-*urethanofluorenone*, m. p. 204°, and a *dinitro*-derivative, m. p. 256—257°; 2-*benzamidofluorenone*, m. p. 237—238°, yields a 3-*nitro*-derivative, m. p. 218—220°, and 2-amino-fluorenone yields almost entirely the 7-nitro-derivative (I). 1-Nitro-derivatives were not obtained. (I) is converted by diazotisation and boiling into 7-*nitro*-2-*hydroxyfluorenone*, m. p. 298—299°, the *methyl ether*, m. p. 248·5—249·5°, of which is reduced by sodium sulphide to 7-*amino*-2-*methoxyfluorenone*, m. p. 195—196° (*acetyl* derivative, m. p. 236—237°). 2 : 7-Di-aminofluorene has m. p. above 300°. 2-Aminofluorene affords in glacial acetic acid a *tribromo*-derivative, m. p. 198°, which is oxidised by nitrosodimethylaniline and sodium ethoxide to *tribromo*-2-*aminofluorenone*, m. p. 279°. This gives a diazonium salt, stable towards boiling water, but converted by boiling alcohol into a *tribromofluorenone*, m. p. 267—268° (not identical with 2 : (?)6 : 7-tribromofluorenone, Schmidt, A., 1906, i, 28), which is not attacked by alcoholic sodium methoxide, and by boiling alkali into a (?)*dibromo-hydroxyfluorenone*, m. p. 303°. Tribromination of 2-hydroxyfluorene yields an impure *product*, m. p. about 130°, converted by methyl sulphate and alkali into *tribromo*-2-*methoxyfluorene*, m. p. 188°, and a little *dibromo*-2-*methoxyfluorene*, m. p. 121°. The tribromo-derivative is oxidised by chromic acid to *tribromo*-2-*methoxyfluorenone*, m. p. 265—266°, which is hydrolysed by sulphuric acid to *tribromo*-2-*hydroxyfluorenone*, m. p. 273°. 2-Methoxyfluorene affords a slightly impure *nitro*-derivative, m. p. 217°, oxidised to a nitro-2-*methoxyfluorenone*, m. p. 212—218°. This is reduced by sodium sulphide to *amino*-2-*methoxyfluorenone*, m. p. 146—147°, which yields a mixture of yellow, m. p. 236°, and red, m. p. 233°, *acetyl* derivatives. The last three products are thus probably mixtures of isomerides. Attempts to prepare 2-hydroxy-3-nitrofluorenone from (II) by the diazo reaction were unsuccessful.

H. E. F. NOTTON.

Condensation of methyl *iso*butyl ketone with benzaldehyde. C. V. GHEORGHIU and B. ARVENTIEV (J. pr. Chem., 1928, [iii], **118**, 295—302).—Unlike the methyl *n*-alkyl ketones (cf. Harries and Bromberger, A., 1902, i, 792; Scholtz, A., 1910, i, 561), methyl *iso*butyl ketone yields with benzaldehyde the same condensation product, *styryl* iso*butyl ketone*, b. p. 173—180°/13 mm., $d_4^{18.1}$ 0·9781, n_D^{18} 1·5570 (*dibromide*, m. p. 101°; phototropic *semicarbazone*, m. p. 167°) (isomeric *by-product*, m. p. 197°), in presence of either hydrogen chloride or aqueous sodium hydroxide. The constitution of the ketone is confirmed by its oxidation with permanganate to benzoic and *iso*valeric acids, and by the conversion of its liquid *oxime* (*by-product* of oximation, m. p. 141—142°) by nitrous acid into the γδ-*dioxime peroxide*, m. p. 182°, of α-oximino-γδ-diketo-α-phenyl-ε-methylhexane (cf. Harries and Tietz, A., 1904, i, 427).

H. E. F. NOTTON.

Ethylenic isomerism of the phenyl β-*p*-tolyl-styryl ketones. M. BADOCHE (Bull. Soc. chim., 1928, [iv], **43**, 337—343).—The preparation of *phenyl* β-p-*tolylstyryl ketone* (I) by isomerisation of phenyl-*p*-tolyl-β-phenylacetylenylcarbinol or by elimination of hydrogen bromide from α-bromo-β-phenyl-β-*p*-tolylpropiophenone (II) affords essentially the same mixture of *isomerides*, m. p. 109·5—110·5° and 85—86°, the latter being the labile form. On exposure to sunlight or on treatment with hot alcoholic hydrochloric acid the labile form undergoes almost complete conversion into the isomeride, m. p. 109·5—110·5°; the reverse transformation takes place only to the extent of about 10% when the stable form is heated with iodine in a sealed tube at 120—130°. These observations are only consistent with the theory that the labile isomeride is first produced if a further assumption is made, either that the transformation is incomplete in the preparation or that under these conditions the equilibrium is displaced in favour of the labile form. *Phenyl*-p-*tolyl*-β-*phenyl-acetylenylcarbinol*, b. p. 205°/0·7 mm., obtained in 97% yield from magnesium ethyl bromide, phenyl-acetylene, and phenyl *p*-tolyl ketone in ether, isomerises when treated with alcoholic sulphuric acid to (I); the stable isomeride separates on crystallisation from alcohol, the labile form is isolated by Dufraisse's method (A., 1922, i, 534). The ketone (II), m. p. 134—135°, obtained in 91% yield from magnesium *p*-tolyl bromide and bromobenzylideneacetophenone, when treated with quinoline at 185—190° or with pyridine at 130—140° affords the same mixture of isomerides. Either cold or boiling alcoholic potassium hydroxide or sodium ethoxide, or alcoholic potassium acetate eliminates hydrogen bromide but (I) is not formed.

R. BRIGHTMAN.

Action of magnesium organo-derivatives on trisubstituted acetonitriles. (MME.) P. RAMART-LUCAS and F. SALMON-LEGAGNEUR (Bull. Soc. chim., 1928, [iv], **43**, 321—329; cf. A., 1927, 246).—The hydrolysis of the ketimine hydrobromides obtained by the action of magnesium phenyl bromide on trisubstituted acetonitriles is most readily effected with sodium acetate in acetic acid solution. With diphenyl-benzylacetonitrile in xylene, magnesium phenyl bromide scarcely reacts, a small quantity of a *substance*, $C_{17}H_{12}O$ (crude), m. p. 153—154°, being obtained. Magnesium benzyl chloride (3—5 mols.) affords ααβ-triphenylethane in 70% yield, together with dibenzyl, no ketimine derivative being produced. Triphenyl-acetonitrile behaves similarly, and in view of the complete absence of phenylacetonitrile or dibenzyl ketone, the fission of the nitriles is represented: $CR_3{\cdot}CN + CH_2Ph{\cdot}Mg{\cdot}Cl \longrightarrow CR_3{\cdot}C{\cdot}MgCl + (CH_2Ph)_2 + Mg{\cdot}Cl{\cdot}CN$, the mechanism being attributed to the formation of an unstable complex between the magnesium derivative, ether, and ketone in which several atoms are linked by "semivalencies" (cf. Perrin, A., 1927, 1009). Such complexes may yield on dissociation the original products or fresh molecules. The ketimine hydrobromide of phenyl αα-

diphenyl-β-methylpropyl ketone has m. p. 250° (decomp.). R. BRIGHTMAN.

***cyclo*Propane series. XI. *cyclo*Propane derivatives with a tertiary nitro-group attached to the ring.** E. P. KOHLER and P. ALLEN, jun. (J. Amer. Chem. Soc., 1928, **50**, 884—892).—The mechanism of the reaction between bases and *cyclo*propane derivatives previously discussed (A., 1920, i, 59, 61; 1922, i, 457) has been reinvestigated in the case of a tertiary nitro*cyclo*propane. The action of bases on stereoisomeric forms of the compound shows that the same reagent opens the ring at different points. 2-*Nitro*-1-*anisoyl*-2 : 3-*diphenyl*cyclo*propane* (I) is obtained in two isomeric forms, m. p. 187° and 137°. Phenylnitromethane and *p*-methoxyphenyl styryl ketone in presence of sodium methoxide form *γ-nitro-α-anisoyl-βγ-diphenylpropane*, m. p. 164—165° (II). The sodium salt of the latter substance on bromination yielded *γ-bromo-γ-nitro-α-anisoyl-βγ-diphenylpropane*, m. p. 140° (III). Hydrogen bromide was removed by methyl-alcoholic potassium acetate and two forms of (I) were thus obtained. The compound (II) is readily hydrolysed to *β-benzoyl-α-anisoyl-β-phenylethane*, m. p. 155—156° (IV) (*dioxime*, m. p. 180—181°). The ketone (IV) on dissolution in concentrated sulphuric acid yields 2 : 3-*diphenyl*-5-p-*methoxyphenylfuran*, m. p. 94—95° (V). Ozonisation produces no change in either of the isomerides (I). Organic bases or ammonia have no action on the higher-melting isomeride, whilst methyl-alcoholic sodium hydroxide or sodium methoxide produces a sodio-compound which when acidified gives *β-nitro-α-anisoyl-α-benzylidene-β-phenylethane*, m. p. 140° (VI). Decomposition of the ozonide of the latter gives benzaldehyde. A *stereoisomeride* of (VI), m. p. 118°, also yielded benzaldehyde on decomposition of its ozonide. The lower-melting isomeride of (I) is, on the other hand, changed by treatment with alcoholic ammonia, primary and secondary amines, alcoholic sodium hydroxide, and alkoxides, giving rise to an open-chain derivative with loss of nitrous acid. Sodium methoxide yields p-*anisyl γ-methoxy-βγ-diphenylallyl ketone* (VII), m. p. 144—145°, which is very sensitive to acids, yielding either (IV) or (V). The *ethoxy*-derivative corresponding with (VII) has m. p. 89—90°. On ozonising (VII) and decomposing with water, methyl benzoate and *benzoylanisoylmethane*, m. p. 129°, were obtained, the latter being identical with a synthetic product. J. D. FULTON.

New indicators, diveratrylidene and divanillylidene derivatives of *cyclo*hexanone. B. SAMDAHL (J. Pharm. Chim., 1928, [viii], 7, 162—173).—*cyclo*Hexanone and *p*-methyl*cyclo*hexanone condense easily with veratraldehyde, vanillin, and vanillin acetate in the presence of sodium ethoxide or hydrochloric acid. *m*-Methyl*cyclo*hexanone affords similar derivatives less readily. The following compounds are described: *diveratrylidene*cyclo*hexanone*, lemon-yellow, m. p. 149—150°; *diveratrylidene*-p-*methyl*cyclo*hexanone*, m. p. 154—155°; *diveratrylidene*-m-*methyl*cyclo*hexanone*, m. p. 134—135°; *divanillylidene*cyclo*hexanone*, orange, m. p. 179—180° (*acetate*, m. p. 190°); *divanillylidene*-p-*methyl*cyclo*hexanone*, dichroic, orange and yellow, m. p. 169° (*acetate*, m. p. 189°); *divanillylidene*-m-*methyl*cyclo*hexanone*, m. p. 171—172° (*acetate*, m. p. 141—142°). The lemon-yellow form of divanillylidene-*p*-methyl*cyclo*hexanone fluoresces under the action of ultraviolet light, λ 366 μμ, whilst the orange form is unaffected. The divanillylidene*cyclo*hexanones are excellent indicators, changing from greenish-yellow through orange to red when an acid solution is neutralised with alkali. The colour change takes place from p_H 7·8 to 9·4, the change from p_H 8 to 9 being so sensitive that these indicators may be used for measuring p_H in this interval. The indicators are as sensitive as methyl-red and twice as sensitive as methyl-orange or phenolphthalein. S. COFFEY.

Preparation of phenolic ketones by the Hoesch method. A. KORCZYNSKI and A. NOVAKOVSKI (Bull. Soc. chim., 1928, [iv], **43**, 329—337).—Pyrocatechol, quinol, or their ethers do not condense with acetonitrile, benzonitrile, or *p*-chlorobenzonitrile in presence of zinc chloride and hydrogen chloride (Hoesch, A., 1917, i, 342), although resorcinol readily condenses. Anisole and acetonitrile afford a molecular *complex*, $C_9H_{13}ONCl_2$, m. p. 104—112° (decomp.), decomposed by water, alcohol, acetic acid, or chloroform into the original compounds. Diphenyl ether similarly affords only a *substance*, $C_{14}H_{15}ONCl_2$, m. p. 124—126° (decomp.), and negative results were also obtained in both cases in benzene at 80°, amyl alcohol at 100°, and with *p*-bromobenzonitrile. These results agree with the observation that with dihydric or trihydric phenols negatively substituted nitriles give higher yields of phenolic ketones than the unsubstituted nitriles (cf. Houben, A., 1927, 143, 1078). Substitution of a hydroxyl group in the quinol molecule induces condensation in the *ortho*- and *para*-positions, and isomerides of maclurin and partly methylated maclurin have been prepared by this method. The following substituted benzophenones are described: 4-*nitro*-2′ : 4′-*dihydroxybenzophenone*, m. p. 200° (*hydrochloride* of corresponding ketimine); 4-*bromo*-2′ : 4′-*dihydroxybenzophenone* (yield 50%), m. p. 164° (*ketimine hydrochloride*); 4-*nitro*-2′ : 4′ : 6′-*trihydroxybenzophenone* (yield 46%), m. p. 244—245°; 4-*chloro*-2′ : 4′ : 5′-*trihydroxybenzophenone* (yield 55%), m. p. 260°; 4-*chloro*-2′ : 3′ : 4′-*trihydroxybenzophenone* (yield 25%), m. p. 157—158°; 2 : 4 : 5 : 3′ : 4′-*pentahydroxybenzophenone*, m. p. 242° (*ketimine sulphate*) (from the diacetate of protocatechuonitrile); 4-*hydroxy*-3′ : 2′ : 4′ : 6′-*tetramethoxybenzophenone*, m. p. 242° (*ketimine hydrochloride* and *sulphate*), and 2 : 4 : 6-*trihydroxy*-2′ : 6′-*dimethoxybenzophenone*, m. p. 216—218°. R. BRIGHTMAN.

Reaction between duroquinone and Grignard reagents. L. I. SMITH and H. M. CRAWFORD (J. Amer. Chem. Soc., 1928, **50**, 869—883).—The nature of the addition of metallic derivatives to duroquinone (tetramethylbenzoquinone) has been investigated by employing a Grignard reagent, as it has the advantage over sodiomalonic esters of adding to carbonyl systems without giving rise to the complicated oxidation reactions of the latter (cf A., 1926, 836). Magnesium phenyl bromide was employed, and, in common with all other Grignard reagents tried, gave rise to oily products amounting to 80% of the reaction mixture. It is

suggested that a mixture of stereoisomeric products is present (cf. A., 1926, 713). The yield and nature of the products, as well as the accompanying colour changes noted, vary with the order of addition of the reagents in ethereal solution and the amounts of reagent employed. Mono- or di-additive products are obtained according to whether excess of duroquinone or Grignard reagent is employed. The metallic derivatives on decomposition with acid yield keto-enol tautomerides, and with acetyl chloride stable acetates are formed. Besides 1 : 2- and 1 : 4-additive products, diphenyl, hydroduroquinone and its diacetate were normally present as by-products. From equivalent quantities of the reagents were obtained : *1-phenyl-2 : 3 : 5 : 6-tetramethyl-*$\Delta^{2:5}$*-*cyclo*hexadien-1-ol-4-one*, m. p. 203°, which does not react with semicarbazide, phenylhydrazine, or methyl sulphate; *3-phenyl-2 : 3 : 5 : 6-tetramethyl-*$\Delta^{1:5}$*-*cyclo*hexadien-1-ol-4-one*, m. p. 150°, mol. wt. 264, 245 (*acetate*, m. p. 140°; *methyl ether*, m. p. 115°; molecular *compound* with duroquinone, m. p. 95°, and the tautomeride), *3-phenyl-2 : 3 : 5 : 6-tetramethyl-*Δ^{5}*-*cyclo*hexene-1 : 4-dione* (I), m. p. 142°. With semicarbazide the last gives an isomeric *compound*, m. p. 62°, also obtained on attempting methylation. Oxidation with permanganate in acetone, or ozonisation followed by decomposition with water gave an acid, m. p. 170—172°, regarded as α-phenyl-αβ-dimethylsuccinic acid, whilst acetophenone was also recognised. A molecular *compound* of duroquinone with a monophenyl product had m. p. 135°. Using excess of Grignard reagent a diphenyl *compound*, $C_{22}H_{24}O_2$, obviously a mixture, m. p. 115—197°, was obtained (*bromo*-derivative, m. p. 163—164°) which on acetylation gave *3 : 6-diphenyl-2 : 3 : 5 : 6-tetramethyl-*$\Delta^{1:4}$*-*cyclo*hexadiene-1 : 4-diol diacetate*, m. p. 245°, also obtained by further treatment of (I) with Grignard reagent and acetylation. J. D. FULTON.

Sclareol, the principal constituent of essence of sage (*Salvia sclarea*). Y. VOLMAR and A. JERMSTAD (Compt. rend., 1928, **186**, 783—785; cf. B., 1928, 284).—Sclareol, $C_{54}H_{63}O_3$, b. p. 182°/1 mm., $[\alpha]_D^{20}$ −6·12° (in alcohol), is probably an unsaturated tertiary alcohol of the cholesterol group; it gives a red colour with a solution of trichloroacetic acid in chloroform, or with concentrated sulphuric acid, and a green colour with a mixture of the latter reagent and acetic anhydride. There is no evidence that it contains alkoxyl, keto-, or phenolic groups. Whilst very inert towards most reagents, it is oxidised by an acetone solution of potassium permanganate to a neutral *substance*, $C_{17}H_{30}O_2$, m. p. 97°, which rapidly changes to a resin, and *sclareolic acid*, $C_{18}H_{35}O_2\cdot CO_2H$, m. p. 160·5° (*silver* salt described), which possesses a blue fluorescence in solutions in organic solvents. Oxidation of sclareol with chromic acid yields a neutral *substance*, $C_{18}H_{30}O_2$, m. p. 125°. G. A. C. GOUGH.

Catalytic hydrogenation of carotin. L. ZECHMEISTER, L. VON CHOLNOKY, and V. VRABELY (Ber., 1928, **61**, [*B*], 566—568).—Carotin, $C_{40}H_{56}$, readily absorbs eleven mols. of hydrogen when dissolved in *cyclo*hexane or ether in the presence of spongy platinum, yielding *perhydrocarotin*, $C_{40}H_{78}$. The wax-like product, m. p. about 40°, slowly separates from ethereal solution in colourless needles, m. p. 65° (corr.). The hydrogenated compound is stable towards halogen. Carotin must hence have mainly an aliphatic structure. Decolorisation of carotin occurs before hydrogenation is complete. H. WREN.

Refractive and dispersive power of santonin and of some of its isomerides and derivatives. I. Santonin, parasantonide, and α- and β-metasantonin. G. BANCHI (Gazzetta, 1928, **58**, 77—95).—Largely a summary of the work that has been done on refractivity of organic substances and its application to the structure of molecules. The various formulæ proposed for santonin are discussed. The refractive indices and densities of solutions of santonin and of its derivatives mentioned above in chloroform have been determined. It is stated that the results agree best with the structural formulæ for santonin put forward by Francesconi and by Angelo and Marini. O. J. WALKER.

Membranes of spores and pollen. I. *Lycopodium clavatum*, L. F. ZETSCHE and K. HUGGLER (Annalen, 1928, **461**, 89—108).—Extraction of *Lycopodium clavatum* spores with acetic acid does not remove hydrocaffeic acid or albumins (cf. A., 1927, 767); these are removed, however, by a subsequent extraction with hydrochloric acid or alkali. Alternatively, they may be removed in one stage by extraction with alkali. The membrane remaining (25% of the original spores) contains no lignin, and when treated with diacetylorthonitric acid gives pure cellulose (about 2% of the crude spores). By boiling the crude spores with 5% alkali and extracting with alcohol and water (both boiling) a residue corresponding with 23—25% of the spores is obtained. This after prolonged digestion with hydrochloric acid, followed by boiling with 5% alkali, affords a new brownish-yellow substance, *sporonin*, $(C_{10}H_{16}O_3)_x$. This appears to be a chemical individual, since the reactions which can be effected with it are reproducible with great exactness. Sporonin contains 1·26% OMe and forms about 21% of the crude spores. It is insoluble in all common solvents, contains neither carbonyl nor carboxyl groups, and is very stable towards mineral acids, alkalis, and heat, beginning to decompose first at 300°. When heated in glycerol with potassium hydroxide, it affords *anhydrosporonin*, $C_{90}H_{132}O_{31}$. Bromine converts sporonin in cold carbon tetrachloride into *bromosporonin* I, whilst free bromine gives *bromosporonin* II. These, unlike sporonin, are not readily attacked by nitric acid. Bromosporonin I is converted by cold alkali into *bromosporonin* III, the latter being brominated in carbon tetrachloride to *bromosporonin* IV. Hydrogen peroxide oxidises sporonin in glacial acetic acid solution to *oxidosporonin*, $C_{90}H_{111}O_{31}$, or $C_{90}H_{148}O_{31}$. Boiling acetic anhydride converts sporonin into a *compound* containing 13% Ac, which, however, on hydrolysis gives a *substance* other than sporonin. Methyl sulphate and alkali transform sporonin into a *substance* containing 2·2% OMe. E. E. TURNER.

Pectin substances. III—VII. K. SMOLEŃSKI and W. WŁOSTOWSKA (Rocz. Chem., 1927, **7**, 591—692).—III. The composition of beetroot pectin is given, and of a number of galacturonides and arabans,

extracted by various methods from pectin. These substances contain various proportions of protein, hexuronic acids, galactoside and galacturonide groups, araban, galactan, methoxy- and acetoxy-groups, and mineral matter, the galactan fraction of the extract rising as more energetic methods of extraction are applied.

IV. On acid hydrolysis of galacturonides and araban, the acetic acid is first eliminated, then methyl alcohol, then araban and galactan, and finally galacturonide groups. Very energetic hydrolysis yields a strongly-reducing *polymeride* of *galacturonic anhydride*, $(C_6H_8O_6)_n$, $[\alpha]_D$ +216°, insoluble in 75% alcohol, not possessing acetoxy- and methoxy-groups, free from galactan, and containing more than 90% of galacturonic acid. Among the products of hydrolysis were found galactose and arabinose, the latter originating mainly from arabans, which part from their arabinose groups far more readily than do galacturonides.

V. Alkaline hydrolysis eliminates acetic acid and methyl alcohol, yielding sodium pectinate, containing galacturonic acid, araban, and galactan in the same proportions as the original galacturonide. Sodium pectinate, on acidification, loses its araban and galactan groups; thus warming for 4 hrs. with sulphuric acid yields *polygalacturonic acid*, $(C_6H_8O_6)_n$, $[\alpha]_D$ +250° (*methyl* ester, $[\alpha]_D$ +228°), containing more than 90% of galacturonic acid, and free from galactan. This differs from the above-mentioned polymeride of galacturonic anhydride in its smaller solubility in water, in not reducing Fehling's solution, and in optical rotation.

VI. From the final products of the hydrolysis of galacturonides and araban, *α-galacturonic acid hydrate*, $C_6H_{10}O_7,H_2O$, m. p. 110—112°, $[\alpha]_D$ +49·9°, was isolated. This has a reducing power of 80% of that of galactose, and on oxidation with nitric acid yields 85% of the quantity of mucic acid given by galactose. Further hydrolytic products are acetic acid amounting to 11·5% of simple and 5—5·5% of compound galacturonide, methyl alcohol, in quantity corresponding with 5% of compound and 7% of simple galacturonide, a small quantity of glyoxylic acid, *d*-galactose, and *l*-arabinose, the last-named being the sole product of the acid hydrolysis of arabans. Dextrose and glycuronic acid are not found.

VII. The following are the probable constituents of beet pectin: *arabano-galactano-galacturonide*, a polymeride of the calcium magnesium salt of the monomethyl ester of arabo-galacto-acetyldigalacturonic acid, $(C_{26}H_{38}O_{22})_n$; *araban*-a, $(C_5H_8O_4)_n$, easily disintegrated by acid hydrolysis; *araban*-b, difficultly hydrolysed by acids; a degradation product of the first-mentioned substance; simple *galacturonide*, which is a polymeride of the calcium magnesium salt of the methyl ester of acetyldigalacturonic acid, $(C_{15}H_{10}O_{13})_n$, and finally galactan, $(C_6H_{10}O_5)_n$. Alkaline hydrolysis of the arabano-galactano-galacturonide yields pectinic acid, $\{[C_5H_7O_4\cdot CO_2H]_2\cdot(C_6H_{10}O_5)\cdot(C_5H_8O_4)\}_n$, a polymeride of arabo-galacto-digalacturonic acid, $(C_{23}H_{34}O_{21})_n$, whilst alkaline hydrolysis of the simpler galacturonide or acid hydrolysis of pectinic acids yields polygalacturonic acid, a polymeride of digalacturonic acid, $[(C_5H_7O_4\cdot CO_2H)_2]_n$, or $(C_{12}H_{16}O_{12})_n$.

R. TRUSZKOWSKI.

Oxidation of reactive methylene groups. W. TREIBS and H. SCHMIDT (Ber., 1928, **61**, [*B*], 459—465).—Hydrocarbons containing an ethylenic linking in the ring are oxidised by a solution of chromium trioxide in acetic anhydride (carbon tetrachloride or other suitable diluent may be employed if required) mainly with production of unsaturated alcohols and ketones, the methylene group vicinal to the double linking being attacked. In spite of the use of an excess of the reagent, a portion of the hydrocarbon remains unattacked, whilst another portion suffers further oxidation. Thus, α-pinene yields verbenol and verbenone, whilst carveol and carvone are obtained from dipentene. *cyclo*Hexene affords *cyclo*hexenol and an unsaturated ketone. 1 : 2 : 3 : 4-Tetrahydronaphthalene yields 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene and the corresponding alcohol. Terpineol gives an unsaturated glycol, $C_{10}H_{18}O_2$, b. p. about 165°/20 mm. With terpenes containing a hemicyclic double linking, oxidation mainly attacks the linking itself. Thus sabinene and sabinol yield cuminaldehyde, *iso*propyl*cyclo*hexenone, and cymene. Camphene affords camphenilone, camphenilanaldehyde, and camphenilanic acid. Similarly, fenchocamphorone, fenchenilanaldehyde, and fenchenilanic acid are obtained from α-fenchene. β-Pinene gives a saturated acid, $C_{10}H_{16}O_2$, and an aldehyde. Δ^{α}-Octene gives octoic acid, (?) a ketonic aldehyde, $C_8H_{14}O_2$, and unsaturated alcohols. α-Phellandrene affords cuminaldehyde, unsaturated alcohols, $C_{10}H_{16}O$, and cymene. The products from sabinene, camphene, and fenchene are similar to those obtained by autoxidation.

H. WREN.

Reimer–Tiemann reaction in the alicyclic series. O. FERNANDEZ (Anal. Fis. Quím., 1928, **26**, 33—39).—If substances of the type of menthol are first treated with sodium, a reaction takes place with chloroform or bromoform in the cold in presence of powdered caustic alkali. Carbon monoxide is evolved on warming, and this is thought to be evidence of the initial formation of an unstable aldehyde. The final products of the reactions are halogenated compounds considered to be dichloro- or dibromo-methyl ethers. Menthol yielded (?) *dichloromethyl menthyl ether*, b. p. 128°/14 mm., unsaponifiable by alkali, and not reduced by zinc and acid. Borneol and terpineols yielded impure products apparently containing small amounts of similar compounds. Benzoylacetone yielded only benzoic acid under the conditions of reaction. Allyl alcohol yielded *dibromomethyl allyl ether*, b. p. 90—110°/15 mm.

R. K. CALLOW.

Constitution of Indian turpentine from *Pinus longifolia*, Roxb. IV. P. P. PILLAY and J. L. SIMONSEN.—See B., 1928, 274.

Genetic relationships in the sylvestrene group. O. ASCHAN (Annalen, 1928, **461**, 1—26, and Svensk Kem. Tidskr., 1927, **39**, 165—178).—Careful fractional distillation of Finnish pine oil, of balsam turpentine oil which had previously been strongly superheated with steam, and of "sulphate" turpentine oil (sulphate-cellulose manufacture) showed the presence of the two terpenes isodiprene and pinonene. The former has d_4^{20} 0·8561, $[\alpha]_D^{20}$ +5·37°, and n_D 1·47536 and is apparently identical with Simonsen's Δ^3-carene (J.C.S., 1920,

117, 570; 1925, 127, 2494), whilst the latter is apparently Δ^4-carene (Simonsen, *loc. cit.*) (oxidation gives pinonic acid). The pinonene was converted into a monohydrochloride, b. p. 75—80°/11 mm. (affording sylvestrene when boiled with aniline), and dipentene dihydrochloride. Similarly, the isodiprene, b. p. 167—170°, gave a monohydrochloride, b. p. 80—85°/10 mm. (converted by boiling aniline into sylvestrene), together with dipentene dihydrochloride. The nitrosate of isodiprene has m. p. (taken rapidly) 146° (cf. Simonsen, *loc. cit.*, 1920).

[With I. Krohn.]—Diprene, prepared by Aschan (A., 1924, i, 1212) from isoprene, gives a dihydrochloride (m. p. now given as 52·5°), which is identified as that of sylvestrene and (1) is convertible into a terpin, m. p. 127°, identical with Baeyer's terpin from carvestrene, and (2) is converted by a boiling acetic acid solution of potassium acetate into carvestrene. Repetition of Baeyer's original synthesis of carvestrene from carone showed that Baeyer's crude carvestrene was a mixture, from which a definite substance, re-named carveprene, b. p. 183—186°, has been isolated. Carveprene gives the same *dihydrobromide*, m. p. 48—49°, as diprene, so that diprene also is a *meta*-cymene derivative.

The author concludes (cf. Simonsen, 1925) that sylvestrene is formed as a result of the treatment to which turpentine oils are submitted and is not necessarily an original constituent of the natural oil. The matters referred to in the title are discussed briefly. E. E. Turner.

Products of the addition of chlorine and bromine to pinene and their de-chlorination. I. L. Kondakov (Ber., 1928, 61, [*B*], 479—481; cf. A., 1905, i, 798).—A theoretical comment on the work of Aschan (this vol., 296). H. Wren.

Campherol. T. Asahina and M. Ishidate (Ber., 1928, 61, [*B*], 533—536).—Campherol, m. p. 216—217°, $[\alpha]_{D}^{17}$ +38·9° in ethyl alcohol, present as the glycuronic acid derivative in the urine of dogs to which camphor has been administered and isolated therefrom by hydrolysis with hydrochloric or sulphuric acid, is reduced by sodium amalgam and water to camphor in satisfactory yield, but when oxidised with nitric acid gives only small amounts of camphoric acid. The camphorquinone derived from it by treatment with dichromate in glacial acetic acid is a mixture of isomerides, one of which affords camphoric acid when oxidised with hydrogen peroxide in alkaline solution, whereas the other remains intact and is identified as 5-ketocamphor. Campherol is therefore a mixture of 3- and 5-hydroxycamphor (cf. Magnus-Levy, A., 1907, i, 228). H. Wren.

Reaction of caryophyllene. D. T. Gibson (J.C.S., 1928, 750—751).—When caryophyllene is treated with a solution of ethyl diazoacetate in caryophyllene in presence of finely-divided copper at 180—200°, there is formed a *cyclo*propane ester (cf. Deussen, this vol. 70), hydrolysed by alcoholic potassium hydroxide to the corresponding *acid*, $C_{16}H_{25}\cdot CO_2H$, m. p. 165°, $[\alpha]_{5461}$ −40° in alcohol. The presence of caryophyllene in supa oil (B., 1927, 172) is demonstrated by this reaction. H. Burton.

Cyclic derivatives of acetonedicarboxylic acid. II. J. Litynski and R. Małachowski (Rocz. Chem., 1927, 7, 579—584).—Methylation of 4 : 6-dihydroxy-α-pyrone by means of diazomethane yields 4 : 6-*dimethoxy-α-pyrone*, m. p. 105·5—106°, which on heating with methyl alcohol yields *dimethyl β-methoxyglutaconate*, b. p. 138°/18 mm. The monomethyl derivative was obtained as follows: 6-hydroxy-4-acetoxy-α-pyrone yielded on methylation 6-*methoxy-4-acetoxy-α-pyrone*, m. p. 66—67°, which on hydrolysis gave 4-*hydroxy-6-methoxy-α-pyrone*, m. p. 146—147·5°. R. Truszkowski.

Behaviour of dixanthylene when heated. A. Schönberg and O. Schütz (Ber., 1928, 61, [*B*], 478—479).—Dixanthylene is colourless at the temperature of liquid air, pale yellow with a greenish tinge at the ordinary temperature, and green at 280°. It melts to a dark greenish-blue liquid. Its behaviour is thus analogous to that of dianthrone. Wizinger's hypothesis (A., 1927, 764) that the behaviour of the latter substance is dependent on the presence of the carbonyl group is therefore doubtful. H. Wren.

Absorption spectra of fluorescein, fluoran, and related compounds. W. R. Orndorff, R. C. Gibbs, and C. V. Shapiro (J. Amer. Chem. Soc., 1928, 50, 819—828; cf. A., 1926, 884).—The red and yellow forms of fluorescein (A., 1927, 671) have identical absorption spectra in neutral alcoholic solution. Both forms are quinonoid, since their absorption curves differ entirely from those of lactonoid compounds such as fluoran, 3:6-dichlorofluoran, and fluorescein diacetate, the absorption curves of which resemble one another. The absorption spectra of fluorescein in 75% formic acid, 93% sulphuric acid, and in an alcoholic solution of hydrogen chloride are all very similar, probably owing to salt formation in each case. In alcoholic solution with 1 mol. of potassium hydroxide the absorption is similar to that in neutral solution, but excess of reagent causes a marked change in absorption, owing to formation of the dipotassium salt. In 33% aqueous potassium hydroxide fluorescein gives an orange solution which changes to purple and finally to pink on long keeping. The absorption alters during these colour changes (cf. Baeyer, A., 1910, i, 249), which are attributed to (i) opening of pyrone ring, (ii) possible production of carbinol followed by further disruption. A. McGookin.

***l*-Hydroxyproline and *l*-proline.** J. Kapfhammer and R. Eck (Z. physiol. Chem., 1927, 170, 294—312).—*l*-Hydroxyproline and *l*-proline are precipitated by Reinecke's salt (cf. Terada, this vol., 542) from hydrolysed gelatin solution from which arginine has been removed as flavianate. The precipitated salts are shaken with warm copper sulphate solution through which sulphur dioxide is passed and the cuprous "Reineckate" is removed by filtration. The filtrate, after being freed from thiocyanate and chromium, is evaporated to dryness in a vacuum; *l*-proline is extracted with absolute alcohol, leaving *l*-hydroxyproline undissolved. From 200 g. of gelatin are thus obtained 172 g. of mixed Reineckates," giving 7·5 g. of pure *l*-proline, $[\alpha]^{20}$ −84·9° (in water), −95·2° (in alkali), −54·5° (in hydrochloric acid) [picrate, m. p. 152—154°; "Reineckate"

$C_5H_9O_2N,C_4H_7N_6S_4Cr$, m. p. 199° (decomp.)], and 14 g. of *l*-hydroxyproline, $[\alpha]_D^{20}$ −80·6° (in water) [hydrochloride, decomp. above 190°; *picrate*, m. p. 188°; "Reineckate," m. p. 248° (decomp.)].

l-Proline, unlike *l*-hydroxyproline, in alcoholic solution gives, with cadmium chloride, a precipitate of a double *compound*, $C_5H_9O_2N,CdCl_2,H_2O$; the copper salt, $C_{10}H_{16}O_4N_2Cu$, p-*toluenesulphonyl* derivative, m. p. 130—133°, and 2 : 4-*dinitrophenyl* derivative, m. p. 136°, are also described. The preparation of Reinecke's salt, $NH_4[Cr(SCN)_4(NH_3)_2]$, is detailed. C. HOLLINS.

Condensation of pyruvic acid with amines and aldehydes. II. S. WEIL and (MLLE.) F. GOLDBERG (Rocz. Chem., 1927, 7, 585—590).—Prolonged boiling in alcoholic solution of a mixture of pyruvic acid, ethyl *p*-aminobenzoate, and benzaldehyde yields 4-p-*carbethoxyphenylimino*-2-*phenyl*-1-p-*carbethoxyphenyl*-5-*ketopyrrolidine*, m. p. 203—204°, together with some 2-phenyl-1-*p*-carbethoxyphenyl-4 : 5-diketopyrrolidine, which also yields the above product on condensation with ethyl *p*-aminobenzoate. By varying the aldehyde used in the above reaction, the following products were obtained: with vanillin, 4-p-*carboxyethylphenylimino*-2-(3-*methoxy*-4-*hydroxyphenyl*)-1-p-*carbethoxyphenyl*-5-*ketopyrrolidine*, m. p. 159°; with piperonal, the corresponding 2-(3′ : 4′-*methylenedioxyphenyl*) derivative, m. p. 219°, together with the *diketo*-derivative, m. p. 156—157°; with salicylaldehyde, the corresponding 2-o-*hydroxyphenyl* derivative, m. p. 219°, and with *p*-dimethylaminobenzaldehyde the corresponding 2-p-*dimethylaminophenyl* derivative, m. p. 176°. R. TRUSZKOWSKI.

Action of αζ-di-iodo-*n*-hexane on amines. A. MULLER and E. ROLZ (Ber., 1928, 61, [*B*], 570—574).—αζ-Di-iodo-*n*-hexane, b. p. 141—142°/10 mm., is prepared in 73% yield by the action of red phosphorus and iodine on *n*-hexane-αζ-diol, obtained by reduction of methyl adipate with sodium and alcohol. It is converted by methylamine into *N*-methylhexamethyleneimine, identified by direct comparison of the methiodides, m. p. 265° (corr.; slight decomp.), and the corresponding chloroplatinate, m. p. 233° (corr.; decomp.), with those of the products derived from αζ-dibromo-*n*-hexane and *p*-toluenesulphonamide (Muller and Sauerwald, this vol., 43). Von Braun's conception of the product as a derivative of α-pipecoline therefore requires correction. *NN*-Dimethyl-α-pipecolinium chloroplatinate decomposes at 246° instead of at 222°, as recorded by von Braun (A., 1920, i, 821). Ring contraction therefore does not occur during the action of αζ-di-iodo-*n*-hexane on methylamine. Similarly, αζ-di-iodo-*n*-hexane and piperidine afford hexamethylenepiperidinium iodide, $[CH_2]_6>NI<[CH_2]_5$, m. p. 273° (corr.; slight decomp.), the constitution of which if confirmed by its formation from hexamethyleneimine and αε-di-iodo-*n*-pentane. On the other hand, αε-di-iodo-*n*-pentane and α-pipecoline afford 2-*methylpentamethylenepiperidinium iodide*, m. p. 268°. H. WREN.

Oxidation of *N*-benzoylhexamethyleneimine. A. MULLER [with H. CLOSTERMEYER] (Ber., 1928, 61, [*B*], 568—570).—*N*-Benzoylhexamethyleneimine is oxidised by potassium permanganate in water at 50° to ε-benzamido-*n*-hexoic acid, m. p. 80—81° (corr.), in 44% yield, thus confirming the constitution assigned to the base (this vol., 43). H. WREN.

Manufacture of isatins and *N*-arylsulphonyl derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1928, 224.

Stereoisomerism in polycyclic systems. IV. Two stereoisomerides of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene. W. H. PERKIN, jun., and S. G. P. PLANT (J.C.S., 1928, 639—646; cf. this vol., 72).—Elimination of carbon dioxide from 2 : 3-dihydroquinindene-12-carboxylic acid, m. p. 297° (decomp.) (lit. 277—278°), yields 2 : 3-dihydroquinindene, which is reduced by tin and hydrochloric acid in aqueous-alcoholic solution, giving a mixture of the two stereoisomeric 2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindenes* (A), m. p. 67° [*acetyl* derivative, m. p. 102°; *benzoyl* derivative, m. p. 174°; *picrate*, m. p. 193° (decomp.)], and (B), an oil, b. p. 284°/762 mm. (*acetyl* derivative, m. p. 87°; *benzoyl* derivative, m. p. 161°; *picrate*, m. p. 158°). The proportion of (A) to (B) is about 1 to 3. When 2 : 3-dihydroquinindene is reduced electrolytically, the proportion of (A) to (B) is about 1 to 12. No conclusive evidence as to which is the *cis*- and which the *trans*-isomeride is available. The existence of the two modifications can be accounted for by the Sachse–Mohr theory of multiplanar rings. The influence of the strain conditions existing in the two molecules on their relative amounts of formation is considered. The experimental results are in accordance with the deductions which can be drawn from the space-models. M. CLARK.

Preparation of pyridine derivatives [iododichlorides] etc. DEUTS. GOLD- U. SILBER-SCHEIDEANSTALT.—See B., 1928, 244.

Action of ethoxyacetyl chloride on magnesyl pyrroles. A. SANNA and G. CHESSA (Gazzetta, 1928, 58, 121—127).—Magnesium 2-pyrryl iodide reacts in ether with ethoxyacetyl chloride to give 2-*ethoxyacetylpyrrole*, b. p. 173°/10 mm. (*phenylhydrazone*, m. p. 163°); 3-magnesium 2-methylindolyl iodide similarly yields 3-*ethoxyacetyl*-2-*methylindole*, m. p. 157° (*phenylhydrazone*, m. p. 90°), and magnesium carbazyl iodide yields N-*ethoxyacetylcarbazole*, m. p. 70°. E. W. WIGNALL.

Compound of *d*-alanyl-*l*-tryptophan with *d*-alanyl-*l*-tryptophan anhydride. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1927, 171, 93—100).—During the preparation of *d*-alanyl-*l*-tryptophan by warming *d*-bromopropionyl-*l*-tryptophan with ammonia, a *substance* was isolated which appears to be the compound, 1 dipeptide +1 anhydride, decolorising at 270°, m. p., after sintering, 280°. It contains no free amino-group. It has a mol. wt. corresponding with the double molecule. A mixture of molecular equivalents of the dipeptide and the anhydride gives an absorption in the ultra-violet very similar to, but not quite identical with that of the compound. The optical rotatory power of the mixture is also slightly different from that of the compound. By boiling in methyl-alcoholic solution the compound is quantitatively transformed into the anhydride. H. D. KAY.

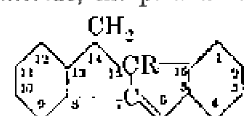
Preparation of quinoline derivatives. I. G. FARBENIND.—See B., 1928, 244.

Quinoline derivatives. VII. 4-Amino-2-phenylquinoline derivatives. H. JOHN [with E. WUNSCHE] (J. pr. Chem., 1928, [ii], **118**, 303—313).—The following derivatives of 2-phenylquinoline have been obtained by condensing 4-chloro-2-phenylquinoline (Wenzel, A., 1895, i, 70) with the appropriate amine in a sealed tube at the temperature given in parentheses: 4-*diisoamylamino*- (150—160°), m. p. 61°; 4-*anilino*- (180—200°), m. p. 182° (*picrate*, m. p. 233—234°); 4-p-*toluidino*- (200—210°), m. p. 173° (*ethiodide*, m. p. 219°); 4-m-4′-*xylidino*- (200—210°), m. p. 151° (*picrate*, m. p. 237°); 4-ψ-*cumidino*- (180—200°), m. p. 188°; 4-α-*naphthylamino*- (170—210°), m. p. 177—178° (*picrate*, m. p. 246°); 4-β-*naphthylamino*- (180—200°), m. p. 185° (*picrate*, m. p. 219°), and 4-*benzylamino*- (180—190°), m. p. 147° (*picrate*, m. p. 241°). The chloro-derivative gives with *o*- (230°) and *p*- (180—200°) anisidines, *substances*, m. p. 279° and 183°, respectively; with 4-amino-2-phenylquinoline hydrochloride (240°), *di-2-phenyl-4-quinolylamine*, m. p. 253·5°, and with hydrazine (150—160°), *2-phenyl-4-quinolylhydrazine*, m. p. 143° (*acetyl* derivative, m. p. 184—185°), from which *benzaldehyde-2-phenyl-4-quinolylhydrazone*, m. p. 151°, sintering from 100° (*picrate*, m. p. 256°), and *acetophenone-2-phenyl-4-quinolylhydrazone*, m. p. 195—196° (*picrate*, m. p. 112°), are prepared. The *hydrochlorides*, *sulphates*, *mercurichlorides*, *chromates*, *ferrocyanides*, and *periodides* of the above bases are described. H. E. F. NOTTON.

Tautomerism in the pyridine series. Diphenylpyridylmethane and its derivatives. A. E. TSCHITSCHIBABIN and S. W. BENEVOLENSKAJA (Ber., 1928, **61**, [*B*], 547—555).—Phenyl 2-pyridyl ketone is converted by magnesium phenyl bromide in ethereal solution into *diphenyl-2-pyridylcarbinol*, m. p. 105° [*chloroplatinate* (+2H_2O); *picrate*, m. p. 173° (decomp.)], which is reduced by hydriodic acid in glacial acetic acid to *diphenyl-2-pyridylmethane*, m. p. 63° [*chloroplatinate*, m. p. 182° (decomp.); *picrate*, m. p. 172°]. *Diphenyl-2-pyridylmethane methiodide*, m. p. 222—224°, is transformed by concentrated alkali hydroxide into *1-methylpyrid-2-onediphenylmethide*, dark reddish-violet needles, m. p. 147°, soluble in water to a strongly alkaline solution; the presence of the phenyl groups facilitates the production of the pyridonemethide and enhances its stability. *Diphenyl-4-pyridylcarbinol*, m. p. 235° [*chloroplatinate*, m. p. 203°; *picrate*, m. p. 101—103° (decomp.), prepared analogously from phenyl 4-pyridyl ketone, differs in an unexplained manner from the compound, m. p. 203°, described previously. Both carbinols are stable towards air and potassium permanganate, so that the possibility that the phenyl groups in one of them have suffered oxidation (by air) with production of a fluorene derivative appears excluded. The carbinol, m. p. 235°, is reduced to *diphenyl-4-pyridylmethane*, m. p. 125° (*chloroplatinate*, m. p. 201° after darkening; *picrate*, m. p. 172°), whereas that of m. p. 203° affords *diphenyl-4-pyridylmethane*, m. p. 111—112°. *Diphenyl-4-pyridylmethane methiodide*, m. p. 159—161° (from the base, m. p. 125°), is converted into *1-methylpyrid-4-onediphenylmethide*, m. p. 113°. H. WREN.

Dyes derived from quinoline-2 : 3 : 4-tricarboxylic acid. J. D. TEWARI and S. DUTT (J. Indian Chem. Soc., 1928, **5**, 59—62; see also A., 1927, 969, 1006).—Quinoline-2 : 3 : 4-tricarboxylic acid condenses with phenols either alone or in the presence of stannic chloride or sulphuric acid to give the following dyes of the phthalein type: *phenol*-, m. p. above 280°; *resorcinol*-, m. p. 194° (yellowish-green fluorescence); *phloroglucinol*-, m. p. above 280°; *pyrogallol*-, m. p. above 280°; m-*diethylaminophenol*- m. p. 220° (brown fluorescence); m-*phenylenediamine-quinoline-2 : 3 : 4-tricarboxylein*, m. p. above 280° (green fluorescence). The dyes are probably produced by condensation of the phenol with the oxygen atom of the 3-carbon in the intermediate anhydride. G. A. C. GOUGH.

New transformations of indolenines [indeno-ψ-indolines] and indolinols [dihydroindenoindolines]. H. LEUCHS [with D. PHILPOTT, P. SANDER, A. HELLER, and H. KOHLER] (Annalen, 1928, **461**, 27—46).—2-Ethyl-1-hydrindone affords a phenylhydrazone which is converted by boiling alcoholic zinc chloride into the *zincichloride*, $(C_{17}H_{15}N)_2,ZnCl_2$, of 15-*ethylindeno-ψ-indoline* (I; R=Et). The latter has b. p. 202—204°/14 mm., and (+¼H_2O), m. p. 79—80° (efferv. at 150°) [*hydrochloride*, m. p. 124—126° (decomp.); *picrate*, m. p.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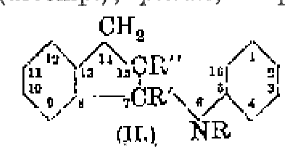
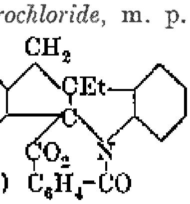

(II.)

173—175°], and is converted by acetic anhydride and sodium acetate at 100° into *7-acetoxy-6-acetyl-15-ethyl-7 : 15-dihydroindenoindoline* (II; R=Ac, R′=OAc, R″=Et), m. p. 125—126°. The latter is transformed (1) by boiling methyl alcohol into *7-methoxy-6-acetyl-15-ethyl-7 : 15-dihydroindenoindoline* (II; R=Ac, R′=OMe, R″=Et), m. p. 105°, (2) by warm hydrochloric–acetic acid into the corresponding 7-*hydroxy*-compound (II; R=Ac, R′=OH, R″=Et), m. p. 159—161°, unaffected by diazomethane or acetic anhydride, and (3) by methyl-alcoholic ammonia at 100° into the corresponding 7-*amino*-compound (II; R=Ac, R′=NH_2, R″=Et), m. p. 138—139°. Benzoic anhydride converts 15-ethylindeno-ψ-indoline into *7-benzoyloxy-6-benzoyl-15-ethyl-7 : 15-dihydroindenoindoline* (as II), m. p. 179—181° when slowly heated. From this compound are obtained, by methods similar to those detailed above, the 7-*methoxy*-6-*benzoyl* compound, m. p. 125—126°, the 7-*hydroxy*-6-*benzoyl* compound, m. p. 145·5—146·5°, and the 7-*amino*-6-*benzoyl* compound, m. p. 130° (*hydrochloride*, m. p. 231—233°). The ethylindeno-ψ-indoline is converted by phthalic anhydride at 160° into the *phthaloyl* compound (III), m. p. 200—201°, which is unaffected by boiling methyl alcohol or by acetic–hydrochloric acid at 100°. Methyl-alcoholic ammonia converts the ethylindeno-ψ-


(III.)

indoline into 7-*amino*-15-*ethyl*-7 : 15-*dihydroindenoindoline* (II; R=H, R'=NH_2, R''=Et), m. p. (+H_2O) 95° (loss of NH_3; sinters at 85°). This substance gives ammonium chloride when treated in chloroform with hydrogen chloride. Reduction of ethylindeno-ψ-indoline affords 15-*ethyl*-7 : 15-*dihydroindenoindoline*, pale green, m. p. 101—102° (*hydrochloride*, decomp. 230—233°; *picrate*, m. p. 115° and 170—172°; 6-*acetyl* derivative, m. p. 128°).

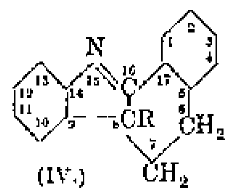
By methods similar to the above, 2-phenyl-1-hydrindone is converted into 15-*phenylindeno*-ψ-*indoline* (I; R=Ph), m. p. 182—183°, sintering at 178° [*hydrate*; *hydrochloride*; *picrate*, m. p. 185—186° (decomp.) or 115°], 7-*acetoxy*-6-*acetyl*-15-*phenyl*-7 : 15-*dihydroindenoindoline*, m. p. 168°, and the corresponding 7-*methoxy*-6-*acetyl* (m. p. 160—161°) and 7-*hydroxy*-6-*acetyl* (m. p. 183—184°) compounds. The phenylindoline combines with ammonia to give 7-*amino*-15-*phenyl*-7 : 15-*dihydroindenoindoline*, m. p. 145° (loss of NH_3), and with phenylhydrazine to give the corresponding 7-*phenylhydrazino*-derivative, m. p. 224—226°, also formed by heating phenylhydrindone with phenylhydrazine at 140—150°.

The compounds obtained previously from 2-benzyl-1-hydrindone (A., 1913, i, 855; 1925, i, 1281) are not derivatives of *lin*-indenoquinoline as formerly supposed, but are strictly analogous to those described above. Thus, the diacetyl compound, $C_{26}H_{23}O_3N$ (1925), is 7-*acetoxy*-6-*acetyl*-15-*benzyl*-7 : 15-*dihydroindenoindoline* (II; R=Ac, R'=OAc, R''=CH_2Ph), convertible into the 7-*amino*-6-*acetyl* compound, m. p., when taken rapidly, 118—120° (sinters and decomp.) (hydrate?) or 147—148°; the amino-compound is accompanied by some 7-*hydroxy*-6-*acetyl*-compound, m. p. 198° (*acetyl* derivative, m. p. 174°). The previously described dibenzoyl compound, $C_{36}H_{27}O_3N$, is converted by methyl-alcoholic ammonia into the 7-*amino*-6-*benzoyl* compound, m. p. 219—220°, which on benzoylation gives the 7-*benzamido*-6-*benzoyl* compound, m. p. 255—258°.

The previously described base, $C_{22}H_{17}N$, *i.e.*, 15-*benzylindeno*-ψ-*indoline* (I; R=CH_2Ph) as it is now identified, forms a *methiodide*, m. p. 165—168° (decomp.), converted by silver carbonate in acetone into 7-*hydroxy*-6-*methyl*-15-*benzyl*-7 : 15-*dihydroindenoindoline*, m. p. 147—148°. The hydrochloride of the $C_{22}H_{17}N$ base reacts (1) with aqueous sodium hydrogen sulphite to give *sodium* 15-*benzyl*-7 : 15-*dihydroindenoindoline*-7-*sulphonate* (II; R=H, R'=SO_3Na, R''=CH_2Ph), m. p. 115—120° (efferv.), and (2) with methyl-alcoholic ammonia to give 7-*amino*-15-*benzyl*-7 : 15-*dihydroindenoindoline*, m. p. 124°, or (+MeOH) 110—115° (efferv.; NH_3 loss), or (from ether or light petroleum) 100—105° (decomp.). Hydrogen chloride or picric acid regenerates the base $C_{22}H_{17}N$ from the amino-compound. The hydrochloride of the base $C_{22}H_{17}N$ is partly converted by hydrazine (100° in methyl alcohol) into the expected 7-*hydrazino*-compound, and when reduced gives 15-*benzyl*-7 : 15-*dihydroindenoindoline*, m. p. 85—86° (*picrate*, m. p. 184°; 6-*acetyl* derivative, m. p. 85—86°, efferv. at 100°), which with diazomethane affords the 6-*methyl* derivative, m. p. 81° (*picrate*, m. p. 166—170°, sintering at 155°).

Ring homologues of some of the above compounds

have been obtained from 1-keto-2-benzyltetrahydronaphthalene. Boiling hydrochloric acid converts the tarry phenylhydrazone of the latter into the *hydrochloride*, m. p. 194—196° (decomp.), of 8-*benzyl*-6 : 7-*dihydro*-αβ-*naphth*-ψ-*indoline* (IV; R=CH_2Ph), m. p. 104—106° [*picrate*, m. p. 180—182° (decomp.)], which is unaffected by phenylhydrazine at 130°, or by acetic or benzoic anhydride, but is reducible to 8-*benzyl*-6 : 7 : 15 : 16-*tetrahydro*-αβ-*naphth*-ψ-*indoline*, m. p. 84—86° (*picrate*, m. p. 179—181°).



(IV.)

Di-β-phenylethylmalonic acid (A., 1924, i, 972) decomposes normally to give *di*-β-*phenylethylacetic acid*, m. p. 49—50°. The *amide*, m. p. 164—165°, of the latter, was obtained during the purification of 1-*keto*-2-β-*phenylethyltetrahydronaphthalene*, b. p. 232—234°/12 mm. (*semicarbazone*, m. p. 166—167°; *phenylhydrazone*, m. p. 98°). This ketone, prepared by the action of phosphorus pentachloride on the acetic acid derivative (cf. this vol., 287), has been converted into 8-β-*phenylethyl*-6 : 7-*dihydro*-αβ-*naphth*-ψ-*indoline*, not obtained pure [*hydrochloride*, m. p. 215—223° (decomp.); *picrate*, m. p. 170—171°], and not reacting with phenylhydrazine or with acetic or benzoic anhydride. E. E. TURNER.

Internally complex salts of the di-indyl- and dipyrryl-methenes. I. Constitution of Kunz's di-indylmethene-copper compound. O. SCHMITZ-DUMONT and E. MOTZKUS (Ber., 1928, **61**, [*B*], 580—586).—Evidence is adduced in favour of the view that the product of the action of copper acetate on 2-methylindolyl-2'-methylindolenemethane (Kunz, A., 1925, i, 1318) is a true copper salt containing univalent metal. It may therefore be regarded as an internally complex salt. The purely additive nature of the other metallic compounds described by Kunz is therefore doubtful. Potassium reacts with 2-methylindolyl-2'-methylindolenemethane in presence of liquid ammonia with evolution of hydrogen and production of the *potassium* derivative, $C_{19}H_{15}N_2K$. When this compound is treated with cuprous bromide or iodide in pyridine or cuprous iodide in ammonia, the copper compound, $C_{19}H_{15}N_2Cu$ (cf. Kunz, *loc. cit.*), is immediately produced. It is also prepared by the use of tetrammine copper nitrate, one half of the base suffering oxidation. The nature of the compound is established by the quantitative regeneration of the methene from it by the protracted action of concentrated formic acid at the atmospheric temperature or by potassium cyanide in aqueous pyridine. The presence of univalent copper in the product derived from tetrammine copper nitrate is placed beyond doubt by the formation of a colourless solution when it is decomposed by hydrochloric acid in an atmosphere of nitrogen and the solution is subsequently rendered ammoniacal. H. WREN.

Optically active hypnotics. C.-M. HSUEH and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 855—859).—Pharmacological tests with the *d*-, *l*-, and *dl*-isomerides of 5-ethyl-5-*sec*.-octylbarbituric acid show that there is practically no difference in their hypnotic action or toxicity. The view that physical properties

are the chief factors in determining hypnotic action is strengthened. The following are mentioned: *d*- and *l*-*sec.*-octyl alcohols, $[\alpha]^{25}$ $\pm 9\cdot 9°$; *dl*-*sec.*-octyl bromide, b. p. 61°/3 mm., 66°/6 mm., 72°/14 mm., d_4^{25} 1·0878, 1·4442; *l*-*sec.*-octyl bromide, b. p. 60°/3 mm., 71°/14 mm., d_4^{25} 1·0982, n^{25} 1·4475, $[\alpha]_D^{25}$ —34·25°; *d*-*sec.*-octyl bromide, $[\alpha]^{25}$ +34·2; *ethyl* dl-*ethyl*-sec.-*octylmalonate*, b. p. 135—140°/3 mm., 137—142°/6 mm., 158—165°/17 mm., 170—175°/27 mm., d_4^{25} 0·9434, n_D^{5} 1·4365; *ethyl* d-*ethyl*-sec.-*octylmalonate*, b. p. 137—138°/3 mm., d_4^{25} 0·9323, n_D^{25} 1·4370, $[\alpha]_D^{25}$ +8·22°; *ethyl* l-*ethyl*-sec.-*octyl malonate*, $[\alpha]_D^{25}$ —8·07°, other constants the same as those of the *d*-isomeride; dl-5-*ethyl*-5-sec.-*octylbarbituric acid*, m. p. 126—127°; d-*acid*, m. p. 107°, $[\alpha]^{25}$ +7·0° in alcohol; l-*acid*, $[\alpha]_D^{25}$ —7·02° in alcohol. J. D. FULTON.

Carbonylbisamino-acids and their transformation products. F. WESSELY and M. JOHN (Z. physiol. Chem., 1927, **170**, 167—182; cf. Wessely and Sigmund, A., 1926, 1235).—The ether-soluble products of the action of pyridine at the ordinary temperature on phenylalanine-*N*-carboxylic anhydride contain two stereoisomeric α-(5-*benzyl*-3-*hydantoin*)-β-*phenylpropionic acids*,

$$CH_2Ph\cdot CH(CO_2H)\cdot N\!<\!\begin{matrix}CO\cdot NH\\ |\\ CO\cdot CH\cdot CH_2Ph\end{matrix} \quad (Ia),$$

p. 234—235°, and (I*b*), m. p. 170° (+1·5H_2O), the yields being 40% and 10%, respectively. By hydrolysis with hot *N*-alkali each of these gives the same two stereoisomeric *carbonylbisphenylalanines*, $CO[NH\cdot CH(CO_2H)\cdot CH_2Ph]_2$ (II*a*), m. p. 211—212° (*ethyl* ester, m. p. 144—145°), and (II*b*), m. p. 185° (*ethyl* ester, m. p. 140°). The acid (II*a*) or its ester is converted by boiling hydrochloric acid into the original hydantoin (I*a*), whilst (II*b*) gives the hydantoin (I*b*). Hydrolysis of each ester yields the stereoisomeric acid. Synthetic carbonylbisphenylalanine ethyl ester, m. p. 129°, obtained by phosgenation of phenylalanine ester, cannot be separated into its constituents (II*a* and *b* esters), but is hydrolysed by alkali to the easily separable acids (II*a*) and (II*b*), from which the individual ethyl esters are obtained by means of diazoethane. From the synthetic ester mixture or the synthetic acids hydantoins identical with (I*a*) and (I*b*) are obtained; the *ethyl* ester of (I*a*) has m. p. 148°. All the above m. p. are corrected.

Glycine-*N*-carboxylic anhydride with pyridine gives in small yield hydantoin-3-acetic acid, m. p. 201°, sublimes at 180°/0·1 mm., also prepared by the action of hydrochloric acid on *carbonylbisglycine*, m. p. 204° (uncorr.; cf. Morel, A., 1906, i, 730, whose product is different), which is obtained by hydrolysis of its ethyl ester. C. HOLLINS.

Synthesis of the polypeptide hydantoin glycyl-3-methylphenylalaninehydantoin. (MISS) D. A. HAHN and (MISS) J. EVANS (J. Amer. Chem. Soc., 1928, **50**, 806—818; cf. A., 1926, 180, 181).—Although two isomerides of 4-benzylidenehydantoin are known (Johnson and Bates, A., 1915, i, 88), the methyl and ethyl esters of the derived 1-acetic acid and its 1 : 3-dimethyl derivative are known only in one form. Ethyl 4-benzylidenehydantoin-1-acetate yields the free acid, m. p. 248—249° (cf. Johnson and Bates, A., 1916, i, 504), which gives the *methyl* ester, m. p. 180·5—181·5°. Methylation of this ester or of the potassium salt of the acid gives two isomeric *methyl 3-methyl-4-benzylidenehydantoin-1-acetates*, m. p. (A) 65·5—66·5°, (B) 98·5—99·5° (the latter, pale yellow). Potassium 4-benzylidenehydantoin-1-acetate gives a potassium derivative which is methylated to *potassium 3-methyl-4-benzylidenehydantoin-1-acetate*, m. p. 255—256° (corresponding *silver* compound, decomp. 235°). The potassium salt yields the free *acid* (C), m. p. 186·5—187·5°. An *isomeride* (D), m. p. 198·5—199·5°, is prepared from (B) by hydrolysis or from (C) by the action of acid. Methylation of (C) with methyl sulphate or methyl iodide gives (A), whilst the use of methyl alcohol yields (B). (A) is converted into (B) by acid. On hydrogenation in presence of palladium, (A) and (B) both give *methyl 3-methyl-4-benzylhydantoin-1-acetate*, m. p. 93—93·5°, whilst the corresponding free *acid*, m. p. 136·5—137·5°, is formed by reduction of (A), (B), (C), or (D) with hydriodic acid. Hydrolysis of 3-methyl-4-benzylhydantoin-1-acetic acid yields α-methylamino-β-phenylpropionic acid and glycine. 4-Benzylidenehydantoin on methylation yields 1 : 3-*dimethyl-4-benzylidenehydantoin*, m. p. 83—84°, which is reduced by hydriodic acid to 1 : 3-*dimethyl-4-benzylhydantoin*, m. p. 86·5—87°. Hydrolysis of the latter gives α-methylamino-β-phenylpropionic acid and methylamine. The stability of hydantoins substituted in the 4-position is decreased by substitution in the 3-position (cf. Wheeler and Hoffman, A., 1911, i, 498; Hahn and Evans, this vol., 74). The absorption spectrum curves of the isomeric 4-benzylidenehydantoins and of the 3-methyl-4-benzylidenehydantoin-1-acetic acids seem to indicate geometrical isomerism. The curves for methyl 4-benzylidenehydantoin-1-acetate and methyl 3-methyl-4-benzylhydantoin-1-acetate are shown. (A) on keeping turns oily with formation of benzaldehyde. In ultraviolet light, (A) and (B) produce small amounts of a solid, m. p. 278°. Under the same conditions (D) yields a substance, m. p. 292°. A. MCGOOKIN.

Production of *iso*naphthyridine and its derivatives. DEUTS. GOLD- U. SILBER-SCHEIDEANSTALT.—See B., 1928, 244.

Production of carbonyldicarbamide by oxidation of uric acid and allantoin, and its metabolism. A. SCHITTENHELM and K. WARNAT (Z. physiol. Chem., 1927, **171**, 174—178).—Uric acid in the presence of dilute ammonia gives on warming with hydrogen peroxide a good yield of carbonyldicarbamide. The latter substance may also be obtained by allowing allantoin, in faintly alkaline solution, to react for several hours with hydrogen peroxide. Carbonyldicarbamide is incompletely oxidised in the body; if administered intravenously either to dogs or to human subjects a large proportion is recoverable unchanged from the urine.

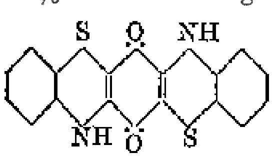
H. D. KAY.

Thiocyanoacetone and derivatives. J. TCHERNIAC (Ber., 1928, **61**, [*B*], 574—579; cf. J.C.S., 1919, **115**, 1071).—A reply to Hantzsch (this vol., 187). The action of hydrochloric acid on thiocyanoacetone has been investigated previously (*loc. cit.*) by the author. The formation of methylrhodim from chloro-

acetone and hydrogen carbonate occurs with 41% yield; the compound is more readily prepared from chloroacetone and ammonium thiocarbamate than by Hantzsch's method (*loc. cit.*). Hantzsch's process for the preparation of thiocyanoacetone gives a product the "appreciable volatility of which at the atmospheric temperature" is due to the presence of more than 20% of volatile impurities. Homogeneous thiocyanoacetone, b. p. 74°/>1 mm., d^{15}_{15} 1·1892, is difficultly volatile when its simple structure is considered. The product of the action of ammonia on thiocyanoacetone is methylrhodim, not aminomethylthiazole. Chloromethylrhodim (Hantzsch's 5-chloro-4-methylthiazol-2-one), after purification from light petroleum, forms colourless crystals, m. p. 149°. The considerations on which the author's formula for methylrhodim are based are discussed in detail.

H. WREN.

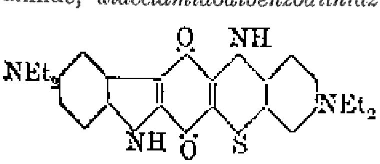
Dibenzodithiazinequinones, vat dyes. R. SHIBATA (Tech. Rep. Tôhoku Imp. Univ., 1928, 7, 53—71, and J. Soc. Chem. Ind. Japan, 1927, 30, 438—445; cf. *ibid.*, 1925, 28, 156, 892).—*o*-Aminothiophenol condenses with *p*-benzoquinone in boiling 80% acetic acid to give *dibenzodithiazinequinone* (I).



(I.)

2 : 5-Dichloro-3 : 6-dianilino-*p*-benzoquinone is converted by sodium sulphide into the *disodium* derivative of the corresponding 2 : 5-dithiol. The disodium derivative is converted by methyl sulphate into 2 : 5-*dianilino*-3 : 6-*di-methylthiol*-p-*benzoquinone*, m. p. 238—239°, and by dilute acid into the free dithiol, which is oxidised by boiling nitrobenzene to (I). Nitric and acetic acids oxidise (I) to a *sulphoxide*, $C_{18}H_{10}O_4N_2S_2$ (*sodium* derivative), reduced by sodium hydroxide and hyposulphite to (I). Fusion of 2 : 5-dianilino-*p*-benzoquinone with sulphur (205—210°, sealed tube) also affords (I).

From 2 : 5-*dichloro*-3 : 6-*di*-p-*toluidino*-p-*benzoquinone* (prepared from chloranil and *p*-toluidine), *dimethyldibenzodithiazinequinone* was obtained, and from *p*-amino-dimethyl- and -diethyl-aniline *di-dimethylamino-* and *di-diethylamino-dibenzodithiazinequinone* (all as I). Similarly, from *p*-aminoacetanilide, *diacetamidodibenzodithiazinequinone* was obtained, and this was hydrolysed with indifferent success to the *di-amino*-derivative of (I). In the synthesis of the tetraethyldiamino-derivative a by-product was isolated, regarded as (II). This, and all of the thiazines now described, may be used as vat dyes.



(II.)

E. E. TURNER.

from the Chinese drug "Kuh-seng." T KONDÔ (Arch. Pharm., 1928, 266, 1—19).—This paper is a re-publication, with many additions and corrections (?), of work already described (A., 1921, i, 882; 1922, i, 269). "Kuh-seng" is the dried root of *Sophora flavescens*, Ait., and is called in Japanese "Kurara" or "Matorigusa." It forms an important constituent of the Japanese remedy "Shinkyogan." Matrine is isolated in four polymorphic forms, viz., α-form, needles or prisms, m. p. 76°; β-form, rhombs, m. p. 87°; γ-form, a liquid, b. p. 223°/6 mm., d^{35}_4 1·088, $n^{35.4}_D$ 1·52865; δ-form, prisms, m. p. 84°. A petroleum solution of the β-form yields at 22—24° the α- and δ-forms, whilst at 10° a solution of the α-form yields the β-form. The γ-form represents the freshly redistilled base, and is converted into the β-form on keeping. Matrine has $[\alpha]^{10}_D$ +39·11°. The *dichromate*, *chloroaurate* (m. p. 199°), *chloroplatinate* (decomp. 249°), and (mono)*methiodide* (m. p. 211°) are described. When matrinic acid hydrochloride is distilled with zinc dust (A., 1921, i, 882, states that matrine hydrochloride itself was so distilled) it yields the *base*, b. p. 87°/20 mm., the formula of which should be $C_{10}H_{19}N$, not $C_{10}H_9N$, together with matridine, $C_{15}H_{26}N_2$. When *potassium matrinate*, $C_{15}H_{25}O_2N_2K$, m. p. 239°, is treated with ammonium chloride, matrinic acid (*loc. cit.*), decomp. 222°, $[\alpha]^{18}_D$ +19·87° (*chloroaurate*, m. p. 181°; *chloroplatinate*, decomp. 245°; *carbonate*, m. p. 216°; *sodium* salt, m. p. 201°), is obtained. Matrinic acid is dehydrated, reproducing matrine, when treated with acetic anhydride or benzoyl chloride, or when attempts are made to esterify it, but when potassium matrinate is treated with methyl iodide the *methiodide* of *methyl* N-*methylmatrinate*, m. p. 217—219°, is obtained. The corresponding *methochloride*, *mercurichloride* (m. p. 126°), *chloroplatinate* (decomp. 250°), and *chloroaurate* (m. p. 178°) are described. At 100° the tertiary nitrogen atom takes up another equivalent of methyl iodide, giving an unstable *dimethiodide*, m. p. 145—146°. When the hydroxide corresponding with the monomethiodide is heated under diminished pressure it decomposes into methyl alcohol and *methyl* N-*methylmatrinate*, b. p. 210—212°/10 mm., $[\alpha]^{18}_D$ −21·23°. The base eventually obtained by reducing matrine (*loc. cit.*) is here named *bismatridine*. When potassium matrinate is distilled with soda-lime it yields pyrrole-like *compounds*, $C_{11}H_{15}N$, b. p. 59—65°/13 mm., $C_{12}H_{15}N$, b. p. 95—105°/3 mm., and others of higher b. p. All these are insoluble in potassium dihydrogen phosphate, together with a small quantity of a *hydrocarbon*, m. p. 64°. From that portion of the distillate which dissolved in potassium dihydrogen phosphate there were eventually isolated by fractionation three bases, viz., in the fraction of highest b. p. matrine, *α-matridine*, and *β-matridine*. α-Matridine, $C_{12}H_{20}N_2$, is an unstable oil, b. p. 132—134°/6 mm., $[\alpha]^{18}$ −18·75°, d^{15} 1·025, 1·5283. The *picrate* (decomp. 288°), *chloroplatinate* (decomp. 289°), and *methiodide* are described. It is a secondary–tertiary base. On acylation the equivalent of 1 mol. of water is taken up; thus *acetyl-α-matridine*, m. p. 160°, has the composition $C_{12}H_{19}N(OH)\cdot NHAc$. The analogous *benzoyl* derivative has m. p. 153°, and a *derivative* is also obtained by interaction with phenylcarbimide. β-Matrinidine, $C_{13}H_{20}N_2$, is likewise an oil, b. p. 174—176°/6 mm., $[\alpha]^{18}_D$ +1·63°, d^{30} 1·100, n^{30}_D 1·56205 (*picrate*, m. p. 184°; *chloroplatinate*, decomp. 214°; *chloroaurate*, m. p. 106°). This also is a secondary–tertiary base and a (mono)*methiodide* is described. Matrine and both α- and β-matridines all yield 1 mol. of methyl iodide when subjected to the action of hydriodic acid under H. Meyer's conditions, but the action, like

that with sparteine, is slow, and it is doubtful whether methylimino-groups are really present.

Matrine being a lactam, it might be expected to undergo ring scission, like other acylamido-compounds, when treated with phosphorus pentachloride, but actually it yields two new compounds, as follows: *matrine monochloride*, $C_{15}H_{22}ONCl$ (decomp. 240—242°), the *chloroplatinate* of which decomposes in solution to give succinic acid, and a *compound*, $(C_{10}H_{18}NCl)_2H_2PtCl_6$, decomp. 309°. The corresponding *base* is obtained as an oil when matrine monochloride is oxidised by dilute potassium permanganate solution, succinic acid being also formed. *Matrine dichloride*, $C_{15}H_{24}ON_2Cl_2$, m. p. 146° (*chloroaurate*, decomp. 224—225°), yields on treatment with cold potassium hydroxide a *base*, $C_{15}H_{24}O_2N_2$, which is reduced by sodium amalgam and acetic acid to matrine, and with hot potassium hydroxide gives another *base*, $C_{14}H_{25}O_2N$. Matrine is considered to contain at least a pyrrolidine ring, but beyond that no conclusions are reached regarding its constitution.

W. A. SILVESTER.

Microchemical reactions of atropine. M. WAGENAAR (Pharm. Weekblad, 1928, 65, 197—201).—The properties and microchemical reactions of the alkaloid are reviewed. The most suitable reagents are bromine in potassium bromide, and iodine in potassium iodide; the periodide formed with the latter is especially characteristic.

S. I. LEVY.

Amino-oxides of alkaloids. V. *N*-Oxides of ψ-tropine and of tropacocaine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1928, [iv], 43, 364—367; cf. this vol., 310).—Tropacocaine, m. p. 49°, when treated with hydrogen peroxide in acetone gives an -*oxide*, $C_{15}H_{19}O_3N$, m. p. 152—153° (*hydrochloride*, m. p. 200°), which on reduction with sulphur dioxide or nascent hydrogen yields the original base, and on hydrolysis with concentrated hydrochloric acid the N-*oxide* of ψ-tropine, m. p. 229° [*hydrochloride*, m. p. 286°; *picrate*, m. p. 257° (decomp.)]. With acetic anhydride the *N*-oxide of tropacocaine yields O-*benzoyl*-N-*acetylnor*-ψ-*tropine*, hydrolysed by *N*-alcoholic potassium hydroxide to N-*acetylnor*-ψ-*tropine*, m. p. 127°, or by 20% sulphuric acid or concentrated potassium hydroxide to nor-ψ-tropine. The latter is also obtained by hydrolysis of the *diacetylnor*-ψ-*tropine* formed when the *N*-oxide of ψ-tropine is similarly treated with acetic anhydride.

R. BRIGHTMAN.

Alkaloid in spurious Angostura bark. J. TROGER (Pharm. Zentr., 1928, 69, 209—217).—A new *alkaloid* extracted from a bark purporting to be *Cusparia trifoliata*, Engler, but of which the true character is unknown, has m. p. 167°, but gives no crystalline derivatives save a *perchlorate* and *methiodide*. The analyses, not concordant, indicate a formula $C_{21}H_{26}O_3N_2$ (mol. wt. found, 352·5) which is also that of yohimbine and quebrachine. The alkaloid dissolves in alkali or in acid. Its individuality follows from its recovery from the well-crystallised and characteristic perchlorate.

S. I. LEVY.

Aporphine alkaloids. I. Synthesis of 5:6-dimethoxyaporphine. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 581—591; cf. A., 1925, i, 576).—*o*-Nitrophenylacetyl chloride condenses with β-veratrylethylamine, giving 2′-*nitrophenylaceto*-β-3:4-*dimethoxyphenylethylamide*, m. p. 112°, converted by the action of phosphorus pentachloride on a cold chloroform solution into 2′-*nitro*-6:7-*dimethoxy*-1-*benzyl*-3:4-*dihydro*iso*quinoline* (I), m. p. 132° [*hydrochloride*, m. p. 228° (decomp.)]. The base (I) yields a *methiodide* (II), m. p. 208°, decomposed by alkaline fission into *o*-nitrotoluene and 6:7-dimethoxy-2-methyl-3:4-dihydro*iso*quinolone. Reduction of the methiodide (II) with zinc dust and very dilute sulphuric acid gives 2-(4′:5′-*dimethoxy*-2′-β-*methylaminoethyl*)*phenylindole* (III), m. p. 132° (*monohydrochloride*; *monoacetyl* derivative, m. p. 138°). Treatment of the compound (III) with nitrous acid yields a *substance*, m. p. 178°, regarded as 2-(4′:5′-*dimethoxy*-2′-β-*methylaminoethyl*)*phenyl*-3-*oximinoindole*. Reduction of the methiodide (II) with zinc dust and hydrochloric acid in strongly acid solution gives 2′-*amino*-6:7-*dimethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline* (IV), an oil [*dihydrochloride*, m. p. 243—244° (decomp.); *monoacetyl* derivative, m. p. 153—154°], together with a small quantity of an isomeric oily *base* [*dihydrochloride*, m. p. 186° (decomp.); *nitrosoamine*] regarded as 2-(4′:5′-*dimethoxy*-2′-β-*methylaminoethyl*)*phenyldihydroindole*. The base (IV), after diazotisation and treatment with copper powder, gives a poor yield of 5:6-*dimethoxyaporphine*, m. p. 136—137° [*hydrochloride*, m. p. 258° (decomp.); *methiodide*, m. p. 223°].

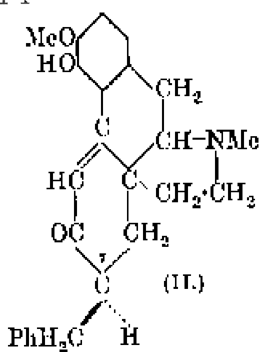
M. CLARK.

Determination of strychnine as silicotungstate. E. STUBER and B. KLJATSCHKINA (Arch. Pharm., 1928, 266, 33—38).—Azadian's method (A., 1914, ii, 307) of determining the alkaloids in nux vomica is trustworthy, but his conversion factor (ratio of the weight of the ash to that of the alkaloid in the precipitate) is too high. His figure (0·498) does not agree with that calculated from Bertrand's formula for the salt, and it is now shown that strychnine silicotungstate has no simple molecular composition. The composition, however, is constant, no matter whether the precipitation is carried out in a weakly or strongly acid solution, hot or cold, etc. The precipitate is almost insoluble in water or dilute nitric acid. From the many experimental results the conversion factor 0·422 is obtained.

W. A. SILVESTER.

Condensation of certain aldehydes with ketones of the morphine group. J. M. GULLAND (J.C.S., 1928, 702—706).—A solution of dianhydro-6-aminopiperonaldihydrohydroxycodeinone (A., 1926, 83) in concentrated sulphuric acid shows no fluorescence, thus differing from the simpler methylenedioxyquinolines and from dianhydro-6-aminopiperonalthebainone (J.C.S., 1923, 123, 998). This anomalous behaviour might be considered to weaken the evidence in favour of the fact that dihydrohydroxycodeinone contains a $-CO·CH_2-$ grouping, but it is now shown that dihydrocodeinone, which undoubtedly contains this grouping, condenses with 6-aminopiperonal yielding *dianhydro*-6-*aminopiperonaldihydrocodeinone*, m. p. 270—271·5° (*methiodide*, decomp. 260°), which exhibits no fluorescence in concentrated sulphuric acid. The presence of one reactive methylene group in phenolic ketones of the morphine series is readily

demonstrated by preparation of crystalline benzylidene derivatives, but attempts to show the presence of a second methylene group by condensation with 6-aminopiperonal were unsuccessful. The following are described: *benzylidenehydroxydihydrothebainone*, m. p. 188°; benzylidenethebainone (I), m. p. 233° [methiodide, m. p. 195—197° (decomp.)]; piperonylidenethebainone, m. p. 176°. Catalytic reduction of compound (I) by palladous chloride solution yields a mixture of two *benzylthebainones*, (II), (A), m. p. 229° (*semicarbazone*, m. p. 155—160°), and (B), m. p. 179° (*semicarbazone*, m. p. 140—145°; *oxime*, m. p. 152°), presumably stereoisomeric about carbon atom 7. These substances are isomeric with but different from *benzylidenethebainol*, m. p. 100—102°, obtained by condensation of benzaldehyde and thebainol.



M. CLARK.

Colour reactions of morphine. L. EKKERT (Pharm. Zentr., 1928, **69**, 198—199).—The colorations obtained when traces of morphine and related alkaloids are treated in concentrated sulphuric acid solution with hydrogen peroxide are described.

S. I. LEVY.

Hydroferro- and hydroferri-cyanides of the alkaloids. II. W. M. CUMMING and D. G. BROWN (J.S.C.I., 1928, **47**, 84—86T).—A continuation of previous work (cf. A., 1925, i, 572). The hydroferro- and hydroferri-cyanides of the following are described: sparteine, cinchonidine, hydrastine, nicotine, pilocarpine, piperine, narceine, ecgonine, codeine, and morphine. Ecgonine, narceine, and codeine are decomposed by potassium ferricyanide in acid and in neutral solution; in alcoholic solution, hydroferricyanic acid gives precipitates which decompose almost immediately. A table is given showing the constitutions of the salts and their percentage iron content. A method for the preparation and determination of hydroferrocyanic acid is included.

Phenoxy- and tolyloxy-, especially *m*-tolyloxy-derivatives of phosphorus trichloride and thiophosphoryl chloride. W. BROEKER (J. pr. Chem., 1928, [ii], **118**, 287—294).—Dichloro-*o*-tolyloxyphosphine has b. p. 106°/11 mm.; chlorodi-*o*-tolyloxyphosphine, b. p. 190°/11 mm., and tri-*o*-tolyloxyphosphine, b. p. 238°/11 mm. (cf. Strecker and Grossmann, A., 1916, i, 442). *m*-Cresol and phosphorus trichloride give a mixture, separable by fractionation, of *dichloro*-m-*tolyloxyphosphine*, b. p. 114°/12 mm.; *chlorodi*-m-*tolyloxyphosphine*, b. p. 198°/11 mm., and *tri*-m-*tolyloxyphosphine*, b. p. 248—250°/12 mm. (cf. Michaelis, A., 1898, i, 417). These are converted by sulphur at the temperature given in parentheses into *dichloro*-m-*tolyloxyphosphine sulphide* (200°), b. p. 138°/12 mm.; *chlorodi*-m-*tolyloxyphosphine sulphide* (175°), m. p. 33—34°, b. p. 218°/11 mm., and *tri*-m-*tolyloxyphosphine sulphide* (190°), m. p. 40—41°, b. p. 270—272°/12 mm., respectively.

H. E. F. NOTTON.

Manufacture of crystallised arsenobenzenes. A. ALBERT.—See B., 1928, 244.

Antimony. II. Derivatives of tri-*p*-tolylstibine. A. E. GODDARD and V. E. YARSLEY (J.C.S., 1928, 719—723).—When tritolylstibine dihalides are heated under reduced pressure, a halogenotoluene distils off, leaving the ditolylhalogenostibine (cf. A., 1926, 508). The following are described: *di*-p-*tolylchlorostibine*, *di*-p-*tolylbromostibine*, m. p. above 290°, and *di*-p-*tolyliodostibine*, m. p. 233°. When tri-*p*-tolylstibine is heated in an atmosphere of carbon dioxide in methyl alcohol saturated with hydrogen chloride, a very small quantity of *di*-p-*tolylstibinic acid*, sintering at 230°, m. p. 260°, is obtained (cf. Schmidt, A., 1922, i, 1204). When tri-*p*-tolylstibine is treated in hot acetone solution with 5*N*-sodium hydroxide and 3% hydrogen peroxide solution, di-*p*-tolylstibinic acid and *di*-p-*tolylstibine trichloride*, sintering at 130°, m. p. 141—142°, are obtained (cf. Schmidt, *loc. cit.*). Tri-*p*-tolylstibine, on treatment with cold fuming nitric acid, gives *tri*-m-*nitrotri*-p-*tolylstibine dinitrate*, m. p. 182° (decomp.). Hydrolysis of the dinitrate by a large excess of phosphorous acid gives *tri*-m-*nitrotri*-p-*tolylstibine oxide*, m. p. 225°. Reduction of the dinitrate with zinc dust and ammonia in alcoholic solution gives *tri*-m-*aminotri*-p-*tolylstibine*, m. p. 92°, converted by the Sandmeyer reaction into *tri*-m-*iodotri*-p-*tolylstibine*, sintering at 136°, m. p. 146°.

M. CLARK.

Preparation of organo-mercury compounds [diphenyl series]. F. HEIN and K. WAGLER.—See B., 1928, 244.

Mol. wt. of phycoerythrin and phycocyan. T. SVEDBERG and N. B. LEWIS (J. Amer. Chem. Soc., 1928, **50**, 525—536; cf. following abstract).—Phycoerythrin and phycocyan, proteins of the globulin class, have been prepared from aqueous extracts of *Ceramium rubrum* and the absorption of visible and ultra-violet rays has been determined. The mol. wts. of these proteins in dilute phosphate solutions, determined by the centrifugal sedimentation equilibrium method (cf. Svedberg and Fahraeus, A., 1926, 340; Svedberg, *ibid.*, 677) and the method of sedimentation velocity (Svedberg, A., 1927, 716; Svedberg and Nichols, *ibid.*, 99), are 208,000±8000 for phycoerythrin and 106,000±5000 for phycocyan. Variations in the concentration of the protein or the p_H have no significant influence on the value, and the results obtained with visible and long and short ultra-violet rays are in good agreement. The mol. wts. of these proteins, like that of hæmoglobin, may be regarded as a multiple of that of egg-albumin (34.500±1000). A sample of phycoerythrin, prepared from *Ceramium rubrum* and kept for 17 years under a saturated solution of ammonium sulphate covered with toluene, was found to consist of molecules of mol. wt. 208,000 and about 30% of molecules of one sixth to one eighth this size, but no separation of these substances by recrystallisation was possible.

A. WORMALL.

Chromoproteins of red algæ. I. R. LEMBERG (Annalen, 1928, **461**, 46—89; cf. preceding abstract).—Phycoerythrin and phycocyan have been extracted

from *Ceramium rubrum* and from *nori* (Japan). The former in winter contains about 1·9% of total pigment, of which 15—25% is phycoerythrin. In the spring, the total pigment present is only about 0·9%, of which about 35% is phycoerythrin. *Nori* contains 1·7—2·2% of total pigment, of which 32—50% is phycoerythrin. Incomplete investigations of the similar pigments in *Phyllophora nervosa* and *Rhodomela subfusca* are recorded.

Phycoerythrin is very strongly fluorescent. The effects of alkali, ammonia, zinc chloride, cuprammonium solutions, concentrated sulphuric acid, bromine water, hydrogen peroxide, ammonium sulphide, sulphurous acid, and Molisch's reagent are mentioned. Phycocyan is less fluorescent than phycoerythrin. That from *Ceramium* forms large, rhombic leaflets, showing dichroism in polarised light. That from *nori* has a different crystalline form. The effect of different hydrogen-ion concentrations on aqueous solutions of both pigments has been investigated. Phycoerythrin has an appreciable calcium content, but no other metal could be detected. Scission of phycoerythrin with pepsin in acid solution produces "*phycobitin.*" Solutions of phycoerythrin and phycocyan obey Beer's law. E. E. TURNER.

Basic proteins. A. KOSSEL and W. STAUDT (Z. physiol. Chem., 1927, **171**, 156—173).—A new protamine *alalongine* has been isolated from the sperm of *Tynnus alalonga*. It is very similar to salmine in physical properties and chemical constitution. From the sperm of *Sagenichthys ancylodon* a tyrosine-free protamine, also having properties similar to those of salmine but with a lower arginine content, has been obtained.

The methods of separation and analysis of an α-cyprinine, *leuciscine*, from the sperm of the carp (*Leuciscus nitilus*) are described. It contains 30% of lysine, 14% of arginine, and 3% of histidine. Tables are given of the occurrence and properties of basic proteins in the sperm of various fishes and invertebrates. H. D. KAY.

Effect of boiling in acid solution on hæmateric acid and its iron compound. A. PAPENDIECK (Z. physiol. Chem., 1927, **171**, 85—92).—To esterify hæmin it is necessary to adopt very careful precaution to avoid further change in the molecule. On the other hand, both hæmateric acid and its iron compound may be esterified by boiling with alcohol containing dilute hydrochloric acid for at least an hour. The *ester* produced shows a first absorption band in ethereal solution which is symmetrical about 6325 Å. Towards higher concentrations of alcoholic hydrogen chloride (20%) or of aqueous mineral acids the molecule is less stable, and after boiling for 1 hr. the spectrum of hæmatoporphyrin may be observed in an ethereal extract of the reaction mixture. Hæmatoporphyrin is also produced when a hæmateric acid solution in 25% hydrochloric acid is kept for a year in the dark in a closed vessel, or is exposed, in a thin layer, to sunlight for 2 hrs. H. D. KAY.

Constitution of proteins. III. S. GOLDSCHMIDT (Z. physiol. Chem., 1927, **170**, 183—185; cf. A., 1927, 474).—An error in drawing the curves for the action of alkaline hypobromite on carbonyldiglycylglycine is corrected, and results in agreement with those of Brigl and Held (A., 1926, 630) are obtained which show that this compound is an exception to the general rule that open-chain ·NH·CO· linkings are unattacked by alkaline hypobromite. C. HOLLINS.

Halogenated proteins. IX. Chloro-ovoprotein. A. J. J. VANDEVELDE (Rec. trav. chim., 1928, **47**, 458—463).—When dry ovoprotein is acted on for some months with a solution of chlorine in carbon tetrachloride there is formed *chloro-ovoprotein* (N, 10·06; Cl, 17·5%). When treated with water, aqueous potassium hydroxide, or ethyl alcohol at the ordinary temperature, the major part of the chlorine is removed. Bromo-ovoprotein (A., 1924, i, 678) and chloro-ovoprotein have the same composition.

Chloro-, *bromo-*, and *iodo-caseins* have been prepared (cf. A., 1927, 65) by the direct action of the halogens on casein, and they contain 11·6, 21·3, and 19·8% of halogen, respectively. A chloropeptone (cf. A., 1924, i, 779) could not be obtained. H. BURTON.

Sulphonation of amino-acids and polypeptides. I. P. BAUMGARTEN (Z. physiol. Chem., 1927, **171**, 62—69).—Glycine, cystine, tyrosine, and glycylglycine have been sulphonated by shaking in cold aqueous solution with *N*-pyridiniumsulphonic acid, in presence of potassium carbonate. The following compounds have been isolated: *potassium salt of glycine*-N-*sulphonic acid*, $+1H_2O$, decomp. 150°; *glycine*-N-*sulphonic acid*, from the potassium salt and perchloric acid, decomp. 132°; *compound of* N-*glycylglycinesulphonic acid with glycylglycine*, $+5H_2O$, not removed even after drying over phosphoric oxide in a vacuum at 110°; *compound of* NN'-*cystinedisulphonic acid with cystine*, very hygroscopic powder; *potassium salt of* ON-*tyrosinedisulphonic acid*, very hygroscopic crystalline powder, +1EtOH, retained in a vacuum at 110°. H. D. KAY.

Behaviour of polypeptides and their derivatives towards dilute alkalis or acids. IV. Polypeptides derived from *l*-cystine. E. ABDERHALDEN and W. KOPPEL (Z. physiol. Chem., 1927, **170**, 226—230; cf. A., 1927, 686, 1099).—At 17° and at 37° *N*- and 0·5*N*-alkalis hydrolyse all polypeptides containing glycyl residues (*e.g.*, diglycyl-*l*-cystine), but dileucylcystine is unattacked, and diglycyldi-*dl*-leucyl-*l*-cystine gives glycine and dileucyl-*l*-cystine. *N*-Hydrochloric acid is without action in each case. C. HOLLINS.

Stability of certain polypeptides and diketopiperazines containing serine towards enzymes and reaction changes. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1927, **171**, 78—84).—From glycyl-*dl*-serine, dl-*leucylglycyl*-dl-*serine* has been prepared (m. p. 233°, yield about 50%). The tripeptide is esterified by passing hydrogen chloride into the methyl-alcoholic solution. After keeping the ester for some days in presence of ammonia, dl-*leucyl*(*glycyl*-dl-*serine*) *anhydride* (decomp. 245°) separates, and is purified by dissolving in ethyl alcohol and precipitating with ether. On incubation with trypsin, leucine is removed from this compound. Dilute sodium hydroxide at 37° readily

hydrolyses glycyl-*dl*-serine, the above tripeptide, and the anhydride. H. D. KAY.

Comparative experiments on the fission of silk-peptone and dipeptides with so-called glycine eluates. A. FODOR and R. SHOENFELD (Z. physiol. Chem., 1927, **170**, 231—245, 246; cf. A., 1925, ii, 857; 1926, 866).—The fission both of silk-peptone and of dipeptides by eluates of glycine proceeds best at p_H 8 (Fodor and Epstein, A., 1925, i, 1214), but there is an appreciable difference in the rates of fission, the glycine present having a greater inhibitive effect with dipeptides than with the peptone. Addition of glycine does, in fact, have this effect in the case of leucylglycine and, more markedly, of glycylglycine. The difference is diminished if a second absorbate (kaolin) be introduced. Addition of kaolin or of chloroform fails to bring about conditions under which only peptone fission proceeds. The precipitate obtained by adding chloroform to the glycine eluate has the physico-chemical and chemical properties of a protein. The activities of the eluate towards peptone and dipeptides maintain a constant ratio both when the eluate is kept for 3 weeks under aseptic conditions, and when it is activated by means of chloride ions.

A polemical note against Grassmann (A., 1927, 794) is added. C. HOLLINS.

Natural organic compounds of colloidal character. II. Degree of association and reactivity of gelatin solutions. M. FRANKEL (Z. physiol. Chem., 1927, **170**, 247—263; cf. A., 1927, 726).—De-association of gelatins, *e.g.*, by prolonged gentle heating, does not affect the course of subsequent peptisation, the same end-products being obtained, but the rate of hydrolysis may be greatly accelerated. C. HOLLINS.

Hydrolysis of wool by sodium sulphide. W. KÜSTER, W. KUMPF, and W. KOPPEL (Z. physiol. Chem., 1927, **171**, 114—155).—If wool is shaken with 3% sodium sulphide, part goes readily into solution, and after 125 hrs. it dissolves completely. Ammonia is given off during the process, and both dialysable and undialysable nitrogenous hydrolysis products are formed. The non-dialysable products are partly soluble and partly insoluble in water. The insoluble portion, which becomes more acidic in properties with increasing time of hydrolysis, forms a readily soluble sodium salt. The protein may be precipitated from this with acetic acid. From examination of the hydrolysis product obtained by the action of sodium sulphide it is concluded that wool contains at least two proteins, different in chemical composition. One of these (the more resistant to sulphide hydrolysis) contains only one seventh of the histidine nitrogen of the less resistant moiety, which is richer generally in basic amino-acids. After 125 hrs. the portion still insoluble in water (precipitated by neutralising the undialysable portion of the hydrolysis products with acetic acid) shows marked difference in amino-acid content from those of wool itself, or from the similarly isolated product after hydrolysis for 1 hr. (Van Slyke's method). There were considerable quantitative differences in the amounts of amino-acids and diketopiperazines produced by autoclaving (*a*) the original wool, (*b*) the protein precipitated as above after 125 hrs., with water at 150°. H. D. KAY.

Titration of amino-acids and proteins, using indicators. K. FELIX and H. MÜLLER (Z. physiol. Chem., 1927, **171**, 4—15).—A series of amino-acids and dipeptides has been titrated with acid and alkali using thymol-blue p_H (1·2—2·8) and alizarin-yellow (p_H 10·1—12·1) as indicators. With the exception of the carboxyl groups of arginine, ornithine, and proline, and the amino-group of taurine, all the amino-acids and dipeptides investigated may be fairly accurately titrated. Dibenzoylarginine gives anomalous results. By mixing known amounts of amino-acids and dipeptides, model protein hydrolysates have been made. Provided arginine is not present, these may be titrated with the above indicators, but with arginine in the mixtures the quantity of acid required to titrate the basic groups against thymol-blue may be greatly in excess of the theoretical. Thus, using thymol-blue, the hydrolysates from protamines or other proteins containing much arginine may give too high titration values. H. D. KAY.

M.-p. and b.-p. determinations. L. W. WINKLER (Arch. Pharm., 1928, **266**, 45—62).—The apparatus described gives more trustworthy results than that officially prescribed in the German Pharmacopœia. The m.-p. apparatus consists of a wide-necked flask within which hangs a wide tube. Both contain sulphuric acid, or pentachloroethane for temperatures below 140°. The liquid in the inner tube is stirred by moving both thermometer and m.-p. tube together. The m.-p. tube itself is 4—5 mm. diameter and 20—25 cm. long, and the substance is previously melted within it, then cooled so as to form a thin coating round the bottom. The temperature at which this becomes transparent is taken as the m. p. The following revised figures, among others, are given for various medicinal chemicals: adalin, 118·8°; anæsthesin, 89·8°; atophan, 215·1°; benzophenol, 38·8°; bromural, 144·9°; duotal, 88·1°; caffeine, 236·8°; luminal, 175·3°; novatophan, 58·3°; pyramidone, 106·5°; theophylline (anhydrous), 272·3°; trichloroacetic acid, 57·3°. Substances which decompose on melting are not previously fused, but are rubbed round the bottom of the tube. The method is suitable also for simple cryoscopic observations on mixtures.

The b.-p. apparatus consists of a tube 25—30 cm. long and 12 mm. wide with a somewhat narrower neck. About 1 cm. at the bottom is filled with clean uniform grains of pumice and the thermometer bulb is protected by a brass sheath resting on the pumice. Enough of the liquid, *e.g.*, about 1 c.c., is introduced to cover the thermometer bulb. The apparatus is heated over wire gauze. From the observed b. p. 0·55° is subtracted, this being the difference in temperature between the liquid and the vapour above it in this apparatus. B. p. are given for various liquids between ethyl chloride (12·0°) and methyl salicylate (221·1°). Tables are given showing the use of the apparatus in detecting and determining alcohol in ether and in chloroform. By determining the b. p. of water simultaneously with any other determination a

correction can be applied which dispenses with the use of the barometer. W. A. Silvester.

Determination of oxygen in organic compounds. G. G. Glockler and L. D. Roberts (J. Amer. Chem. Soc., 1928, **50**, 828—831).—The apparatus and method are described for conducting semi-micro-combustions of compounds containing carbon, hydrogen, and oxygen in a closed apparatus. A measured volume of oxygen is enclosed, the compound completely burnt, and the residual oxygen measured. The results are approximate, but serve to confirm the presence of oxygen in organic compounds. A. McGookin.

Determination of [labile] halogens in organic compounds. S. Krishna and J. Swarup (J. Amer. Chem. Soc., 1928, **50**, 798—801).—A modification of Kux's method is described for the determination of labile halogen alone or in presence of stable halogen. The method is not applicable to benzyl chloride, chloral hydrate, and compounds containing nitro-groups. A. McGookin.

Volumetric determination of amino-nitrogen. K. Linderstrøm-Lang (Z. physiol. Chem., 1928, **173**, 32—50).—The compound is titrated in acetone solution (100—200 c.c. of 99% acetone to 10 c.c. of an aqueous solution) with $0\cdot1N$-alcoholic-hydrochloric acid using benzeneazo-α-naphthylamine as indicator. The titration is accurate to within 0·02—0·04 c.c. of acid, and is not affected by any of the usual buffer solutions, by ammonia, or by ammonium chloride. J. Stewart.

Determination of sulphinic group and ferric [iron]. S. Krishna and H. Singh (J. Amer. Chem. Soc., 1928, **50**, 792—798).—Sulphinic acids give quantitative precipitates (Thomas, J.C.S., 1909, **95**, 342) of the type $(R\cdot SO_2)_3Fe$ in acid solution with ferric salts, and the presence of other metals, like cobalt, nickel, chromium, aluminium, and ferrous iron, or of other negative groups, *e.g.*, the carboxyl group, does not affect the reaction. Good results were obtained for benzene-, *p*-toluene-, 1 : 4-dichlorobenzene-2-, 1-chloro-4-nitrobenzene-2-, benzoic acid-3-1 : 4-dibromobenzene-2-, *p*-chlorobenzene-, *p*-acetanilide-, salicylic acid-4-, benzene-1 : 3-di-, cinnamic acid-4-, and *p*-anisyl-sulphinic acids. The ferric salts of all but the last-named acid were analysed. A. McGookin.

Interference of nitro- and azo-groups on the Zerewitinoff method for the determination of active hydrogen. H. Gilman and R. E. Fothergill (J. Amer. Chem. Soc., 1928, **50**, 867—869).—The presence of an azo-group gives rise to high values in the determination of active hydrogen. Values for active hydrogen higher than those obtained by Zerewitinoff are recorded for the complexes of *p*-aminoazobenzene and anthranilic acid with trinitrobenzene. The presence of nitro- and azo-groups is suggested as an explanation. J. D. Fulton.

Biochemistry.

Inhalation, retention, and exhalation of dusts and fumes by man. I. Concentrations of 50—450 mg. per cubic metre. P. Drinker, R. M. Thomson, and J. L. Finn (J. Ind. Hygiene, 1928, **10**, 13—25).—The amounts of dusts and fumes of known composition retained and expired by man have been determined as a function of the concentration, length of exposure, and rate of breathing. Suspensions of zinc oxide fume (particles 0·15 and 0·4 μ) and of marble dust (particles 0·3—6 μ) were employed. The percentage retentions obtained were $55\pm9\cdot4$. The concentrations inhaled varied from 50 to 450 mg./m.^{3}, the exposure from 5 to 45 min., and the rates of breathing from 6 to 18 respirations per min. No appreciable variation of retention with concentration of fume was detected. E. A. Lunt.

Variations in the uric acid content of blood relative to respiratory functions; asphyxial hyperuricæmia. L. Binet and R. Fabre (Compt. rend., 1928, **186**, 973—975).—The proportion of uric acid in the blood of dogs, which in the normal condition has the values total blood, 0·09—0·16, plasma, 0·03—0·06 g./litre, is increased 17—18% during asphyxiation, the amount of the increase depending on the period of asphyxiation. The excess of uric acid is eliminated and the value returns to normal 15 min. after return to normal respiration. J. W. Baker.

Carbon dioxide of the blood. S. Kato (J. Biochem. Japan, 1927, **8**, 167—185).—The carbon dioxide dissociation curves of horse blood, plasma, and serum, of a suspension of the corpuscles in physiological saline solution, and of the laked blood were studied. The curves for plasma and serum are identical and similar to that of a $0\cdot3M$-hydrogen carbonate solution. The carbon dioxide content of defibrinated blood at any carbon dioxide pressure is less than that of the serum and corpuscles taken separately, and it is suggested that the presence of corpuscles suppresses the carbon dioxide-combining ability of the serum. The carbon dioxide contained in the corpuscles is combined with the hæmoglobin. The carbon dioxide content of the blood decreases slightly with increasing oxygenation. Blood in equilibrium with air free from carbon dioxide is slightly more acidic than the serum under the same conditions, and on mixing these there is a liberation of carbon dioxide. W. A. Richardson.

Combination of carbon dioxide with oxyhæmoglobin. S. Kato (J. Biochem. Japan, 1927, **8**, 187—194).—The carbon dioxide dissociation curves of oxyhæmoglobin solutions dialysed to different degrees have been studied, and it is found that the equation $V^1=\alpha P^{1/n}$ is applicable, where V^1 is the concentration of carbon dioxide expressed as a volume percentage of a standard hæmoglobin solution,

P is the pressure of carbon dioxide with which the solution is in equilibrium, and α and n are constants for each solution. The lower the salt content of the solution the higher is the amount of carbon dioxide combined, and it is concluded that the amount of carbon dioxide adsorbed decreases when the degree of aggregation of the hæmoglobin is increased. The amount of carbon dioxide adsorbed by hæmoglobin at 37° is less than at 18°, and this is the main cause of decrease in the carbon dioxide capacity of the blood with rise of temperature.

W. A. Richardson.

Photographic methods of estimating the percentage saturation of hæmoglobin with various gases. I. Ratio of oxyhæmoglobin to carboxyhæmoglobin. H. Hartridge and F. J. W. Roughton (J. Physiol., 1928, **64**, 405—414).—A method is described for obtaining photographs of the absorption spectra of oxyhæmoglobin, carboxyhæmoglobin, or mixtures of the two pigments. The plates are analysed by the selenium densitometer or by a visual apparatus, the mid-point of the α-band being determined to within about 0·03 mm. A calibration curve relating the percentage of carboxyhæmoglobin to the position of this mid-point is obtained by photographing a series of known mixtures of the two pigments, and an unknown solution can then be determined by recording and analysing its photograph on the same plate as the calibrating exposures. The accuracy of the method is greater than that of the reversion spectroscope and has the further advantage of permanency of records.

R. K. Cannan.

Apparatus for the analysis of blood-gases. L. Condorelli (Arch. sci. biol., 1926, **9**, 146—151; Chem. Zentr., 1927, ii, 2217).—The gases are collected at atmospheric pressure. The apparatus can also be used for the gasometric determination of urea.

A. A. Eldridge.

Action of carbon monoxide in absence of hæmoglobin, and some properties of the respiratory ferment. O. Warburg (Naturwiss., 1927, **15**, 546; Chem. Zentr., 1927, ii, 2202).—Carbon monoxide acts on living cells in general, reversibly inhibiting respiration. The substance in the cell with which the carbon monoxide reacts behaves very similarly to hæmoglobin. The attachment of hæmoglobin to carbon monoxide is firmer than to oxygen, whilst with the respiratory ferment (an oxidase) the reverse is the case. The affinity for carbon monoxide is greater in the dark than in light. The effect of different wave-lengths is considered.

A. A. Eldridge.

Colloid chemistry of hæmoglobin. I. B. Jirgensons (Biochem. Z., 1928, **194**, 140—150).—In presence of organic substances (*e.g.*, alcohol, *iso*propyl alcohol, urea, pyridine, acetone, glycerol, etc.) the visible spectrum of hæmoglobin (a mixture of oxy- and met-hæmoglobin) changes, the three bands at 525—550, 575—585, and 629—639 $\mu\mu$ becoming positions of which are 520—550 and 560 (or 565)—580. Capillary-inactive organic substances act more slowly than capillary-active, whilst salts have no effect. A moderate rise of temperature, to 40° for capillary-active and to 70° for capillary-inactive substances, favoured this spectral change.

P. W. Clutterbuck.

Protein grouping of hæmoglobin. J. Barcroft (Bull. Soc. Chim. biol., 1928, **10**, 279—282).—It is suggested that the differences between the hæmoglobins from various animals are due to differences in the structure of the component globins and probably not to the formation of isomeric hæmoglobins by variation in the position of attachment of the hæmatin to the globin.

G. A. C. Gough.

Decomposition of oxyhæmoglobin with pepsin-hydrochloric acid. K. Felix and A. Buchner (Z. physiol. Chem., 1927, **171**, 276—289).—When pepsin acts on oxyhæmoglobin acidic and basic groups are set free in equivalent amounts. No basic groups other than amino-groups appear and it is therefore unlikely that the glyoxaline ring is involved to any great extent.

J. Stewart.

Iron. II. Labile iron of blood, and its relation to hæmoglobin. III. Distribution of labile iron between blood-corpuscles and -plasma, and its behaviour. G. Barkan (Z. physiol. Chem., 1927, **171**, 179—193, 194—221).—II. Earlier experimental work (A., 1925, i, 1482) is confirmed. The reaction is now shown to be complete in acid or alkaline solution, no porphyrins are detected, and there is no relationship between the iron content of hæmoglobin and the amount of iron easily separated by the action of dilute hydrochloric acid. Either a small, variable part of the hæmoglobin is more loosely attached than the main portion, or the greater part of the hæmoglobin molecule must be admixed with a small, variable amount of material the iron of which is loosely attached.

III. By far the greater part of the easily separated iron of blood comes from the corpuscles. The iron of the washed stromata is only a fraction of that existing in the corpuscles, and is all in the easily separated form. Neither periods of anæmia nor of regeneration of blood affect the content of labile iron. Even large doses of iron will raise a subnormal only to a normal value. Transference of iron from blood-corpuscles to plasma takes place slowly when non-coagulable blood is kept.

J. Stewart.

Action of potassium cyanide and potassium ferricyanide on certain respiratory pigments. S. F. Cook (J. Gen. Physiol., 1928, **11**, 339—348).—Oxygen is liberated from echinochrome and hæmerythrin by both salts, from hæmoglobin by potassium ferricyanide only, from hæmocyanin by potassium cyanide only.

E. A. Lunt.

Oxidation processes occurring in the system plasma-potassium ferricyanide. G. Litarczek (J. Physiol., 1928, **65**, 1—14).—Plasma or serum to which potassium ferricyanide has been added absorbs oxygen from the air. Hæmoglobin can replace the ferricyanide, but ferric chloride or ferrocyanide cannot. The removal of ether-soluble lipins greatly reduces the oxygen consumption of the system and the extracted lipins have some power of autoxidation on the addition of ferricyanide or hæmoglobin. These facts indicate an error in the determination of the

oxygen capacity of blood by the ferricyanide method. The extent of the error will be a function of the time taken in analysis, the lipin concentration of the blood, and the concentration of ferricyanide. The method of Van Slyke is probably the only accurate one for lipæmic bloods. R. K. CANNAN.

Action of carbon monoxide and light on hæmin catalysis. H. A. KREBS (Biochem. Z., 1928, **193**, 347—349).—Carbon monoxide and light affect the catalysis by hæmin of the oxidation by molecular oxygen of cysteine to cystine in the same way as they affect the respiration of living substance. P. W. CLUTTERBUCK.

Sources of error in detection of blood in clinical and forensic cases. I. Oxidising action of commercial ether. II. Bromine content of commercial hydrogen bromide–acetic acid as a source of error in the identification of blood by conversion into Nencki's hæmatoporphyrin. III. Possibility of confusion of hæmoglobin and hæmatin with iron porphyratin of vegetable food. O. SCHUMM (Z. physiol. Chem., 1927, **172**, 38—49).—I. Discrepancies in tests for blood pigments by the acetic acid–ether method, with spectroscopic identification of pyridine-hæmochromogen, are due to the oxidising action of the ether used. Pure α-hæmatin, or defibrinated human blood in acetic acid, or a suspension of hæmin in acetic acid, is readily oxidised under the conditions of the test, and since this destructive action is of considerable magnitude, appreciable amounts of pigment may be affected. When chloroform is used instead of ether no destruction occurs. The oxidative power of the ether is reduced by treatment with anhydrous potassium carbonate and redistillation, or preferably by shaking with one tenth its volume of 15% potassium hydroxide, and redistillation. This purified ether enables positive reactions to be obtained for occult blood in fæces when the ordinary ether gives negative results. Several samples of anæsthetic ether investigated showed no hæmatin-destroying action. The destructive action runs parallel with the oxidative power of the ether, the latter being measured by the liberation of iodine from potassium iodide solutions and the oxidation of ferrous sulphate or ferrous ammonium sulphate; anæsthetic ether with a small amount of hydrogen peroxide added behaves in the same way as commercial ether. Satisfactory purification of the latter for these tests can thus be effected by shaking with potassium iodide solution, followed by washing with potassium hydroxide solution and then with water.

II. The identification of blood stains by treatment with acetic acid saturated with hydrogen bromide to produce Nencki's hæmatoporphyrin often fails with traces of blood owing to the presence of free bromine in commercial hydrogen bromide–acetic acid solutions.

III. Positive spectroscopic hæmatin reactions have been obtained with acetic acid–chloroform extracts of oat preparations. The necessity of considering the iron porphyratin content of the residues from vegetable food when testing for occult blood is emphasised. A. WORMALL.

Blood concentration in marine fishes. F. G. HALL (J. Biol. Chem., 1928, **76**, 623—631).—The previous results (A., 1926, 634) regarding the increased concentration of various constituents of the blood of fishes during asphyxia are confirmed; the greatest increase is in the iron content and the least in the nitrogen content. There is increased combining power for oxygen, but this is not proportional to the increase in hæmoglobin concentration owing to the coincident accumulation of acid; the latter, together with the retention of toxic substances, are the ultimate causes of death of the fish in asphyxia. C. R. HARINGTON.

Absorption spectra of blood from man, ox, and frog. G. A. AKOVBIANTS and V. A. HAMBURTZEV (Zhur. exp. Biol. Med., 1927, **4**, 751—761).—The relation between *KdC* and λ is determined spectrophotometrically for blood. The absorption remains the same on increased dilution, provided the same number of molecules are present in the path of the light. CHEMICAL ABSTRACTS.

Is succinic acid present in ox blood? B. FLASCHENTRÄGER and G. LOHR (Z. physiol. Chem., 1928, **174**, 302—305).—No succinic acid could be isolated from about 50 litres of fresh defibrinated ox blood, and the amount present, if any, cannot be greater than 0·2 mg.-%. A. WORMALL.

Hydrogen-ion concentration of blood corpuscles. H. TAYLOR (J. Physiol., 1927, **63**, 343—356).—The hydrogen-ion activities were calculated from observed *P.D.* at a collodion membrane separating laked blood-corpuscles from a dilute sodium hydrogen carbonate–sodium chloride solution. The p_H of human corpuscles varied from 7·47 to 6·95, whilst that of the corresponding sera varied from 7·70 to 7·26. Similar relations held for goose blood, which, at the same partial pressure of carbon dioxide, appeared to be slightly alkaline to human blood. R. K. CANNAN.

Origin of plasma-proteins. M. KOMATSU (J. Biochem. Japan, 1927, **7**, 447—456).—The great reduction of the albumin/globulin ratio in hæmatoporphyrin rabbits is accompanied by an increase of the nitrogen/sulphur ratio in the liver tissue and simultaneous diminution in muscle tissue. Both liver and muscle may contribute to the production of blood-protein, the former contributing protein rich in sulphur, and the latter protein poor in sulphur. CHEMICAL ABSTRACTS.

Plasmalogen. I. Absorption of plasmalogen and the conditions for the establishment of alimentary plasmalogenæmia. R. FEULGEN, K. IMHAUSER, and M. WESTHUES (Biochem. Z., 1928, **193**, 251—263).—Plasmalogen, the precursor of the aldehyde plasmal, is present in animal food and is absorbed from the intestine either when given as flesh or as a phosphatide emulsion prepared therefrom. It produces alimentary plasmalogenæmia, whereas free plasmal does not, since the latter either is not absorbed or is immediately retained or chemically changed, probably in the intestinal wall, so that it no longer gives the fuchsin–sulphurous acid reaction. Whereas plasmalogen, intravenously injected, can be detected for an hour in the serum, plasmal similarly injected

disappears so quickly that it cannot usually be detected at all. The tissues must be responsible for the reaction, since blood *in vitro* does not attack either plasmalogen or plasmal. In the stomach, part of the plasmalogen is converted into plasmal by the acid present and only the plasmalogen remaining is responsible for plasmalogenæmia (cf. A., 1927, 369, 370, 894). P. W. CLUTTERBUCK.

Plasmalogen. II. Behaviour of plasmalogen in the serum of the newly born. K. IMHÄUSER (Biochem. Z., 1928, **193**, 416—422).—Newly-born calves have traces of plasmalogen in the serum, only about 1/20 of that of the adult animal, whereas the serum-plasmalogen content of the mother is normal. From birth, there is a daily increase until, after 1—2 months, the adult value is reached.

P. W. CLUTTERBUCK.

The saponifiable reducing carbohydrate of blood-plasma. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, **10**, 261—271).—The hypothesis that the "immediately reducing blood-sugar" (A., 1927, 690) is a hexosediphosphate is rejected on comparing its properties with the latter. Hexosediphosphate, unlike the blood-carbohydrate, is not completely precipitated by mercuric nitrate and is only partly hydrolysed under conditions which hydrolyse the blood-carbohydrate. Living yeast, which does not consume hexosediphosphate, removes the entire content of "immediately reducing blood-sugar" from the plasma of horse's blood.

G. A. C. GOUGH.

Unfermentable residue of free blood-sugar. E. J. BIGWOOD and A. WUILLOT (Bull. Soc. Chim. biol., 1928, **10**, 272—273).—In connexion with previous work (A., 1927, 1102) it is found that the reducing power of lævulose is not altered by digestion with sulphuric acid (0·125—2·0*N*) for 1 hr.

G. A. C. GOUGH.

So-called protein-sugar of blood-plasma. E. J. BIGWOOD and A. WUILLOT (Bull. Soc. Chim. biol., 1928, **10**, 274—278).—The enhancement of the reducing power of blood-plasma on treatment with dilute acids at 130° (A., 1914, ii, 682; 1925, i, 714) is confirmed; it is shown, however, that only 4% of the sugars, liberated possibly from combination with protein, are fermented by yeast. G. A. C. GOUGH.

Effect of dextrose and dihydroxyacetone on the blood-sugar value. K. UCHIDA (Biochem. Z., 1928, **194**, 111—127).—The effect of previous feeding of carbohydrate or protein on the utilisation of injected dextrose and dihydroxyacetone by normal and depancreatised dogs, and dogs the pancreatic ducts of which had been tied 6 months before the experiment, is investigated. With a protein-rich and carbohydrate-free diet, symptoms with normal dogs on injecting dextrose are similar to those in depancreatised dogs and the effect is even greater in dogs the ducts of which are ligatured. On the other hand, utilisation of injected dihydroxyacetone is not affected by previous feeding, but depancreatised dogs utilise the triose less readily than normal dogs. The readier utilisation of triose compared with hexose is less marked in dogs having the duct tied.

P. W. CLUTTERBUCK.

Micro-method for the determination of dihydroxyacetone in blood. F. SILBERSTEIN and F. RAPPAPORT (Biochem. Z., 1928, **194**, 105—110).—A modification of the Hagedorn–Jensen sugar determination is employed as a micro-method for the determination of dihydroxyacetone.

P. W. CLUTTERBUCK.

Attempt to detect methylglyoxal as an intermediate product of glycolysis. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, **193**, 464—467).—It was not found possible to detect, by means of semicarbazide, the formation of methylglyoxal during glycolysis in horse's or dog's blood after addition of dextrose. P. W. CLUTTERBUCK.

Ammonia content of and ammonia formation in blood. I. Ammonia formation in the kidney. II. E. GOTTLIEB (Biochem. Z., 1928, **194**, 151—162, 163—176).—I. The ammonia-nitrogen content of the arterial and venous blood of fasting dogs is 0·03 mg./100 c.c. In all but one experiment, the blood-ammonia was not preformed. Ammonia formation proceeds in dog's blood from the moment of removal of the sample with decreasing velocity, depending on the temperature and to a smaller extent on the p_H, a greater ammonia formation occurring with more alkaline reaction (p_H 12).

II. Experiments are described which support the theory of Nash and Benedict (A., 1922, i, 191, 483) of the formation of ammonia by the kidney. In four experiments considerable amounts of ammonia were detected in the urine which had not come from the blood, whilst in six other experiments considerably more ammonia was detected in the venous blood from the kidney than was present in the arterial blood. P. W. CLUTTERBUCK.

Application of the hypobromite method to the determination of minute quantities of ammonia and especially of the non-protein nitrogen of the blood. V. ENGELHARDT and N. LYUBIMOV-KREMLEVA (Zhur. exp. Biol. Med., 1927, **6**, 26—39).

CHEMICAL ABSTRACTS.

Determination of carbamide in blood. F. W. FOX (Biochem. J., 1928, **22**, 545—547).—A description of a macro- and a micro-method based on the determination of the ammonia produced by the action of urease directly and without previous aeration.

S. S. ZILVA.

Effect of blood preservatives on urea determination. R. A. KILDUFFE and E. G. SPRINGER (Arch. Path. Lab. Med., 1927, **4**, 396—397).—The results of the determination of urea in blood are affected by the use of a mixture of thymol and sodium fluoride as a preservative. CHEMICAL ABSTRACTS.

Influence of sodium fluoride and thymol on determination of urea by urease method. A. E. OSTERBERG and E. V. SCHMIDT (J. Biol. Chem., 1928, **76**, 749—754).—Addition to blood of a 10 : 1 mixture of sodium fluoride and thymol in quantities of 10 mg. per c.c. as recommended by Sander (*ibid.*, 1923, **58**, 1) interferes with the determination of urea by retarding the action of urease; 3 mg. per c.c. of the preservative have no effect (cf. Roe and others, this vol., 192). C. R. HARINGTON.

Ferricyanide micro-method in blood analysis. L. Flatov (Biochem. Z., 1928, **194**, 132—139).—The author's method for the determination of uric acid by addition of excess of ferricyanide and titrating the excess with sodium indigotinsulphonate (A., 1926, 1283) is extended to the determination also of blood-sugar, glutathione, thiazine, copper, and iron.

P. W. Clutterbuck.

Determination of chlorides in blood by Volhard's method. N. Ivanovski (Zhur. exp. Biol. Med., 1927, **4**, 631—636).—The blood (0·05 c.c.) in water (1 c.c.), after complete hæmolysis, is boiled with nitric acid (5 drops) and 3% hydrogen peroxide solution (1 drop). After cooling, water (3 c.c.) and exactly 1 c.c. of 0·01*N*-silver nitrate solution are added, the excess being titrated with ammonium thiocyanate in the presence of ferric alum.

Chemical Abstracts.

Determination of phosphate in a few drops of serum. T. Brehme and E. M. Lepski (Klin. Woch., 1927, **6**, 1905—1906; Chem. Zentr., 1927, ii, 2411).—Tisdall's method is modified for use with 0·12 c.c. of serum.

A. A Eldridge.

Calcium metabolism. II. Calcium content of corpuscles, plasma, and serum. III. Calcium and the coagulation of blood. C. P. Stewart and G. H. Percival (Biochem. J., 1928, **22**, 548—558, 559—570).—II. True plasma contains 10—20% more calcium than does the corresponding serum. In citrated plasma the amount is less than in true plasma to an extent depending on the amount of citrate added. The corpuscles contain no more than traces of calcium. In plasma the concentration of ionic and of diffusible calcium appears to be equal to that in serum. It is suggested that during the coagulation of blood some of the non-diffusible calcium is precipitated.

III. The effect of sodium citrate, fluoride, chloride, and oxalate on the coagulation time of ox blood and on the concentration of calcium, diffusible calcium, and ionic calcium of the corresponding serum has been studied. It is concluded that some complex calcium compound incapable of filtration through a collodion membrane is essential for the coagulation of blood. Calcium ions are not necessary and it is possible that they may even have an inhibitory effect.

S. S. Zilva.

Blood composition and blood clotting. A. Gigon and R. Boulenaz (Biochem. Z., 1928, **194**, 83—90).—Serum from clotted blood contains more carbon than serum of defibrinated blood and the latter more than plasma of blood treated with sodium fluoride. The total nitrogen values do not run parallel with these carbon values. Sodium fluoride added to blood to make the concentration 1% considerably changes the composition of the blood, serum, and plasma. The plasma of whipped fluoride blood is richer in carbon than the plasma of unwhipped fluoride blood.

P. W. Clutterbuck.

Proteolytic enzymes of blood-serum. IX. Different behaviour of sera in the stages of metamorphosis of Anura. M. von Falkenhausen, H. J. Fuchs, and M. Schubert (Biochem. Z., 1928, **193**, 269—275).—The sera of various cold-blooded animals at a particular stage of development react with the fibrin of a later stage of development in the same way as with foreign fibrin, but with fibrin of an earlier stage it behaves like immune serum to its own normal fibrin, causing a decrease in residual nitrogen. Serum of the completely developed frog, however, behaves to the fibrin of the various stages of development as to foreign protein (cf. A., 1926, 536, 1166; 1927, 787).

P. W. Clutterbuck.

Immuno-chemical investigation of globin and globin derivatives. F. Ottensooser and E. Strauss (Biochem. Z., 1928, **193**, 426—463).—From the weak antigen hæmoglobin there is formed by careful preparation, a strongly antigenic globin which behaves atypically as a basic protein. The derivatives nitro- and amino-globin which are not or only faintly basic are strongly and typically antigenic. Specific globin precipitation takes place best at p_H 8·1—8·3. An attempt to stabilise concentrated globin solutions sufficiently for anaphylactic experiments proved unsuccessful. The results of a large number of specificity experiments are tabulated.

P. W. Clutterbuck.

Formation of blood and bile pigments in the incubated hen's egg. Y. Sendju (J. Biochem. Japan, 1927, **7**, 191—196).—The hæmoglobin content of the developing hen's egg increases very slowly up to about 22 mg. during the first 14 days of incubation and then very rapidly up to 140 mg. by the end of the 19th day. The bile pigments show exactly the same course of development except that they first appear on the 7th incubation day.

Chemical Abstracts.

Formation of enzymes in the developing egg. W. Engelhardt and R. Waehner (Zhur. exp. Biol. Med., 1927, **5**, 335—343).—The total catalase and lipase contents of the hen's egg were determined. Both enzymes increase very greatly, but the catalase shows a transitory slight decline at an early stage. The course of the lipase formation runs very nearly as a logarithmic curve, whereas the curve of the catalase production runs convex to the abscissa. The peroxidase reaction occurs simultaneously with the appearance of hæmoglobin.

Chemical Abstracts.

Content of phospholipins in the submaxillary gland, and the physiological activity of this gland. R. Caminade, A. Mayer, and H. Vallée (Ann. physiol. physicochim. biol., 1927, **3**, 89—93; Chem. Zentr., 1927, ii, 2203).—Dog's submaxillary gland contains 0·34% (calculated on the dried material) of phospholipins.

A. A. Eldridge.

Calcium content of heart muscle. R. Kapeller and H. Kutschera-Aichbergen (Biochem. Z., 1928, **193**, 400—408).—The calcium content of four ox hearts and of four hearts of normal adult men was 25—25·7 mg.-%, the value being very constant and no difference between the left and right sides being found. In a case of insufficiency of the left side, this side showed a decreased and the right side a somewhat increased calcium content. In two cases of valvular disease the calcium content of both chambers was decreased.

P. W. Clutterbuck.

Potassium and calcium contents of peripheral nerve fibres. A. Simon and J. Szelöczey

(Biochem. Z., 1928, **193**, 393—399).—Determination of the potassium and calcium contents of the sciatic nerves of a large number of rabbits are tabulated. Both contents show considerable individual variations. The two nerves of the same rabbit contain roughly the same amounts of calcium, but the amount of potassium varies. The nerves contain no indiffusible potassium or calcium. Both potassium and calcium diffuse out of the cut nerve constantly for 24 hrs. The calcium content of the nerves changes under the action of cocaine *in vivo*, but not regularly. There diffuses during 2 hrs. from one cut nerve into saline containing 0·5% of cocaine hydrochloride more calcium than from the other nerve of the same rabbit into saline. P. W. CLUTTERBUCK.

Comparison of the nucleic phosphorus balance of the organs of different species of vertebrates. M. JAVILLIER, A. CREMIEU, and H. HINGLAIS (Bull. Soc. Chim. biol., 1928, **10**, 327—337).—The nucleic, the transitional (A., 1927, 791), the lipoid, and the total phosphorus of the organs of different species of vertebrates was determined. The nucleic phosphorus of the organs of individuals of the same age and physiological state is constant. The order of the nucleic phosphorus content of the organs (spleen, liver, kidney, brain, and muscle) is generally the same throughout different species, but the ratio of nucleic phosphorus to lipoid phosphorus and especially the total phosphorus figures show greater variations. The transitional phosphorus is invariably greatest in the muscle. G. A. C. GOUGH.

Nucleic phosphorus balance and the phosphorus relations in some complete organisms (chiefly invertebrates). M. JAVILLIER and A. CREMIEU (Bull. Soc. Chim. biol., 1928, **10**, 338—341).—The nucleic, lipoid, transitional, insoluble, and the total phosphorus contents were determined for dried and fresh bodies of members of typical classes of invertebrates. Although considerable variations were observed, the ratios of lipoid phosphorus to total phosphorus—insoluble phosphorus for these animals, and also for some vertebrates, are of the same order. G. A. C. GOUGH.

Guanidine determinations on some invertebrates by a colorimetric phosphotungstic acid method. M. M. ELLIS (Biochem. J., 1928, **22**, 353—361).—The alcoholic extracts of the tissues after having been freed from proteins, fatty material, lipochromes, etc. were precipitated with phosphotungstic acid and the phosphotungstates extracted with methyl alcohol. This last extract contained the guanidine phosphotungstates, which were determined by means of the nitroprusside reaction. Four invertebrates, *Purpura lapillus*, *Calanus helgolandicus*, *Ligia oceanica*, and *Carcinus mœnas*, in which animal tissues other than muscle alone were extracted, showed the presence of guanidines by the above method. Pure samples of molluscan muscle from freshly-collected limpets and from unattached limpets in which the foot muscle had been in prolonged contraction were found to be free from both creatine and guanidine. S. S. ZILVA.

Iodine in gorgonian corals. K. SUGIMOTO (J. Biol. Chem., 1928, **76**, 723—728).—The horny axial skeleton of various gorgonian corals contains iodine in amounts varying from 0·11 to 2·63% of the dry weight. 3 : 5-Di-iodotyrosine has been isolated from the skeleton of *Plexaura flexuosa*. C. R. HARINGTON.

Iodine as a biological element. XII. Iodine content of the normal animal. XIII. Effect on iodine content of an animal of ingestion of small amounts of inorganic iodine. XIV. Effect of a single administration of inorganic iodine on the blood-iodine value. E. MAURER and H. DUCRUE (Biochem. Z., 1928, **193**, 356—359, 360—363, 364—371; cf. A., 1926, 1167; 1927, 169, 481).—XII. The iodine contents of the tissues of five normal rabbits vary considerably in the different animals and quite independently of the iodine contents of the thyroid gland of those animals.

XIII. By administration of small amounts of inorganic iodine to such animals, the iodine content of every tissue was increased, but to different extents, and this increase was almost completely lost in 24 hrs. by excretion.

XIV. The power of the organism to retain iodine in the blood is different for different animals. Whereas in man, after administration of iodine, a return to normal blood-iodine values occurs in 24 hrs., in rabbits and sheep this occurs only in 6—11 days. P. W. CLUTTERBUCK.

Relationship between state of maturity and chemical composition of the whiting, *Gadus merlangus*. H. O. BULL (J. Marine Biol. Assoc., 1928, **15**, 207—218).—The muscles of *G. merlangus* show no change in composition during the ripening of the gonads or with age. The amount of fat in the liver, very low in immature fishes, is at a maximum just after the ripening of the gonads, and it then decreases. Males are richer in liver-fat than females. The protein content of the liver is higher in immature than in mature fish. W. O. KERMACK.

Artificial albuminous cells. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], **7**, 32—35; cf. this vol., 238).—When dropped from a height on to concentrated nitric, sulphuric, or hydrochloric acid, particles of egg-albumin give rise to cell-like structures. A drop of egg-albumin, compressed under a cover-slip, to the edge of which 50% sulphuric acid is applied later, gives a cellular structure closely resembling a plant-tissue. This and other similar results emphasise the importance of diffusion for the formation of cells. T. H. POPE.

Cholesterol and lipoid phosphorus of bile; variations during feeding with various materials after "blockade" of the reticulo-endothelial system and after splenectomy. S. LEITES (Arch. exp. Path. Pharm., 1928, **129**, 108—121).—The cholesterol content of the bile is not markedly influenced by administration of olive oil with or without cholesterol or of oleic acid, and appears to be slightly increased after administration of flesh or of lecithin. The total and lipoid phosphorus of the bile is not always increased after administration of lecithin. Blockade of the reticulo-endothelial system causes an increase of the cholesterol in the bile, whilst splenectomy causes a decrease both in cholesterol and in lipoid phosphorus. W. O. KERMACK.

Determination of acetaldehyde in cerebrospinal fluid. P. THOMAS and E. MAFTEI (Compt. rend. Soc. Biol., 1927, **96**, 1042—1043; Chem. Zentr., 1927, ii, 469).—The cerebrospinal fluid is neutralised with phosphoric acid, 96% alcohol is added, and the acetaldehyde in the distillate is determined colorimetrically with a magenta-sulphurous acid solution, the comparison solution being standardised titrimetrically. A. A. ELDRIDGE.

Determination of globulin in cerebrospinal fluid. S. VON NADOR-NIKITITS (Klin. Woch., 1927, **6**, 1709; Chem. Zentr., 1927, ii, 2089).—The method consists of precipitation with ammonium sulphate in a calibrated sedimentation tube.
A. A. ELDRIDGE.

Boltz cerebrospinal fluid test (acetic anhydride-sulphuric acid). L. D. CADY (Arch. Neurol. Psych., 1927, **18**, 565—571).—The bluish-pink or lilac colour developed on adding acetic anhydride and sulphuric acid to positive general paralytic cerebrospinal fluids is not due to cholesterol, and is not given by aqueous extracts of brain tissue, brain lecithin, urea, uric acid, nucleic acid, calcium lactate, or tyrosine. The active compound, which is present in blood, is destroyed by treatment with ether, alkali, nitric acid, or hydrogen peroxide, is precipitated by protein precipitants, and is not dialysable in presence of proteins. CHEMICAL ABSTRACTS.

Relation between urea in blood and saliva. A. BERGMAN and I. BARG (Rev. Soc. Med. Interna, 1927, **3**, 605—611).—Determination of urea in the saliva and blood-serum of healthy and diseased subjects showed that the concentrations in each were closely parallel, and the same variation occurred in each after oral administration of urea. If the normal amount in blood-serum is taken as 20—40 mg.-%, the corresponding amount in saliva is 30—50 mg.-%.
R. K. CALLOW.

Ash of human milk. O. LAXA (Lait, 1927, **7**, 617—621; Chem. Zentr., 1927, ii, 2078).—The dialysable portion of human milk contains sulphate; calcium phosphate is present in a non-dialysable form. Numerous analytical data comparing the composition of the ash of human milk with that of cow's milk are given. A. A. ELDRIDGE.

Phosphorus compounds of milk. IV. Presence of adenine nucleotide in milk. H. D. KAY and P. G. MARSHALL (Biochem. J., 1928, **22**, 416—418).—Adenine nucleotide associated with some other phosphoric ester with similar precipitation reactions and solubilities is present in milk in concentrations of the order of 3 mg. per 100 c.c.
S. S. ZILVA.

Physical properties and chemical composition of the amniotic and allantoic fluids of the embryo chick. T. KAMEI (Z. physiol. Chem., 1927, **171**, 101—113).—Fluids from embryos were investigated after incubation for 9, 14, and 17 days. The sp. gr. of amniotic fluid rises from 1·006 at 9 days to 1·06 at 14 days, and falls to 1·04 at 17 days; that of allantoic fluid rises from 1·006—1·007 at 9 days to 1·016 at 14 days and 1·02 at 17 days. Amniotic fluid is distinctly hypotonic to hen's serum throughout; allantoic fluid is still more hypotonic. Sodium chloride is the main constituent of the ash. In the ash from amniotic fluid there is a relatively high proportion of silica. Sugar is absent from both fluids. The nitrogen content of both the fluids rises to a maximum at 14 days. There is more urea in the allantoic than in the amniotic fluid throughout incubation. Uric acid is absent from the amniotic fluid, but present in the allantoic fluid (0·01—0·02%). The concentration of both creatine and creatinine in the allantoic fluid increases throughout the period of incubation; both appear to be absent from the amniotic fluid. H. D. KAY.

Role of tryptophan in the animal organism. S. DEMIANOVSKI (Biochem. Z., 1928, **193**, 245—250).—Silkworms either diseased or existing under unfavourable conditions secrete more tryptophan in their silk than do healthy worms cultivated under favourable conditions. P. W. CLUTTERBUCK.

Iron metabolism. IV. Iron content of urine. W. LINTZEL (Z. Biol., 1928, **87**, 157—166).—Experiments are described which show that the Neumann–Hanslian method for the determination of small amounts of iron in urine is inaccurate. By combining Neumann's procedure for the separation of iron with the author's colorimetric method of determination as ferric thiocyanate, a satisfactory method has been evolved. It is concluded that normal human urine contains no iron. E. A. LUNT.

Indican in examination of urine. E. SCHLECHT (Pharm. Ztg., 1928, **73**, 355).—Since indican has a powerful reducing action, urine containing it may give positive reactions with Nylander's and Fehling's solutions when no sugars are present. S. I. LEVY.

Preparation of creatinine from urine. M. TERADA (Z. physiol. Chem., 1927, **170**, 289—293).—The mixed potassium ammonium salt of Reinecke's acid, obtained by melting together potassium dichromate and ammonium thiocyanate, gives with creatinine solutions a precipitate of the creatinine *salt*, $C_4H_7ON_3[Cr(SCN)_4(NH_3)_2]H$, m. p. 175°. The salt similarly precipitated from urine is contaminated with a substance richer in carbon, but may be obtained pure from urine which has been acidified and treated with animal charcoal, by dissolving in 120 pts. of warm water, filtering at 15°, and crystallising at 0°. C. HOLLINS.

Condition of the uric acid in urine. R. ASCOLI (Arch. sci. biol., 1926, **9**, 152—160; Chem. Zentr., 1927, ii, 2205).—A discussion. It is concluded that the uric acid is present in the molecular or practically molecular disperse condition. Further, any additive product of uric acid cannot be colloidal.
A. A. ELDRIDGE.

Determination of urobilinogen in fæces and urine by the new extraction method. A. ADLER and M. BRESSEL (Deut. Arch. klin. Med., 1927, **155**, 326—341; Chem. Zentr., 1927, ii, 2090).—Ehrlich's urobilinogen reaction is quantitative only under definite conditions. In the chloroform extract of urine or fæces the conversion of the chromogen into urobilin takes place much more slowly than in urine or after addition of alcohol, being maximal when 1 c.c. of Ehrlich's reagent and 2 c.c. of absolute

alcohol are added to 2 c.c. of chloroform extract. Normally, 1—3 mg. per day appear in the urine; in urine and fæces together, 100 mg.

A. A. ELDRIDGE.

Electrodialysis or electro-osmosis. Physico-chemical characteristics of normal and pathologically altered blood-serum. L. REINER (Biochem. Z., 1928, **193**, 313—314).—A reply to Lasch and Reitstotter (this vol., 192). P. W. CLUTTERBUCK.

Colour reaction in blood-serum. A. GROSS (Deut. med. Woch., 1927, **53**, 1642; Chem. Zentr., 1927, ii, 2515).—On addition of sodium indigotinsulphonate or methylene-blue solution to serum, colour change takes place in certain pathological conditions. Fuchsin solution normally becomes violet, but in disease carmine-red. The reaction is ascribed to a displacement of the protein equilibrium.

A. A. ELDRIDGE.

Experimental anæmia produced by *Clostridium Welchii*. Chemical analysis of the blood. J. A. KILLIAN M. B. PATTERSON, and L. KAST (Arch. Int. Med., 1928, **41**, 370—384).—Acute intoxication of rabbits with the products of *Clostridium Welchii* grown in broth culture results in a decrease in erythrocytes and hæmoglobin, an increase in non-protein nitrogen but not in urea-nitrogen or amino-nitrogen, a marked increase in the icterus index, and, during the earlier stages of the intoxication, a slight decrease in cholesterol and an increase in sugar.

W. O. KERMACK.

Mineral metabolism in anaphylaxis. A. SCHITTENHELM, W. ERHARDT, and K. WARNAT (Klin. Woch., 1927, **6**, 2000; Chem. Zentr., 1927, ii, 2554).—In anaphylactic shock, rabbits show increased blood-potassium. A. A. ELDRIDGE.

Influence of normal and cancerous blood-serum on pancreatic lipase action and the effect of ionic and colloidal lead. R. F. CORRAN and W. C. M. LEWIS (Biochem. J., 1928, **22**, 451—463).—Normal serum has an augmenting effect on the action of lipase. Sera from cancer patients are less potent in this respect. Lead in both the ionic and colloidal forms increases the lipolytic augmentation of both normal and cancerous sera. This effect manifests itself whether the compound is present in amounts either sufficient or insufficient to cause a precipitate with serum. It was found with commercial olive oil emulsion that the variation in the order of mixing of the reactants yields quantitatively different results for the effect of ox serum on lipase action and that filtration through filter-paper has no effect on the activity of the glycerol extract of lipase. With pure olive oil and sodium oleate as emulsifying agent it was found that in concentrations up to 0·2 g. of oleate per 100 c.c. of the mixture this salt acts on the extent of fat hydrolysis as an augmenter, whilst beyond this concentration the augmentative effect diminishes and with a concentration of 0·5 g. of oleate per 100 c.c. of mixture the effect is less than in the absence of the oleate. Sodium oleate acts also as an accelerator of the rate of hydrolysis. S. S. ZILVA.

Metabolism of tumours. I. S. EDLBACHER and K. W. MERZ (Z. physiol. Chem., 1927, **171**, 252—263).—Mammalian sarcomata and carcinomata, like granulations, polypi, and embryonic tissues, have an abnormally high content of arginase. High content of arginase is not, however, characteristic of sarcomata in birds: Rous' chicken-sarcoma has a relatively small arginase content. J. STEWART.

Metal-fume fever. V. Results of the inhalation by animals of zinc and magnesium oxide fumes. K. R. DRINKER and P. DRINKER (J. Ind. Hygiene, 1928, **10**, 56—70).—Rabbits, rats, and cats exposed to the fumes of zinc oxide plus 10% of carbon dioxide show depressions in body temperature the extent and duration of which vary with the time of exposure. Contrary to the existing data on metal-fume fever in man, no significant abnormal rise in temperature follows. A similar but milder reaction occurs when magnesium oxide is substituted for zinc oxide. Autopsies indicate varying degrees of peribronchial leucocytic infiltration. Experiments on the zinc concentrations of various organs following inhalation of zinc oxide fumes indicate that the liver, gall bladder, bile, kidney, and possibly the pancreas are involved in the excretion of zinc. E. A. LUNT.

Determination of bile acids in the serum in hepatic disease. K. SCHALSCHA and K. LANDÉ (Klin. Woch., 1927, **6**, 1939—1942; Chem. Zentr., 1927, ii, 2509).—In various forms of hepatic disease with icterus the concentration of bile acids in the serum was 2—17 mg.-%, the amount falling or disappearing in severe parenchymatous injury.

A. A. ELDRIDGE.

Elimination of chlorine in hepatic disease after treatment with various chlorides. B. KRISS and L. POLLAK (Wien. klin. Woch., 1927, **40**, 1251—1254; Chem. Zentr., 1927, ii, 2554).—Normally, the elimination of chlorine is practically independent of the cation, but is slightly subnormal for sodium. In hepatic disease or œdema there is considerable retention of chlorine when sodium is administered simultaneously, but good chlorine diuresis with simultaneous administration of potassium or ammonium salts. Infection is accompanied by marked retention of chlorine.

A. A. ELDRIDGE.

Variation of protein in blood-serum in acute infection. A. SCHOCH (Schweiz. med. Woch., 1926, **56**, 1017—1022; Chem. Zentr., 1927, ii, 469).—In pneumonia the serum-protein at first diminishes, and is later increased. The methods of Reiss, Robertson, Nageli and Rohrer, and Kjeldahl are compared.

A. A. ELDRIDGE.

Inflammation. III. Carbohydrate metabolism of the inflamed tissue in initial stages of injury. F. BRICKER and F. SUPONIZKA (Arch. exp. Path. Pharm., 1928, **129**, 100—107).—The venous blood from a rabbit's ear injured by hot water contains more sugar and more amylase than the venous blood from the uninjured ear. It therefore appears that inflamed tissue breaks down polysaccharides more rapidly and is less able to utilise carbohydrate than normal tissue. W. O. KERMACK.

Non-protein sulphur of the blood in certain pathological conditions. W. DENIS, G. R. HERRMANN, and L. REED (Arch. Int. Med., 1928, **41**, 385—402).—Normally the inorganic sulphate fraction of

the blood is entirely confined to the plasma, but in cases of nephritis where increase of non-protein sulphur occurs it appears to diffuse into the red blood-cells. There does not appear to be any direct relation between the retention of non-protein nitrogen and inorganic sulphate, or between the latter, the neutral sulphur fraction, or the chlorides.

W. O. KERMACK.

Urinary proteins not originating in blood. W. A. THOMAS, K. W. SCHLEGEL, and E. ANDREWS (Arch. Int. Med., 1928, **41**, 445—448).—Immunological methods are used to demonstrate that the protein which first appears in the urine of dogs suffering from albuminuria produced experimentally in its early stages is not serum-protein, but that serum-proteins appear after a short time when the permeability of the renal epithelium has increased.

W. O. KERMACK.

Concentration ratio of aromatic substances between serum and urine in renal health and disease. E. BECHER, S. LITZNER, and F. DOENECKE (Munch. med. Woch., 1927, **74**, 1656—1657; Chem. Zentr., 1927, ii, 2509).—Normally the concentration ratio for phenols and indican between the urine and serum is greater than that for nitrogen. The ratio falls in renal insufficiency to a greater extent than does that of urea. For indican the serum value may be higher than the urine value. A. A. ELDRIDGE.

Properties of pure bilirubin and its behaviour towards the van den Bergh reagent. D. T. DAVIES and E. C. DODDS (Brit. J. Exp. Path., 1927, **8**, 316—325).—Changes in the behaviour of bilirubin towards the diazo-reagent are due either to change in p_H or to the occurrence of an oxidative change in the pigment. Bilirubin can be oxidised to biliverdin in the circulation. CHEMICAL ABSTRACTS.

Rickets in dogs. Metabolism of calcium and phosphorus. A. T. SHOHL and H. B. BENNETT (J. Biol. Chem., 1928, **76**, 633—642).—Investigation of calcium and phosphorus metabolism affords a better indication of the development of rickets than does examination of the bones. In dogs, as in rats, rickets is associated with diminution in the balances of calcium and phosphorus; the calcium balance remains positive, whilst the phosphorus balance may become negative, and this more marked deficiency in retention of phosphorus is observed even on diets rich in phosphorus but poor in calcium.

C. R. HARINGTON.

Metabolism in scurvy. I. Lactic acid excretion of scorbutic guinea-pigs. H. L. SHIPP and S. S. ZILVA (Biochem. J., 1928, **22**, 408—415).—The concentration of lactic acid (about 0·01%) as established by Clausen's method in the urine of adult and young scorbutic guinea-pigs is fairly constant. The decline in weight of the animals in the premortal phase is usually associated with polyuria. There is no increase, however, in the concentration of lactic acid in this condition nor is the polyuria associated with albuminuria. A similar increase in the volume of the urine takes place in guinea-pigs declining in weight on a restricted diet containing a sufficiency of the antiscorbutic factor. It is, therefore, not specific of scurvy in guinea-pigs. S. S. ZILVA.

Disturbance of sugar metabolism in trypanosomiasis and spirochætosis. K. SCHERN (Biochem. Z., 1928, **193**, 264—268).—The variations in blood-sugar of two normal rabbits and of two rabbits and a horse after trypanosome infection are tabulated, the values for the infected animals showing sudden changes, hypoglycæmia followed by hyperglycæmia.

P. W. CLUTTERBUCK.

Plasma and corpuscular chlorides in peptic ulcer. L. BLOCH and A. M. SERBY (Arch. Int. Med., 1928, **41**, 415—419).—Marked individual variations occur in the chloride content of plasma and corpuscles, but no significant alteration from normal could be detected in cases of peptic ulcer, nor does any relation appear to exist between the gastric acidity and the blood-chlorides. W. O. KERMACK.

Changes in the blood as reflecting industrial damage. S. MEYER (J. Ind. Hygiene, 1928, **10**, 29—55).—Results of blood examinations are given in the cases of workers suffering from industrial disease due to the inhalation of fumes from benzene, toluene, xylene, naphthalene, aromatic nitro-compounds (dinitrobenzene, trinitronaphthalene, etc.), arsine, thallium, and hydrocyanic acid. In all cases examined there was an increase in the lymphocyte count and a decrease in the neutrophile count. E. A. LUNT.

Aerobic and anaerobic metabolism of the common cockroach (*Periplaneta orientalis*). III. J. G. DAVIS and W. K. SLATER (Biochem. J., 1928, **22**, 331—337).—Lactic acid accumulates during anaerobiosis in the cockroach. The relation between the concentration of lactic acid and the period of anaerobiosis at 14° and 18° is approximately linear. This relationship does not obtain at 25°, in which circumstance there is a noticeable drop in the output of lactic acid during the second hour. This lactic acid accumulation returns to the resting value during the recovery process within 3 hrs. The excess lactic acid amounts to only about one fifth of that calculated from the oxygen debt (cf. Davis and Slater, A., 1927, 66) on the assumption that the recovery takes place as in vertebrate muscle. If, on the other hand, it is assumed that all the lactic acid is burnt without recovery, then the excess lactic acid agrees within the limits of experimental error with that calculated from the oxygen debt.

S. S. ZILVA.

Anaerobic metabolism of the earth-worm (*Lumbricus terrestris*). J. G. DAVIS and W. K. SLATER (Biochem. J., 1928, **22**, 338—343).—The earth-worm goes into debt for oxygen when it is kept under anaerobic conditions, using an excess volume of oxygen during recovery in air equal to that which it would have consumed during the anaerobic period. In the absence of oxygen lactic acid accumulates in the tissues of the worm, the amount in a given time being related to the oxygen debt in the same way as in isolated vertebrate tissue. Thus in distinction to the cockroach there is a re-synthesis of glycogen (see preceding abstract).

S. S. ZILVA.

Metabolism of embryonic tissue in serum. S. KUMANOMIDO (Biochem. Z., 1928, **193**, 315—321).—Anaerobic glycolysis of normally growing cells of

chick and rat embryos, of the chorion, and of embryonic hearts is much smaller in the animal's own serum than in Ringer's solution. The difference is greatest with chick embryos, glycolysis being 49% greater in Ringer's solution than in serum. The effect is not lost by dialysing the serum against Ringer's solution nor by heating it for 30 min. at 55°.

P. W. CLUTTERBUCK.

Placental function. I. Carbohydrate metabolism (III and IV). G. DELLEPIANE (Riv. ital. ginecol., 1926, 5, 216—240, 328—337; Chem. Zentr., 1927, ii, 2206).—Fresh, antiseptically autolysed placental tissue is glycogenolytic, but not glycolytic or glycogenetic; hence the glycolysis of living and surviving placenta is not a simple function of specific, pre-existing enzymes. Experiments suggest that the placenta regulates the carbohydrate metabolism between mother and child. A. A. ELDRIDGE.

Influence of various sugars on the respiratory quotient. E. P. CATHCART and J. MARKOVITCH (J. Physiol., 1927, 63, 309—324).—Current conceptions of the non-protein respiratory quotient as a combustion quotient are criticised. It is suggested, rather, that it represents the equilibrium carbohydrate–fat plus the oxidation of carbohydrate for energy purposes. The rise in R.Q. following the administration of 50 g. of dextrose to a subject was much slower than when the same amounts of sucrose, galactose, lævulose, or dihydroxyacetone were given. These differences are not due to greater rates of absorption or to preferential oxidation of the latter substances. R. K. CANNAN.

Comparison of the effects of dextrose and dihydroxyacetone on metabolism. M. W. GOLDBLATT (Biochem. J., 1928, 22, 464—473).—The experiments were carried out on normal and starving human subjects. There is a much greater oxygen intake and higher respiratory quotients following the administration of dihydroxyacetone as compared with dextrose. The former is not an effective antiketogenic substance and such antiketogenesis as it does exert does not take place simultaneously with the maximum rise in oxygen intake as it does in the case of dextrose. The hypoglycæmia which occurs in man after administration of dihydroxyacetone does not occur in the rabbit. S. S. ZILVA.

Immediate products of glycogenolysis in mammalian muscle and liver. W. W. SIMPSON and J. J. R. MACLEOD (J. Physiol., 1928, 64, 255—266).—Muscle was ground in liquid air immediately after removal from a decapitated cat and then kept at the ordinary temperature. The glycogen almost entirely disappeared in 30 min. There was only a slight increase in inorganic phosphate and free sugar and the increase in lactic acid did not parallel the fall in glycogen. There are, as yet, unidentified intermediate products. In the liver the lactic acid does not increase, but free sugar increases in proportion to the fall in glycogen. R. K. CANNAN.

Lactic acid content of resting mammalian muscle. H. A. DAVENPORT and H. K. DAVENPORT (J. Biol. Chem., 1928, 76, 651—658).—The lactic acid content of the gastrocnemius muscle of guinea-pigs and rats, when removed from the anæsthetised animal, was found to be about 15 mg.-%; much higher values were obtained on analysis of the muscle even immediately after death of the animal.

C. R. HARINGTON.

Production of lactic acid and phosphoric acid in "rigor after thawing." L. DE CARO (Atti R. Accad. Lincei, 1927, [vi], 6, 607—612).—Fletcher (A., 1914, i, 227) has shown that the freezing of striated mammalian muscle is accompanied, not by formation of lactic acid, but by a change which determines the more rapid production of this acid when thawing commences. The author finds that the formation of phosphoric acid in muscle from the frog, toad, and dog proceeds parallel to that of lactic acid and that this behaviour persists unaltered after suppression of the morphological structure of the muscular tissue. The chemical changes involved in "rigor after thawing" are the same as those occurring in other normal or experimental forms of muscular contraction. T. H. POPE.

Chemical changes in muscle. II. Invertebrate muscle. III. Vertebrate cardiac muscle. E. BOYLAND (Biochem. J., 1928, 22, 362—380).—The change of glycogen into lactic acid accompanies activity in invertebrate muscle in the same way as in the muscle of vertebrate animals; the quantity of lactic acid produced under various conditions is different for different species. The heart muscle of invertebrates differs from that of vertebrate animals in not producing less lactic acid than the skeletal muscle of the same animal and in not producing lactic acid in excess of the glycogen present. It is suggested that the excess production of lactic acid in vertebrate cardiac muscle may be derived from the inositol of the muscle. The muscles of crustacea, lamellibranchs, and gastropods appear to act as stores for glycogen. Muscles of lamellibranchs and gastropods usually contain large quantities of glycogen which cannot be converted into lactic acid by the muscle under known optimal conditions for this change. S. S. ZILVA.

Changes in muscle following repeated faradic stimulation. I. G. EMBDEN and H. HABS. **II.** H. HABS (Z. physiol. Chem., 1927, 171, 16—39, 40—61).—I. The *biceps femoris* muscle of one leg of a rabbit may be "trained" by daily faradic stimulation (up to 10 min. per day, 60 stimuli per minute). If after 2—6 weeks the animal is killed, the "trained" muscle shows a remarkable increase in its glycogen content, which may reach in some cases three times that of the control muscle. The "trained" muscle loses its extra glycogen only very slowly on going out of "training." There is also a small increase in creatine content. There is no constant difference in the phosphoric acid partition between the "trained" and "untrained" muscle.

II. Inorganic phosphate is liberated from the hashed "trained" muscle at 0° much more slowly than from the untrained muscle. The diminution in ability to synthesise phosphoric esters which occurs on keeping hashed muscle at 0° is much lower in "trained" than in "untrained" muscle. Ammonia

formation is also slower in "trained" muscle. "Untrained" muscle goes into rigor earlier than "trained" muscle. These differences suggest that deep-seated change in the colloidal condition of the muscle is brought about by "training." H. D. KAY.

Influence of the "training" of muscles on their creatine content. A. PALLADIN and D. FERDMANN (Z. physiol. Chem., 1928, **174**, 284—294).—Experiments have been carried out on rabbits to determine the changes in the creatine, total nitrogen, water, and glycogen content of muscle on tetanisation. The creatine content of a muscle tetanised by an induction current is always reduced compared with that of the non-stimulated muscle, but this decrease is not real and is due to an increase in the water content; thus no change occurs in the creatine nitrogen or total nitrogen expressed as percentage of the dry weight of the muscle. The *biceps femoris* muscle of a rabbit "trained" by stimulation for 3 min. twice per day for 5—15 days has a significantly higher creatine content than the "untrained" control muscle, and this increase is quite marked even after 5 days' "training." The total nitrogen shows no change and the creatine nitrogen accounts for 5·0—5·5% of the total nitrogen in the "trained" muscle and 4·1—5·0% in the control muscle. The water content is approximately constant and thus the increase in creatine is real and persists for some time after the last stimulation; 6 days after the last stimulation, however, no difference between the creatine contents of the "trained" and the "untrained" muscles can be observed, although the increase in glycogen content persists longer. The conclusion is reached that the stimulations effect an increased storage of the substances required to furnish energy for muscle contraction (cf. Embden and Habs, Skand. Arch. Physiol., 1926, **49**, 122). A. WORMALL.

Phosphagen. P. EGGLETON and G. P. EGGLETON (J. Physiol., 1928, **65**, 15—24; cf. A., 1927, 271, 990).—The rate of disappearance of phosphagen from a resting muscle under anaerobic conditions greatly exceeds the rate of lactic acid production. The breakdown of phosphagen, in fatigue, rigor, or incubation in hydrogen carbonate solutions, leads to the production of free creatine in amount roughly corresponding with the phosphagen which has disappeared. The re-synthesis of phosphagen in a fatigued muscle is very rapid in an atmosphere of oxygen, greatly exceeding the re-synthesis of glycogen from lactic acid. Under anaerobic conditions the phosphagen lost by resting muscle is completely accounted for by the inorganic phosphate produced, but in activity part of the phosphorus appears as organic phosphoric esters. When muscle is incubated in the presence of fluoride all the phosphorus appears as organic esters. The phosphoric ester produced in fatigue is identical with Embden's "lactacidogen." R. K. CANNAN.

Different phosphagen content of rapidly contractile and slowly contractile striated muscle. G. MARTINO (Atti R. Accad. Lincei, 1928, [vi], 7, 79—82).—Of the muscles of the rabbit and pigeon, those capable of the more rapid contraction contain the more phosphagen (cf. Eggleton and Eggleton, A., 1927, 271) and the less inorganic phosphorus. T. H. POPE.

Relation of diet to quality of fat produced in the animal body. W. E. ANDERSON and L. B. MENDEL (J. Biol. Chem., 1928, **76**, 729—747).—On a constant diet of wheat and milk the iodine value of the body-fat of growing rats decreases with increasing body-weight. On diets containing much fat, the body-fat did not always approximate to the composition of the ingested fat; a diet rich in protein or carbohydrate and low in fat resulted in deposition of body-fat with a low iodine value. Alteration in the character of the body-fat was most rapidly brought about by preliminary depletion of the fat deposit by starvation before transference to a new type of diet. C. R. HARINGTON.

Cholesterol metabolism. H. BEUMER (Klin. Woch., 1927, **6**, 1749; Chem. Zentr., 1927, ii, 2079).—Intravenous injection of cholesterol into a milk-fed infant led to its rapid and complete elimination by the liver. A. A. ELDRIDGE.

Synthesis and absorption of cholesterol. H. DAM (Biochem. Z., 1928, **194**, 188—196).—Determination of cholesterol in fresh hen's eggs and in fully developed chick embryos showed an increase of 10% in the embryo, an amount too small to decide whether synthesis has occurred. Cholesterol compounds, detected by heating with acetic acid and extracting with ether, could not be found either in hen's eggs or in the embryos. After feeding with free cholesterol or with cholesteryl palmitate, the amount of cholesterol in the eggs is increased by about 20%. P. W. CLUTTERBUCK.

Biological significance of the unsaponifiable matter of oils. IV. Absorption of higher alcohols. H. J. CHANNON and G. A. COLLINSON (Biochem. J., 1928, **22**, 391—401).—The order of the degree of absorption by the rat of the alcohols is as follows: phytol, oleyl alcohol, cetyl alcohol, cholesterol. Their solubilities in bile salt fall in the same order. The presence of unsaponifiable substances in the diet increases the unsaponifiable fraction of the liver, the cholesterol in this fraction tending to rise at the same time. S. S. ZILVA.

Availability of the calcium in calcium lactate in man. F. W. HEYL and M. C. HART (J. Amer. Pharm. Assoc., 1928, **17**, 225—232).—The average daily intake and output of calcium, phosphorus, and magnesium in normal subjects on a calcium-deficient and acidotic diet with varying additions of calcium lactate and milk have been examined. The diet, which was not deficient in vitamins, required the addition of approximately 9·5 g. of calcium lactate over a period of 10 days to establish calcium equilibrium. This represents 2·5 or more times as much calcium as is necessary when using milk. Both with milk and calcium lactate the urinary calcium was markedly increased. The urinary phosphorus excretion was decreased and phosphorus retention secured by the ingestion of calcium lactate. In this diet the original Ca : P ratio was 2 : 9, and the favourable influence on phosphorus metabolism may be due to the establish-

ment of a more favourable balance of 14 : 9. In the case of milk experiments, a ratio of 5 : 9 produced a more decided phosphorus retention. In the case of magnesium metabolism, calcium lactate caused slightly increased losses in three of the five subjects. E. H. SHARPLES.

Nucleic phosphorus balance in mice deficient in lipoid-soluble nutriment. M. JAVILLIER, H. ALLAIRE, and S. ROUSSEAU (Bull. Soc. Chim. biol., 1928, **10**, 294—300).—Since it is possible that vitamin-*A* acts as a "catalyst" in the multiplication of cells, the course of avitaminosis in mice has been examined in order to determine whether this state is reflected in abnormal nucleic phosphorus values. Whilst the insoluble phosphorus values are considerably higher in the animals deficient in the vitamin, the very slightly lower transitional, lipoid, and nucleic phosphorus values obtained do not support any definitive conclusion. G. A. C. GOUGH.

Losses of sulphur due to hæmolysis and its fate in the organism. M. LOEPER, R. GARSIN, A. LESURE, and J. TONNET (Bull. Soc. Chim. biol., 1928, **10**, 316—321).—A discussion of the metabolism of sulphur. Sulphur is liberated in the oxidised form by hæmolysis and by the proteolysis of albumin (which liberates sulphur even under aseptic conditions). The liberated sulphur is partly utilised by the tissues and partly excreted in the urine.

G. A. C. GOUGH.

Creatinine and uric acid metabolism. II. Ingestion of proteins and amino-acids and the hourly elimination of creatinine and uric acid. H. ZWARENSTEIN (Biochem. J., 1928, **22**, 307—312). —Ingestion of glycine, alanine, or a purine-free protein meal (egg-white and cheese) is without effect on the hourly output of uric acid or creatinine. On the other hand, the ingestion of a meal rich in uric acid or creatinine precursors, such as meat, causes a large increase in the excretion of these two catabolites. The effect of the differences in the calorific value of the diet on the tissue metabolism may be a cause of the variation in uric acid and creatinine excretions.

S. S. ZILVA.

Production of carbonyldicarbamide by oxidation of uric acid and allantoin and its metabolism. A. SCHITTENHELM and K. WARNAT.—See this vol., 530.

Detection of alcohol in forensic practice. F. SCHWARZ (Deut. Z. ges. gerichtl. Med., 1927, **10**, 377—407; Chem. Zentr., 1927, ii, 2516).—A detailed discussion. A. A. ELDRIDGE.

Rate of narcotic action of homologous and isomeric monohydric alcohols. L. LENDLE (Arch. exp. Path. Pharm., 1928, **129**, 85—92).—The rate of narcotic action increases with length of the chain. *tert.*-Amyl alcohol acts less rapidly than *n*-amyl, *sec.*-amyl, and *iso*amyl alcohols.

W. O. KERMACK.

Causes of the differences in pharmacological actions of optical isomerides. E. KEESER (Arch. exp. Path. Pharm., 1928, **129**, 236—255).—Optical isomerides have the same effect on the surface tension of liquids even although these are optically active or contain an optically active substance in solution. They have, however, different effects on the viscosity of solutions of gelatin and on the viscosity of certain optically active liquids. The degrees of adsorption of optical isomerides on optically active adsorbents such as red blood-cells are probably equal, apparent differences being due to other influences such as unequal rates of destruction. Differences have, however, been detected between the rates of diffusion of optical isomerides into an optically active gel. The bearing of these results on the mode of pharmacological action is discussed. W. O. KERMACK.

Detoxification of and immunity production to ricin by sodium ricinoleate. E. B. CARMICHAEL (Proc. Soc. Exp. Biol. Med., 1926, **24**, 5—7).—The detoxifying influence of sodium ricinoleate on ricin has been investigated in the case of the rabbit. Solutions of ricin containing 400—2000 lethal doses can be injected subcutaneously into rabbits without causing death if mixed with 0·2—0·5 g. of sodium ricinoleate. An immunity to the lethal dose of ricin is developed and the sera of the animals thus treated have antiricin properties.

E. A. LUNT.

Influence of purine diuretics on inorganic phosphates of blood and urine. A. BOLLIGER (J. Biol. Chem., 1928, **76**, 797—807).—Purine diuretics cause diminution in the concentration of inorganic phosphorus in the blood and in its excretion in the urine; the effect was least marked with caffeine.

C. R. HARINGTON.

Effect of salicylates on nitrogen metabolism with special reference to the effect of the cation of the salt. G. P. GRABFIELD and E. KNAPP (J. Pharm. Exp. Ther., 1928, **32**, 341—350).—The effect has been determined of lithium, sodium, and potassium salicylates on the nitrogen metabolism of normal individuals. The dose of salicyl ion was 6 mg. per pound of body-weight administered three times a day. An increase of 10% in the total urinary nitrogen, total sulphur, total sulphate, and inorganic sulphate, and a 30% increase in uric acid excretion resulted. Increase in the total nitrogen excretion occurred immediately after the sodium salt was given, but a delay of 2 days followed the administration of the potassium salt. The increase in uric acid excretion was most prompt after the administration of the lithium salt and least prompt after the administration of the potassium salt.

E. A. LUNT.

Relation of synthalin to carbohydrate metabolism. R. BODO and H. P. MARKS (J. Physiol., 1928, **65**, 83—99).—In the whole animal synthalin produces hypoglycæmia and death. Relief of the hypoglycæmia seems only to postpone the fatal result. In the perfused muscle preparation synthalin increases the disappearance of dextrose. The sugar is not converted into glycogen nor is it oxidised, but the lactic acid concentration of the blood increases and the respiratory quotient rises above unity. In the whole animal the liver is depleted of glycogen and is unable to react to adrenaline. There is evidence for a toxic effect of synthalin on the liver and the circulation. R. K. CANNAN.

Influence of phloridzin on inorganic metabolism. A. O. Kastler (J. Biol. Chem., 1928, **76**, 643—649).—Administration of phloridzin to dogs over a period of 7 days caused diminution of the potassium and increase in the phosphorus of the blood without coincident changes in the urinary excretion of these elements. C. R. Harington.

Biological determination of the amounts of cardio-active glucosides absorbed by the heart of the frog. E. Rothlin and T. Oliaro (Compt. rend., 1928, **186**, 901—902).—Scillarin *A*, *B*, and the natural mixture of glucosides (Stoll, Schweiz. med. Woch., 1927, **49**, 1169) arrest the action of the frog's heart at the following maximum dilutions, 1 in 900,000, 1,300,000, and 1,000,000, respectively. The amounts of these substances, 0·00009 mg., 0·000145 mg., and 0·000105 mg., respectively, absorbed by a heart during the cessation of action are determined in the following way: a known amount of the glucoside solution, of a concentration higher than the minimum effective, is passed through separate isolated hearts until it fails to stop the beating; at this stage its concentration has fallen to that of the minimum effective and hence the amount of glucoside absorbed by the hearts may be calculated. G. A. C. Gough.

Enzymic processes as the cause of Gottlieb's detoxication of digitalis substances fixed by the heart. O. Steppuhn and J. Nolle (Biochem. Z., 1928, **193**, 409—415).—By keeping active digitalis substances in heart muscle-pulp undergoing autolysis, a decrease of the toxicity of the heart-active constituent occurs, due probably to its hydrolysis. It is suggested that a similar enzymic process in frog's heart muscle explains the detoxication observed by Gottlieb (cf. Arch. exp. Path. Pharm., 1918, **83**, 117). P. W. Clutterbuck.

Supposed influence of polarised light on the deterioration of digitalis. W. R. Bond and E. W. Gray (J. Pharm. Exp. Ther., 1928, **32**, 351—358).—Experiments have been carried out with reference to the deterioration of digitalis with age under various conditions of storage. The potency of the preparations was tested by intravenous injection into cats. It is concluded that the potency of digitalis preparations is not lowered by exposure either to ordinary or to polarised light (cf. Macht and Krantz, B., 1927, 346). E. A. Lunt.

Chemistry of vegetative stimulation. Alleged role of ions. L. Jendrassik and A. Czike (Biochem. Z., 1928, **193**, 285—299).—In solutions poor in potassium, the action of pilocarpine on the large intestine, stomach, uterus, œsophagus of rabbits, and on the urinary bladder of rabbits and cats is the reverse of that of potassium. Adrenaline stimulates (in the absence of calcium) and calcium inhibits rabbit's uterus. With frog's stomach calcium and adrenaline are antagonistic. With cat's intestine, adrenaline in the absence of calcium inhibits and calcium stimulates. P. W. Clutterbuck.

Influence of allyl groups on the pharmacological action of various amines. E. Brauchli and M. Cloetta (Arch. exp. Path. Pharm., 1928, **129**, 72—84).—By the action of allyl bromide on the parent bases the following compounds have been obtained: *allyltetrahydro*-β-*naphthylamine* [*hydrobromide*, m. p. 236°; *hydrochloride*, m. p. 225° (decomp.)]; *diallyltetrahydro*-β-*naphthylamine*, b. p. 164—165°/9 mm.; *diallyltetrahydro*-β-*naphthylmethylamine*, b. p. 172—173°/10 mm.; *diallyltyramine*, b. p. 184—185°/10 mm.; *diallylphenylethylamine* (*hydrobromide*, m. p. 125°); *diallylephedrine* (*hydrobromide*, m. p. 170°); *diallyl*-n-*butylamine*, b. p. 54—55°/10 mm., and *diallyl*-i-*amylamine*, b. p. 65—66°/9 mm. The parent bases all raise the blood pressure, but these allyl derivatives without exception lower it when administered to dogs. W. O. Kermack.

Toxicity of aromatic nitro-compounds. Dinitrophenol. Koelsch (Zentr. Gewerbehyg., 1927, **14**, 261—268; Chem. Zentr., 1927, ii, 2082).—The maximum tolerated dose (by the mouth) of 2 : 4-dinitrophenol is 0·02—0·03 g. per kg. body-weight; 0·05 g. is rapidly fatal. Simultaneous administration of alcohol increases the toxicity. The critical dose by absorption through the skin is 8—10 times as great as that by the mouth. The kidneys are damaged, and there appears to be a general injury to protoplasm. A. A. Eldridge.

Mechanism of action of arsenic and related elements. II. Role of oxygen in hæmolytic activity of hydrogen phosphide or its lowest oxidation product. III. Hæmolytic activity of hydrogen sulphide at increased oxygen concentration. IV. Hæmolysis by hydrogen sulphide. Action of colloidal sulphur formed. V. Conditions for hæmolysis by salts of hydrogen iodide. R. Labes (Arch. exp. Path. Pharm., 1928, **129**, 150—158, 159—175, 176—192, 193—201).—II. Hydrogen phosphide does not hæmolyse red blood-cells in the absence of air, but small concentrations (1/200 mol. per litre) effect hæmolysis if oxygen is admitted.

III. Similarly, hydrogen sulphide effects hæmolysis of red blood-cells provided sufficient oxygen is present. Serum tends to inhibit this action of hydrogen sulphide.

IV. When hydrogen sulphide is passed into a suspension of red blood-cells containing sodium sulphite under conditions suitable for the formation of colloidal sulphur, rapid hæmolysis occurs, but colloidal sulphur produced in other ways may not cause hæmolysis.

V. Iodides and iodates are not hæmolytic under conditions in which free iodine effects rapid hæmolysis. Iodides thus exhibit a certain similarity to the hydrides of arsenic, phosphorus, and sulphur in that an oxidation product is actively hæmolytic. W. O. Kermack.

Effect of arsenic compounds on excretion of sulphur. F. P. Underhill and A. Dimick (J. Pharm. Exp. Ther., 1928, **32**, 359—365).—The subcutaneous injection of arsenious oxide into the dog increases the ethereal sulphate and neutral sulphur fraction of the urinary sulphur. No consistent variations were detected when the administration was made by mouth. Serial administration of neosalvarsan is associated with increase of the

neutral sulphur fraction of the urine. These results lend support to Voegtlin's hypothesis for the behaviour of compounds of arsenic in the body.

E. A. LUNT.

Histochemical detection of gold. Distribution of "sanocrysin" in, and its elimination from, the normal and tuberculous body. S. KUROSU (Z. ges. exp. Med., 1927, **57**, 77—110; Chem. Zentr., 1927, ii, 2329—2330).—"Sanocrysin" is detected in microscopical sections by treatment with stannous chloride. It is found chiefly in the kidneys; gold particles accumulate in the lungs, spleen, and liver of animals. Deposition was abnormally great in tuberculous organs, as well as in non-tubercular inflammation.

A. A. ELDRIDGE.

Pharmacology of the iodine ion. W. WADI (Arch. exp. Path. Pharm., 1928, **129**, 1—42).—A comprehensive investigation of the action of iodides and of the thyroid gland on the organism as a whole and on the body-weight, on the separate organs of the body, on the blood, on the mechanism of heat regulation, on sensitiveness to lack of oxygen, and on the respiratory exchange.

W. O. KERMACK.

Behaviour of magnesium hydroxide towards solutions of mercuric chloride and salts of tervalent arsenic. M. RAKUZIN and E. ITZKIN (Trudy nauc. chim.-farm. inst., 1926, 109—114).—The antitoxic effect of magnesium hydroxide on mercuric chloride is superior to that on arsenites, but inferior to that of charcoal on mercuric chloride. Neither magnesium hydroxide nor charcoal acts on sodium cacodylate.

CHEMICAL ABSTRACTS.

Pharmacology of a mercury colloid. E. UGOLOTTI (Arch. Farm. sperim., 1928, **44**, 145—168).—The colloid used was prepared by heating mercuric chloride with fresh egg-albumin in presence of sodium hydroxide and heating the gel thus obtained with water at 100° to form the sol. This colloid is black and highly stable, neither boiling nor addition of an equal volume of 10% sodium chloride solution causing its flocculation; barium chloride precipitates it, and addition of acid results in reversible gel-formation. It is negatively charged and exhibits Tyndall's phenomenon.

Experiments with rabbits, guinea-pigs, and dogs show that, when the colloid is administered subcutaneously, the more stable part having the finer micelles is absorbed, causing toxic phenomena, degeneration and necrosis of the renal and hepatic epithelia, rapid loss of flesh, and death, whereas the coarser, less stable part becomes granular and is diffused through the tissues at the point of introduction. Experiments *in vitro* do not reveal any antiseptic action of the mercury in the colloidal condition.

T. H. POPE.

Distribution of the respiratory enzyme between carbon monoxide and oxygen. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, **193**, 334—338).—Regarding iron as the respiratory enzyme, its distribution between carbon monoxide and oxygen is shown to be dependent, not only on temperature, but also to a less extent on the salt concentration of the solution in which the yeast (*Torula utilis*) is suspended (cf. A., 1927, 1221).

P. W. CLUTTERBUCK.

Influence of the wave-length on the distribution of the respiratory enzyme. Absorption spectrum of the respiratory enzyme. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, **193**, 339—346).—The changes of distribution of the respiratory enzyme between carbon monoxide and oxygen, in yeast suspensions, with the wave-length (from 366 to 700 $\mu\mu$) of the light to which they are exposed is investigated and the results are tabulated. In order to compare the dV/di values for the different wave-lengths, the blue mercury line 436 $\mu\mu$ is taken as reference line, when W, the photochemical action, becomes $(dV/di)\lambda/[(dV/di)\times 436]$, or, working in quanta, W_1—$436W/\lambda$. Plotting W_1 against λ and assuming that differences are dependent on differences in absorption, the curve obtained, which has the form of a hæmin spectrum, becomes the absorption curve of the respiratory enzyme or of its compound with carbon monoxide.

P. W. CLUTTERBUCK.

Kinetics of catalase. S. M. MAXIMOVITSCH and E. S. AVTONOMOVA (Z. physiol. Chem., 1928, **174**, 233—250).—The kinetics of the decomposition of hydrogen peroxide by blood-catalase have been studied with varying amounts of hydrogen peroxide and catalase. The whole process consists of two simultaneous independent reactions, the enzymic decomposition of hydrogen peroxide by catalase and the inactivation of catalase by hydrogen peroxide. The former reaction is unimolecular and deviations from this law are due to the second reaction. Formulæ are given which, under certain conditions, enable the amount of hydrogen peroxide decomposed or the catalase power of the solution to be determined.

A. WORMALL.

Decomposition of hydrogen peroxide by liver catalase. J. WILLIAMS (J. Gen. Physiol., 1928, **11**, 309—337).—The velocity of decomposition of hydrogen peroxide by catalase has been determined as a function of (*a*) concentration of catalase, (*b*) concentration of hydrogen peroxide, (*c*) hydrogen-ion concentration, (*d*) temperature. From the similarity of the results obtained with those of known absorption processes it is concluded that the reaction involves adsorption of hydrogen peroxide at the catalase surface and that it involves two reactions, viz., the catalytic decomposition of hydrogen peroxide and the "induced inactivation" of catalase by the nascent oxygen produced and still adhering to the catalase surface. The critical increment for the former reaction in the range 15—20° is of the order of 3000 g.-cal., and the optimum p_H 6·8—7·0. Values calculated for the critical increment of the latter reaction are irregular and rise from 8000 in the range 10—15° to 30,000 in the range 15—20° and also increase as the concentration of hydrogen peroxide is increased.

E. A. LUNT.

Lactic dehydrogenase. A cell-free enzyme preparation obtained from bacteria. M. STEPHENSON (Biochem. J., 1928, **22**, 605—614).—The enzyme is obtained by autolysing suspensions of *B. coli* in a phosphate buffer at p_H 7·6 and centrifuging and filtering the resulting solution. The preparation in the presence of methylene-blue actively dehydrogenates lactate and also much more slowly

α-hydroxybutyrate. The enzyme is not affected by cyanide. It differs from the intact cell in its behaviour towards lactate, not only in specificity, but also in the fact that it cannot reduce molecular oxygen except in the presence of a carrier such as methylene-blue. S. S. ZILVA.

Soluble dehydrogenases. T. THUNBERG (XII Int. Cong. Physiol., 1926, 161; Chem. Zentr., 1927, ii, 445).—Seeds are ground with 5 parts of 0·05*N*-dipotassium hydrogen phosphate solution, and the mixture is centrifuged and filtered; the filtrate is colloidal and macroscopically homogeneous. Various specific donators are described. A. A. ELDRIDGE.

Effect of lipin on the dehydrogenating power of tissue. K. TSUNEYOSHI (J. Biochem. Japan, 1927, 7, 267—272).—Lecithin and cholesterol neither promote nor retard the dehydrogenation reaction of tissue, but in greater concentrations both produce an inhibiting effect. CHEMICAL ABSTRACTS.

Aldehyde oxidase of the potato. F. BERNHEIM (Biochem. J., 1928, 22, 344—352).—The enzyme will oxidise all aldehydes but none of the other hydrogen donators tried. The system will reduce methylene-blue, Clark's dyes, and quinones, besides nitrates. The p_H activity curves for the nitrate and methylene-blue reductions have been obtained. The action of the enzyme is not dependent on traces of iron. The enzyme was prepared from potato juice by precipitation with ammonium sulphate, redissolving the precipitate, clearing the solution with charcoal, and adsorbing the active principle on kaolin in acid solution. The enzyme was eluted from the adsorbent with sodium carbonate solution. Methylene-blue is reduced very slowly by the untreated potato juice. S. S. ZILVA.

Effect of temperature on the oxidation of pyruvic and fumaric acids by tissue. K. TSUNEYOSHI (J. Biochem. Japan, 1927, 7, 259—261).—The oxygen-consuming power of tissue is maximal at 38°. CHEMICAL ABSTRACTS.

Biological importance of heavy metals as catalysts. Biological action of the water of the [illegible] hot springs. III. K. HARPUDER (Biochem. [illegible], 1928, 193, 372—379; cf. A., 1927, 320, 1088).—[illegible] dialysis of serum against the water of the Wiesbaden hot springs, its peroxidase and oxidase action is increased, but its catalase activity and its power to reduce methylene-blue are decreased. Dialysis causes an increase in the iron content of the serum and the [illegible] constituent remains active in serum after keeping a long time in air. P. W. CLUTTERBUCK.

Phosphate ion and hydrolysis by pancreatic lipase. E. R. DAWSON and B. S. PLATT (J. Gen. Physiol., 1928, 11, 357—360).—The validity of the relationship used by Lynn (cf. A., 1927, 390) [Activity of [illegible] K, in [illegible] with the effect of the phosphate ion in certain biological processes has been examined in the case of the hydrolysis of ethyl butyrate by lipase in the presence of p_H [illegible] ion. The results show that this expression is not valid and [illegible] tions are advanced to account for the observed deviations. E. A. LUNT.

Nature of the action of pancreatic extract on the inhibition of lactic acid formation in muscle. D. R. MCCULLAGH (Biochem. J., 1928, 22, 402—406).—The pancreatic factor which inhibits the formation of lactic acid by muscle enzymes (Foster and Woodrow, A., 1924, i, 897; Foster, A., 1925, i, 1495) when added to an aqueous extract of muscle containing lactic acid-forming enzymes prevents the formation of lactic acid and the disappearance of carbohydrate, causes an increase in free phosphate, and prevents the esterification of phosphate even in presence of fluoride. This factor is present in traces in many other tissues from various species of mammals. S. S. ZILVA.

Nuclein metabolism. XVII. Liver-nucleotidase. W. DEUTSCH (Z. physiol. Chem., 1927, 171, 264—275).—A study of the preparation and purification of liver-nucleotidase, its activity, and the inhibiting action of glycerol. J. STEWART.

Structure of polypeptides and the proteolytic enzymes. R. NAKASHIMA (J. Biochem. Japan, 1927, 7, 399—403).—A comparison of the digestion by erepsin of glycylaspartic acid and glycylasparagine shows that the amidation considerably increases the effectiveness of the enzyme. CHEMICAL ABSTRACTS.

Fractional enzymic hydrolysis of histone. E. WALDSCHMIDT-LEITZ and G. KUNSTNER (Z. physiol. Chem., 1927, 171, 290—315).—The amounts of peptide and of free amino-acids produced from histone sulphate (prepared from calf's thymus) by various sequences of proteolytic enzymes are determined. J. STEWART.

Effect of ferrous and manganous ions on enzymes. Biological action of the water of the Wiesbaden hot springs. IV. K. HARPUDER (Biochem. Z., 1928, 193, 380—383).—Investigation of the action of ferrous and manganous ions in 1×10^{-2} to $0·5\times10^{-4}M$-concentrations on unpurified salivary amylase, pepsin, and trypsin shows that, whereas with ptyalin and pepsin heavy metals inhibit in higher and accelerate in lower concentrations, the acceleration being greater for the amylase than for pepsin, with trypsin a small inhibition is detected only with high concentrations of iron. P. W. CLUTTERBUCK.

Ultrafiltration of pancreas ferments. E. LAGRANGE and E. SUAREZ (Compt. rend. Soc. Biol., 1927, 96, 963; Chem. Zentr., 1927, ii, 445).—Bechhold and König's apparatus is modified. 7% Cellulose nitrate acetate is impermeable to trypsin, practically so to lipase, partly so to amylase, and permeable to vitellase. 10% Cellulose acetate is impermeable to trypsin, lipase, and vitellase, and partly so to amylase. Relatively pure vitellase can thus be prepared. A. A. ELDRIDGE.

Specificity of animal proteases. XI. Pepsin. E. WALDSCHMIDT-LEITZ and G. KÜNSTNER (Z. physiol. Chem., 1927, 171, 70—77).—In the hydrolysis of four typical proteins—egg-albumin, caseinogen, gelatin, and histone—by pepsin, the ratio of amino-groups liberated to carboxyl groups liberated is 1. (Amino-groups were determined by Van Slyke's method, carboxyl groups by titration in 90% alcoholic

solution.) The peptide linking is, in the main, the mode of union of the constituent amino-acids of enzymically hydrolysable proteins. H. D. KAY.

Pepsin hydrolysis. S. P. L. SØRENSEN and L. KATSCHIONI-WALTHER. [With a note on **Indicators** by K. LINDERSTRØM-LANG] (Z. physiol. Chem., 1928, **174**, 251—277).—In view of the conflicting results of other workers on the relationship between the increase of free acid groups and that of free amino-groups on peptic digestion of proteins, a critical examination of the usual methods of analysis has been made; Van Slyke's method for determination of amino-nitrogen is not suitable for natural proteins or the products of peptic digestion. Digestion of caseinogen, gliadin, and gelatin by pepsin in acid solution results in the liberation of equal amounts of acid groups (determined by formol titration and by Willstätter's method) and basic groups (determined by the Linderstrøm-Lang method; this vol., 313). Previous failures to obtain a ratio of unity are due to errors which have been avoided by modifications of the above methods. The liberation of equal amounts of acidic and basic groups indicates that peptic hydrolysis, like other proteoclastic hydrolyses, consists of a splitting of peptide linkings. Linderstrøm-Lang has investigated the possibility of using certain triphenylmethane dyes as indicators for the acetone–hydrochloric acid titration method for determination of amino-nitrogen (*loc. cit.*); 2 : 4 : 2 : 4′ : 2″-pentamethoxytriphenylcarbinol gives values similar to those obtained when naphthyl-red is used for the titration of glycine and of peptic hydrolysates of caseinogen. No control is necessary with the former indicator, but a sharper end-point is obtained with naphthyl-red. A. WORMALL.

Adsorption of pepsin. K. KIKAWA (J. Biochem. Japan, 1927, 7, 389—398).—Pepsin is not adsorbed by kaolin, but is adsorbed by alumina in slightly acid medium, optimally at p_H 4·6 for acetate and 3·8 for citrate buffer. The nature of the anion does affect the adsorption. The adsorption with alumina is reversible, and by combining adsorption with electrodialysis the pepsin solution can be concentrated to 0·03 of its volume without loss of activity.
CHEMICAL ABSTRACTS.

Pepsinometric method; pepsin determination. J. ROOS (Deut. med. Woch., 1927, **53**, 1693; Chem. Zentr., 1927, ii, 2412).—In the action of activated pepsin on adipose tissue, a small digestion causes a relatively large volume change. A. A. ELDRIDGE.

Effect of chemicals on glycerophosphatase. K. INOUYE (J. Biochem. Japan, 1927, 7, 433—439). —Fluorine ions markedly inhibit the action of glycerophosphatase, and in high concentration destroy the enzyme, whilst citrate and calcium ions are practically without effect. Fluoride ions and glycerol shift the optimum p_H to the alkaline side (6·1 and 5·0, respectively). CHEMICAL ABSTRACTS.

Origin of creatine. E. ABDERHALDEN and P. MÖLLER (Z. physiol. Chem., 1927, **170**, 212—225; cf. Abderhalden and Buadze, A., 1927, 696).—The earlier experiments are confirmed and Riesser's suggestion that choline plays an important part in the formation of creatinine (A., 1922, i, 791) is supported. Addition of choline and/or arginine to a suspension of fresh liver and muscle of dogs or rats produces notable increase in total creatine and creatinine; the result with choline alone seems to depend on the presence of arginine and arginase in the liver used. A similar increase is observed when urea instead of arginine is added with choline.
C. HOLLINS.

Action of yeast oxidoreductase on some probable intermediate products of alcoholic fermentation and on crotonaldehyde. A. LEBEDEV (Z. physiol. Chem., 1927, **172**, 50—55).—The action of yeast oxidoreductase on acetaldehyde, methylglyoxal, dihydroxyacetone, glyceraldehyde, sodium lactate, and crotonaldehyde in the presence of methylene-blue has been determined. The first two compounds are oxidised at approximately the same rate, in contrast to the results with milk oxidoreductase, which does not oxidise methylglyoxal readily (cf. A., 1927, 76). These observations support the view that methylglyoxal is an intermediate product in alcoholic fermentation, although this substance is not directly fermented by living yeast. The rate of oxidation of glyceraldehyde by the yeast enzyme is at least double that for acetaldehyde, but with dihydroxyacetone no oxidation or very slight oxidation occurs. Crotonaldehyde is oxidised almost as readily as acetaldehyde, whilst sodium lactate, which is not acted on by the milk oxidoreductase (*loc. cit.*), is oxidised to a slight extent only. Activation of hydrogen occurs with glyceraldehyde or dihydroxyacetone in the presence of phosphates, and this hydrogen can be given up to methylene-blue without the intervention of the enzyme, and it is concluded that the action of the oxidoreductase is concerned only with activation of labile hydrogen atoms, the term " hydrogenactivase " being suggested for this enzyme. A. WORMALL.

Pyruvic acid. C. NEUBERG and E. SIMON (Z. physiol. Chem., 1927, **171**, 1—3).—Polemical against Haehn and Glaubitz (A., 1927, 902).

Point of attack of co-zymases in the fermentation of dextrose and hexosediphosphoric acid. A. GOTTSCHALK (Z. physiol. Chem., 1927, **170**, 264—273).—For the dismutation of acetaldehyde by washed, dried bottom yeast and also for the fermentation of hexosediphosphate a smaller addition of co-zymase (boiled and filtered cow's milk) is required than for the fermentation of dextrose; these facts support the suggestion (cf. A., 1926, 544; Meyerhof, *ibid.*, 95) that co-zymases behave during phosphorylation as co-phosphatases. C. HOLLINS.

Oxidase reaction in bacteria. III. Nature of the oxidase reaction. M. NISHIBE (Japan. Med. World, 1927, 7, 128).—It is not considered probable that the oxidase reaction is due to iron catalysis; the active principle of the oxidase reaction in bacteria may be an oxidative enzyme, iron acting as a secondary factor by increasing the intensity of the reaction.
CHEMICAL ABSTRACTS.

Deamination and synthesis of *l*-aspartic acid in presence of bacteria. R. P. COOK and B.

Woolf (Biochem. J., 22, 474—481; cf. Quastel and Woolf, A., 1926, 868).—Eleven species of bacteria consisting of strict aerobes, facultative anaerobes, and strict anaerobes have been investigated. At 37° and p_H 7·4 they all deaminate aspartic acid anaerobically to succinic acid. This reaction is completely prevented by the presence of inhibitors such as 2 or 4% propyl alcohol, 0·1*M*-sodium nitrite, or toluene. In addition, all the four facultative anaerobes can effect a reversible equilibrium, aspartic acid $\rightleftharpoons$ fumaric acid + ammonia. The four strict aerobes and three strict anaerobes examined show no trace of this reaction, which is unaffected by the presence of the inhibitors. Well-boiled bacteria have no deaminating effect on aspartic acid. All the bacteria used completely deaminate glycine, alanine, and glutamic acid in the absence of inhibitors. S. S. Zilva.

Nitrogen metabolism of nitrogen-fixing bacteria. W. V. Halversen (Iowa State Coll. J. Sci., 1927, 1, 395—410).—*Rhizobium leguminosarum* and *Azotobacter chroococcum* were employed, with Moore's dextrose–Ashby's solution and dextrose–Ashby's solution with excess of lime. The amino-nitrogen increased with age until a maximum was reached. The first product of nitrogen metabolism is ammonia, since this accumulates during the first few days of maximum growth, but gradually diminishes as the source of carbohydrate is exhausted. In presence of excess of lime, *Rhizobium* fixes an unusually large amount of nitrogen. Tyrosine or hydroxy-acids were always present; nitrites and nitrates were absent. Sørensen's method for determining amino-nitrogen is untrustworthy for bacterial cells, and Van Slyke's method employs volumes too small for young cultures. Chemical Abstracts.

Production of pyruvic acid by certain nodule bacteria of the *Leguminosæ*. J. A. Anderson, W. H. Peterson, and E. B. Fred (Soil Sci., 1928, 25, 123—131).—Small amounts of pyruvic acid were produced in the fermentation of various sugars by the lucerne nodule organism. H. J. G. Hines.

Relation of the growth of certain micro-organisms to the composition of the medium. III. Effect of the addition of growth-promoting substances to the synthetic medium on the growth of *Streptothrix corallinus*. V. Reader (Biochem. J., 1928, 22, 434—439).—The substance in tryptic beef broth that exerts a stimulating action on the growth of *S. corallinus* (A., 1927, 903) is organic, water-soluble, and dialysable and is not precipitated by either neutral or basic lead acetate. It is also present in yeast preparations, rabbit muscle, serum, and wheat embryo. It is associated with the anti-neuritic vitamin in fractions from yeast up to the 0·1 mg. per pigeon dose stage. S. S. Zilva.

***Meningococcus* as a source of growth factor for *Streptothrix corallinus*.** J. Orr-Ewing and V. Reader (Biochem. J., 1928, 22, 443—444).—*Meningococcus* type I can grow in a meat extract medium which has been completely freed from the *S. corallinus* growth factor. On re-testing the meat extract medium after the growth of the former it is found to be capable of supporting good growth of the latter. S. S. Zilva.

Relation of glycerol in culture media to the growth and chemical composition of tubercle bacilli. E. R. Long and L. L. Finner (Amer. Rev. Tuberculosis, 1927, 16, 523—529).—The glycerol (in Long's synthetic medium) promotes acid-fastness and yield, and is regarded as a progenitor of the waxy constituents of the bacillus. The lipin content is increased only with high concentrations of glycerol. Chemical Abstracts.

Digestion of pectin and methylglucose by various organisms. H. W. Coles (Plant Physiol., 1926, 1, 379—385).—Only those organisms commonly occurring in the soil are capable of attacking pectin and 3-methylglucose with the production of acid and gas. Chemical Abstracts.

Chemical action of quinones on proteins and amino-acids. E. A. Cooper and R. B. Haines (Biochem. J., 1928, 22, 317—325).—Quinones readily undergo decomposition in aqueous solution in the presence of light and the change is accompanied by a fall in the bactericidal power. Benzoquinone is from 4 to 17 times as active as a germicide as toluquinone, the ratio depending on experimental conditions. The latter is, however, somewhat more diffusible through a membrane and more readily adsorbed by colloids than benzoquinone. Alcohol increases the germicidal power of benzoquinone to a much greater extent than that of phenol and toluquinone. The interaction of benzoquinone and glycine is also greatly accelerated in the initial stages by alcohol. Whilst there is relatively only a small difference in the apparent reactivity of the quinones towards yeast, bacteria, proteins, peptones, peptides, and even certain amino-acids, benzoquinone reacts up to seven times as readily as toluquinone with other amino-acids. Toluquinone is adsorbed to a somewhat greater extent than benzoquinone by charcoal and deaminoalbumin. The difference, however, is not sufficiently great to justify the conclusion that adsorption is the primary factor in the protein experiments and probably the small differences in the uptake of benzoquinone and toluquinone by proteins have a structural explanation. The germicidal power of the quinones is to an important degree associated with the reactivity towards the simpler cell constituents. S. S. Zilva.

Mechanism of adrenaline hypoglycæmia. E. Geiger (Arch. exp. Path. Pharm., 1928, 129, 93—99).—Administration of adrenaline to an animal brought into a state of tetany by over-ventilation causes a lowering of the blood-sugar, but this does not happen when the vagus is cut. Plasma removed from the animal when in the hypoglycæmic state is able to cause increase in the uptake of dextrose by the red blood-corpuscles (cf. Loewi, A., 1927, 795). It is concluded that the hypoglycæmia is a result of the liberation of insulin from the pancreas following central stimulation through the vagus. W. O. Kermack.

Action of adrenaline on purine metabolism. G. Taubmann (Arch. exp. Path. Pharm., 1928, 129, 43—51).—The increase in the excretion of purine

compounds after administration of adrenaline is not due to the leucocytosis which is provoked.
W. O. KERMACK.

Fat metabolism. II and III. A. LOW and R. PFEILER (Biochem. Z., 1928, **193**, 276—277, 278—280).—II. Adrenaline injected subcutaneously into rabbits causes an increase in blood-cholesterol.

III. Under the action of adrenaline, transport of fat occurs from the periphery to the liver. The glycogen content of the liver is usually greatly reduced, but in individual cases it is increased, especially when the glycogen content of the liver is initially small owing to starving.
P. W. CLUTTERBUCK.

Formation of sugar from fatty acids in depancreatised dogs injected with adrenaline. I. L. CHAIKOFF and J. J. WEBER (J. Biol. Chem., 1928, **76**, 813—832).—Treatment of fasting depancreatised dogs with adrenaline causes an increased excretion of dextrose which cannot be accounted for as arising from any source other than fat; under these conditions there is also increased excretion of phosphorus in the urine. C. R. HARINGTON.

Reaction of adrenaline with novocaine. H. LANGECKER (Arch. exp. Path. Pharm., 1928, **129**, 202—235).—Solutions containing a mixture of novocaine and adrenaline become yellow slowly in the cold and more rapidly when hot, the physiological action of the adrenaline meanwhile becoming weaker. The reaction appears to consist first in the oxidation of adrenaline to a rose-coloured *o*-quinone derivative, this reaction being catalysed by novocaine, and, secondly, in the condensation of this substance with novocaine to form a yellow compound. Other aromatic amines react with adrenaline in an analogous way and a yellow colour may also be developed when pyrocatechol, quinol, or one of their derivatives is used in place of adrenaline. W. O. KERMACK.

Crystalline insulin. III. Nature of the sulphur linking and the isolation of cystine and tyrosine from hydrolysed crystalline insulin. V. DU VIGNEAUD, H. JENSEN, and O. WINTERSTEINER. **IV. Isolation of arginine, histidine, and leucine.** H. JENSEN, O. WINTERSTEINER, and V. DU VIGNEAUD. **V. Distribution of nitrogen.** O. WINTERSTEINER, V. DU VIGNEAUD, and H. JENSEN (J. Pharm. Exp. Ther., 1928, **32**, 367—385, 387—396, 397—411).—III. Conditions are described for the preparation of crystalline insulin from the impure product; cystine and tyrosine have been isolated as products of hydrolysis of this material. From a comparison of the total sulphur content with the cystine content of insulin, it is concluded that insulin contains some sulphur compound other than cystine.

IV. The presence of arginine, histidine, leucine, and lysine in crystalline insulin has been proved by their isolation from the hydrolysate of this substance. By means of the method of Koessler and Hanke the amount of histidine in insulin is shown to be 2·6%.

V. The Van Slyke method for determining the nitrogen distribution in proteins has been used in the examination of the nitrogen distribution in crystalline insulin, and a comparison is made of the results obtained with those of other authors. E. A. LUNT.

Insulin-like substance of yeast. U. VON EULER (Biochem. Z., 1928, **194**, 197—203).—A yeast extract prepared with 25% alcohol and 1% hydrochloric acid shows in a vacuum in a system containing fresh muscle-pulp, methylene-blue, dextrose, and phosphate, a typical insulin action, the optimal effect being at a concentration of 10^{-8} g./c.c. The preparation (50 mg.) injected subcutaneously into rabbits causes either no, or only an insignificant, lowering of blood-sugar. The result of the methylene-blue experiment, however, suggests that only a very small amount of the active substance is present in the preparation and the blood-sugar effect must therefore be small.
P. W. CLUTTERBUCK.

Insulin and amino-acid catalysis [of the oxidation of dextrose and lævulose by hydrogen peroxide]. J. M. ORT.—See this vol., 487.

Preliminary hyperglycæmia after [administration of] insulin. M. GUARDABASSI (Ann. fac. med. chir., 1926, **29**, 147—177; Chem. Zentr., 1927, ii, 2322).—Subcutaneous, particularly intraperitoneal, administration of insulin is followed by an increase of blood-sugar, particularly with thyroid-fed animals, but not with thyroidectomised animals. The hyperglycæmia is observed in diabetes, and in disease or after removal of the suprarenals, but not in castrated animals. A. A. ELDRIDGE.

Fate of sugar in the animal body. VIII. Influence of insulin on utilisation of dextrose, lævulose, and dihydroxyacetone. C. F. CORI and G. T. CORI (J. Biol. Chem., 1928, **76**, 755—795).—Earlier experiments (cf. A., 1926, 1271; 1927, 790) on the utilisation of dextrose and lævulose, with and without extra insulin, have been repeated and extended. The general effect of excess of insulin is to cause slightly increased oxidation of the sugar, diminished deposition of glycogen in the liver, and much increased deposition of glycogen in the muscles. The normal rate of absorption of dihydroxyacetone is intermediate between those of dextrose and lævulose, and the effect of insulin on its utilisation is of the same type. With dextrose and dihydroxyacetone, the predominant effect of excess of insulin is on glycogen storage; with lævulose, on oxidation. Slightly greater heat production is observed during utilisation of these carbohydrates when excess of insulin is present. The influence of various physiological factors of absorption is discussed.
C. R. HARINGTON.

Influence of thyroid and insulin on the oxidases of various organs. K. MORI (Folia endocrinol. japon., 1927, **2**, 40—41, 122—152).—The oxidase content of rabbits' organs (especially heart and kidney) is increased by injection of insulin; a further increase is caused by simultaneous injection of dextrose. Thyroxine has a similar effect on the heart and kidney. The increase following simultaneous injection of insulin and thyroxine is greater than that produced by each hormone alone. The loss in oxidases caused by thyroidectomy may be repaired by injection of insulin. CHEMICAL ABSTRACTS.

Effect of toxæmia on tolerance for dextrose and on the action of insulin. J. S. Sweeney (Arch. Int. Med., 1928, **41**, 420—427).—Rabbits to which diphtheria toxin had been administered so as to decrease their sugar tolerance responded normally to the action of insulin when this hormone was injected. It is inferred that the toxin affects the sugar tolerance by inhibiting the production of insulin.

W. O. Kermack.

Insulin and fat metabolism. J. Hepner and O. Wagner (Biochem. Z., 1928, **193**, 187—191).—After large doses of insulin to starving animals formation of fat occurs during aseptic autolysis of the liver. The fasting animal reacts to large doses of insulin in the opposite way to the depancreatised animal. Insulin contains two hormones, one regulating carbohydrate, and the other fat, metabolism, the latter not being destroyed by tryptic digestion. The fact that small doses of insulin cause increase of glycogen and decrease of fat in the liver and that large doses have the opposite effect is due to the antagonism of these two substances (cf. A., 1927, 1222).

P. W. Clutterbuck.

Effect of nickel and cobalt salts on insulin hypoglycæmia. M. A. Magenta (Rev. Soc. Argentina Biol., 1927, **3**, 687—690).—Injections of copper, nickel, and cobalt salts (2—5 mg. per kg.) into dogs caused slight hyperglycæmia. Injections of 0·01—1 mg. per kg. of nickel and cobalt salts slightly counteracted the hypoglycæmic effect of simultaneous doses of insulin (cf. Bertrand and Machebœuf, A., 1926, 869, 971; Blatherwick and Sahyun, A., 1927, 1115; Labbe, Roubeau, and Nepreux, this vol., 206, 321).

R. K. Callow.

Female sexual hormone (menoformone). IV. Influence on metabolism and resistance. E. Laqueur, P. C. Hart, and S. E. de Jongh (Deutsch. med. Wochschr., 1926, **52**, 1331—1333; Chem. Zentr., 1927, ii, 1484).—Menoformone specifically increases the metabolism of castrated female (but not male) rats; the substance is soluble in water, thermostable to 360° (in aqueous or 10% potassium hydroxide solution to 170°). It is resistant to pancreatic ferment and pepsin; it is decomposed by strong oxidising agents, but not by reduction. Volatility or sublimation could not be detected.

A. A. Eldridge.

Preparation and properties of a female sexual hormone (menformone) in water-soluble form. E. Lacquer, P. C. Hart, and S. E. de Jongh (Lancet, 1927, i, 1126—1128; cf. following abstract).—Fresh placenta is minced, boiled with benzene, and the benzene residue extracted with 80% alcohol; the extract is evaporated, the dry residue dissolved in water to which some hydrochloric acid is added, and kept at 2° for 12 hrs. Some preparations failed to give reactions for sulphur or histidine.

Chemical Abstracts.

Preparation and properties of ovarian hormone in water-soluble form. F. Dickens, E. C. Dodds, and D. J. T. Brinkworth (Lancet, 1927, i, 1015—1016, 1182—1183).—The aqueous residue left on vacuum distillation of an (70%) acetone extract of a mixture of pig ovaries and dry picric acid is filtered, and the dry residue extracted with acid alcohol. The precipitate obtained on addition to the extract of acetone (15 vols.) is washed with ether and dried in a vacuum. The active principle contains sulphur, histidine, and tryptophan.

Chemical Abstracts.

Ovarian hormone. B. P. Wiesner (Nature, 1928, **121**, 498—499).—A re-statement and discussion of physiological results.

A. A. Eldridge.

Sexual glands and metabolism. V. Influence of lipoid extracts of testes and prostate on nitrogen metabolism and development of genital organs. V. Korenchevsky. **VI. Influence of water-soluble testicular and prostatic extracts on nitrogen metabolism and development of genital organs.** V. Korenchevsky and M. Schultess-Young (Biochem. J., 1928, **22**, 482—490, 491—503).—V. Lipoid fractions have been prepared from testes and prostate, which, although possessing insignificant activity separately, when injected simultaneously increased the nitrogen metabolism of rabbits. None of the fractions was able to prevent atrophy of the sexual organs of castrated rats.

VI. Water-soluble extracts, from which insulin-like substances had been removed, were prepared from testes and prostate; these raised the nitrogen metabolism of rabbits and rats to some extent whether injected singly or together. A review of work on male sexual hormones is given in these two papers.

H. W. Dudley.

Active principles of the posterior lobe of the pituitary gland. I. Demonstration of the presence of two active principles. II. Separation of the two principles and their concentration in the form of potent solid preparations. O. Kamm, T. B. Aldrich, I. W. Grote, L. W. Rowe, and E. P. Bugbee (J. Amer. Chem. Soc., 1928, **50**, 573—601).—The oxytocic and pressor principles of the posterior lobe have been separated and obtained as stable, water-soluble powders; the acetone-desiccated gland material is extracted with 0·25% acetic acid, the extract concentrated at a low temperature, the proteins and the active principles are precipitated with ammonium sulphate, and the principles extracted from the precipitate with glacial acetic acid, followed by fractionation using various organic solvents (acetone, ether, and light petroleum) and subsequent purification. No decomposition occurs during the process, and the combined components show activities identical with those of the original extract. The preparation of the pressor principle (for which the term β-hypophamine is suggested) is 80 times as potent and the oxytocic preparation (α-hypophamine) more than 150 times as potent as the International Standard Powdered Pituitary. The principles have not been obtained crystalline, but both are basic. Experiments on rabbits seem to indicate that the diuretic–antidiuretic action of the posterior lobe of the pituitary is due to the pressor principle. The development of a tolerance to the pressor principle by a rapid succession of intravenous injections of relatively large amounts is identical with that obtained with impure pituitary extracts, but no depressor action is observed with the

pure preparation. The two principles are being manufactured for experimental clinical use under the trade names "oxytocin" and "vasopressin," and a preliminary discussion of the therapeutic indications is presented. A. WORMALL.

Di-iodotyrosine and thyroid substance. Knipping's gas metabolism method. F. HOFFMANN (Z. ges. exp. Med., 1927, **57**, 68—76; Chem. Zentr., 1927, ii, 2408).—3 : 5-Di-iodo-*l*-tyrosine (3—5 g.) does not affect human metabolism similarly to thyroxine.
A. A. ELDRIDGE.

Thyroxine and allied substances. I. J. H. GADDUM (J. Physiol., 1927, **64**, 246—254).—The diminution in length of tadpoles which occurs several days after immersion in solutions of thyroid preparations is shown to occur also in solutions of natural and of synthetic thyroxine. Di-iodothyroxine was much less effective and deiodothyroxine was inactive. Di-iodotyrosine had very little activity by comparison with thyroxine. The test may be regarded as a specific quantitative biological test for thyroxine.
R. K. CANNAN.

Evaluation of vitamin-*A* by means of the growth of rats. E. M. HUME and H. H. SMITH (Biochem. J., 1928, **22**, 504—521).—From the results obtained with graded doses of spinach and of butter and from the results of other workers it is concluded that the growth response of the rat to vitamin-*A* after a depletion period is as follows. There is no recovery on a small dose. On a rather larger dose there is subnormal growth graded quantitatively to the dose with premature slackening. On a still larger dose there is normal growth for a time, followed by premature slackening. With an optimal dose normal growth to maturity is achieved. The peculiar character of the growth obtained with sub-optimal doses is disproportionate to the supply of vitamin after depletion and cannot be maintained subsequently. It is suggested that the evaluation of vitamin-*A* is best made by dispensing with the depletion period.
S. S. ZILVA.

Colour tests for vitamin-*A*. Application to naturally occurring products. S. G. WILLIMOTT and F. WOKES (Lancet, 1927, ii, 8—11).—The arsenic chloride and antimony chloride tests are most sensitive; then follow the concentrated sulphuric acid and phosphoric anhydride tests, and finally the trichloroacetic acid and pyrogallol tests. Vitamin-*A* is not markedly absorbed by charcoal used to remove carotin and xanthophyll, and the colour tests are not qualitatively affected by the presence of vitamin-*D*. Destruction of vitamin-*A* continued after cod-liver oil had been removed from the action of rays from a mercury-vapour lamp. CHEMICAL ABSTRACTS.

Vitamins of commercially concentrated orange juice. S. G. WILLIMOTT (Biochem. J., 1928, **22**, 535—544).—Five c.c. of orange concentrate diluted to the strength of the original juice were adequate in vitamin-*A* for the rat and 10 c.c. of this diluted preparation were adequate in vitamin-*B*.
S. S. ZILVA.

Vitamin-*B* content of malt extract. A. L. BACHARACH and E. ALLCHORNE (Biochem. J., 1928, **22**, 313—316).—Several brands of commercial malt extract have been found to be rich sources of that vitamin which will restore to normal growth rats on a diet devoid of water-soluble growth-promoting factors. The vitamin is derived from the unmalted flour.
S. S. ZILVA.

Dietary requirements for fertility and lactation. XIII. Storage of fat-soluble vitamins for lactation; cod-liver oil requirements of suckling young. XIV. Biological determination of vitamin-*B* requirements for lactation. XV. Relation to infant mortality of inefficient secretion of vitamin-*B* by lactating rat. B. SURE (J. Biol. Chem., 1928, **76**, 659—671, 673—683, 685—700).—XIII. Rats transferred at the birth of their young from a complete diet to one deficient in fat-soluble vitamins retained sufficient vitamins for lactation, but on re-breeding such rats, either sterility or increased infant mortality was observed. Administration of very small amounts of cod-liver oil to the suckling young enabled the latter to grow when the mother was suffering from deficiency of fat-soluble vitamins; no evidence was obtained of the necessity of a specific fat-soluble vitamin other than vitamins-*A* and -*D* during lactation.

XIV. The vitamin-*B* requirements of lactating rats were determined by observing their response to additions of vitamin-*B* to a deficient diet at the point when the growth of the young had come to a standstill; a preparation of vitamin-*B* was obtained by dissolving out the vitamin with sodium hydroxide from an adsorbate of baker's yeast on fuller's earth.

XV. Direct administration of yeast to the young gave much better growth and less mortality of the latter than administration of the same amount of yeast to the mother; the high mortality of young rats whose mother is on a diet deficient in vitamin-*B* is therefore due both to the large requirements of suckling young in respect of this vitamin, and also to the fact that the vitamin received by the mother is excreted only to the extent of about 40% in the milk.
C. R. HARINGTON.

Fundamental food requirements for growth of the rat. III. Yeast and yeast fractions as a supplement to synthetic rations. IV. Coprophagy as a factor in the nutrition of the rat. C. KENNEDY and L. S. PALMER (J. Biol. Chem., 1928, **76**, 591—606, 607—622).—III. The purified diet which, although presumably complete except for vitamin-*B*, has been shown previously (A., 1927, 1115) to be unsatisfactory for the growth of rats, may be completely supplemented by addition of 0·6 g. of dried yeast per day, but not by various yeast concentrates, autoclaved yeast, or wheat-embryo extract; in presence of the last-named as a source of vitamin-*B*, however, the remaining necessary factor may be supplied in the form of alcohol-extracted or autoclaved yeast or the yeast residue after removal of the Osborne and Wakeman concentrate. This remaining factor is apparently not bios; it is similar to but not identical with vitamin-B_2.

IV. Loss of weight in rats on the purified diets (see above) was not observed when coprophagy was permitted, nor when commercial caseinogen was substituted for the purified protein; the growth-promoting factor present in the fæces was alcohol-

but not ether-soluble and was destroyed by autoclaving for more than 30 min. C. R. HARINGTON.

Antineuritic yeast concentrates. IV. Further purification of yeast vitamin-*B* (curative). H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1928, **22**, 419—433; cf. A., 1925, i, 1516; A., 1927, 904).—Highly active fractions (0·027 mg. per day per pigeon) have been prepared. Phosphotungstic acid and chloroplatinic acid can be used in purifying yeast vitamin-*B*. The solubility of the vitamin in ethyl alcohol varies with the activity of the preparation and with the p_H of the solution treated with the alcohol. It is not soluble in chloroform, carbon tetrachloride, ether, acetone, or ethyl acetate. Heating for 1 hr. with 0·5*N*-sodium hydroxide destroys the curative power of the vitamin completely at an activity of 0·06 mg.; heating for 10 min. with 0·1*N*-sodium hydroxide does not inactivate it appreciably. The vitamin may become more unstable to alkali in the presence of other substances. It is stable to oxidising and certain reducing agents. The yield of the charcoal concentrates from brewer's yeast is not quite as high as that obtained by this process from baker's yeast. Two forms of yeast vitamin-B_1 possibly occur in an aqueous extract of yeast. S. S. ZILVA.

Relation of vitamin-B_1 to the growth-promoting factor for a *Streptothrix*. R. A. PETERS, H. W. KINNERSLEY, J. ORR-EWING, and V. READER (Biochem. J., 1928, **22**, 445—450).—Parallel tests on the pigeon and *S. corallinus* have been made during the course of numerous fractionations of yeast concentrates. The most active vitamin-B_1 preparations have the same relative growth-promoting powers as preparations 100 times less pure. Sufficient treatment with alkali always inactivates the curative properties for pigeons, but the purer extracts after such treatment still retain growth-promoting activity. Vitamin-B_1 and the bacterial growth-promoting factor are not identical. The two principles fractionate, however, in parallel. Since the *Streptothrix* factor is present in the charcoal concentrates it is not identical with vitamin-B_2.
S. S. ZILVA.

***Streptothrix corallinus* in the determination of vitamin-B_1.** J. ORR-EWING and V. READER (Biochem. J., 1928, **22**, 440—442).—A method capable, with certain limitations, of replacing pigeon tests is described. It is based on the comparison of the growth of *S. corallinus* in a medium containing the vitamin fraction of unknown potency with that in a medium containing a concentrate of known pigeon dosage. S. S. ZILVA.

Existence of two active factors in vitamin-*B* complex. W. D. SALMON, N. B. GUERRANT, and I. M. HAYS (J. Biol. Chem., 1928, **76**, 487—497).—By treatment of a solution of vitamin-*B* with fuller's earth it is possible to effect a selective adsorption of the beri-beri-preventing factor (B_1) if the amount of fuller's earth employed be such that it becomes saturated with adsorbed material; repeated treatments of this nature fail, however, to remove the last traces of vitamin-B_1, which must be destroyed by heat in order to furnish a preparation containing exclusively vitamin-B_2. C. R. HARINGTON.

Effect of light on vitamin synthesis in plants. V. G. HELLER (J. Biol. Chem., 1928, **76**, 499—511).—Both vitamins-*A* and -*C*, especially the latter, are formed to some extent in the germination and early growth of seedlings in the dark, but their formation is much accelerated by exposure to light; vitamin-*B* is not, in any circumstances, formed during the early stages of growth. C. R. HARINGTON.

Antiscorbutic vitamin value of some Peking fruits. K. L. HSÜ (Chinese J. Physiol., 1928, **2**, 41—44).—"Red fruit," *Cratægus pinnatifida*, contains considerable quantities of vitamin-*C*, whilst "*Haitang Pirus spectabilis*, and the persimmon *Diospyros kaki* are poor in this vitamin.
W. O. KERMACK.

Influence of ultra-violet light on the vitamin-*C* content of milk. A. HOTTINGER (Klin. Woch., 1927, **6**, 1793—1797; Chem. Zentr., 1927, ii, 2553).—The irradiation does not cause loss of vitamin-*C*. The vitamin-*C* content of various preserved milks is considered. A. A. ELDRIDGE.

Immediate action of a vitamin [*C*]. N. BEZSSONOFF (Compt. rend., 1928, **186**, 914—916; cf. A., 1925, i, 751).—The immediate result of even partial avitaminosis (*C*) in adult guinea-pigs is the accumulation of toxic substances (probably phenolic) in the system; when a diet containing vitamin-*C* is given, an increase in the elimination of toxic substances occurs (shown by the increase in the bromine titre of the urine) and the animals gain weight.
G. A. C. GOUGH.

Assay of the antirachitic vitamin-*D*. K. M. SOAMES and J. C. LEIGH-CLARE (Biochem. J., 1928, **22**, 522—527).—The conclusion of Steenbock and his colleagues that the growth curve of the animal on an otherwise adequate diet can be employed for the assay of vitamin-*D* is substantiated. Two diets used for this purpose, one containing 20% of wheat embryo and another 50% of hog-millet as a source for vitamin-*A*, are described. It is confirmed that lucerne meal contains too much vitamin-*D* to be used as supply for vitamin-*A* in the determination of the former diet.
S. S. ZILVA.

Biological assay of antirachitic lipoids tested by a new rachitogenic régime on rats. L. RANDOIN and R. LECOQ (Ann. Falsif., 1928, **21**, 68—75).—A simple diet that will establish experimental rickets in young rats in a constant way consists of meat peptone 17 parts, dried ground brewer's yeast 3, butter fat 5, olive oil 5, sucrose 65, salt mixture Z 84, 4, and calcium lactate, 1. The fats are added to the ground mixture of the other ingredients and the mixture is kept in closed containers.
D. G. HEWER.

Detection of the antirachitic factor in grass grown in the dark on an artificial nutritive solution. II. W. VÖLTZ and W. KIRSCH (Biochem. Z., 1928, **193**, 281—284).—The authors' previous result (A., 1927, 904) that grass grown on soil in complete darkness has an antirachitic action is confirmed. Grass grown on a nutritive solution of salts in absolute darkness, to the same height as the grass grown on soil, has a smaller dry substance content and a somewhat smaller antirachitic effect. The

active substance is not absorbed through the roots, but is formed within the plant. P. W. CLUTTERBUCK.

Specificity of ergosterol as parent substance of vitamin-*D*. O. ROSENHEIM and T. A. WEBSTER (Nature, 1928, **121**, 570).—Contrary to Windaus and Holtz (Nachr. Ges. Wiss. Gottingen, 1927), digitaligenin is not activated by irradiation; an alcoholic solution was employed, since olive oil becomes antirachitic when irradiated. Moreover, the absorption spectrum of digitaligenin differs from that of ergosterol, and remains unchanged on irradiation. The results, together with the known inactivity of irradiated coprosterol, dihydrocholesterol, dihydrositosterol, cholesterol, sitosterol, stigmasterol, cholesterilene, oxycholesterilene, dihydroergosterol, *iso*ergosterol, *neo*ergosterol (this vol., 425), squalene, nerolidol, or ψ-ionone, support the view that ergosterol is the specific parent substance of vitamin-*D*.

A. A. ELDRIDGE.

Photochemical oxidation of ergosterol. A. WINDAUS and J. BRUNKEN. See this vol., 424.

Photochemical activation of sterols in the cure of rickets. R. J. FOSBINDER, F. DANIELS, and H. STEENBOCK (J. Amer. Chem. Soc., 1928, **50**, 923—927).—Cholesterol purified by treatment with alcoholic potassium hydroxide followed by repeated crystallisation from alcohol was exposed for varying periods to monochromatic light from a spectrometer, the mercury line 265 $\mu\mu$ being employed for the most part, as experiments with different lines in the spectrum had shown that only those wave-lengths shorter than 313 $\mu\mu$ were effective. Calculations on the basis of the quantum theory and assuming Einstein's law of photochemistry show that 2×10^{-8} g. of vitamin-*D* is sufficient to produce calcium deposition in a rachitic rat fed on the activated cholesterol.

J. D. FULTON.

Activation of cholesterol at liquid oxygen temperature. C. E. BILLS and F. G. BRICKWEDDE (Nature, 1928, **121**, 452).—Cholesterol, when irradiated by ultra-violet light at $-183°$, becomes antirachitic; it is concluded that the activation consists in rearrangement, and not in oxidation. The temperature coefficient of vitamin formation is low; that of the spontaneous deterioration of unactivated ergosterol is high. A. A. ELDRIDGE.

Activation of ergosterol at $-180°$. T. A. WEBSTER and R. B. BOURDILLON (Nature, 1928, **121**, 502).—Vitamin-*D* has been obtained by irradiation of ergosterol in alcoholic solution at $-180°$ to $+78°$ (cf. preceding abstract). A. A. ELDRIDGE.

Biochemical relationships of phenols. I. Quinol. R. C. HUSTON and H. D. LIGHTBODY (J. Biol. Chem., 1928, **76**, 547—558).—Addition of 0·01—0·1% of quinol to a diet deficient in vitamins-*A* and -*D* caused improvement in growth and calcification of rats; further, the quinol increased the beneficial effect of adding cod-liver oil to such diets. Larger amounts of quinol caused retardation of growth. The occurrence of ophthalmia was retarded or prevented by the quinol. C. R. HARINGTON.

Photo-activity of oils and their antirachitic power. E. REKLING (Acta Radiol., 1926, **5**, 517—552; Chem. Zentr., 1927, ii, 952).—Cod-liver oil is already "photo-active"; linseed and olive oils become so on irradiation in presence of oxygen. Photo-activity depends on the hydrogen content, *i.e.*, on the so-called Russel effect. Photo-activity and antirachitic power are not parallel.

A. A. ELDRIDGE.

p_H of gastrointestinal tract in dogs in relation to diet and rickets. D. M. GRAYZEL and E. G. MILLER, jun. (J. Biol. Chem., 1928, **76**, 423—436).—On a normal diet the reaction of the whole gastrointestinal tract of dogs is acid, varying from p_H 7·0 in the colon to p_H 3·0 in the stomach; a rickets-producing diet shifts the reaction towards the alkaline side, whilst addition of cod-liver oil to such a diet, or irradiation of the animals, restores the normal acidity. Variations in the fat, protein, or carbohydrate of the diet, and irradiation of animals on a normal diet, have no effect on the reaction of the gastrointestinal contents. C. R. HARINGTON.

Bird feathers and antirachitic vitamin-*D*. W. ROWAN (Nature, 1928, **121**, 323—324).—It is suggested that feather oil may contain vitamin-*D*.

A. A. ELDRIDGE.

Oxidative destruction of vitamin-*A* and -*E* and the protective action of certain vegetable oils. H. A. MATTILL (J. Amer. Med. Assoc., 1927, **89**, 1505—1508).—Development of rancidity in unsaturated animal fats is accompanied by destruction of vitamin-*A* and -*E*. The development of rancidity is promoted by ferrous iron, and retarded by hydroxyl groups. CHEMICAL ABSTRACTS.

Vitamin-*E*. II. Destructive effects of certain fats and fractions thereof on the antisterility vitamin in wheat germ and wheat-germ oil. H. M. EVANS and G. O. BURR (J. Amer. Med. Assoc., 1927, **89**, 1587—1590).—Some fats and oils contain substances which counteract the effect of vitamin-*E*. The substances increase with rancidity, but the amount is not parallel to the acid value of the fat. Much of the antivitamin in commercial oleic acid can be concentrated in the unsaponifiable fraction.

CHEMICAL ABSTRACTS.

Vegetable assimilation and respiration. XVII. Diurnal rhythm of assimilation in leaves at "limiting" concentrations of carbon dioxide. XVIII. Relation between stomatal opening and assimilation. E. J. MASKELL (Proc. Roy. Soc., 1928, B, **102**, 467—487, 488—533).—XVII. The rate of carbon assimilation has been determined during 24 hr. periods in the leaves of *Prunus laurocerasus* as a function of the light intensity and of the concentration of carbon dioxide in mixtures of air and carbon dioxide at atmospheric pressure. The results show that the nocturnal depression in assimilation is not due to any decrease in efficiency of the photosynthetic mechanism, nor to diurnal changes in respiration rate.

XVIII. It is shown by means of Darwin's porometer method that diurnal and seasonal rhythms of stomatal opening occur in the leaves of *P. laurocerasus* which run parallel with the observed diurnal and seasonal rhythms of assimilation rate.

E. A. LUNT.

Carbon dioxide nutrition of the forest. D. FEHER (Biochem. Z., 1928, **194**, 213—214).—A correction of a previous paper (cf. A., 1927, 385).
P. W. CLUTTERBUCK.

Effect of radioactivity on chlorophyll-containing or chlorophyll-free cells. J. STOKLASA, J. PENKAVA, and J. BARES (Sborn. Českoslov. Akad. Zemed., 1927, **2**, 57—104; Chem. Zentr., 1927, ii, 945—946).—The intensity of respiration of the cells is greatly increased by the presence of emanation issuing from the ground or of the α-rays emitted by it, the production of carbon dioxide being increased by 40—90%. α-Rays stimulate all the enzymic processes if sufficient oxygen is present; β- and γ-rays are chiefly effective in activating glycolytic enzymes. There results an anoxybiotic degradation of carbohydrate, yielding first lactic acid and then alcohol and carbon dioxide, acetaldehyde and acetic acid being produced from alcohol. The β-rays are surface-activating and therefore synthetic, the α-rays disintegrative, decomposing complexes, and apparently assisting oxidation by isolation of the organic iron groups. A. A. ELDRIDGE.

Characters of cells attaining great age. D. T. MACDOUGAL and F. L. LONG (Amer. Nat., 1927, **61**, 385—406).—A study of medullary and cortical cells of *Echinocactus wislizenii*, which live for 100 yrs. or more. Carbohydrates decrease and the osmotic value of the cell sap diminishes with age. Crystals and insoluble inclusions increase, and the pentosan component of protoplasm wastes.
CHEMICAL ABSTRACTS.

Exosmosis of dissolved substance from storage tissue into water. W. STILES (Protoplasma, 1927, **2**, 577—601).—The roots or tubers of red beet, carrot, turnip, parsnip, Jerusalem artichoke, and potato were examined. When tissue was immersed in water at 20°, vitality was retained for 2—3 days only, exosmosis of electrolytes and other solutes continuing until the tissues were dead. With continuous movement in water, and daily opening of containers, vitality continued for 3—4 weeks, apparently owing to removal of oxygen and carbon dioxide diffusion shells. Increase of dissolved substances in distilled water was followed by a decrease, indicating absorption by the tissue. A mechanism of solute absorption by plant cells is suggested. CHEMICAL ABSTRACTS.

Effect of soil acidity on the growth and composition of leguminous plants. A. I. VIRTANEN (Biochem. Z., 1928, **193**, 300—312).—When leguminous plants are grown in sand containing considerable amounts of nitrogen, without the assistance of nodule bacteria, their growth decreases with increasing acidity, but not so rapidly as when they are grown in nitrogen-free sand with the help of bacteria. Clover shows good growth in strongly nitrogenous soils (moors) even at p_H 4·5, whereas no growth occurs in soils poor in nitrogen under p_H 5. Red clover thrives better in nitrogen-free sand with the help of the bacteria than with ammonium nitrate in absence of the bacteria. The reverse is true of white clover, whilst bastard clover and peas thrive equally well on either. The roots of these plants, when dependent on bacteria for their nitrogen supply, are strong, but there is little fibrous root, whereas, when dependent on the nitrogen of ammonium nitrate, they are chiefly of the fibrous variety. The nitrogen content of the plants increases considerably with decrease of soil acidity. With peas, the phosphorus content decreases with increase of acidity, as does also the potassium content, but to a smaller extent. With clover, the phosphorus and potassium contents differ with soil acidity in the same sense, but to a much smaller extent.
P. W. CLUTTERBUCK.

Physiology of apples. VII. The sugars of apples with especial reference to the lævulose-dextrose ratio. D. I. EVANS (Ann. Bot., 1928, **42**, 1—28).—Dextrose and lævulose are determined in apple juice by a method depending on their differential oxidation by an alkaline solution of iodine at 5°. The acid and sugar (sucrose, dextrose, and lævulose) constants of various varieties of apples have been determined. The former varies with the species. The variation in sugar content with variety is not more marked than the variation in one particular species due to soil variation. For apples the ratio of dextrose to lævulose is 2·5 : 1 and approximates in the Bramley seedling to the sucrose/acid ratio. There is a slight decrease in the reducing sugar content on storage at 1°. E. A. LUNT.

Physiology of apples. VIII. Methods of determining the dry weight of apple pulp. H. K. ARCHBOLD (Ann. Bot., 1928, **42**, 29—38).—Decomposition of certain of the solids present in apple juice takes place when their aqueous solutions are heated under varying pressures at 50°. Dry-weight determinations on apple juice under such conditions are thus inaccurate and only drying in a vacuum at the ordinary temperature for 3 weeks gives trustworthy results. A method suitable for rapid routine analysis is described in which the time allowed for desiccation at 50° at atmospheric pressure is such that the error due to incomplete desiccation compensates for the error due to chemical decomposition, giving results accurate to within 2%. E. A. LUNT.

Physiology of fruit trees. II. Effects of ringing, double ringing, and dis-budding on the starch content and cambial activity of two-year-old apple shoots. T. SWARBRICK (J. Pomology, 1928, **6**, 296—312).—Continuation of previous work (cf. A., 1927, 797). W. O. KERMACK.

Physiological significance of pyrogallol tannins. MICHEL-DURAND (Compt. rend., 1928, **186**, 514—517).—In chestnut leaves the total amount of pyrogallol tannins remains constant during the autumn fading, but there is a decrease in free tannins (acetone-soluble), which are transformed into adsorbed tannins (insoluble in acetone). In young etiolated oaks the free tannins decrease like the simple sugars, but the adsorbed tannins remain constant; possibly the former are used as food in the respiratory process; this conclusion, however, is not confirmed in the case of young etiolated chestnut trees.
B. W. ANDERSON.

Detection and physiology of urea in the higher plants. K. TAUBOCK (Oesterr. bot. Z., 1927, **76**, 43—56; Chem. Zentr., 1927, ii, 2330).—An acetic acid extract of the tissue or section, prepared on a micro-

scope slide or in a micro-extraction apparatus, is treated with solid xanthydrol, yielding doubly-refracting dixanthylcarbamide, insoluble in acetic acid or methyl alcohol, and soluble in hot alcohol.

A. A. ELDRIDGE.

Energy content and energy storing of plants in relation to the carbon and nitrogen contents. A. ZBOROVSZKY (Biochem. Z., 1928, **193**, 122—138).—The carbon and nitrogen contents, the C/N ratio, and the heat values obtained by burning 1 g. of dried substance are tabulated for a variety of plants grown in different years. With leguminous plants, the heat value and carbon content show corresponding variations and the C/N ratio lies between 9 and 15. Plants dried slowly in air have a lower heat value and carbon and nitrogen content than plants dried quickly at 100°, the decrease consisting about equally of nitrogenous and non-nitrogenous constituents. During the course of development, especially in the early stages, an increase in heat value and carbon content is obtained, whereas the nitrogen content per g. of dry substance usually decreases. With non-leguminous plants the C/N ratio usually increases during development, but with horse-bean it remains practically constant.

P. W. CLUTTERBUCK.

Effect of length of day on the growth and chemical composition of the tissues of certain economic plants. M. A. H. TINCKER (Ann. Bot., 1928, **42**, 101—140).—The effect of curtailed periods of daylight on the growth of certain plant species is described, and it is suggested that the length of day affects the rate of stem growth and the utilisation of the carbohydrates formed, and thus influences the C/N ratio and the production of flowers.

E. A. LUNT.

Transport of carbohydrates in the cotton plant. I. Diurnal variation in the carbohydrates of leaf, bark, and wood, and the effects of ringing. T. G. MASON and E. J. MASKELL (Ann. Bot., 1928, **42**, 189—253).—Diurnal variations in concentration of the total sugars in the bark are due to variations in sucrose concentration, and the downward transport of carbohydrate occurs in the bark rather than in the wood.

E. A. LUNT.

Formation of starch in cereals; the carbohydrates of the leaves and stems of the rice plant. H. BELVAL (Compt. rend., 1928, **186**, 781—783; cf. A., 1923, i, 1274).—The leaves of the rice plant contain more sucrose and less reducing sugars than the stems. Since the rotatory powers of the sugar solutions from both parts of the plant are approximately identical after inversion, it is probable that the only reducing sugars present are the inversion products of sucrose. The amount of sugars increases towards the autumn.

G. A. C. GOUGH.

New maltose-producing plant, *Schizopepon Fargesii*, Garnepain. H. COLIN and R. FRANQUET (Compt. rend., 1928, **186**, 890—891).—The tubers of this plant, better known as *Actinostemma paniculatum*, Maxim, contain 7% of maltose, 12% of starch, and very small amounts of sucrose and hexoses in October, whilst the underground roots, on which the tubers grow, are devoid of maltose. When dried at the ordinary temperature the maltose is completely replaced by a mixture of sucrose and monoses. The latter constitute the major part of the sugars of the tubers at other periods.

G. A. C. GOUGH.

Cell membrane of plants. II. M. LUDTKE (Ber., 1928, **61**, [*B*], 465—470; cf. A., 1927, 960).—Treatment of bamboo with chlorine dioxide and sodium sulphite yields fibres which, when treated with sodium hydroxide or ammoniacal copper oxide in transverse or diagonal section to the axis, exhibit stratification. By further action of ammoniacal copper oxide or acids, a film can be detached from the fibre which, according to colour reactions and chemical properties, cannot consist of carbohydrates. The film separates the layers of the bamboo membrane, which probably consist mainly of cellulose. Interaction of cellulose or similar carbohydrates with iodine or ammoniacal copper oxide is therefore not possible unless the protective film is ruptured or opportunity for diffusion exists. On anatomical grounds, a chemical union between lignin or pectin and the carbohydrates of the cell-wall is considered impossible in all cases in which the substances are separated by a film. *Bambusa, Avena sativa, Secale cereale, Typha angustifolia, Populus tremula, P. nigra, Alnus glutinosa, Betula verrucosa, Picea excelsa, Pinus sylvestris, Pirus malus, P. aucuparia, Fagus silvatica, Quercus pedunculata*, and *Svietenia mahogoni* give negative reactions towards zinc chloride-iodine and sulphuric acid-iodine; except in the last two instances, these reactions become positive when the film is mechanically ruptured by grinding the specimens. Cellulose di- and tri-acetate, di- and tri-nitrate, di- and tri-ethyl- and di- and tri-methyl-cellulose, and cellulose xanthate do not react with iodine reagents.

H. WREN.

Pectin. II. Determination of the individual pectic substances in nature. D. R. NANJI and A. G. NORMAN (Biochem. J., 1928, **22**, 596—604).—The tissues are desiccated by drying at 95° in a steam-oven and are extracted with water at 85°. The aqueous extract is then precipitated by alcohol, the precipitate redissolved, hydrolysed, and precipitated finally as calcium pectate. Results are given for certain leaves, cereal grains, and fruits.

S. S. ZILVA.

Constitution of the hemicellulose of timber. M. H. O'DWYER (Biochem. J., 1928, **22**, 381—390; cf. A., 1926, 983).—Eighty % of hemicellulose-*A* from beech wood 80 yrs. old could be readily acetylated, but only 20% of the same substance from an older beech and from oak heartwood responded to this treatment. Methylation of the residue from acetylation in the case of oak brought about an increase in the methoxyl content. On re-methylation the compound showed a large increase in ash, due to the formation of a sodium compound. The hemicelluloses from both beech and oak contain a certain percentage of methoxyl of which about half exists in the form of an ester. The remainder seems to bear a different character, as it resists drastic methods of de-esterification. Hemicelluloses may be transition products in the change from pectic substances to lignin.

S. S. ZILVA.

Wheat proteins. A. KIESEL and A. CHARITONOVA-CHOLODKOVSKA (Zhur. exp. Biol. Med., 1927,

4, 548—550).—In an attempt to characterise wheat proteins the total and amino-nitrogen, optical properties, and drop number of gliadin and glutenin solutions were determined for different species.

CHEMICAL ABSTRACTS.

Chemical characterisation of proteins in pure races. A. KIESEL, A. BELOZERSKI, and S. SKVORZOV (Zhur. exp. Biol. Med., 1927, **4**, 538—546).—Differences in the histidine and tyrosine content of protein from different species of peas and beans are described. CHEMICAL ABSTRACTS.

Allantoic acid, a new nitrogenous principle of plants. R. FOSSE (Bull. Soc. Chim. biol., 1928, **10**, 301—307).—See A., 1927, 284.

Seeds of *Nepeta Cataria*. S. M. GORDON (Amer. J. Pharm., 1928, **100**, 155—156).—Extraction of the seeds, which contained 7·5% of water, with light petroleum yielded 22·90% of oil having d^{25} 0·7391, 1·4802, saponification value 183·9, and iodine value 103. E. H. SHARPLES.

Seed fats of the *Umbelliferæ*. I. *Heracleum sphondylium* and *Angelica sylvestris*. T. P. HILDITCH and E. E. JONES (Biochem. J., 1928, **22**, 326—330).—The ether-extracted fats were saponified and the lead salts from the crude mixture of fatty acids were examined. The presence of palmitic, stearic(?), petroselic, oleic, and linoleic acids was established in the extracts from the seeds of both plants. A partial estimate of the quantitative composition of the fatty acids is computed. A large proportion of non-fatty matter, mainly esters of lower fatty acids and alcohols in the case of *Heracleum*, and esters of valeric and other acids in the case of *Angelica*, was also extracted from the seeds. S. S. ZILVA.

Use of the bleaching action of chlorine in the rapid detection of fatty oils and the investigation of some other substances and structures of green cells. K. B. BLACKBURN and M. THOMAS (Proc. Univ. Durham Phil. Soc., 1927, **7**, 202—207).—A method of demonstrating oil in green cells by the combined use of osmic acid and chlorine water is described. Tannic acid does not interfere with the test. Starch grains can be shown by subsequent treatment with aqueous iodine. W. E. DOWNEY.

Aldehydes of *Pinus Jeffreyi*. S. M. GORDON (Amer. J. Pharm., 1928, **100**, 156—161).—The last fractions from the steam-distillation of the oil from *P. Jeffreyi* contain octaldehyde and nonaldehyde and *l*-α-pinene. 98% of the volatile products of the oleo-resin consists of *n*-heptane (cf. Kremers, A., 1921, i, 705). E. H. SHARPLES.

Essential oil of *Lippia hastulata* (Grisebach). L. PEREYRA (Univ. Nac. Tucuman Mus. Hist. Nat., 1926, No. 8, 3—13).—The oil has d^{15} 0·9207, n_D^{20} 1·4541, α_D^{15} 53° 5′ (? 53·5°), b. p. 100—195°, saponification value 28·9, and probably contains free alcohols 23·85, total alcohols 31·79, aldehydes 3 vol.-%, terpenes 50—55%. CHEMICAL ABSTRACTS.

***Lippia Hastulata* (Griseb.), Hieronymus.** E. H. DUCLOUX and C. ALBIZZATTI (Rev. Fac. Cienc. quim. La Plata, 1927, **4**, No. 2, 47—56; Chem. Zentr., 1927, ii, 1969—1970).—Analytical data are recorded. The essential oil has d^{15} 0·9133, n_D^{15} 1·4520, $[\alpha]_D$ +53·33°, f. p. −25·3°, saponif. value 13·95. A. A. ELDRIDGE.

Shoots of *Pinus maritima*. G. DUPONT and M. SOUM (Bull. Inst. Pin, 1927, 39—40; Chem. Zentr., 1927, ii, 1969).—The shoots (69·26% water) yielded (undried) an ethereal extract containing 7·64% of the dried substance. Of this, the oil volatile in steam had d_0^{15} 0·8843, n_D^{1} 1·4682, $[\alpha]_D$ −6·38°; the resin and fat contained 24% of neutral fat and esters, 71·3% of acids (67·4% of resin acids).

A. A. ELDRIDGE.

***Werneria proposa*, Philippi.** F. ZELADA (Univ. Nac. Tucuman Mus. Hist. Nat., 1927, No. 10, 3—17).—The plant extract contained a glucoside and an essential oil (d^{15} 0·8871, n^{20} 1·4965, α 0°, saponification value 17·60). The resin containing the glucoside had acid value 184·7, saponification value 260·78, iodine value 664·2. CHEMICAL ABSTRACTS.

Ouabain content of *Acocanthera Schimperi* from Eritrea. S. BERLINGOZZI and D. MIGLIACCI (Boll. Chim. farm., 1928, **67**, 33—35).—This plant contains in its wood 0·3%, and in its leaves 0·1% of the glucoside (cf. Arnaud, A., 1888, 848), as estimated by the fatal dose of an aqueous extract injected into a dog. E. W. WIGNALL.

Comparison of *Ephedra equisetina* and *E. sinica* and their seasonal content of ephedrine. C. T. FENG and B. E. READ (Chinese J. Physiol., 1928, **2**, 87—95).—*Ephedra equisetina* and *E. sinica* contain about four times as much ephedrine in the autumn as in the spring. At the time of maximum alkaloidal content, *E. equisetina* contains 1·75% and *E. sinica* 1·32% of alkaloid, the former being richer in ephedrine both absolutely, and relatively to other alkaloids. W. O. KERMACK.

Determination of filicin in extract of male fern. H. FLUCK (Bull. Sci. pharmacol., 1927, **34**, 266—272; Chem. Zentr., 1927, ii, 470).—Fromme's method is preferred, and is slightly modified; 84 g. of the filtered barium hydroxide solution of filicin are employed, the precipitated filicin is treated successively with 30, 20, 15, and 10 c.c. of ether, and the filicin is dried for 1 hr. at 100—102°.

A. A. ELDRIDGE.

Cortex of *Iodina rhombifolia* (Hoock et Arn.), Reiss. M. AWSCHALOM (Rev. Fac. Cienc. quim. La Plata, 1927, **4**, No. 2, 33—45; Chem. Zentr., 1927, ii, 1969).—Analytical results are given, and the method of extraction of the saponins (0·578% of the dry substance) is described. A. A. ELDRIDGE.

Constituents of *Typha angustata*, Bory et Chaub. M. FUKUDA (Bull. Chem. Soc. Japan, 1928, **3**, 53—56).—The alcoholic extract of the pollen of *Typha angustata* contains palmitic acid and an amorphous flavone glucoside which is hydrolysed by dilute acid to dextrose and *iso*rhamnetin, identical with a synthetic specimen (cf. Robinson, A., 1926, 1149). H. E. F. NOTTON.

Solubility of phosphorus compounds contained in seeds. Z. KOEHLER (Rocz. Chem., 1927, **7**, 692—706).—The total mineral, phytinic, and organic phosphorus contents of a number of seeds were determined. Extraction with 0·1—1·0% hydro-

chloric acid removed only mineral phosphorus; more concentrated acid also extracted phytinic phosphorus.
R. TRUSZKOWSKI.

Phosphatides of *Daucus carota*. V. GRAFE and H. MAGISTRIS (Z. wiss. Biol., Abt. 3 Planta, Arch. wiss. Bot., 1926, 2, 429—437; Chem. Zentr., 1927, ii, 1156).—The differences between denatured and native phosphatides are discussed. A diaminomonophosphatide from *Daucus carota* yields as fission products palmitic, oleic, and glycerophosphoric acids, choline, and carbohydrates.
A. A. ELDRIDGE.

Relations of the phospholipin in seeds to other constituents. N. B. GUERRANT (J. Agric. Res., 1927, **45**, 1001—1019).—The phospholipin content of sorghum seeds varies considerably with different varieties and among individual seeds of the same variety. Cereals contain smaller proportions, but beans, peas, and cotton seed are characterised by very high values. There seems to be no definite relationship between the amount of phospholipin and any other constituent present in seeds, although high phospholipin content is generally coincident with high fat and protein values. During the maturing of sorghum seeds there is a steady increase of phospholipin, but this does not account for the whole increase in total phosphate content during the same period. During the germination period of seeds there is a decrease in fat, protein, water-soluble phosphorus, and phospholipin. It is suggested that the phosphorus in seeds passes through a water-soluble condition before combining with lipins to form vital plant tissue.
A. G. POLLARD.

Essential oils of *Chenopodium rigidum* (arcayuyo) and of *Satureia eugenoides* (muna-muna). F. ZELADA (Univ. Nac. Tucuman Mus. Cienc. Nat., 1925, (sep.), 5—19).—Oil of *Chenopodium rigidum* has d 0·8780, α_D +1° 9′ (? 1·9°), n_D^{20} 1·4770, b. p. 182—183°, m. p. —20°, saponification value 19·3, and consists chiefly of terpene hydrocarbons, with small quantities of alcohols and phenols. Oil of *Satureia eugenoides* has d^{15} 0·9144, α_D^{20} 18° 9′ (? 18·9°), n_D 1·4759, b. p. 183—194°, m. p. —20°, saponification value 62·7, and probably contains free alcohols 48·8, ethers 21·26, and phenols 8·0%.
CHEMICAL ABSTRACTS.

***Banisteria Caapi*, Spr. A South American intoxicant.** L. LEWIN (Arch. exp. Path. Pharm., 1928, **129**, 133—149).—The alkaloid *banisterine*, $C_{13}H_{12}ON_2$, m. p. 257° (*hydrochloride*, m. p. 260—270° with browning), is extracted from the South American plant *B. Caapai* belonging to the family *Malpighiaceæ*. Its physiological action on man and animals is described. Banisterine may be identical with harmine.
W. O. KERMACK.

Microchemical detection of organically combined sulphur and magnesium in plants. G. KLEIN (Oesterr. bot. Z., 1927, **76**, 15—24; Chem. Zentr., 1927, ii, 2329).—Neuberg's hydrogen peroxide method does not completely oxidise organic sulphur; the material is instead exposed for several hours to bromine vapour, the excess of which is removed by volatilisation or by means of ammonia. The sulphate is precipitated with calcium chloride, the crystals of calcium sulphate being observed on the next day. Magnesium compounds are removed from plant sections by extended treatment with water.
A. A. ELDRIDGE.

Iodine as plant nutrient. A. STROBEL and K. SCHARRER (Naturwiss., 1927, **15**, 539; Chem. Zentr., 1927, ii, 2319).—Application of sodium iodate, *e.g.*, to beet and spinach, causes a considerable increase in the iodine content of the plant, but iodine is not therefore necessarily a plant nutrient.
A. A. ELDRIDGE.

Copper as a normal component of plants. A. QUARTAROLI (Annali Chim. Appl., 1928, **18**, 47—63).—A number of soils of various characters are found to contain 0·0008—0·0140% of copper (cf. this vol., 96) and 0·0147—0·1280% of manganese, the proportion of the total manganese which is soluble in 5% acetic acid solution being considerably greater than that of the total copper. When treated with very dilute copper sulphate solution, fine soil rapidly absorbs the copper and renders it insoluble; the copper adheres firmly to the colloidal material and is not to any great extent rendered soluble by subsequent treatment with successive quantities of water. Of 90 different kinds of seeds examined, 44 contain more copper than manganese, and only when manganese is present in exceptionally large amount is the relative proportion of copper very small. In general, seeds of cereals are low, and leguminous seeds and also seeds of garden plants high in copper content. The large proportions of copper in many seeds constituting the normal nutriment of many birds explains the high copper content of the feathers. Thus, copper appears to be an element necessary to the life of plants. The biological function of the elements is discussed.
T. H. POPE.

Biology of uranium. J. STOKLASA and J. PĚNKAVA (Biochem. Z., 1928, **194**, 15—77).—Small amounts of uranyl nitrate stimulate the assimilation of elementary nitrogen by bacteria, the effect being especially marked in presence of oxygen, whilst ammonia production is not stimulated. Concentrations of uranyl nitrate above $3{\cdot}125\times10^{-6}$ g.-atom/litre of medium are toxic. Germination experiments show that very dilute uranyl nitrate ($3{\cdot}125\times10^{-6}$—5×10^{-4} g.-atom/litre) accelerates the growth of embryos, higher concentrations being toxic and inhibiting growth, particularly of the roots. Photosynthetic assimilation of carbon dioxide is assisted by uranium. In presence of potassium hydrogen carbonate, increased photosynthetic assimilation is obtained only in absence of uranium, there being an antagonistic action between uranium, radium, and potassium. The presence of uranium in the culture fluid of plants causes a great increase in the amount of water transpired. In water culture experiments uranyl nitrate ($1{\cdot}4\times10^{-3}$—$4{\cdot}2\times10^{-3}$ g.-atom/litre) assisted photosynthesis, assimilation of carbon dioxide, formation of tissue, and assimilation of nitrogen by the roots. Similar amounts of uranium, however, have an injurious effect if the experiments are carried out in the dark. Analysis of whole plants (*Zea Mais* and *Polygonum fagopyrum*) shows that the greater the production of new plant tissue, the greater is the amount of phosphate assimilated and that under conditions in which phosphate is decreased, it is

replaced by increased silicate, chloride, and sulphate. In experiments with *Beta vulgaris*, *Soja hispida*, and *Vicia faba*, it is shown that uranium becomes stored in the seeds arising from plants the growth of which has been accelerated by uranium and so the growth of the second, third, and fourth year crops is also accelerated. Uranium $\beta+\gamma$- or γ-rays depress the growth of embryos and the development of roots and cotyledons, but β- and γ-rays increase photosynthesis. When plants are grown in shade, irradiation with uranium nitrate injures them, but the effect is counteracted by irradiation with ultra-violet light. Addition of small amounts of uranyl nitrate to soils, *e.g.*, for cereals 2—3 kg., for leguminous plants 2—5·3 kg., for sugar beet 8—10 kg., and for *Solanum tuberosum* 3—4 kg. per hectare, makes plants more resistant to parasites.

P. W. CLUTTERBUCK.

Zinc in plant biochemistry. M. GRAČANIN (Biochem. Z., 1928, **194**, 215—230).—Whereas zinc acts as a typical stimulator of the living processes of heterotrophic plants, it injures higher autotrophic green plants. Zinc sulphate in small amounts stimulates germination of some culture plants, but only until the embryo sends out its first leaves, the activating power being lost as soon as the plant becomes able to form new living material by means of its chlorophyll cells. When, however, the power of the chloroplasts is inhibited by lack of light, the activating influence is again evident. The extent of activation by zinc sulphate increases with rise of temperature and especially with increase of light intensity. Concentrations of zinc sulphate greater than 0·001*M* always cause acute injury to *Lamium album* and *Glechoma hederacea*, whilst lower concentrations cause chronic injury accompanied by decrease of the chlorophyll content of the chloroplasts. Very small concentrations of zinc sulphate cause a decrease of chlorophyll in *Mnium undulatum* and *Elodea canadensis*, the loss running parallel with the increase of zinc sulphate, with the increase of temperature and of light intensity. In diffused light, *M. undulatum* after 10 days still contained considerable amounts of chlorophyll, whereas with the same concentration of uranium in sunlight, the chlorophyll completely disappears. Leaves of *L. album* after loss of chlorophyll by the action of uranium, regenerate the pigment on treating with 0·125*M*-sugar solution. This reversibility is only partly obtained in *M. undulatum* leaves.

P. W. CLUTTERBUCK.

Behaviour of chemical fertilisers and other organic and inorganic substances during the germination and the early stages of plant growth. B. MAGRINI (Arch. Farm. Sperim., 1927, **44**. 93—122).—Lo Monaco (Staz. sperim. Agrar. Ital., 1924, **57**, 219) has advanced the theory that the effect of chemical fertilisers is due not to the fact that they replace what has been removed from the soil by crops, but to the stimulation of the action of the root hairs by the soluble constituents of the fertilisers. Evidence in support of this view is cited and the results are given of experiments on the influence on the germination and early growth of barley corns of dilute solutions of hydrochloric, nitric, sulphuric, and phosphoric acids, ammonia, sodium nitrate, ammonium sulphate, superphosphates, chlorine, bromine, neo-superphosphate (prepared by the action of a current of chlorine on a mixture of phosphorite with substances rich in ternary groups, such as sawdust, straw, hay, algæ, rice or wheat husk, etc., in fine condition), and "clumin." Some of the results obtained, such as the beneficial effects of dilute acids and the retarding effects of calcium salts on the development of the plant embryo, run counter to current views.

T. H. POPE.

Liberation of ammonia by the roots of plants during acid poisoning. D. PRIANISCHNIKOV (Biochem. Z., 1928, **193**, 211—215).—The power to liberate ammonia and to neutralise acid of the roots of pea, oats, and lupin embryos after dipping them in acid is followed quantitatively. The separation of ammonia by the pea begins earlier and the neutralisation of the acid takes place to a greater extent than with oats, but the pea is more sensitive to acid and withering takes place earlier. Lupin embryos, which contain a greater store of protein, possess this power even to a greater extent.

P. W. CLUTTERBUCK.

Toxicity of colloidal arsenic to plants. R. H. CARR (Proc. Indiana Acad. Sci., 1927, **36**, 185—187).—Colloidal arsenic (0·3 g. per gallon of water) is more toxic to geranium plants than non-colloidal arsenic (1·0 g. per gallon).

CHEMICAL ABSTRACTS.

Liberation of free iodine by sea-weed. P. DANGEARD (Compt. rend., 1928, **186**, 892—894).—The liberation of free iodine by many species of sea-weed, which is apparently due to specific cells situated near the surface of the plant, occurs in the natural state and continues until the plants are dry.

G. A. C. GOUGH.

Formation of diastase by *Aspergilli*. H. KNAPP (Zentr. Bakt. Par., 1927, II, **71**, 372—398; Chem. Zentr., 1927, ii, 2073).—The diastase formation of *Aspergillus oryzæ*, *A. flavus*, *A. parasiticus*, and *A. effusus* is dependent on the temperature during growth and the age of the culture; rapid, luxuriant growth on a medium containing no excess of nutrient is preferable. Spore formation prevents diastase formation; once formed, the enzyme remains unchanged.

A. A. ELDRIDGE.

Occurrence of phytase in yeasts and in *Aspergillus oryzæ*. C. SHIMODA (Zentr. Bakt. Par., 1927, II, **71**, 232—247; Chem. Zentr., 1927, ii, 2074).—For the preparation of phytin, rice bran, after extraction with ether and alcohol, was extracted with 1·5% hydrochloric acid, and the filtered liquid boiled with ammonia. The precipitate was extracted with 0·2% hydrochloric acid, protein was precipitated by boiling, ammonia added, the precipitate extracted with acetic acid, reprecipitated with ammonia, and redissolved in acetic acid. From the crude phytin, after complete removal of phosphoric acid, ammonia, and acetic acid, a product (a calcium magnesium inositolhexaphosphate) soluble in cold water was obtained. Yeasts and moulds can grow in a medium containing phytin as the only source of phosphorus, decomposing it by means of a phytase. The optimal temperature is 55—60° and p_H 2·2—4·4.

A. A. ELDRIDGE.

Nitrate assimilation in moulds. G. Klein (Z. physiol. Chem., 1928, **174**, 278—283).—A reply to the criticism by Kostytschev (A., 1927, 703) of the work of Klein, Eigner, and Muller (A., 1926, 1280).

A. Wormall.

Urea in fungi and its significance. N. N. Iwanov (Z. physiol. Chem., 1927, **170**, 274—288).—The urea content of certain fungus fructifications increases greatly during ripening but diminishes and may vanish in the ripe spores; in many examples the urea reached a maximum of about half the total nitrogen. The increase in urea content is accompanied by considerable loss of non-nitrogenous material as carbon dioxide, and that some of the latter is used in the synthesis of urea is confirmed by a largely increased production of urea when gaseous ammonia or an ammonium salt is supplied during the ripening period. It is suggested that urea plays in fungi a similar role to that of other amides (asparagine, glutamine) in green plants. The production of urea by bacteria is also observed. C. Hollins.

Biochemical differences between sexes in Mucors. IV. Enzymes which act on carbohydrates and their derivatives. S. Satina and A. F. Blakeslee (Proc. Nat. Acad. Sci., 1928, **14**, 229—235).—Comparative tests were made with 24(+) and (−) Mucor races, included in 10 species and 8 genera, to determine the possibility of a given carbohydrase being present in one sex and not in the other, but with negative results. The cultures were grown on a mineral nutrient solution to which, after inoculation, the carbohydrate in question was added. Two control dishes were kept for each experiment, in one of which the cultures were grown on the mineral nutrient solution, and in the other on the same solution to which an equal volume of 1% dextrose solution was added. The cultures in the first control dish germinated, but did not grow further, whilst those in the second dish developed a mycelium and later a felt with aerial hyphæ and fructifications. When the fungus did not contain the hydrolytic enzyme capable of converting the carbohydrate, the growth in the experimental dishes was similar to that in the first control dish. If, however, the carbohydrate was hydrolysed the cultures grew well. Thus, by examining the growth of the cultures, the presence of enzymes could be shown. The conclusions arrived at were confirmed by p_H determinations, and by other tests. In many cases no sugar could be found in the nutrient solution, especially when the fungus was most developed, showing that it was used up as soon as formed. No definite conclusion with regard to the occurrence of carbohydrases in the fungus can be reached by testing for reducing sugars, unless the tests are made on successive days. Trehalase, maltase, and emulsin were present in all the tested species; amylase and glycogenase in all but one. Lactase was found in races of 4 species and invertase and inulase in races of 2 species only. Of the species tested, Cunninghamella contained the greatest number of carbohydrases, whilst species of the genus Mucor and Parasitella contained the fewest. The relative values for Mucor development of several carbohydrates and derivatives are as follows: trehalose, maltose, salicin, amygdalin, starch, glycogen, mannitol, lactose, sucrose, and inulin. Amygdalin, however, yields hydrocyanic acid and ultimately kills the fungus. A. J. Mee.

Plant diseases. X. Fermentation of pentoses by *Fusarium Lini*. XI. *Fusarium Lini* and the pyruvic acid theory of alcoholic fermentation. M. G. White and J. J. Willaman (Biochem. J., 1928, **22**, 583—591, 592—595).—X. When the organism is grown on xylose, arabinose, or rhamnose the main products are mycelium, carbon dioxide, ethyl alcohol, and a small amount of organic substance precipitated by lead; 95—99% of the carbon is thus accounted for. Of these three pentoses xylose is utilised the most efficiently for alcohol production and arabinose for growth. Rhamnose is utilised very poorly for either. During the course of growth the ratio of carbon dioxide to ethyl alcohol is constantly shifting, due to the consumption of alcohol by the fungus.

XI. The intermediate products in the pyruvic acid theory of alcoholic fermentation may be utilised by the organisms (the hydroxy-derivative of methylglyoxal was used). Ethyl alcohol has not been found in the cultures. S. S. Zilva.

Preparation of collodion tubes and membranes. T. Huzella (Biochem. Z., 1928, **194**, 128—131).—Collodion tubes are made by dipping glass tubes into a concentrated solution of invert-sugar and then, after allowing the sugar layer to solidify, into collodion solution. On dipping into water, the tubes will readily slip off the glass. For making fine tubes, suitable for use as artificial capillaries, fine strings of the sugar are similarly employed.

P. W. Clutterbuck.

Universal extraction apparatus. K. Zipf (Biochem. Z., 1928, **193**, 207—210).—Two modifications of the Soxhlet apparatus are described which permit the extraction of dry powders by solvents or of aqueous solutions by a solvent either specifically lighter than or heavier than water (*e.g.*, ether or chloroform). P. W. Clutterbuck.

Nephelometric determinations and micro-determinations using the Vernes–Bricq–Yvon photometer. D. Leroy and M. Taillandier (Compt. rend. Soc. Biol., 1927, **97**, 557—559; Chem. Zentr., 1927, ii, 1495).—The apparatus is suitable for the determination of chlorides, sugars, urea, and uric acid in blood, urine, and cerebrospinal fluid.

A. A. Eldridge.

Determination of mol. wt. by means of the centrifuge. T. Svedberg (Tekn. Tidskr., 1927, **57**, Kemi, 64—69; Chem. Zentr., 1927, ii, 1736; cf. A., 1927, 99, 716).—The mol. wt. of ovalbumin is 34,400; those of phycocyan and phycoerythrin are approx. 100,000 and 200,000, respectively. The mol. wt. of hæmocyanin is at least 10^6. A 3% solution of hæmocyanin forms an unstable gel which prevents molecular diffusion, but on dilution diffusion takes place. There is possibly a connexion between this fact and the role of hæmocyanin as an oxygen-carrier. A. A. Eldridge.

Congo-red as deproteinising agent. E. Mislowitzer (Klin. Woch., 1927, **6**, 1240—1241; Chem. Zentr., 1927, ii, 1060).—Congo-red is a convenient deproteinising agent. It is quickly flocculated

by aluminium as well as by hydrogen ions, but an excess of aluminium salt is to be avoided. Blood (3 c.c.) is diluted with distilled water (30 c.c.), 3% Congo-red solution (10 c.c.) is added, and then a few drops of concentrated aluminium chloride solution.

A. A. ELDRIDGE.

Determination of sugar by means of Fehling's solution and centrifuging. W. S. ILJIN (Biochem. Z., 1928, **193**, 322—325).—A modification of Bertrand's method is described in which the cuprous oxide is separated and washed in a centrifuge tube. Tables show the weight of copper corresponding with 1—25 mg. of dextrose and with 1—45 mg. of maltose.

P. W. CLUTTERBUCK.

Determination of two kinds of sugar in a solution. W. S. ILJIN (Biochem. Z., 1928, **193**, 326—333). —A method is described for the determination of dextrose, maltose, and lactose in mixtures of the sugars by means of Fehling's solution and polarimetric tests, and also a method for determining two sugars in admixture by hydrolysis. P. W. CLUTTERBUCK.

Micro-determination of blood-sugar. K. DRESEL (Biochem. Z., 1928, **194**, 466—472).—By keeping dry for 24 hrs. filter papers on which was absorbed a known amount of blood, the mean loss in sugar, determined by the Hagedorn–Jensen method, was only 2·5%, whereas when stored in corked flasks in a moist atmosphere the loss may be 32·7%. The time of heating (3 min.) in the Hagedorn method with zinc hydroxide is sometimes too small, the results being 6% higher, in isolated cases, after heating for 30 min. P. W. CLUTTERBUCK.

Determination of reducing sugars by the ferricyanide method. A. IONESCO-MATIU (Bull. Soc. Chim. biol., 1928, **10**, 252—260).—See this vol., 398.

Determination of nitrogen. II. T. SHIMODA (J. Biochem. Japan, 1927, **7**, 473—488).—A modified micro-Kjeldahl method, suitable for blood and urine, is described. CHEMICAL ABSTRACTS.

Determination of quinine. B. P. SHVEDSKI (Zhur. exp. Biol. Med., 1927, **4**, 605—613).—Quinine, even 1 in 200,000, can be determined by Mayer's potassium mercuric iodide reagent. Ethereal blood extracts may give high values. Five min. after the injection of 0·5 g. of quinine hydrochloride into animals, 82—95% has disappeared from the blood.

CHEMICAL ABSTRACTS.

Determination of solubility of digitoxin. K. SAMAAN (J. Egypt. Med. Assoc., 1928, **11**, 16—21).— From an investigation of the time required to arrest the heart of frogs, using a series of solutions of digitoxin of known concentrations, the solubility of digitoxin in either distilled water or Ringer's solution is found to be approximately 1 : 120,000 at 18·5°.

O. J. WALKER.

Determination of cholesterol. H. DAM (Biochem. Z., 1928, **194**, 177—187).—The composition of the precipitate obtained by precipitating cholesterol in alcoholic solution with digitonin varies with the amount of precipitant in excess. Washing with alcohol redissolves a little of the precipitate and it is therefore better to wash with a saturated solution of cholesterol digitonide. The amount of cholesterol is finally calculated by use of a curve. When the total cholesterol in a tissue extract is determined after previous treatment with sodium ethoxide, too low results are obtained. A more accurate method for determining the total cholesterol, when the amount of cholesterol ester is small, consists of determining the free cholesterol by the digitonin method and then determining the ester in the filtrate colorimetrically.

P. W. CLUTTERBUCK.

Methods of determining the p_H of body fluids. E. J. BIGWOOD (Bull. Soc. Chim. biol., 1928, **10**, 15—241).—A lecture with full bibliography.

Use of quinaldine-red for the determination of p_H in an acid medium. I. M. KOLTHOFF (Biochem. Z., 1928, **194**, 78—82).—Quinaldine-red changes from colourless to red at p_H 1·4—3·2. The indicator constant at 23° is $1{\cdot}77\times10^{-3}$, corresponding with a pK_I of 2·75, the temperature modulus being 0·007 per 1°. The salt error is rather large. In 0·1N-potassium chloride the p_H correction is +0·17 and in 0·5N-potassium chloride, +0·38. 2 : 4 : 2′ : 4′ : 2″-Pentamethoxytriphenylcarbinol is better than quinaldine-red for p_H determinations. P. W. CLUTTERBUCK.

Applicability of the quinhydrone electrode and its biological uses. S. MORI (J. Biochem. Japan, 1927, **7**, 411—431).—The quinhydrone method is applicable to a solution of p_H <8·5, and gives trustworthy results for blood or serum. Isoelectric points (p_H) are: albumin 6·04, albumose 6·25, peptone 5·54. In titrating hydrochloric acid containing any of these substances, the end-point must be taken at the corresponding isoelectric point. The fixation of hydrogen ions in a solution of peptones in hydrochloric acid accords with the Freundlich adsorption formula.

CHEMICAL ABSTRACTS.

Determination of chloride in biological fluids. R. K. CHRISTY and W. ROBSON (Biochem. J., 1928, **22**, 571—574).—The excess of silver nitrate in deproteinised solutions after precipitating the chlorides is titrated with standard potassium iodide in acid solution in the presence of potassium di-iodate and soluble starch. The error involved in the method is less than 1%. S. S. ZILVA.

Volumetric micro-determination of phosphorus and its application to biological analyses. M. JAVILLIER and D. DJELATIDES (Bull. Soc. Chim. biol., 1928, **10**, 342—355).—Amounts of phosphorus of the order of 1 mg. may be determined in animal tissues by the following method. After destruction of the organic matter by the Kjeldahl method, the residue is treated with ammonium molybdate at 100° and the precipitate, which under these conditions has the formula $8[(NH_4)_3(MoO_3)_{12}PO_4],(NH_4)_2(MoO_3)_8SO_4$, is removed and washed with aqueous alcohol. The molybdic acid in this is then reduced by treating a solution in ammonia, acidified with sulphuric acid, with aluminium foil. By titration of the resultant reducing agent with 0·05N-potassium permanganate, the phosphorus value of the original sample may be calculated. G. A. C. GOUGH.

Micro-colorimetric method for the determination of sodium. L. T. POULSSON (Biochem. Z., 1928, **193**, 423—425).—A modification of the Barrenscheen–Messiner method (this vol., 96) is described.

P. W. CLUTTERBUCK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1928.

General, Physical, and Inorganic Chemistry.

Highly accurate method for interferometric wave-length determinations, and its application to a preliminary determination of krypton lines for a German standard metre in terms of light waves. A. P. Weber (Physikal. Z., 1928, **29**, 233—239).—In view of the use of interferometric methods in fixing standards of length, the relative merits of the Fabry–Perot etalon and the Koster absolute interference comparator methods have been studied at the Physikalisch-Technischen Reichsanstalt. The krypton spectrum possesses advantages over the cadmium spectrum in that the latter shows only one entirely suitable line, the standard red line, whereas several lines are available in the discharge from pure krypton. The following wave-lengths have been measured relative to the cadmium line 6438·5033 A. (in air at 20°, 760 mm., and 10 mm. moisture): green cadmium, 5085·8490, red krypton, 6456·3241, yellow, 5870·9463, yellowish-green, 5649·5924, violet, 4502·3790, green, 5400·5919, the two lines last named being measured relative to the other krypton lines. Pending further investigations in different countries on the krypton yellowish-green line, the use of the cadmium red line as a standard is continued.

R. A. Morton.

Coefficient of absorption in lead of the γ-rays from thorium-C'' and radium-C. L. Bastings (Phil. Mag., 1928, [vii], **5**, 785—793).—Measurements of the absorption in lead of the γ-rays from thorium-C'' and radium-C have shown that the absorption coefficient in the case of the former increases with the thickness of the lead penetrated, whilst in the case of the latter it decreases. This result is in general agreement with Compton's theory of scattering of radiation, since whilst the γ-rays from radium-C are distributed over a moderate range of wave-lengths with no outstanding gaps or preponderating concentration of energy, those from thorium-C'' are almost monochromatic. A. E. Mitchell.

Reversal of helium lines. T. Takamine and T. Suga (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 83—91).—See this vol., 209.

Spectra and atoms. A. Fowler (J.C.S., 1928, 764—780).—A lecture.

Spark spectrum of neon. H. N. Russell, K. T. Compton, and J. C. Boyce (Proc. Nat. Acad. Sci., 1928, **14**, 280—283).—A new series of lines of considerably shorter wave-length than those previously described has been discovered in the spark spectrum of neon. A vacuum spectrograph was used, the spectrum being excited by electron impacts at controlled voltages between a Wehnelt cathode and a wire-grid anode, the pressure in the spectrograph being kept at less than 0·005 of that in the discharge tube. This work, together with previous observations of de Bruin, has enabled 203 lines to be classified in 59 multiplets. A table is given stating the term values of all the states of Ne II so far identified. The mean quantum defects of the various states are also given, and compared with those of O II, to which they show close similarity. The ionisation potential was found to be 40·9±0·05 volts. A. J. Mee.

Spark spectrum of argon. I. T. L. de Bruin (Z. Physik, 1928, **48**, 62—66).—Theoretical. The deepest quadruplet term of the A II spectrum has been determined. An analogy is drawn between the spectrum of A II and Ne II. W. E. Downey.

Energy levels of the hydrogen atom according to the Dirac quantum theory of electrons. W. Gordon (Z. Physik, 1928, **48**, 11—14).—Mathematical. It is shown that Dirac's theory leads to Sommerfeld's fine-structure formula.

W. E. Downey.

Natural vibrations in the infra-red of beryllium oxide, magnesium oxide, calcium oxide, and zinc oxide. S. Tolksdorf (Z. physikal. Chem., 1928, **132**, 161—184).—The infra-red transmission spectra of the above oxides have been studied in the range 2—22 μ. In every case the lattice vibration is anharmonic. Magnesium oxide and calcium oxide give, corresponding with their simple cubic lattice structure, simple spectra, each having one fundamental. The hexagonal lattices of beryllium oxide and zinc oxide each appear to possess three fundamentals. Using the values obtained for the natural frequencies, ν, to calculate the values of $\beta\nu$, where β is the quotient of Planck's constant by Boltzmann's constant, gives results in fair agreement with those derived from m. p., compressibilities, and specific heats, respectively. R. Cuthill.

Structure of the fluorine spectrum (F I). T. L. de Bruin (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 944—951).—A theoretical term scheme has been deduced for the fluorine spectrum (F I) on the basis of the theory of complex spectra developed by Heisenberg (A., 1925, ii, 729), Hund (*ibid.*, 912), and Pauli (*ibid.*, 339). This is in fairly good agreement with experimental results. M. S. Burr.

Structure of the second order spectrum of sulphur (S II). J. Gilles (Compt. rend., 1928, **186**, 1109—1111; cf. Bloch and Bloch, A., 1927, 1117).—

Five multiplets of rays corresponding with the combinations $ans.^4P-anp.P^4$, $ans.^4P-anp.^4D$, $anp.^4P-and.^4D$, $anp.^4D-and.^4D$, and $anp.^4D-and.^4F$ have been recognised for the S II spectrum, and are tabulated. The S II and O II spectra are analogous.

J. GRANT.

Absorption spectra of nitric oxide. M. LAMBREY (Compt. rend., 1928, **186**, 1112—1114; cf. A., 1927, 808).—The absorption spectrum of nitric oxide is made up of two families of doublets located in the long and short wave-length regions, respectively, some of the doublets of the latter being partly superposed on those of the former. Each of the components is a resolvable band, and there is a single absorption minimum corresponding with a null ray. Formulæ are given representing the rays.

J. GRANT.

Origin of the spectrum of the solar corona. M. SAHA (Nature, 1928, **121**, 671—672).—A discussion of the method whereby certain light elements may give rise to the coronal spectrum. For lithium, beryllium, and boron, the force of radiation would more than balance the force of gravity, so that the element could be retained in the solar atmosphere only in the ionised form; corresponding lines for the non-ionised elements are not found in the Fraunhofer spectrum, but the identification of lines of the ionised elements is doubtful. The possibility of silicon, carbon, and other elements giving rise to prohibited transitions is also discussed, and the author's views are supported by experimental evidence derived from the behaviour of thallium. A. A. ELDRIDGE.

Stark effect and series limits. [MISS] J. M. DEWEY and H. P. ROBERTSON (Nature, 1928, **121**, 709—710).—An upper limit is obtained for the energy of quantised orbits in a hydrogen-like atom, and it is shown that various types of unquantised orbits having negative energies exist. A. A. ELDRIDGE.

Excitation of the auroral green line in active nitrogen. J. KAPLAN (Nature, 1928, **121**, 711).—The auroral green line has been excited in active nitrogen produced by a condensed discharge in a mixture of nitrogen and oxygen (4%); the wave-length was determined as 5577·5 Å. With decreasing amounts of oxygen the line, at first intense, gradually disappeared. A red line, 6654·8 Å., possibly identical with an unclassified oxygen line at that wave-length, was also observed. The dissociation of the oxygen molecule and the excitation of the atom are considered not to occur in a single act.

A. A. ELDRIDGE.

Mn II spectrum excited by rare gas ions. J. G. BLACK and O. S. DUFFENDACK (Science, 1927, **66**, 401—402).—Rare gas ions on contact with manganese atoms ionise them and excite them to the degree that the ionising potential of the rare gas exceeds that of manganese (7·4 volts). Argon (ionisation potential 15·4 volts) gives manganese lines originating in the ^7P and ^5P levels; with neon (ionisation potential 21·5 volts), $^7P-^7D$ lines were strong.

A. A. ELDRIDGE.

Extension of the violet CN band system to include the CN tail bands. F. A. JENKINS (Physical Rev., 1928, **121**, 539—558).—Wave-numbers of band-lines are tabulated for thirteen of the CN tail bands as excited by interaction of acetylene with active nitrogen. The tail bands are merely members of the ordinary CN sequences, with high vibrational quantum numbers. The constants B' and B'' were evaluated. The vibrational term-differences obtained from the calculated band-origins satisfy the combination principle. The assignment of the tail bands to the violet CN system makes this the first known system having some bands shaded towards the violet and others towards the red; also the frequencies of the bands of a given sequence may pass through a maximum. A. A. ELDRIDGE.

Certain multiplets in the spectra of Nb III and Nb IV. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], **31**, 520—526).—By applying the irregular doublet law to known data for the triad of multiplets ^3DF, $^3DD'$, and ^3DP $(ds-dp)$ in the two-electron systems Sr I and Y II, the corresponding multiplets for Zr III and Nb IV have been identified; similarly the triad of multiplets $^4F'D'$, $^4F'F$, and $^4F'G'$ (d^2s-d^2p) in the three-electron systems Y I and Zr II has been extended to Nb III, and the stronger lines of the $^4F'G'$ multiplet to Mo IV. A. A. ELDRIDGE.

Zeeman effect and Stark effect of hydrogen in wave mechanics. Force equation and virial theorem in wave mechanics. A. E. RUARK (Physical Rev., 1928, [ii], **31**, 533—538).—Theoretical. The Zeeman levels of hydrogenic atoms are determined by a new method. The formulæ for the first-order Stark effect and for the Paschen–Back effect can be obtained similarly. A. A. ELDRIDGE.

Absorption and scattering of mercury vapour for the line 2536 Å. J. Z. ZIELINSKI (Physical Rev., 1928, [ii], **31**, 559—568).—The absorption coefficient of the radiation (λ 2356 Å.) excited in mercury vapour by a beam from a mercury arc is unchanged by admission of air up to 4 mm. pressure, although the resonance radiation is strongly quenched; in a vacuum the scattering coefficient is equal to the absorption coefficient. A. A. ELDRIDGE.

Intensities in the hydrogen spectral series. F. G. SLACK (Physical Rev., 1928, [ii], **31**, 527—532).—Theoretical intensities of the components of the most important lines of the first six series of the hydrogen spectrum are computed and tabulated, together with the probability coefficients for the components and lines. A. A. ELDRIDGE.

Series spectra of potassium and calcium. I. S. BOWEN (Physical Rev., 1928, [ii], **31**, 497—502).—Series designations are given for some extreme ultra-violet lines in the spectra of K III, K IV, Ca IV, and Ca V; additional lines in the K II spectrum are identified. The series lines in the spectrum of Ca III are tabulated with series designations. The term values give the ionisation potential of K II as 31·7 volts, and that of Ca III as 51·0 volts.

A. A. ELDRIDGE.

Reflexion of atoms by a crystal. A. ELLETT and H. F. OLSON (Physical Rev., 1928, [ii], **31**, 643—647).—For cadmium and mercury atoms striking a rock-salt surface the incident and reflected beams are

equally inclined to the normal. Sodium is not reflected. Hydrogen gives irregular results.

A. A. ELDRIDGE.

Continuous absorption in sodium vapour. B. TRUMPY (Z. Physik, 1928, **47**, 804—813).—From measurements of the continuous absorption by sodium vapour in the neighbourhood of the convergence frequency of the principal series, it is shown that the coefficient for the continuous absorption diminishes rapidly with increasing frequency, and at 2300 Å. attains a value approximately one half that obtaining at the convergence frequency. The results are discussed from the point of view of Sugiura's theory.

J. W. SMITH.

Behaviour of hydrogen and mercury at the electrode surfaces of spectrum tubes. M. C. JOHNSON (Proc. Roy. Soc., 1928, **A**, **118**, 695—708).—If an aluminium cathode is exposed to mercury vapour and then washed for a long time in streams of hydrogen without further admission of mercury, the resulting domination of mercury lines over the hydrogen spectra, and the increase in rate of cathode disintegration, are accompanied by a decrease in the proportion of the spectrum of hydrogen due to neutralisation of protons, as deduced from the Doppler effect. With aluminium electrodes, the mercury spectrum appears instantaneously; it is almost instantaneous with a nickel cathode if there is gas connexion with a second tube containing aluminium, but with an isolated nickel cathode the mercury spectrum is fainter and requires a greater mercury pressure. In badly-contaminated tubes, the gradual saturation of the absorbing sodium or silver and the gradual weakening of the mercury spectrum at the electrodes are functions of the time during discharge, not of the intervals of time between. Admission of mercury to all tubes continues to decrease the resistance of the tube after admission has ceased for as long as 10 min. When solid, a mercury cathode can be made to disintegrate electrically in a way distinct from its thermal disintegration, but the disintegration layer from the aluminium cathode after mercury contamination is of aluminium, and is due neither to thermal nor to electrical disintegration of mercury. It is suggested that when a gas known to be liable to multiple ionisation is admitted to the tube, the increased energy of its ions effects what has been impossible for the steady proton bombardment, viz., a partial break-up of the protective layer of oxygen on the aluminium cathode, thus allowing the gases in the aluminium structure to diffuse out.

L. L. BIRCUMSHAW.

Emission of light by flames containing sodium and the absorption of light by mercury vapour. H. A. WILSON (Proc. Roy. Soc., 1928, **A**, **118**, 362—366).—The relative light intensities due to 1, 4, and 9 sensibly equal Bunsen flames, arranged in a row and supplied with sodium by the same sprayer, were found to be 1 : 2 : 3, within the limits of error. Using solutions with concentrations of sodium proportional to 1, 4, 9, and 16 in the sprayer, the light intensities for any number of flames from 1 to 9 were found to be as 1 : 2 : 3 : 4. These results confirm Gouy's conclusion (Ann. Chim. Phys., 1879, **18**, 5) that $I \propto \sqrt{\rho d}$ (when ρd is not extremely small), where I is the light intensity emitted in a direction perpendicular to the flame surface, d is the flame thickness, and ρ the amount of sodium per unit volume. Gouy's square-root law may be simply explained by taking into account the fact that the sodium atoms absorb the light at the centres of the D lines much more strongly than that at the edges. The experimental results on the emission of light by sodium flames and on the absorption of resonance radiation in mercury vapour (Hughes and Thomas, A., 1927, 1118) are shown to be consistent with the view that the atoms absorb light like simple damped oscillators.

L. L. BIRCUMSHAW.

Theory of scattering of slow electrons. J. HOLTSMARK (Z. Physik, 1928, **48**, 231—243).—Using a method previously developed (Faxén and Holtsmark, A., 1927, 1119), the scattering of slow electrons in argon and the effective cross-section of the argon atom for small electron velocities are calculated. A general agreement is found with the data of Rusch (A., 1926, 989) and of Brüche (A., 1927, 1119). The minimum scattering cross-section is obtained approximately. The calculations are made on the basis of the field worked out by Pauling (A., 1927, 394) and by Hartree (this vol., 216). The minimum appears to be a general property for all centrally symmetrical atoms, in agreement with the latest experimental results of Brüche. The calculation for neon is not in such good agreement as for argon. The diffusing cross-section is also calculated.

A. J. MEE.

Corona discharge in helium and neon. L. G. H. HUXLEY (Phil. Mag., 1928, [vii], **5**, 721—737).—Measurements of the potentials necessary to start a discharge between a cylinder and a coaxial wire in pure helium and in pure neon have been made. It has been found that the starting potential depends on the polarity of the electrodes and that whilst at pressures less than about 8 mm. the starting potential is greater when the wire is positive, the reverse is the case for higher pressures. This result is not in agreement with the theory that the discharge is maintained by the action of electrons in ionising the gas molecules by collision and of the positive ions in liberating electrons from the cathode, since the negative discharge would then be started always by the smaller potential. The velocities of the positive ions in helium and neon have been measured and the molecules are shown to present towards positive ions of certain velocities large reductions in effective diameter, and the mean free paths in neon of the positive ions are shown to be about five times those in helium.

A. E. MITCHELL.

Electrical properties of monatomic gases. J. S. TOWNSEND and S. P. MACCALLUM (Phil. Mag., 1928, [vii], **5**, 695—700).—In an investigation of the electrical properties of neon it has been found that small traces of diatomic impurities may be removed in a few seconds by the action of a high-frequency discharge from either internal or external electrodes. The effect of impurities on the electrical properties of the gas has been shown to be more noticeable in a wide tube, where the force required to maintain the

discharge is comparatively small, than in a narrow tube, where a larger force is required. The purification is explained on the previous results of Townsend and Donaldson (*ibid.*, 179) that in similar discharges the positive ions and electrons do not recombine to any appreciable extent in the gas. The disappearance of ions from the gas is then attributable primarily to the diffusion of the electrons to the walls of the tube, leaving the gas positively charged. The repulsion of the positive ions to the wall quickly establishes a stable distribution in which positive ions and electrons reach the wall simultaneously. Losses are balanced by the process of ionisation of molecules by electron collision and a steady state is maintained. The easily ionised molecules of diatomic gases are thus driven by the force of the positive charges into contact with the tube wall, where they remain for a considerable time and do not affect the electrical properties of the free monatomic gas. It is thus concluded that atoms of monatomic gases are ionised by electron collisions and that the development of heavy currents in these gases is chiefly due to this process, a conclusion which is in disagreement with other theories.

A. E. MITCHELL.

Quantum theory of the Ramsauer effect. J. R. OPPENHEIMER (Proc. Nat. Acad. Sci., 1928, **14**, 261—262).—The Ramsauer effect can be accounted for by consideration of electronic resonance and spin. Two first-order cross-sections for the elastic collision of an electron and a hydrogenic atom can be calculated, corresponding with initial orbital wave-functions respectively symmetric and antisymmetric in the co-ordinates of the impacting electron and the atomic electron. The symmetric wave-function gives a greater cross-section than that calculated without resonance, whilst the anti-symmetric function gives a cross-section vanishing for some small velocity for each angle of deflexion. The total cross-section shows a sharp minimum at about 1 volt. In the general case, both symmetric and antisymmetric wave functions will occur, but for atoms having only paired electrons (*e.g.*, helium, argon, methane) the cross-section is given by the antisymmetric function alone and may, therefore, pass through a minimum for sufficiently low velocities. For any particular case the whole problem must be solved. Minima in cross-sections have been observed for argon and krypton.

A. J. MEE.

Electric moment of alkali atoms. J. J. WEIGLE (Physical Rev., 1928, [ii], **31**, 672—675).—The electric moments of sodium, potassium, and rubidium atoms, respectively, are computed by an "inaccurate" method as 0·18, 0·24, and 0·27 $\times 10^{-18}$ g.$^{\frac{1}{2}}$cm.$^{\frac{3}{2}}$sec.$^{-1}\varepsilon$, respectively. The values, being negligible, are in accord with Bohr's theory.

A. A. ELDRIDGE.

Low-voltage arcs in iodine. H. F. FRUTH (Physical Rev., 1928, [ii], **31**, 614—628).—The minimum radiating potential of the iodine atom is 6·5 volts, the ionising potential of the atom 8·0, and the ionising potential of the molecule 9·5 volts. At 4·9 volts the spectrum contained the lines 2062, 2535, and 3135 Å., the continuous band 3460 Å., and several groups of bands. Arc lines appear at slightly higher voltages, and spark lines at 8 volts. The continuous bands at 4080, 4300, and 4800 Å. are observed for molecular, but not atomic, iodine. A band system at 2224—2050 Å., and two groups at 2880, 2833, 2776, 2716 Å. and 2480, 2379, 2290, 2243 Å., were observed.

A. A. ELDRIDGE.

Positive ion kinetics. G. P. HARNWELL (Physical Rev., 1928, [ii], **31**, 634—642).—Measurements of the mean free path and energy loss per collision of positive ions of potassium and cæsium in helium, neon, argon, hydrogen, and nitrogen accord with a free path approximately equal to the kinetic theory value and with an energy loss considerably less than would be expected.

A. A. ELDRIDGE.

Motion of conducting electrons. A. E. MALINOVSKI (Z Physik, 1928, **47**, 859—885).—A detailed description of the experiments previously recorded (A., 1927, 504). The negative results obtained are theoretically discussed and the conclusion is reached that the magnitude of the electromagnetic motion of the conducting electrons is not influenced by the self-induction of the conductor.

J. W. SMITH.

Electrical conductivity in flames. P. LENARD (Ann. Physik, 1928, **85**, [iv], 730—744).—A general review.

W. E. DOWNEY.

Ion rays. E. WEITKAMP (Physikal. Z., 1928, **29**, 217—223).—For salts from which the same ion is emitted, a parallelism is shown to exist between the m. p. and the temperature at which emission begins. At lower temperatures the emission falls off with time, but at and above the m. p. the emission is constant. Addition of graphite to the salt-containing anode results in a reduction of the emission to as little as 1/10 to 1/20 of the original current. Small additions of iodine slightly increase, and larger quantities of iodine markedly decrease the emission. In the case of cadmium iodide, no difference appears when dry air is admitted after the substance has been maintained and allowed to cool in a vacuum, whereas moisture greatly increases the emission.

R. A. MORTON.

Origin of magnetism based on the structure of atoms. K. HONDA (Proc. Imp. Acad. Tokyo, 1928, **4**, 12—15).—A qualitative discussion of the author's theory that ferro- and para-magnetism is due to nuclear electrons, whilst diamagnetism is attributed to the outer, or optical, electrons of the atom. Diamagnetic atoms have definite magnetic moments comparable with those of the ferro- or para-magnetic atoms, but owing to their large angular moments, they cannot be magnetised. In the latter case, it is assumed (after Rutherford) that the angular moments of protons and electrons in the nucleus, revolving in opposite directions, almost cancel one another, whilst the theory of the gyroscope is applied to show that in the former case a diatomic model cannot be magnetised but may be diamagnetised.

J. GRANT.

Reflexion of positive rays by a platinum surface. G. E. READ (Physical Rev., 1928, [ii], **31**, 629—633).—A study of the relative amount of reflexion of lithium and potassium ions at a platinum

surface under various conditions, and of the angle distribution of the reflected rays.

A. A. ELDRIDGE.

Revision of at. wt. of uranium. Analysis of uranous chloride. O. HÖNIGSCHMID and W. E. SCHILZ (Z. anorg. Chem., 1928, **170**, 145—160).—By preparing and analysing uranous chloride by the methods previously used for the bromide (A., 1914, ii, 662; 1916, ii, 484) the value of the ratio $UCl_4 : 4Ag$ has been found to be 0·880524, giving 238·14 for the at. wt. of uranium. For the fused chloride, d_4^{25} is 4·725.

R. CUTHILL.

Precision measurements in radioactivity. L. BASTINGS (J. Sci. Instru., 1928, **5**, 113—122).—The factors introducing error into gold-leaf electrometer measurements are discussed. An experimental technique and a gold-leaf electrometer are described, by means of which results can be obtained consistent to 1 in 1000.

C. W. GIBBY.

β-Rays of proto-actinium. O. HAHN and A. VON GROSSE (Z. Physik, 1928, **48**, 1—10).—The absorption curves for the secondary β-radiation of proto-actinium have been measured and μ, the absorption coefficient in aluminium, is found to be 126 cm.$^{-1}$ Comparison of the curves with those for radio-actinium suggests that the β-radiation of proto-actinium is not due to impurity. The γ-radiation which accompanies secondary β-rays was detected. This γ-radiation of proto-actinium is found to be more penetrating than the β-rays from the active precipitate of actinium.

W. E. DOWNEY.

Velocities of α-particles from radium-*C*, thorium-*C* and -*C′*. G. H. BRIGGS (Proc. Roy. Soc., 1928, A, **118**, 549—557).—The value of $H\rho=MV/E$ for an α-particle from radium-*C* has been redetermined, the apparatus for producing the magnetic deflexion being modified (cf. A., 1927, 392, 393). From the value found, $3{\cdot}993\times10^5$ e.m.u., and the theoretical value of E/M, 4814·8, calculated from recent determinations of the at. wt. of helium and the value of the Faraday, taking into account the relativity correction for the increase in mass of the α-particle, the initial velocity of α-particles from radium-*C* is found to be $1{\cdot}923\times10^9$ cm./sec. The values found by Rutherford and Robinson were $H\rho=3{\cdot}983\times10^5$ and $V=1{\cdot}922\times10^9$ (cf. A., 1914, ii, 789). The initial velocities of α-particles from thorium-*C* and -*C′* are found to be $1{\cdot}705\times10^9$ and $2{\cdot}053\times10^9$ cm./sec. respectively. These results are compared with those deduced from the Geiger relation $V^3=kR$, and found to be in good agreement. A table is given showing the velocities of α-particles from other radioactive substances, the results being deduced from the author's velocity curve for α-particles from radium-*C* (*loc. cit.*) and from Geiger's determination of the ranges (Z. Physik, 1921, **8**, 45).

L. L. BIRCUMSHAW.

Energy stages of atoms and molecules and their relationship to chemical union. J. FRANCK (Ber., 1928, **61**, [*B*], 445—459).—A lecture.

H. WREN.

Penetrating radiation. J. CLAY (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1115—1127).—Measurements of the penetrating or ultra-γ-radiation have been made at Bandoeng, Java, from February to July. There appears to be a daily variation in intensity with a minimum at about 8 a.m., which is always maintained, although the average value for the day may vary with the season. Absorption experiments indicate that there are at least two different kinds of rays, with possible mass absorption coefficients of 17×10^{-3} cm.$^{-1}$ and 4×10^{-3} cm.$^{-1}$, which are greater than those found by Millikan and Cameron (Physical Rev., 1926, [ii], **28**, 851). The wave-lengths calculated from these are 3×10^{-11} and $0{\cdot}8\times10^{-11}$ cm., respectively. The intensity of the radiation appears to decrease with increasing altitude at first and then to increase. A penetrating radiation was also observed in a rock-salt mine in Stassfurt.

M. S. BURR.

Non-appearance of the recombination luminescence in the reaction between alkali and halogen atoms. V. KONDRATJEV (Nature, 1928, **121**, 571—572).—The exciter of chemiluminescence in the reaction between alkali atoms and halogens is considered to be a molecule, NaCl′, having an excess of energy and existing as an energy-rich molecule for a sufficiently long time to meet a sodium atom. The curves for the potential energy of the systems (M)(X) and $(M^+)(X^-)$ as a function of the distance r between two nuclei intersect at a point r_c at which the valency electron of the metal can be "adiabatically" transferred to the halogen atom. The molecule M^+X^- (MX′) formed in this way from the neutral atoms can exist for a comparatively long time in a high vibrational state. The energy of vibration of such a molecule can be increased by the absorption of the temperature radiation to a quantity $Q+J-E$, where Q is the heat of reaction $M+X=MX$, J the ionising potential of the cation, and E the electron affinity of the anion; in the chemiluminescence spectrum, lines the excitation energy of which exceeds Q do in fact appear. In the region $r<r_c$, spontaneous transition followed by emission of light may be expected, but visible radiation is not observed. Radiation may be expected in recombination of one normal and one excited atom, the curves (M′)(X) or (M)(X′) and $(M^+)(X^-)$ of which do not intersect. The curves (K)(I) and $(K^+)(I^-)$ do not intersect, whereas the curves (Na)(I′) and $(Na^+)(I^-)$ intersect; in the chemiluminescence spectrum of the former, but not the latter, reaction, a large continuous band is observed.

A. A. ELDRIDGE.

Disappearance of gases into glass under the action of the electric discharge. J. TAYLOR (Nature, 1928, **121**, 708—709).—In experiments in which positive ions obtained in various gases at low pressures by means of an electrodeless discharge were pulled out by an electric field to the walls of a glass bulb immersed in molten sodium nitrate, (*a*) for hydrogen, oxygen, and nitrogen the quantity of gas disappearing is directly proportional to the quantity of electricity transferred through the glass walls, (*b*) for hydrogen, every electron charge passed involves the disappearance of one hydrogen molecule, (*c*) for oxygen and nitrogen, every two electron charges passed involve the disappearance of one atom, (*d*) for helium, no disappearance of gas occurred. The

effect is not an accelerated diffusion, but appears to arise from an electrolytic decomposition of the glass probably resulting, with hydrogen, in the formation of water which penetrates deeply into the glass structure. A. A. ELDRIDGE.

Energy of the helium atom and of the positive ion of the hydrogen molecule. B. N. FINKELSTEIN and G. E. HOROWITZ (Z. Physik, 1928, **48**, 118—122).—Mathematical. W. E. DOWNEY.

Statistical theory of the transition between two excited states of an atom. K. BOLLERT (Z. Physik, 1928, **48**, 98—110).—Theoretical. W. E. DOWNEY.

Wave mechanics of rotating electrons. J. FRENKEL (Z. Physik, 1928, **47**, 786—803).—Mathematical. An extension of a former theory (A., 1926, 773). J. W. SMITH.

Wave equations of the electron. C. G. DARWIN (Proc. Roy. Soc., 1928, A, **118**, 654—680).—Mathematical. Dirac's recent work on the quantum theory of the electron (this vol., 344, 456) is discussed, and his system is treated by the ordinary methods of wave calculus instead of by the non-commutative algebraical methods. The relationship of his equations to previous theories is considered, and it is shown that Schrödinger's equation and the pair of equations derived empirically by the author (cf. A., 1927, 916) are successive approximations to Dirac's. The equations are solved for the motion of an electron in a central field, and are shown to be expressible in terms of spherical harmonics and to lead to a doublet structure for the spectrum. The discussion of the radial functions is shown to lead exactly to the original Sommerfeld expression for the energy levels in the case of hydrogen. A few points connected with the free electron, the emission of radiation from an atom, and its magnetic moment are reviewed, the rules of combinations are considered, and a discussion of the Zeeman effect is outlined.

L. L. BIRCUMSHAW.

Statistical method for estimating some properties of atoms and its application to the theory of the periodic system of the elements. E. FERMI (Z. Physik, 1928, **48**, 73—79).—Theoretical. The electrons in heavy atoms may be considered as a kind of atmosphere, and their distribution round the nucleus may be calculated by a statistical method.

W. E. DOWNEY.

Anomalous effective cross-section of similar atoms when suffering collisions of the second kind. W. SCHÜTZ (Z. Physik, 1928, **48**, 67—72).—Polemical against Orthmann and Pringsheim (this vol., 338) and von Keussler (A., 1927, 491).

W. E. DOWNEY.

Change of wave-length in light scattering. C. V. RAMAN (Nature, 1928, **121**, 619).

Absorption coefficients. H. G. DE LASZLO (J. Physical Chem., 1928, **32**, 503—506).—A summary of the methods used to measure absorption coefficients of solutions and pure liquids. L. S. THEOBALD.

Absorption spectra of formaldehyde and carbon monoxide: close relationship between these two molecules. V. HENRI and S. A. SCHOU (Compt. rend., 1928, **186**, 1050—1052).—The ultra-violet absorption spectrum of formaldehyde corresponds with a bivalent molecule, and is analogous in many respects to that of carbon monoxide, having a system of triplets with the same intervals. The inter-combination absorption bands $^1S-^3P$ occurring in the latter correspond with the resonance rays of the bivalent atoms. J. GRANT.

Arc spectrum of Kasolo uraninite. J. VERHAEGHE (Bull. Acad. roy. Belg., 1928, [v], **14**, 18—30).—Crude uraninite may be utilised to give a continuous arc spectrum suitable for the investigation of absorption spectra in the ultra-violet. Uraninite itself is insoluble in hydrochloric acid, whilst the crust of secondary minerals dissolves easily. Arc spectra obtained with the solution exhibit the complete spectrum of lead, whilst only the more persistent lines (indicating concentrations between the limits 0·001—2·0%) are recorded for iron, cobalt, nickel, molybdenum, chromium, manganese, vanadium, titanium, lanthanum, magnesium. The following elements can be present only in traces, since only "raies ultimes" were detectable: potassium, strontium, cæsium, tungsten, and thorium. The proportion of iridium present remains doubtful. R. A. MORTON.

Infra-red absorption spectra of acetylene, ethylene, and ethane. A. LEVIN and C. F. MEYER (J. Opt. Soc. Amer., 1928, **16**, 137—164).—The spectra of acetylene, ethylene, and ethane were investigated between 2 and 15 μ. Each gas shows a characteristic type of structure for its vibrational–rotational bands. The three main absorption regions of acetylene have been resolved into individual lines which are alternately intense and faint. These lines have the same average spacing in the three bands. The two minor absorption regions of acetylene were also investigated, and the molecular moment of inertia was computed from the spacing of the fine structure of the principal bands. The value is in agreement with that computed from the classical theory on the assumption of a linear molecular model. Seven regions of absorption were investigated for ethylene. Two were resolved into individual lines with a strong Q branch present in one case and absent in the other. Four of the remaining regions reveal "envelopes" of an identical type, characterised by a sharp Q branch together with P and R branches. The bands in the region of 2·3 μ lack Q branches. The main absorption regions of ethane reveal bands, each consisting of a single succession of absorption maxima.

C. J. SMITHELLS.

Spectroscopic criterion for the benzenoid structure in some types of triphenylmethane derivatives. R. C. GIBBS and C. V. SHAPIRO (Proc. Nat. Acad. Sci., 1928, **14**, 251—252).—It is shown that in every case where the benzenoid structure was to be expected (with one exception), the absorption spectra of the compounds in neutral alcoholic solution include a pair of bands having an average separation of 100 mm.$^{-1}$, and lying in the region between frequency numbers (mm.$^{-1}$) 3500 and 3700. These bands are usually weak, and are sometimes superimposed on the general absorption. The average molecular absorption coefficient for these bands is of the same order of magnitude for all the triphenylmethane derivatives

studied. This observation was applied to coloured solutions, and confirmed the view that benzenoid or lactonoid derivatives were actually present in the solutions even although they might be in equilibrium with quinonoid modifications. *p*-Hydroxytriphenylcarbinol was studied in this way, together with hydration products of benzaurin and aurin etc. There is one exception—dichlorosulphonefluoran, a colourless compound, known to be lactonoid in structure, which, however, gives the above bands.

A. J. MEE.

New diffuse radiations. Y. ROCARD (Compt. rend., 1928, **186**, 1107—1109).—An attempt is made to explain the new diffuse radiations described by Raman (this vol., 461) on the basis of the author's theory (this vol., 354), as the optical beats due to the various oscillation frequencies of the electric moment of the molecules. J. GRANT.

Absorption spectra of anthracene derivatives. I. E. DE B. BARNETT, J. W. COOK, and T. E. ELLISON (J.C.S., 1928, 885—890).—Substitution in the *meso*-positions of anthracene has very little effect on the spectrum (in alcohol), which is merely shifted as a whole, but is independent of the mass of the substituent. Destruction of the bridge linking by reduction to 9 : 10-dihydroanthracene, however, causes the spectrum to become similar to that of an alkyl derivative of benzene. Derivatives of anthrone in which tautomeric change is impossible owing to replacement of the methylene hydrogen atoms of anthrone by non-mobile groups give a characteristic absorption curve. As would be expected from considerations of transannular tautomerism (this vol., 52), 1 : 5-dichloroanthrone has bands of both the anthracene type and the anthrone type. It is established that the reactive bromo-compound of 1 : 5-dichloro-9-benzylanthracene has a structure corresponding with those of the colourless series of compounds derived from it, but it is not possible to decide between the two alternative structures for these compounds (cf. *loc. cit.*). R. CUTHILL.

Optical analogue of the Compton effect. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, **121**, 711).—The presence in the light scattered by fluids of wave-lengths differing from those of the incident light is demonstrated. It is suggested that an incident quantum of radiation may be scattered by the molecules of a fluid either as a whole or in part.

A. A. ELDRIDGE.

Shape and intensities of infra-red absorption lines. D. M. DENNISON (Physical Rev., 1928, [ii], **31**, 503—519).—An expression for the shape of an infra-red absorption line is developed. The absorption coefficient may be expressed by means of two damping curves involving the number of molecules per unit volume, the temperature, and the effective diameter. Formulæ are derived which are capable of interpreting the absorption lines of the infra-red hydrogen chloride spectrum; the value $10{\cdot}8\times10^{-8}$ cm. is obtained for the effective diameter. The meaning of this value and the validity of the assumptions are discussed. The effective moving charge of the hydrogen chloride molecule is $\varepsilon=(0{\cdot}199)\times4{\cdot}77\times10^{-10}$ e.s.u. A. A. ELDRIDGE.

Changes produced in the absorption bands of certain organic fluorescent dye solutions by alterations of concentration and temperature. W. E. SPEAS (Physical Rev., 1928, [ii], **31**, 569—578).—Increase in concentration of solutions of rhodamin *B* or eosin produces the same general effect on the absorption bands as a fall of temperature, and *vice versa*. Increase in concentration of alcoholic rhodamin *B* causes an increase in the absorption per molecule and a shift of the bands towards the red. Experiments were also performed with fluorescein, uranin, and resorcinol-benzein. A. A. ELDRIDGE.

Chemiluminescence between alkali metal vapours and tin halides. M. PÓLÁNYI and G. SCHAY (Z. Physik, 1928, **47**, 814—818).—Highly diluted flames of alkali metals burning in stannic chloride, bromide, and iodide emit intense luminescence and continuous bands. The bands extend from 400 to 550 $\mu\mu$ with potassium and stannic chloride, from 405 to 540 $\mu\mu$ with sodium and stannic chloride, from 440 to 600 $\mu\mu$ with sodium and stannic bromide, and from 500 to 620 $\mu\mu$ with sodium and stannic iodide. The intensity is greatest in the middle of the band and decreases symmetrically on each side. From the data the heats of formation of the tetrachloride and trichloride of tin are deduced. The chemiluminescence is explained by supposing a trihalide to be first formed and that this decomposes into the di- and tetra-halides with evolution of light energy. J. W. SMITH.

Band spectrum of water vapour. II. D. JACK (Proc. Roy. Soc., 1928, **A**, **118**, 647—654; cf. A., 1927, 808).—The water-vapour band λ 3428 has been measured and analysed. Comparison of the term differences in this band with those in the bands previously analysed shows that the initial terms are the same for the bands λ 3428 and λ 3064, and the final terms are the same for the bands λ 3428, λ 3122, and λ 2875. This is in agreement with the scheme already proposed (*loc. cit.*). The band λ 3428 corresponds with the transition $0\longrightarrow1$ of the vibrational quantum number. Accurate values are calculated for the moments of inertia of all the bands, to replace the relative values previously given. The values for the state of no vibration are $I_0'=1{\cdot}633$ and $I_0''=1{\cdot}498\times10^{-40}$ g.-cm.^{2}, whilst the corresponding nuclear separations are $r_0'=1{\cdot}022\times10^{-8}$ cm. and $r_0''=0{\cdot}979\times10^{-8}$ cm. in the case of the hydroxyl ion.

L. L. BIRCUMSHAW.

Variation of the absorption coefficients of fluorite and quartz with temperature in the short-wave infra-red. O. REINKOBER and H. KIPCKE (Z. Physik, 1928, **48**, 205—215).—The absorption coefficients of fluorite in the region between 8 μ and 12·5 μ, and of quartz between 3 μ and 6·5 μ, were measured at a series of wave-lengths at different temperatures from 20° to the temperature of liquid air. The curves between absorption coefficient and temperature show that the former decreases in both cases as the temperature is lowered. Extrapolation indicates that at the absolute zero there will still be some absorption. The graph connecting wave-length and the ratio of the absorption coefficients at 20° and at −180° (this being used instead of the exact

temperature coefficient) is drawn, and it is found that for fluorite the relationship is linear. The results agree very well with those of Rubens and Hertz. For quartz the ratio increases rapidly with the wave-length as this approaches the chief absorption region, and there is a minimum in the curve between 3 μ and 7 μ. A. J. MEE.

Widening of absorption bands with pressure. M. C. TEVES (Z. Physik, 1928, **48**, 244—258).—The effect of mixing an inert foreign gas with a vapour on the absorption spectrum of the latter was investigated. The vapours used were benzene and *o*- and *p*-dichlorobenzene (which all have spectra with series of sharp edges showing fine structure due to rotation) and the foreign gas was nitrogen. For pressures of nitrogen up to 10 atm. the broadening of the rotation lines was in accord with the Lorentz collision damping theory. At higher pressures, however, there was a displacement as well as broadening, an increase of absorption energy, and finally appearance of new edges. A curve is given showing the change in $1/\lambda$ for given pressures, and photographs showing the spectrum of benzene, and that with the addition of nitrogen at pressures from 20 to 100 atm. For a given gas added, there is a proportionality between the displacement of the lines and the molecular concentration. Possible causes of the broadening of the lines are discussed, including the Doppler effect, the effect of molecules of the same kind on one another, collision damping (Lorentz theory), and, in detail, the Stark effect due to molecular fields. There appears to be a strong analogy with the Stark effect for atoms, but the effect is of a much greater order of magnitude. The appearance of new edges is analogous to the appearance of normally forbidden lines in the Stark effect. A direct connexion of the displacement with the polarisation is not found. A. J. MEE.

Measurement of spectral photographs. W. HIRSCHEL (Z. Physik, 1928, **48**, 293—294).—The spectral photograph is measured under the microscope by means of a photographed scale. A. J. MEE.

Problem of the normal hydrogen molecule in the new quantum mechanics. S. C. WANG (Physical Rev., 1928, [ii], 579—586).—Theoretical. The following data are obtained for the configuration corresponding with the normal hydrogen molecule: heat of dissociation 3·76 volts, moment of inertia $4{\cdot}59\times10^{-41}$ g. cm.^{2}, nuclear vibration frequency 4900 cm.$^{-1}$ A. A. ELDRIDGE.

Connexion between positive rays and the abrupt change of potential at the cathode for the thermal emission from an oxide cathode. Method of obtaining the energy of emission. G. SCHMERWITZ (Z. Physik, 1928. **48**. 259—275).—Experimental details are given for the determination of the positive-ray current, the anode current, and the abrupt change of potential at the cathode for a tube with a cathode coated with calcium oxide. The electron stream showed no relationship with the change of potential at the cathode; the positive-ray current showed a linear relationship with it for high values, but at about 2·4 volts there was an abrupt change in the curve. Below this voltage there was practically no positive-ray current. In high vacua the same result was obtained, the value being independent of the temperature, and thus of the number of electrons emitted. It is shown that this critical voltage is the equivalent of the energy of emission of the electrons from the calcium oxide. Similar results were obtained with barium oxide and strontium oxide, and these agree with the values obtained by Spanner. A. J. MEE.

High-frequency glow discharge in hydrogen. E. HIEDEMANN (Ann. Physik, 1928, [iv], **85**, 649—686).—Glow discharges excited by constant waves or modulated constant waves show a much sharper separation of the various phases of a discharge than those excited by means of damped waves (*i.e.*, a spark coil as source). A characteristic of these high-frequency discharges is a splitting of the positive column, with the formation of a dark space, shortly before the disappearance of the column. Another characteristic is that a visible glow can be observed at gas pressures of 0·001 mm. Glass fluorescence, on the other hand, is observable at 55 mm. gas pressure. The discharge in hydrogen has been quantitatively studied. Under certain conditions a stratified discharge is obtained. The potentials between the layers under various conditions show relationships to the ionisation potentials of the hydrogen molecule and atom. W. E. DOWNEY.

Dielectric constants and magnetic susceptibilities in the new quantum mechanics. III. Application to dia- and para-magnetism. J. H. VAN VLECK (Physical Rev., 1928, [ii], **31**, 587—613).—Theoretical. The general mathematical theory is modified. It is admitted that Pauli's formula for diamagnetic susceptibility can be applied to molecules as well as to atoms. The paramagnetism of atoms and molecules is discussed. The experimental susceptibilities of oxygen and chlorine dioxide accord with the assumption that the normal states are respectively ^3S and ^2S terms. Calculation of the paramagnetic susceptibility of nitric oxide gives a value in agreement ($\pm1{\cdot}5\%$) with the experimental value (cf. A., 1927, 609, 812). A. A. ELDRIDGE.

Migration of ions from aqueous solutions into glass. F. QUITTNER (Ann. Physik, 1928, [iv], **85**, 745—769).—The migration of cations from metal salt solutions and of hydrogen ions from acid solutions into four Schott glasses at 52° and $2-6\times10^5$ volts/cm. field strength has been investigated. The percentage of the total current carried by alkali metal ions is characteristic for the various glasses and rises with increasing concentration of the solution used as anode. Silver ions wander the most freely, whilst calcium, barium, zinc, and copper, when at all, wander only feebly. With an acid solution or a barium hydroxide solution as anode, the current for the greater part is due to hydrogen ions. W. E. DOWNEY.

Molecular and atomic volumes. XVII. Volumes and magnetic properties of solid cyanides. W. BILTZ [with W. ESCHWEILER and A. BODENSIEK] (Z. anorg. Chem., 1928, **170**, 161—183; cf. A., 1927, 920).—The volume of the cyanide radical in both simple and complex cyanides has been studied

with the aid of density measurements on the solid cyanides. In the cyanides of the univalent metals, the volume is 20—24, which agrees with the value for the zero volume derived from data for other compounds containing the cyanide radical, and is taken as the normal value; in the cyanides of bivalent metals, with the exception of nickel, the volume is greater. The volume in the double cyanides of potassium decreases with increase in the size of the complex, ultimately falling below the normal figure. Replacement of the metal atom in the complex by a metal of higher at. wt. in the same group of the periodic system causes a rise in the volume of the cyanide group, and also, in general, in the solubility in 87—88% alcohol. Substitution of nickel or zinc for the potassium usually gives rise to a considerable expansion, the formation of these cyanides from the component simple cyanides being in some instances attended by an increase in volume. It appears probable here, however, that polymerisation plays some part. The volume of the cyanide radical in other hydrated complex cyanides, calculated from existing data, is nearly normal. Comparison of the molecular volumes of a few fulminates with those of the corresponding cyanides shows that the volume of the oxygen is here less than the zero volume. In the thiocyanates, on the other hand, the sulphur appears to have undergone little, if any, contraction. Measurements of the magnetic susceptibilities of the complex potassium cyanides show that, in accordance with the views of Welo and others, a complex which contains a metal atom in itself paramagnetic is not paramagnetic if it possesses the inert gas configuration. The behaviour of these cyanides as a whole is in excellent agreement with the rule suggested by Sidgwick, according to which there is a tendency for the formation of those complexes with effective atomic numbers equal to the atomic numbers of the following inert gases. In a few instances, however, ferromagnetic metals in complexes having effective atomic numbers not equal to the atomic numbers of inert gases are found to be diamagnetic. The complex *cyanides*, $ZnNi(CN)_4$ (yellow), $NiAu_2(CN)_4$ (white), and $Ni_2W(CN)_8$ (brown), have been obtained from the corresponding potassium salts by precipitation.

R. CUTHILL.

Theory of the birefringence induced by flow in fluids. C. V. RAMAN and K. S. KRISHNAN (Phil. Mag., 1928, [vii], 5, 769—783).—It is shown, from the results of Stokes, that the tensions and pressures in a fluid in a state of viscous flow are such as to cause the orientation of elongated molecules so that their greatest length lies in the direction of the axis of tension and their shortest length along the axis of pressure. It is then shown that the orienting tendency is opposed by the thermal agitation of the molecules resulting in a state of statistical equilibrium determined from Boltzmann's principle. The optical anisotropy of the molecules combined with the orienting tendency is claimed to give rise to the birefringence of the medium, the magnitude of which is proportional to the product of the viscosity and the velocity gradient. This proportionality constant has been designated the Maxwell constant for the liquid and has been expressed in terms of the optical and geometrical anisotropy of the molecule, the refractive index, density, and mol. wt. of the liquid, and Boltzmann's constant. The theory has been used to explain satisfactorily the general features of the phenomena observed from the published results for 172 liquids and quantitative values of the Maxwell constant have been determined. A. E. MITCHELL.

Thermal variation of magnetic rotatory power when the magnetisation coefficient is positive and independent of temperature. H. OLLIVIER (Compt. rend., 1928, 186, 1001—1003).—Paramagnetic substances may be classified according as they obey Curie's, Weiss', or other similar laws, or have paramagnetism independent of the temperature. Becquerel showed that according to Langevin's theory of the orientation of paramagnetic atoms in a field, paramagnetic rotation of the plane of polarisation occurs, which is proportional to the coefficient of mass magnetisation. Assuming the simple additive law expressing this in terms of Verdet's constant, the variation in magnetic potential, and the observed rotation, it is shown for sodium dichromate—a compound shown by Weiss and Collet (A., 1926, 230, 234) to have a constant paramagnetism—that Verdet's constant (referred to unit mass) is independent of temperature between 7° and 61°. A solution of iodine-free zinc iodide (d^0 2·482) was found preferable to carbon disulphide as a comparison substance. It has a Verdet constant 1·36 times as great at 16°, using yellow or mercury green light. It is transparent up to λ 0·3 μ. J. GRANT.

Production of optical activity by circularly polarised light. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, 132, 313—319).—By the action of circularly polarised light on a film of sensitive silver chloride, there is formed colloidal silver which manifests both circular dichroism and circular double refraction. The curves connecting these magnitudes with the frequency of the light are similar to those obtained for the linear anisotropy of the sensitive chloride (cf. this vol., 583). R. CUTHILL.

Refractivity and dispersivity of normal saturated monobasic acids. H. I. WATERMAN and S. H. BERTRAM (Rec. trav. chim., 1928, 47, 576—577).—The work of Nekrassov (A., 1927, 922) is cited by the authors in support of their contention that oscillations occur in the physical constants of homologous series in the liquid state. They maintain that the refraction of the normal monobasic acids shows alternation in the liquid state.

W. A. RICHARDSON.

Anomalous dispersion of ionised gases. IV. Anomalous dispersion of hydrogen; true intensity ratio of the hydrogen lines H_α and A. CARST and R. LADENBURG (Z. Physik, 1928, 48, 192—204).—Hydrogen in a discharge tube was highly ionised by passing through it a current of 0·2—1 amp./cm.^{2}, and the anomalous dispersion of the hydrogen lines H_α and H_β was photographed and measured. The mean of the measurements gave for the ratio of the number of dispersion electrons corresponding with the two lines the value 4·66. According to the quantum theory dispersion formula, this ratio should be equal to a first approximation to the

"strength," of the corresponding quantum switch. The value of f_a/f_β calculated from quantum mechanics is 5·37. The difference between the experimental value for the ratio and that obtained theoretically is beyond the range of experimental error, and can be explained by the influence of negative dispersion. The probability of this is high because of the strong excitation. When corrected the experimental value of f_a/f_β comes to be less than 5·91, but greater than 4·66, between which values lies that obtained theoretically. A. J. MEE.

Rectilinear diameter of ethylene. E. MATHIAS, C. A. CROMMELIN, and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1054—1056).—The densities of liquid ethylene and its saturated vapour have been determined between −145·07° and 7·98°. The rectilinear diameter y=0·22179—0·00061277t, where t is the temperature on the centigrade scale. The critical temperature deduced from this formula is 9·5° and the critical density is 0·21597. The critical coefficient T_k/p_kv_k=3·524. The deviations of the observed from the calculated values of the rectilinear diameter may exceed 1%. In the neighbourhood of the critical point the curve of diameters is slightly concave, and at lower temperatures convex to the temperature axis. M. S. BURR.

Apparent large diameters of molecules for deactivation by collision. B. LEWIS (Science, 1927, **66**, 331—332).—Tolman, Yost, and Dickinson's calculation for nitrogen pentoxide (A., 1927, 604) is erroneous. Whilst collisions between inactive molecules are not considered to occur any more frequently than is usual in the kinetic theory, collisions between active and inactive molecules which cause a transfer of energy and may result in deactivation occur 50 to 66 times as often as required by the kinetic theory; hence the apparent abnormality in diameter for deactivation by collision can be accounted for by increased numbers of collisions. A. A. ELDRIDGE.

Ionised hydrogen molecule. A. H. WILSON (Proc. Roy. Soc., 1928, **A, 118**, 635—647).—Mathematical. The ionised hydrogen molecule is represented by a system which is a particular case of the three-body problem. Applying Schrodinger's method to the system, a wave equation is obtained which is separable in elliptic co-ordinates, and the resulting differential equations can be solved exactly. The relations between the differential equations defining the system are discussed and values obtained for the energies of the various states. The unexpected result appears that no solution is in general possible; solutions will occur only for certain distances apart of the nuclei. It seems probable that these states are illusory, and that there are no positive distances of the nuclei which give states. L. L. BIRCUMSHAW.

Simple method of determining the orientation and structure of crystals with X-rays. W. E. DAWSON (Phil. Mag., 1928, [vii], **5**, 756—767).—An X-ray goniometer has been devised the operation of which depends on the observation of Weissenberg (Z. Physik, 1924, **23**, 229) that if the rotation of a crystal be accompanied by a proportional movement of the recording film the angle traversed by the crystal between successive reflexions may be obtained and thus sufficient data are provided, from one photograph, for the absolute determination of the normal to each set of atomic reflecting planes, and hence also the orientation and space-lattice of the crystal. The method has been employed for the examination of aluminium crystals prepared by the method of Carpenter (B., 1926, 792). The results are in fair agreement with those of Yoshida and Tanaka (A., 1927, 95) for similar crystals except that they tend to show that in such crystals the orientation is at random about the direction of stretching.
A. E. MITCHELL.

Phosphorescence of calcium tungstate induced by X-rays. F. E. SWINDELLS (J. Opt. Soc. Amer., 1928, **16**, 165—173).—The rate of decay of a very phosphorescent sample of calcium tungstate, determined photographically, was found to fit the Becquerel equation, $I^{-x}=a+bt$, from 30 sec. to 5 min. after exposure to X-rays. The phosphorescence of this sample could be detected after 50 hrs. under conditions when the phosphorescence of normal calcium tungstate disappeared in 1 min. The intensity of the phosphorescence was found to be closely proportional to the product of the intensity of the X-rays and the time of exposure up to a limiting value, beyond which there was a negligible increase.
C. J. SMITHELLS.

X-Ray examination of manganese arsenide, iron telluride, nickel stannide, and platinum stannide. I. OFTEDAL (Z. physikal. Chem., 1928, **132**, 208—216).—The values in Å. of a and c, respectively, for the hexagonal elementary cells of the above compounds are: manganese arsenide, 3·716±0·003, 5·704±0·006; platinum stannide, 4·103±0·003, 5·428±0·005; iron telluride, 3·800±0·003, 5·651±0·005; nickel stannide, 4·081±0·002, 5·174±0·003. From the intensity data, the first two definitely appear to have the nickel arsenide structure, and this is probably so with the other two as well.
R. CUTHILL.

Reflexion of X-rays by plane surfaces. H. E. STAUSS (Physical Rev., 1928, [ii], **31**, 491—496).—Measurements of the reflexion of molybdenum $K\alpha_1$ radiation by plane surfaces of glass and quartz, and by sputtered films of nickel, platinum, and silver suggest that the densities of sputtered films of nickel and platinum are less than those of the massive metals, and that that of nickel is smaller the thinner is the film. The surface density of quartz appears to be less than the average density.
A. A. ELDRIDGE.

X-Ray investigation of the structure of some naphthalene derivatives. J. M. ROBERTSON (Proc. Roy. Soc., 1928, A, **118**, 709—727).—The crystal structures of 1 : 2 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene and of 1 : 2 : 3 : 4 : 5 : 8-hexachloro-1 : 2 : 3 : 4-tetrahydronaphthalene examined by the rotating crystal method are found to be closely similar. The former has a 7·9, b 10·3, c 14·2 Å., β 112° 40′, d 1·67; the latter a 7·8, b 12·3, c 13·9 Å., β 116° 14′, d 1·87. The lattices are monoclinic body-centred with four asymmetric molecules in the unit cell, and the most probable space-group is C_s^4. This involves a polar molecule. By means of Bernal's

method of interpretation, indices are assigned to all the reflexions. Information is also obtained as to the approximate location of the halogen atoms, which virtually lie on a different type of lattice. A qualitative examination and comparison of the intensities of the most important reflexions indicate that the two additional substituted chlorine atoms in the hexachlorotetrahydronaphthalene must lie somewhere beneath the other halogens when the structure is viewed along the c axis. The facts are accounted for if it is assumed that the long axis of the molecule coincides with the c axis of the crystal. The intensity distribution in the higher orders of certain planes requires an almost flat carbon ring, as in the graphite structure. L. L. BIRCUMSHAW.

X-Ray study of some simple ethane derivatives. I. and II. (MISS) K. YARDLEY (Proc. Roy. Soc. 1928, **A**, **118**, 449—484, 485—497).—I. A detailed investigation has been made of crystals of hexachloroethane, hexabromoethane, tetrachlorodibromoethane (two forms), pentabromofluoroethane, trichlorotribromoethane, and *s*-βγ-tetrabromo-*n*-butane (two unstable orthorhombic forms, one obtained below 0°). These substances form an isomorphous series, crystallising in the space-group Q_h^{16}. Hexachloroethane has $a:b:c=1{\cdot}1350:1:0{\cdot}6302$; hexabromoethane $a:b:c=1{\cdot}1278:1:0{\cdot}6270$; tetrachlorodibromoethane (symmetrical form), $a:b:c=1{\cdot}1308:1:0{\cdot}6270$; (asymmetrical form), $a:b:c=1{\cdot}1220:1:0{\cdot}6288$; pentabromofluoroethane, $a:b:c=1{\cdot}1012:1:0{\cdot}6098$; trichlorotribromoethane, $a:b:c=1{\cdot}1270:1:0{\cdot}6262$; tetrabromobutane (low-temperature form), $a:b:c=1{\cdot}073:1:0{\cdot}601$; (ordinary temperature form), $a:b:c-1{\cdot}1206:1:0{\cdot}6296$. There are four molecules in the unit cell, each possessing a plane of symmetry parallel to (010). This plane passes through the two carbon atoms and two of the halogen atoms (or the two methyl groups in the case of tetrabromobutane), with the other four halogen atoms arranged in pairs on either side. In the case of hexachloro- and hexabromo-ethane, and probably the tetrabromobutane, the molecules also possess a pseudo-centre which produces additional halvings not expected from space-group considerations. The symmetry of the carbon valencies is deduced from the molecular symmetry and it is shown that the carbon atom possesses two A and two B valencies, possibly identical with the two (2, 1) and two (2, 2) electrons in the outer group of neutral carbon. Composite F curves obtained for hexachloro- and hexabromo-ethane are compared with Hartree's curves for Cl^- and C^{++++} (cf. A., 1925, ii, 735). The formula of both forms of tetrachlorodibromoethane appears to be $CCl_3{\cdot}CClBr_2$.

II. Tetrabromobutane possesses a stable tetragonal form which bears no apparent resemblance to the two forms described above, and has a $8{\cdot}80_6$, c 11·27 Å., d ~·818. The unit cell probably contains four molecules in face-centred positions. Dibromotetramethylethane (βγ-dibromodi*iso*propyl) forms needle-like tetragonal crystals having $a:c=1:0{\cdot}7798$ and d 1·811. There are four molecules in the unit cell occupying approximately face-centred positions, and possessing either a plane or dyad axis of symmetry or both. The molecules themselves simulate tetragonal symmetry. There are two possible types of structure, which are illustrated. Pentamethylbromoethane forms needle-like crystals very similar to those of the tetramethyl compound. The orthorhombic cell has a 21·35, b 10·77, c 7·84 Å., d 0·85; it may be divided into two pseudo-tetragonal parts, the arrangement of molecules in each resembling that in the unit cell of dibromotetramethylethane. The space-group is C_{2v}^{21}. L. L. BIRCUMSHAW.

Theory of absorption and dispersion in X-ray spectra. R. DE L. KRONIG and H. A. KRAMERS (Z. Physik, 1928, **48**, 174—179).—An explanation is put forward for the fact that the effective number of oscillators that must be associated with continuous absorption bands in the case of X-rays in order to give the observed dispersion and absorption, is different from the number of electrons in the shell associated with the particular absorption band concerned. In particular, the case of the K-band is considered, and it is shown why the effective number of oscillators is less than 2. A. J. MEE.

[Crystal structures of] diselenides of iron, cobalt, and nickel. W. F. DE JONG and H. W. V. WILLEMS (Z. anorg. Chem., 1928, **170**, 241—245).—The compounds $NiSe_2$ and $CoSe_2$ have been prepared by heating the monoselenides in a vacuum with selenium; it has not been possible to obtain the corresponding iron salt. In each case the structure is shown by the X-ray diagram to be of the iron pyrites type (A., 1927, 502), the length of the basal edge, the calculated density, and the distance apart of the atomic centres being $5{\cdot}854\pm0{\cdot}003$ Å., 7·18, and 2·41 Å., respectively, for the cobalt compound, and $6{\cdot}022\pm0{\cdot}003$ Å., 6·69, and 2·47 Å. for the nickel compound. R. CUTHILL.

Hexahydrated double sulphates containing thallium. A. E. H. TUTTON (Proc. Roy. Soc., 1928, **A**, **118**, 367—392; cf. A., 1925, ii, 749).—A complete goniometrical measurement and a full optical and volume investigation have been made of perfect crystals of thallium magnesium, thallium ferrous, thallium manganese, and thallium copper sulphates. All these crystallise in the holohedral class of the monoclinic system. For thallium magnesium sulphate, $a:b:c=0{\cdot}7442:1:0{\cdot}5000$, β=106° 30′; for thallium ferrous sulphate, $a:b:c=0{\cdot}7427:1:0{\cdot}4999$, β=106° 16′; for thallium manganese sulphate, $a:b:c=0{\cdot}7454:1:0{\cdot}4964$, β=106° 22′; for thallium copper sulphate, $a:b:c=0{\cdot}7499:1:0{\cdot}5033$, β=105° 33′. The results are in line with those previously obtained for the corresponding zinc, nickel, and cobalt thallium sulphates. Thallium does not entropically replace the alkali metals potassium, rubidium, cæsium, or the ammonium group, but the thallium salts are very nearly isostructural with the analogous ammonium and rubidium salts. One outstanding difference is shown, *i.e.*, a very much higher optical refraction and spectral dispersion. Attention is directed to the remarkably small effect on the crystal form and properties of interchanging the M-metals, in comparison with the marked determinative effect exerted by interchange of the five R-bases.

L. L. BIRCUMSHAW.

Hexahydrated double selenates containing thallium. Completion of the thallium salts and of the whole monoclinic series. A. E. H. TUTTON (Proc. Roy. Soc., 1928, **A**, **118**, 393—426; cf. preceding abstract).—A full crystallographic investigation has been made of a series of double selenates, $R_2M(SeO_4)_2,6H_2O$, containing thallium as the R-metal, and magnesium, ferrous iron, nickel, cobalt, manganese, copper, or zinc as the M-metal. The iron salt has not previously been described, probably owing to the fact that iron reduces selenic acid directly to selenium. Pure *ferrous selenate* may be prepared by the action of dilute selenic acid on ferrous sulphide, and very pale green crystals of *thallium ferrous selenate* are obtained on evaporating excess of ferrous selenate solution with thallium selenate solution under reduced pressure. For thallium magnesium selenate, $a:b:c=0{\cdot}7485:1:0{\cdot}4993$, $\beta=105°\ 36'$; for thallium nickel selenate, $a:b:c=0{\cdot}7456:1:0{\cdot}5019$, $\beta=105°\ 36'$; for thallium cobalt selenate, $a:b:c=0{\cdot}7463:1:0{\cdot}5021$, $\beta=105°\ 40'$; for thallium ferrous selenate, $a:b:c=0{\cdot}7445:1:0{\cdot}5011$, $\beta=105°\ 27'$; for thallium manganese selenate, $a:b:c=0{\cdot}7463:1:0{\cdot}4993$, $\beta=105°\ 29'$; for thallium copper selenate, $a:b:c=0{\cdot}7531:1:0{\cdot}5048$, $\beta=104°\ 59'$.

The results obtained are in every respect analogous to those for the double sulphates containing thallium. The replacement of sulphur by selenium causes all the constants to be slightly shifted, and the relations of the thallium double selenates to the double selenates containing potassium, rubidium, cæsium, and ammonium are almost exactly the same as in the case of the double sulphates. The thallium double selenates are distinguished by exceptionally high refractive indices and molecular refractions, the maximum index of refraction in some cases exceeding that of the very highly refractive monobromonaphthalene. L. L. BIRCUMSHAW.

Longitudinal thermomagnetic potential difference in a bismuth crystal. C. W. HEAPS (Physical Rev., 1928, [ii], **31**, 648—652).—The results suggest that a magnetic field produces a structural change in the atomic system of bismuth, the change in the direction normal to the field differing from that parallel to it. A. A. ELDRIDGE.

Interpretation of the paramagnetism of the iron group. O. LAPORTE (Z. Physik, 1928, **47**, 761—769).—The magneton numbers of the iron group, calculated from purely spectrographic data by means of the relative doublet formula in the manner described by Laporte and Sommerfeld (A., 1927, 86), do not agree with the observed values. The same effect is also shown by the rare earths. Possible explanations of these discrepancies are discussed. J. W. SMITH.

Theory of Heusler's alloy. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1928, **47**, 770—785).—It is shown on metallographic grounds that Richarz' theory of the Heusler alloy anomalies is untenable. The author describes experiments which indicate that the anomalies can be traced to a phase change occurring in the neighbourhood of 130°. J. W. SMITH.

Calculation of the rotatory power of quartz. R. DE MALLEMANN (Compt. rend., 1928, **186**, 1046—1048).—The experimental results of Ze (this vol., 352) are used to deduce the value of the molecular anisotropy which figures in the author's expression for the rotatory power (A., 1927, 610). A value of 30°/mm. was obtained for quartz at λ 0·546 μ (observed value 25·5°/mm.). The agreement is considered satisfactory in view of the indirect method employed and the low experimental accuracy. It is improved if allowance is made for the slight inclination of the plane of principal molecular axes with respect to the ternary crystal axis, the existence of which is indicated by the work of Ze and of Bragg. J. GRANT.

Transmission and reflexion of gold and silver films. W. V. HOUSTON and G. MOORE (J. Opt. Soc. Amer., 1928, **16**, 174—176).—Measurements of the reflecting power and transmission of sputtered films of gold and silver as a function of the wave-length and thickness were made to determine the most suitable coating for the mirrors of interferometers. Between 5000 and 6000 Å. gold and silver are equally good. Above 6000 Å. gold is superior, since for the same reflecting power the transmission is higher. Below 5000 Å. silver is much superior to gold. C. J. SMITHELLS.

Quick and slow decay of luminescence of phosphors of various types of atoms. H. MOSER (Ann. Physik, 1928, [iv], **85**, 687—710).—With oxide phosphors the quick decay outweighs the slow decay, but with selenide phosphors the reverse is the case. Sulphide phosphors, in general, show both processes equally strongly. The total emission shows a strong increase from oxygen, sulphur, to selenium as generic atoms and calcium, strontium, to barium as alkaline-earth atoms. W. E. DOWNEY.

Deformation, rupture, and hardening of crystals. M. PÓLANYI (Naturwiss., 1928, **17**, 285—294).—See this vol., 9.

Magnetic susceptibility of aluminium. C. CHÉVENEAU (Compt. rend., 1928, **186**, 1102—1104).—Very small amounts of iron alloyed with aluminium have very little effect on its magnetic properties, and these effects follow no simple rule, as the iron behaves differently according as it is present in the metallic or ionic state. Iron-free aluminium should be paramagnetic and should have a susceptibility near that obtained for Hoope's "extra-pure" aluminium (Al 99·87%, Fe 0·06%), viz., +0·58. J. GRANT.

Electrical resistance of titanium and zirconium at low temperatures. P. CLAUSING and G. MOUBIS (Physica, 1927, **7**, 245—250; Chem. Zentr., 1927, ii, 2649).—With titanium and zirconium at 70—273° Abs., the dependence of electrical resistance on temperature is normal (cf. Koenigsberger and Schilling, A., 1910, ii, 481). The specific resistance at 273° is $0{\cdot}80\times10^{-4}$ and $0{\cdot}41\times10^{-4}$, respectively, and the temperature coefficient 0·00469 and 0·00438. A. A. ELDRIDGE.

Dielectric constants of dilute solutions of polar liquids in non-polar solvents. J. D. STRANATHAN (Physical Rev., 1928, [ii], **31**, 653—671).—Dielectric constants and densities have been determined at 10°

intervals between f. p. and b. p. for dilute solutions of methyl, ethyl, propyl, and amyl alcohols in benzene, and methyl alcohol in carbon tetrachloride. The electric moments are independent of temperature, being respectively 1·64, 1·74, 1·75, and 1·62 × 10^{-18} for benzene solutions, in agreement with Debye's theory, and in contrast with results for the pure liquid alcohols. A. A. ELDRIDGE.

Magnetic susceptibility of solutions. J. J. WEIGLE (Physical Rev., 1928, [ii], **31**, 676—679).—When a solution of ions of different magnetic susceptibilities is placed in a magnetic field, an almost imperceptible difference exists between the concentrations of the solute in and outside of the field. A. A. ELDRIDGE.

Wave mechanical theory of metallic conduction. J. FRENKEL (Z. Physik, 1928, **47**, 819—834).—Mathematical. J. W. SMITH.

Dispersion by hydrogen-like atoms in undulatory mechanics. B. PODOLSKY (Proc. Nat. Acad. Sci., 1928, **14**, 253—257).—Schrödinger's theory of dispersion is applied to the case of atomic hydrogen, terms of the order of relativistic correction being omitted. The wave-equation is obtained by the operational method of Schrödinger and Eckart, as extended by Epstein. Formulæ are developed giving a result for the dielectric constant in exact agreement with that obtained by Van Vleck, Epstein, and Pauling. Values for the refractive index obtained, however, do not agree very well with the experimental value of Langer, but this may be due to experimental difficulties. A. J. MEE.

Anomalous dispersion of gases in the excited state. I. Dispersion formula of the quantum theory. R. LADENBURG. **II. Anomalous dispersion in excited neon. III. Transition probability and density of excited atoms in neon; statistical equilibrium in the positive column.** H. KOPFERMANN and R. LADENBURG (Z. Physik, 1928, **48**, 15—25, 25—50, 51—61).—I. Theoretical. The connexion between the dispersion formula of the classical theory and that of the quantum theory is discussed with a view experimentally to prove the latter.

II. Anomalous dispersion of light passed through the positive column of a neon discharge tube has been detected in the region of 19 lines in the orange. The dispersion increases with increase of current strength up to 50 mm. The effect of pressure, above 1·3 mm. of mercury, is to cause the anomalous dispersion to decrease.

III. A theoretical discussion of the results obtained in the experiments described in the previous paper. W. E. DOWNEY.

Latent heat of vaporisation as a function of temperature. R. M. WINTER (J. Physical Chem., 1928, **32**, 576—582).—The variation with temperature of the total latent heat of vaporisation is expressed by the relation $\lambda = \lambda_0 (1 - T/T_c)^{0.4}$ for the 22 liquids examined. The values of λ_0, a constant for each liquid, were found graphically from the data of Mills (A., 1909, ii, 861), as well as those of T_c which are in good agreement with observed values. Elimination of the term $1 - T/T_c$ from the above relation and from the relationships found by Sugden for temperature, density, and surface tension (A., 1927, 920) gives $\gamma = \text{constant} \times \lambda^3$, and $\lambda = \text{constant} \times (D - d)^{4/3}$, where D and d are the densities of liquid and vapour, respectively. L. S. THEOBALD.

F. p. and density of pure hydrogen peroxide. A. C. CUTHBERTSON, G. L. MATHESON, and O. MAAS (J. Amer. Chem. Soc., 1928, **50**, 1120—1121).—The m. p. is −0·89°; the liquid has a great tendency to supercool and must be kept within 0·1° below the m. p. and continuously stirred. For the pure peroxide, d^0 is 1·4649; for solutions containing A% by weight of peroxide $d = 0.9486 + 0.005163A$, provided A is 95 or more. S. K. TWEEDY.

Measurement of the true specific heats of nickel by a direct electrical method. (MME.) C. LAPP (Compt. rend., 1928, **186**, 1104—1106).—The specific heats of pure Mond nickel wire have been measured between −175° and 460° by determinations of its variations in temperature when placed in a medium at the required temperature, and heated for a known period by a measured amount of electrical energy. The specific heat increases with temperature up to the Curie point (357·6°), falls between 353·5° and 360·2°, and then increases slowly in the paramagnetic region. J. GRANT.

Anomalous dispersion in thallium vapour. V. K. PROKOVJEV and V. N. SOLOVIEV (Z. Physik, 1928, **48**, 276—285).—The anomalous dispersion of thallium vapour was investigated in the neighbourhood of the lines 3776 and 5353, at different temperatures, from 892° to 1107°. It is found that the ratio of the number of dispersion centres for these lines varies with the temperature according to the Boltzmann law. From this it is shown that the probabilities of the spontaneous transitions $2s \rightarrow 2p_1$ and $2s \rightarrow 2p_2$ (Paschen–Gotze notation) are equal. A. J. MEE.

Thermal conductivities of oxygen and nitrogen. H. GREGORY and S. MARSHALL (Proc. Roy. Soc., 1928, **A**, **118**, 594—607).—The thermal conductivities of oxygen and nitrogen at 0° have been measured, with the object of confirming the result obtained by Gregory and Archer for air (A., 1926, 231), a wide discrepancy existing among the values obtained for this gas by various observers. The apparatus used was the vertical compensated hot-wire type previously employed for determining the thermal conductivity of carbon dioxide (A., 1927, 403). From the curves obtained by plotting absolute thermal conductivities against corresponding mean gas temperatures, it is found that $K_0 = 5.89 \times 10^{-5}$ and 5.80×10^{-5} g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ for oxygen and nitrogen respectively. The temperature coefficients of thermal conductivity, deduced from the slopes of the curves, are 0·00289 and 0·00293 for oxygen and nitrogen, respectively. The results are consistent with those of Gregory and Archer for air at 0°. L. L. BIRCUMSHAW.

Parachor and chemical constitution. IX. Boron compounds. J. J. ETRIDGE and S. SUGDEN (J.C.S., 1928, 989—992; cf. this vol., 416).—Determinations of the density and surface tension of methyl and ethyl borates between 15° and 60 , taken with

Mills and Robinson's data for boron trichloride (A., 1927, 927), give a value of 16·4 for the parachor of boron. Methyl alcohol and methyl borate form a mixture of maximum vapour pressure, with b. p. 55°, and containing 30% of the ester. R. CUTHILL.

Coefficient of expansion of bromoform. A. SHERMAN and J. SHERMAN (J. Amer. Chem. Soc., 1928, **50**, 1119—1120).—The specific volume of bromoform, m. p. 7·7°, between 9° and 50° is given by $0{\cdot}24204\,[1+0{\cdot}00090411(t-7{\cdot}7)+0{\cdot}0_{6}6766(t-7{\cdot}7^{2})]$. S. K. TWEEDY.

Physical constants of bromoform. H. BUHMANN (Arch. Pharm., 1928, **266**, 123—125).—Pure bromoform has d_4^{15} 2·9000, b. p. 146·3°/760 mm., setting-point, +7·4°; another sample had b. p. 147·2°/760 mm. When the latter was mixed with 1% of alcohol 0·7942) the mixture had setting-point +5·4°, b. p. 146·6°. This sample fulfils the requirements of the German pharmacopœia, but the method given there for testing bromoform is unsatisfactory. In determining the proportions volatile between the prescribed limits a Schantz apparatus should be used. W. A. SILVESTER.

Connexion between the coefficient of expansion and the coefficient of compressibility of liquids. V. S. VRKLJAN (Z. Physik, 1928, **48**, 111—117; see also A., 1926, 786; 1927, 103).—Theoretical. W. E. DOWNEY.

Viscosity of mercury. S. ERK (Z. Physik, 1928, **47**, 886—894).—From a critical survey of the existing data on the viscosity of mercury, the most probable values over the temperature range −20° to 340° are deduced and are found to be in agreement with an empirical formula $\log \eta=-2{\cdot}21336(t+184{\cdot}54)/(t+230{\cdot}32)$. The possibility of the mercury slipping over an unwetted surface in some series of experiments is also discussed. J. W. SMITH.

Physical properties of gas-freed sulphur. C. C. FARR and D. B. MACLEOD (Proc. Roy. Soc., 1928, **A, 118**, 534—541).—It is extremely difficult to prepare a sample of sulphur the viscosity of which is independent of previous thermal treatment (cf. A., 1920, ii, 343). This may be due to traces of sulphuric acid, hydrogen sulphide, or sulphur dioxide, which retard the attainment of inner equilibrium between the two varieties and S_λ. Methods are given for the preparation of pure gas-free sulphur by distillation in a stream of carbon dioxide, followed by distillation in a high vacuum, and the relative viscosity of the sulphur so prepared has been measured over the temperature range 163—169°, which is the interval over which sulphur shows high viscosity variations. The viscosity was measured under several conditions of thermal treatment. The results showed that the viscosities between 163° and 169° lie on the same curve whatever the previous heat treatment, and it is considered established that sulphur prepared with care and protected from exposure to air gives reproducible values of the viscosity. From sulphur purified in this way, crystals of S_{III} (mother of pearl sulphur) separate readily. The natural f. p. was found to be 103·8—103·9° (cf. Smith and Carson, A., 1911, ii, 977), the ideal m. p. about 107°. Efforts to obtain rhombic sulphur from sulphur similarly prepared were unsuccessful. It was found possible to supercool liquid sulphur down to 80°, and measurements of the relative viscosity were obtained down to this temperature. The minimum value was at about 155°. L. L. BIRCUMSHAW.

Application of Debye's dipole theory to binary liquid mixtures. J. W. WILLIAMS (Physikal. Z., 1928, **29**, 174—181).—Debye's extension of the Clausius–Mosotti relation has been applied to the calculation of electric moments from the dielectric constants and densities of suitably chosen binary liquid mixtures. Earlier data (A., 1926, 1000; 1927, 819, 1132) are tabulated and the substances investigated divided into three classes: (*a*) molecules exhibiting no electric moment, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, hexane, tin tetraiodide, *p*-xylene, *p*-dinitrobenzene; (*b*) less symmetrical molecules showing a definite dipolar moment, *e.g.*, ethyl ether, *o*- and *m*-dinitrobenzene, etc.; (*c*) molecules for which the existence of a dipolar moment appears doubtful, *e.g.*, *s*-trinitrobenzene, naphthalene, iodine. Within the limits of experimental error, the molecular polarisation and therefore the electric moment of a solute molecule is independent of the nature of a dipole-free solvent. The dipolar moment, as measured in this work, is a quantitative criterion of the polarity of a molecule. R. A. MORTON.

Viscosity of supersaturated solutions. I. I. K. TAIMNI (J. Physical Chem., 1928, **32**, 604—615).—The viscosities of supersaturated solutions of sodium nitrate, sodium chlorate, copper sulphate, sodium thiosulphate, tartaric acid, and sucrose have been determined by means of a modified form of the apparatus devised by Scarpa (Gazzetta, 1920, **40**, 271). The viscosity–temperature curves for the first two substances remain regular, in passing not only through the temperature of saturation, but also through that of spontaneous crystallisation as determined by Miers (J.C.S., 1906, **89**, 413). The curves for the remaining substances were also regular as far as they could be traced (30—45° below saturation temperature), and only one of these substances, copper sulphate, showed any signs of spontaneous crystallisation. The curves for two different concentrations of sodium thiosulphate, tartaric acid, and sucrose show an increasing divergence with a fall in temperature, this being especially noticeable in the case of the last two substances mentioned. L. S. THEOBALD.

Electrical conductivity of silver alloys. M. HANSEN and J. SACHS (Z. Metallk., 1928, **20**, 151—152).—The curves showing the variation of the electrical conductivity with the composition of binary alloys of silver containing cadmium, zinc, magnesium, manganese, tin, antimony, or aluminium within the solid solution range are almost perfect hyperbolas which approach more closely to the axes in the order given. The electrical resistance of these alloys increases almost linearly with increase in the atomic percentage of added element, the steepness of the curves decreasing in the order: antimony, tin, aluminium, manganese, zinc, magnesium, cadmium. As is the case with solid solution alloys of copper (Norbury, B., 1925, 245), the change of resistance produced by

the presence of one atom per cent. of an element in solid solution increases with the distance from the silver group of that group in the periodic system to which the element in question belongs. For elements in the same group, the effect on the resistance is more marked the greater the difference in the atomic numbers of the solute and solvent elements. In general, the hardness–composition curves correspond roughly with the resistance–composition curves, but magnesium has an exceptionally large hardening effect on silver. A. R. POWELL.

Solubility relations of isomeric organic compounds. VII. Mutual solubility of the dinitrobenzenes with the nitroanilines, and of the three chlorobenzoic acids. J. JOHNSTON and E. P. JONES (J. Physical Chem., 1928, **32**, 593—603; cf. Collett and Johnston, A., 1926, 237).—The solubility curves of the nine binary systems formed between the nitroanilines and dinitrobenzenes lie close to the ideal. The small divergences observed bear no apparent relationship to other properties of the systems. Mixed crystals are not formed. The three binary systems of the chlorobenzoic acids are also practically ideal. The three like pairs of the chloro- and bromo-nitrobenzenes form a complete series of solid solutions, but *p*-toluic acid and *p*-chlorobenzoic acid show only partial crystal miscibility. Solubility data are given. L. S. THEOBALD.

Critical solution temperatures and their applications. A. BOUTARIC and G. CORBET (Chaleur et Ind., 1927, 8, 565—568; Chem. Zentr., 1927, ii, 2651).—A discussion, with special reference to the addition of a third component to binary liquid mixtures, particularly hydrocarbons and alcohol, and to the attempted differentiation of fats and oils.
A. A. ELDRIDGE.

Effect of a third substance on the miscibility of binary liquid systems. C. WAGNER (Z. physikal. Chem., 1928, **132**, 273—294).—Theoretical. It is shown thermodynamically that if to a binary liquid mixture there is added a third substance such that for any given ratio of the two components its partial pressure at the small concentrations considered is proportional to its concentration, the temperature range of complete miscibility will be extended or restricted according as the solubility of the third substance in the region of the critical composition is greater or less, respectively, than corresponds with additivity in respect of its solubilities in the two liquids. Equations are derived (*a*) for the composition of the critical phase at any given temperature, (*b*) for the effect of the added substance on the miscibility at constant temperature, and (*c*) for the change in critical solution temperature. From molecular considerations, it appears that an important cause of the solubility of a substance in a binary solvent mixture being less than the value calculated additively from the solubilities in the pure solvents is that the field of force in the vicinity of a solute molecule is generally due to more than one solvent molecule. R. CUTHILL.

Influence of salts on the solubility of water in phenol. R. CERNATESCU (Z. physikal. Chem., 1928, **133**, 31—38).—A continuation of previous work (cf. A., 1927, 416). The effect of the addition of a number of alkali halides and thiocyanates on the solubility of water in phenol has been studied, the temperature at which a mixture of known weights of the 18% phenol layer and the salt becomes homogeneous being measured. The lowering of solubility of water in phenol was obtained from the Rothmund solubility curve. The formula $t=ac^b$, given by Carrington, Hickson, and Paterson for the influence of salts on the critical solution temperature of the system phenol–water (A., 1926, 18), has been applied to the experimental results, and it is found that the cations and anions of the salts investigated, in order of decreasing effect on the solubility of water in phenol, may be arranged as follows: $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, $Rb^{\cdot}$, $Cs^{\cdot}$, and Cl', Br', I', F', SCN'. Unusual results are found with potassium fluoride and with ammonium thiocyanate, which, in the case of the latter salt, may be explained by its greater solubility in the phenol layer compared with the other salts investigated. L. L. BIRCUMSHAW.

Solubility in mixtures of solvents. I. Solubility of picric acid. E. ANGELESCU and D. DUMITRESCU (Z. physikal. Chem., 1928, **132**, 217—234).—The solubility at 12° of picric acid in binary mixtures of solvents has been determined. Taking the solubilities in g./100 g. of solvent as ordinates and the percentage compositions of the solvents as abscissæ, the curves obtained closely resemble those characteristic of the vapour pressures of binary mixtures of liquids. Mixtures of benzene with ethyl ether or ethyl alcohol and of ether with alcohol show throughout positive deviations from the mixture rule, the curve of each system possessing a maximum. This type of curve probably results from combination between the solute and one of the solvents. Mixtures of water with acetone or ethyl alcohol and of acetone with chloroform or carbon tetrachloride exhibit negative deviations throughout, minima being present in the first two systems. The curves for mixtures of alcohol with carbon tetrachloride or chloroform and of benzene with acetone or carbon tetrachloride are intermediate in character between the foregoing two types, each lying partly above the straight line and partly beneath it. For many of the systems examined the results may be expressed over considerable ranges of composition of the solvents by the formula $S_c-S_o-KC^p$, where S_o is the solubility in 100 g. of a pure solvent, S_c is the solubility in 100 g. of this solvent when mixed with C g. of a second solvent, and K and p are constants. This expression will represent every type of solubility curve except that with negative deviations accompanied by a minimum.
R. CUTHILL.

Adsorption of vapours on carbon, and the thermal dilation of the interface. F. GOLDMANN and M. PÓLANYI (Z. physikal. Chem., 1928, **132**, 321—370).—A method is described whereby adsorption isotherms of vapours may be determined by allowing the saturated vapour to remain in contact with the adsorbent at a known temperature until equilibrium is attained, and then removing successive quantities of the vapour by condensation into a tube immersed in liquid air; by sealing off this tube the mass of

vapour removed may be determined. The equilibria are completely reproducible after many months. The adsorption of ethyl chloride, ethyl ether, and carbon disulphide by carbon at $-15\cdot3°$, 0°, and 20°, and of *n*-pentane by carbon at temperatures from $-63\cdot7°$ to 20° was examined; in each case the pressure varied from about 90% of the saturated vapour pressure to 10^{-2} mm. No evidence could be obtained that the adsorption of vapours is caused by capillary condensation. If the vapour above the adsorbent is saturated, the adsorbed layer becomes identical with the film of liquid formed when the adsorbent is immersed in the liquid. The weights of the liquid films of different substances on the same adsorbent are in the same ratio as the densities of the liquids, whilst the volumes of the liquid films are independent of temperature. The thermal expansion of the liquid in films of ethyl chloride, ethyl ether, and *n*-pentane is about 20% less than when the substances are in the ordinary liquid phase. A film of water has a positive expansion coefficient from 0° to 5°. The heat of wetting is greater than the affinity of wetting, and in general decreases as the thickness of the film increases; as saturation is approached there is, however, a sharp increase. The results of the measurements are in good agreement with the potential theory of adsorption. When the quantity of adsorbed vapour ranges from 5 to 80% of the quantity required for wetting the adsorbent, it forms a unimolecular but discontinuous film, which tends to run together as the quantity adsorbed increases; the points on the adsorbent having the greatest potential are the first to be occupied by the vapour. H. F. Gillbe.

Active charcoal. Amorphous state, temperature stability, and relation of adsorptive power to the physical and chemical properties of the charcoal and the adsorbed molecules. O. Ruff and P. Mautner (Z. physikal. Chem., 1928, **26**, 312—356; cf. A., 1925, ii, 1125; 1926, 346; 1927, 305, 1138).—The relation between the adsorptive power of graphite and the nature and state of division of the dissolved substance is discussed. Although the adsorptive activity increases with increase of surface area, there appears to be no simple relation between the state of division and activity. Substances in colloidal solution are more easily adsorbed than those in true solution. Results are given of experiments with four different charcoals to show that the adsorptive power decreases with rise of temperature and with increased duration of heating. From a rontgenographic investigation of supernorit at different temperatures, conclusions are reached as to the influence of temperature and length of heating on the orientation of the carbon atoms to a graphite lattice. The progressive graphitisation of the carbon caused by heating beyond 1000° results in a marked decrease of activity. The adsorption of gases and substances in solution (phenol, methylene-blue, Congo-red, molasses) by a number of commercial active charcoals has been studied, and the influence of impurities and of the porosity of the material and its form is considered. On the basis of the results, a comparison is made of a number of active charcoals for technical purposes. The non-specific and the specific natures of the adsorption are discussed. The specific adsorption represents the sum of two specific effects, one due to the adsorbent and the other to the adsorbed material. The specific effect of the charcoal is the chief factor in molecular adsorption and in the preferential polar adsorption of acids. The polar effect is influenced by the constitutive properties of the adsorbed substance, and a summary is given of data showing the effect of the size of the molecule, ring or chain formation, the presence of double linkings, and of various types of isomerism. L. L. Bircumshaw.

Adsorption and heat of adsorption of sulphur dioxide on carbon. M. Polanyi and K. Welke (Z. physikal. Chem., 1928, **132**, 371—383).—The equilibria and heat changes associated with the adsorption of sulphur dioxide by carbon have been determined for adsorbed layers ranging from a few ten-thousandths to about 3% of the maximum possible. For the lowest values the adsorbed substance is held by forces which have a high energy value (about 20 kg.-cal.), but the sphere of action is restricted. From 0·0005 to 0·0008 of the maximum the adsorption takes place with a much smaller energy change, the adsorbed substance having such mobility that it is to be regarded as a two-dimensional gas, filling the adsorption area to a considerable extent. Further adsorption results in the formation of a condensed film, the latent heat of condensation being manifested by an increase of the heat of adsorption; simultaneously the mobility of the adsorbed molecules decreases. H. F. Gillbe.

Adsorption of gases by chabasite. F. Simon (Z. physikal. Chem., 1928, **132**, 456—459).—The dehydration of chabasite which occurs on heating takes place in stages which show a stoicheiometric relation between the weight of the water and that of the dehydrated silicate. Measurements have been made of the adsorption of argon and of nitrogen by the anhydrous substance at 90·2° Abs. in order to determine whether similar relations obtain. The curves derived by plotting pressure against volume of dissolved gas consist of a series of straight portions, with breaks at the points which correspond with the ratio 1 mol. gas : 1 mol. chabasite. The slope of the curve at this point changes 75% for argon and 85% for nitrogen. The curves exhibit breaks also at 1/3 mol. of gas. The theoretical significance of these observations is discussed. H. F. Gillbe.

Adsorption of sulphur dioxide by titania gel. S. Klosky and A. J. Burggraff (J. Amer. Chem. Soc., 1928, **50**, 1045—1049).—The adsorption at $-22\cdot5°$, 0°, 25°, and 50° agrees with Patrick's equation at lower pressures, but over the whole range is best represented by Polanyi's formula. S. K. Tweedy.

Adsorption of excess ions by positive and negative silver halide and silver thiocyanate sols. A. Lottermoser and W. Petersen (Z. physikal. Chem., 1928, **133**, 69—121).—An exhaustive study has been made, by means of potentiometric measurements, of the adsorption of silver, halogen, and thiocyanate ions by silver halide or thiocyanate sols or gels. In each case, the silver-ion concentration

was measured by electrometric titration, and the number of adsorbed ions was given by the difference between the measured potential and that calculated from Nernst's formula. The results are represented graphically by "potential curves." The amount of adsorption is found to increase with decreasing salt solubility. The adsorption of bromine and iodine ions by negative silver bromide and iodide sols, respectively, is considerably greater than that of silver ions by the corresponding positive sols. The adsorption of thiocyanate ions by negative silver thiocyanate sols is considerably less than that of bromine ions by negative silver bromide sols, although the former are only slightly more soluble than the latter. On account of the change of potential at the equivalence point, a limit is set to the accuracy of the potentiometric titrations. Thus, for silver bromide, iodide, and thiocyanate sols, titrated with $0{\cdot}1N$-silver solution, an accuracy of $\pm 0{\cdot}004\%$ may be obtained. Negative silver chloride and bromide sols are markedly sensitive to light in the neighbourhood of the equivalence point, and decompose with liberation of free halogen and colloidal silver. By determining the liberated halogen, a measure of the photo-sensitiveness of the silver halide might be possible. With positive sols and silver iodide sol, the action of light, so long as the exposure is not too long, has no effect on the potential. Silver iodide and bromide sols may be considered as colloidal electrolytes, for which the greatest part of the adsorption is due to the charging of the sol. In the case of the other sols investigated, which may also be regarded as colloidal electrolytes, the adsorption caused by charging before coagulation is so small as to be unmeasurable. L. L. BIRCUMSHAW.

Adsorption in mixtures of solvents. E. ANGELESCU and V. N. COMANESCU (Kolloid-Z., 1928, **44**, 288—296).—Measurements have been made of the adsorption of picric acid by animal charcoal in benzene, ethyl alcohol, acetone, and in various mixtures of the following pairs of liquids: ethyl alcohol–chloroform, benzene–ethyl ether, ethyl alcohol–ethyl ether, acetone–benzene, ethyl alcohol–benzene, acetone–chloroform, acetone–ethyl alcohol, and acetone–water. The concentration of the picric acid was varied between 2 and 8%. The results show that the ordinary adsorption equation $a=kc^{1/n}$ is applicable to mixtures of solvents. The values of the exponents vary between narrow limits, and the constant k is inversely proportional to the nth root of the solubility l of picric acid in the solvent or mixture of solvents. The product $kl^{1/n}$ is a measure of the affinity between animal charcoal and picric acid and can be used as a measure of the adsorptive power of a specimen of charcoal. Exceptions to these generalisations were found in the mixtures of acetone with water or ethyl alcohol containing a high percentage of acetone. E. S. HEDGES.

Adsorption phenomena in solutions. X. Connexion between adsorption and p_H of solutions. S. PEWSNER (Z. physikal. Chem., 1928, **133**, —128).—A study has been made of the adsorption of carbamide, dextrose, formaldehyde, arsenious acid, phenol, aniline, acetone, hydrogen cyanide, and boric acid by charcoal, in the presence of phosphate or acetate buffer solutions of varying p_H. The curves giving the relation of adsorbed quantity to p_H show either two maxima or two minima in the region p_H 5·0—7·0. The upper limit corresponds with the of pure water, whilst the lower limit, p_H about 5·0, corresponds with the p_H of water in equilibrium with charcoal containing carbon dioxide.

L. L. BIRCUMSHAW.

Adsorption from solutions. W. HEYNE and M. PÓLANYI (Z. physikal. Chem., 1928, **132**, 384—398).—Measurements have been made of the adsorption by carbon of various crystalline organic compounds from aqueous and alcoholic solutions between −21° and 50°. With rise of temperature the affinity of the adsorption process increases in all cases. The maximum quantity adsorbed decreases with temperature much more rapidly than in the case of adsorption of vapours. Both the absolute value of the affinity and the maximum quantity of substance adsorbed are very much less than is found for adsorption from the vapour phase. These differences are ascribed to the work necessary for separating the solvent and solute and for breaking down the crystal lattice. Other observations in favour of this view are that adsorption of a given substance from an organic solvent is less than from water, and that the adsorption of phenol at and near its m. p. are similar to those shown in the adsorption of vapours.

H. F. GILLBE.

Adsorption phenomena in solutions. XI. N. SCHILOV and K. TSCHMUTOV (Z. physikal. Chem., 1928, **133**, 188—201).—Carbon purified by ignition in air differs from that prepared by treating with hydrogen at a high temperature in that it always retains a film of adsorbed carbon dioxide. The hydrolysis of both weak and strong electrolytes brought about by adsorption on carbon has been followed by p_H measurements, and in agreement with observations of the related phenomena of cataphoresis and electro-osmosis, it is found that with a negative adsorbent the anions are adsorbed before the cations. Two stages in the process of adsorption can thus be defined: in the first the charge on the adsorbent increases owing to the adsorption of ions bearing charges of the same sign as that of the adsorbent; in the second ions of the opposite sign are adsorbed and this corresponds with molecular adsorption. This theory is in accordance with the observation that strong electrolytes undergo hydrolysis when in contact with an adsorbent, whereas weak electrolytes merely experience molecular adsorption.

H. F. GILLBE.

[Influence of] electric charge of adsorbent in adsorption. S. SASAKI (J. Biochem. Japan, 1927, **8**, 102—106).—The sign of the charge of carbon particles was determined when these had reached a state of equilibrium with the basic dyes methylene-blue and crystal-violet at 18° and 0°. As the concentration of the dye increases beyond a certain limit, the negative charge on the carbon is reversed. The concentration at which the reversal takes place is lower the lower the temperature, and the lower the proportion of charcoal to solution. The adsorption requires about 2 hrs. to complete. It is suggested

that the mass attraction between charcoal and dye molecules is the chief cause of the adsorption, although this is undoubtedly assisted by electrical attraction.

W. A. RICHARDSON.

Theory of sorption. Mechanism of heterogeneous catalysis. O. SCHMIDT (Z. physikal. Chem., 1928, **133**, 263—303).—The sorption at 1 atm. pressure and at constant temperature between 0° and 150° of gases for which the molecular diameter is less than the mean diameter of the pores of the adsorbent, is found to be expressed by $\log c = a\sqrt{\lambda} - b$, where c is the quantity of gas adsorbed per unit weight of adsorbent, λ the latent heat of evaporation, and a and b are constants which are for a given adsorbent independent of the nature of the gas, but vary with temperature and pressure. The equation, which has also been derived theoretically, is applicable to the adsorption of gases by colloids and by liquids. Deviations are found when chemical reaction takes place readily. If ionisation of the adsorbed gas occurs, forces of attraction, additional to those of van der Waals, are called into play, and the force needed for separation of the molecules of the gas is greater than the calculated values. H. F. GILLBE.

Patrick's theory of adsorption. S. J. GREGG (J. Physical Chem., 1928, **32**, 616—619).—Theoretical. An examination of adsorption data shows Patrick's formula, $V=k(p\gamma/p_0)^{1/n}$ (A., 1920, ii, 417), to be unsatisfactory. The inclusion of γ is unjustifiable, and the substitution of T^{-1} gives a closer agreement with experimental data. Even then the purely empirical formula obtained forms no basis for a theory of adsorption. L. S. THEOBALD.

Surface tension and the structure of the surface of aqueous ammonia solutions. O. K. RICE (J. Physical Chem., 1928, **32**, 583—592).—The surface tension of aqueous ammonia has been measured by a modified capillary-rise method over the concentration range 0—14 g.-mol./litre. Calculations of the adsorption of the ammonia at the surface of the solution appear to show that even at the highest concentration used there are insufficient molecules of ammonia to form a unimolecular layer. Further, it is estimated that the average adsorbed molecule is approximately 10^{-8} cm. from the surface.

L. S. THEOBALD.

Surface tension of non-aqueous salt solutions. P. P. KOSAKEVITSCH (Z. physikal. Chem., 1928, **133**, 1—14).—By means of the capillary-rise method, the surface tensions of a large number of non-aqueous salt solutions have been measured, the solvents including aliphatic alcohols, acids, and ketones, glycerol, pyridine, and furfuraldehyde. The surface tension of the pure solvents is raised by the addition of salts. For concentrated solutions the relation between the surface tension (γ) and salt concentration (C) is linear. For more dilute solutions, three types of $\Delta\gamma$–C curves are found: (1) concave to the C-axis (chiefly ethyl and propyl alcohols); (2) convex to the C-axis (methyl alcohol); (3) a straight line passing through the origin (chiefly non-alcoholic solvents and *iso*amyl alcohol). The greatest negative capillary activity is observed for salt solutions in methyl alcohol; the value rapidly decreases with increase in the length of the carbon chain in the homologous alcohol series. This phenomenon may be connected with the greater degree of association of salts in the higher alcohols. In non-alcoholic solvents, the negative capillary activity is found to vary but little. If the angle between the $\Delta\gamma$–C line and the C-axis is taken as a measure of the negative capillary activity, the order of the alkali metals (in methyl and ethyl alcohols) is the same as that in water, viz., Li>Na>K. By direct comparison of the $\Delta\gamma$ values at equal concentrations of the alkali iodides, however, different results are obtained according to the chosen concentration, since the curves intersect one another. The order of the lyotropic series Cl>Br>I appears to be reversed in non-aqueous solvents.

L. L. BIRCUMSHAW.

Surface tension of aqueous solutions of salts of high mol. wt. G. ETTISCH and R. KOGANEI (Biochem. Z., 1928, **193**, 390—392).—The surface tension–concentration (γ–C) curves of pure aqueous solutions of sodium cholate, glycocholate, and taurocholate show a well-marked minimum, the degree of lowering of the surface tension being larger, and the molar concentration at the minimum being smaller the larger the mol. wt. With sodium cholate, the activity is due to the liberation by hydrolysis of cholic acid. With sodium oleate the γ–C curves are normal and do not show a minimum. The form of the γ–C curves for sodium cholate in serum and plasma is quite distinct from that in egg-albumin, the former resembling the course in 0·005N-sodium hydroxide and not possessing a minimum, whilst the latter resembles the course in distilled water.

P. W. CLUTTERBUCK.

Determination of hydration from surface tension. H. FREUNDLICH and A. SCHNELL (Z. physikal. Chem., 1928, **133**, 151—164).—The surface tension of aqueous *iso*amyl alcohol solutions containing sugar or electrolytes at various concentrations has been measured. Szyszkovski's equation is valid for the mixed solutions. From the results the degrees of hydration of dextrose and sucrose and of a number of sodium and potassium salts have been calculated; the hydration of the anions corresponds with the lyotropic series. The calculated values of the hydration are in agreement with those obtained by other workers from partition and solubility data, but for the sodium and potassium cations the values deviate widely from those derived from mobilities; in the case of the anions no such deviation exists.

H. F. GILLBE.

Molecular orientation at surfaces of solids. II. Work of adhesion of the saturated fatty acids for water. A. H. NIETZ (J. Physical Chem., 1928, **32**, 620—630).—Experimental results previously obtained (this vol., 358) are now discussed. For the saturated fatty acids, the curves obtained by plotting work of adhesion against the number of carbon atoms show a marked alternating effect according as the number of carbon atoms is odd or even. The β-acids with an odd number and the even members lie on a smooth curve, the α-modifications of the odd-numbered members showing the alternating higher values. This is attributed to differences in crystal structure (cf. Garner and Randall, A., 1924, ii,

385). The curves show a minimum at 12—14 carbon atoms, followed by a pronounced increase, and the general trend of the curve is attributed partly to the nature of the adhesional energy–temperature relationships, and partly to the mechanical effects of the length of the carbon chain.

L. S. THEOBALD.

Production of anisotropy on surfaces. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, **132**, 295—302).—The thickness of the anisotropic layer produced on the surface of glass by rubbing (A., 1927, 931) is found by etching to be about 0·3 μ. Similar layers may be produced on almost all solid substances, although with such as readily recrystallise, *e.g.*, lead, they become isotropic after a short time. The nature of the material used to rub the surface does not affect the result. The presence of such films is detected by utilising the fact that they induce anisotropy in thin films of methylene-blue deposited on them. Most other dyes are unsuitable for this purpose, but melted *p*-azoxyanisole and *p*-azoxyphenetole may be used. Anisotropy is also observed on a freshly-fractured surface of glass. R. CUTHILL.

Adhesion. III. Mixtures of two lubricants. (MISS) M. E. NOTTAGE (Proc. Roy. Soc., 1928, **A**, **118**, 607—616; cf. B., 1928, 287).—By means of the method described previously, three pairs of lubricants have been studied—palmitic acid and the normal paraffin $C_{30}H_{62}$, palmitic acid and cetyl alcohol, and phenanthrene and the paraffin $C_{30}H_{62}$. Curves are given showing the relation of adhesion and m. p. of the mixtures to mol. composition, and the structure of the crystalline plate formed on breaking the metal–lubricant joint is illustrated by means of photographs. In the case of the acid–paraffin mixture, the adhesion is in every case greater than that of the pure substances. Both the adhesion and m.-p. curves show a well-defined transition point for a mixture containing about 3 mols. of palmitic acid to 1 mol. of paraffin. From a study of the structure of the crystalline plates, it appears that the transition point is accompanied by a change from a system containing two constituents to a system containing one. Mixtures on the palmitic acid side of the transition point have a latent period of increasing adhesion, those on the paraffin side, one of decreasing adhesion. In the case of the acid–alcohol mixture, the adhesion curve shows three well-defined transition points—at about 30, 50, and 66 mols. % of cetyl alcohol. The m.-p. curve shows transition points at about 30 and 66 mols. % of cetyl alcohol. The second transition point on the adhesion curve is probably due to the presence of cetyl palmitate, and coincides with a change in structure from a two-constituent to a one-constituent system. The addition of $C_{30}H_{62}$ to phenanthrene causes the adhesion of the latter to decrease at first rapidly, then gradually, and finally rapidly again. An ill-defined transition point is shown, corresponding with 46·6 mols. % of paraffin. The m. p. of each constituent is lowered by the addition of the other, the m.-p. curve being continuous and passing through a minimum extending from about 47 to 74 mols. % of $C_{30}H_{62}$. The latent period of phenanthrene is one of decreasing adhesion. L. L. BIRCUMSHAW.

Electron theory of surface energy at the boundary of two amorphous media. B. M. EIDELSON (Physikal. Z., 1928, **29**, 200—204).—Theoretical. R. A. MORTON.

Bubbles, drops, and Stokes' law. II. W. N. BOND and (MISS) D. A. NEWTON (Phil. Mag., 1928, [vii], **5**, 794—800).—The apparently accidental variations observed in the previous work of Bond (*ibid.*, 1927, [vii], **4**, 898) have been further examined and it is shown both theoretically and experimentally that the surface tension of a drop or bubble decreases the terminal velocity. For a given drop or bubble there is a critical radius below which the drop or bubble behaves as a rigid sphere, whilst for appreciably greater radii the surface-tension effect is small. Experiments with different media give results for the critical radii in fair agreement with theory and show that surface tension is the main contributory cause of the departure from Stokes' law.

A. E. MITCHELL.

Diffusion of carbon through tungsten. C. ZWIKKER (Physica, 1927, **7**, 189—193).—Hot tungsten filaments were coated with carbon in an atmosphere of illuminating gas, and diffusion experiments performed at 1970° Abs.; mathematical relations are derived. CHEMICAL ABSTRACTS.

[Semipermeable] diaphragms. I. Measurement of electro-endosmosis. K. ILLIG and N. SCHONFELDT (Wiss. Veroff. Siemens-Konz., 1927, **6**, 171—176).—An apparatus for the measurement of the electro-endosmotic effect is described. The porous diaphragm is arranged to form the junction of two right-angled tubes, so that the whole forms a U-tube with the diaphragm in the centre of the horizontal lower portion. Copper electrodes of the same area are placed at equal distances from opposite sides of the diaphragm. Corks with right-angled capillary tubes of equal and uniform cross-section are placed in the open ends of the U-tube, which is filled with electrolyte so that the horizontal limbs of the capillaries are filled half-way to the ends. The current is supplied from accumulators, and is reversed repeatedly after equal intervals of time, the movements of liquid in the capillaries being measured. S. I. LEVY.

Osmosis of ternary liquids. General considerations. III and IV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1095—1114).—The diagram showing the direction of diffusion of the components of a ternary liquid mixture is discussed, and also the way in which the changes in composition of the diffusing liquids may be determined. M. S. BURR.

Mol. wt. of cellulose nitrate in molten camphor. C. TROGUS and M. ABD EL SHAHID (Naturwiss., 1928, **16**, 315).—Cellulose nitrate containing 13·5% of nitrogen, corresponding with a mean mol. wt. of 286 (2·76 nitro-groups per $C_6H_{10}O_5$), exhibits depressions of the m. p. of camphor in concentrations up to 15% which indicate values between 280 and 315 for the observed mol. wt.

R. A. MORTON.

Von Weimarn's theory of the colloidal state. S. F. SLOKASOFF (Anal. Asoc. Quím. Argentina, 1927, **15**, 237—286).—A lecture. R. K. CALLOW.

Preparation of negatively-charged sols by means of tartaric acid. I. Properties of compounds of oxides of tin and titanium with tartaric acid. A. Dumanski and A. Kniga (Kolloid-Z., 1928, **44**, 273—277).—Measurements have been made of the density, viscosity, optical activity, and electrical conductivity of solutions of tartaric acid containing progressively increasing quantities of stannic hydroxide and titanium hydroxide respectively. The hydroxides were used in a freshly-precipitated condition by adding sodium hydroxide to the tetrachlorides of the metals. The results indicate that the reaction between tartaric acid and stannic or titanium hydroxide can be separated into two stages: in the first stage, both the optical activity and the ionic concentration increase, and in the second stage the optical activity continues to increase whilst the ionic concentration remains constant. The density and viscosity of the solutions increase linearly throughout. It is considered that the second stage denotes a colloid-chemical process, in which the excess of metallic hydroxide is peptised by the tartaric acid. Such solutions exhibit the Tyndall effect. The colloid particles migrate to the anode under a *P.D.* The formation of colloid can be observed when the ratio of tartaric acid to stannic oxide reaches 5 : 1. In the coagulation of stannic oxide sol by sodium, barium, or aluminium chloride Schultze's rule is not followed quantitatively. E. S. Hedges.

Silver hydrosols with particles of uniform size. A. Gałecki and R. Kempf (Rocz. Chem., 1928, **8**, 40—43).—Stable silver hydrosols are prepared by the reduction of silver nitrate by means of white phosphorus. The particles of such hydrolysis are of uniform size and can serve as nuclei for the deposition of silver from its solutions, but not of gold. On the other hand, silver will deposit on similarly prepared gold hydrosol particles. Such silver hydrosols are affected by the presence of electrolytes, and their particles possess a negative charge which diminishes with time. R. Truszkowski.

Stability of coarse particles in solutions. III. Influence of concentration of the disperse phase and of salt on clarification. H. Werner (Ber., 1928, **61**, [*B*], 802—809; cf. A., 1927, 620, 1023).—The rate of sedimentation of suspensions of *Bolus alba* in water and aqueous potassium chloride solution at 20·0±0·1° has been investigated. The formation of aggregates from suspended particles may be a reversible or an irreversible process; from coarse particles it is irreversible. It may affect the falling of the particles and the shrinking of the deposit favourably, unfavourably, or not at all, according to the concentrations. The degree of its action may vary with time. The higher the concentration of the disperse phase, the lower is that of the salt necessary to produce optimal rate of falling of the particles. Every suspension is completely clarified in a relatively short time when the salt has a certain minimum concentration which is independent of that of the suspended particles within very wide limits. The necessary concentration of the salt depends on its nature. The concentration of the salt which just causes clarification of thick suspensions approximates closely to that which is optimal for the falling of the particles and involves the least expenditure of salt. The nature of the deposit varies with the concentration of salt and disperse phase. With high salt concentration, gentle agitation usually causes the production of a very stable layer of foam the height of which increases with the concentration of salt and disperse phase. Analogous results are obtained with suspensions of *Bolus* in magnesium chloride solution and of aluminium oxide in potassium chloride solution. H. Wren.

Charge and particle size. R. Keller (Kolloid-Z., 1928, **44**, 324—326).—The colloidal state of matter is characterised not only by the size of the particles of the disperse phase, but also by a minimal and maximal electrostatic charge with respect to the dispersion medium. The part played by the ions in the charging of a colloid is small, especially in regard to the ions of strong acids and bases. An analogy is drawn between the electrical relations of colloid particles and molecules, and it is considered that in both cases the surface charge shows itself in an electric field through selective adsorption at one of the electrodes. E. S. Hedges.

The crystalline liquid state as a general property of matter. I. Vectorial aggregation, fluid structure, and stream-double refraction of barium sulphate ultramicrocrystals. P. P. von Weimarn (Kolloid-Z., 1928, **44**, 279—288).—The results of a microscopical and ultramicroscopical examination of barium sulphate, precipitated by mixing concentrated solutions of manganous sulphate and barium thiocyanate, support the author's claim that the state of aggregation of the precipitate depends not so much on the properties of the precipitated substance as on the physicochemical conditions of precipitation. Five stages can be distinguished in the precipitation of barium sulphate: (1) chemical reaction, (2) formation of highly supersaturated and associated solution of barium sulphate, (3) production of very concentrated, highly disperse colloidal solution, (4) vectorial aggregation in this colloidal solution, (5) destruction in consequence of aggregative crystallisation (formation of larger ultramicro- or micro-crystals). An increase in viscosity occurs during the processes (1) to (4), the substance changing from a thick oil of syrupy consistence to a gelatinous membrane. In the case of barium sulphate, states (1) and (2) are passed through rapidly. E. S. Hedges.

Electrokinetic and chemical behaviour of alumino-silicates. S. Mattson (Soil Sci., 1928, **25**, 289—311).—On mixing increasing quantities of sodium silicate with an aluminium chloride solution, an electropositive sol, an isoelectric precipitate, and finally (with an excess of silica) an electronegative sol are successively formed. The alumina–silica system forms isoelectric precipitates in which the proportion of silica decreases with an increase in p_H, approaching zero at p_H 7·0, at which the alumina is itself isoelectric. In the presence of active anions the alumina–silica system forms isoelectric precipitates in which the proportion of silica is lower than in the

precipitates which are formed at the same p_H but in the absence of such anions. In the presence of cations the proportion of silica in the isoelectric precipitates is correspondingly increased. The base exchange capacities of the several precipitates prepared were found to increase with the ratio of silica to alumina and to be of the same order of magnitude as those of the natural gels. The hydroxyl ion as well as the cation is absorbed by the natural gel indicating true adsorption instead of the neutralisation of an acid. The mechanism of adsorption and exchange and the pedological significance of these experiments are discussed. H. J. G. HINES.

Immunity [towards staining] of the granule in colloidal solutions. A. BOUTARIC and F. BANÈS (Compt. rend., 1928, **186**, 1003—1005).—Spectrophotometric measurements have shown that eosin is removed from aqueous solution by colloidal solutions of mastic, gold, albumin, casein, or aluminium hydroxide only when the latter are flocculated, and not when they are in the colloidal state. Flocculation was produced by aluminium chloride or by boiling. The exceptional nature of ferric hydroxide and arsenic sulphide sols may be due to flocculation in crystalline granules. The phenomenon is one of true adsorption, and not of occlusion, since the dye is removed even if added after flocculation is complete, and throws light on the selective staining of living as distinct from dead cells by dyes. J. GRANT.

Flow of starch pastes at high and low rates of shear. F. D. FARROW, G. M. LOWE, and S. M. NEALE (J. Text. Inst., 1928, **19**, 18—31T).—The flow of starch pastes and of castor oil in capillary and Couette viscosimeters has been measured at 20° over a range of shear of 300,000-fold; within this range the viscosity of castor oil is constant. A method is described whereby the results of viscosity measurements in these instruments may be used to calculate the simple shearing stress and velocity gradient at a definite point in the fluid. A graph of the values so obtained expresses in a manner independent of the instrument the variation of flow with shearing stress for the liquid investigated. The stress–shear curve for starch pastes is quite continuous and either passes through or terminates close to the origin. Whilst it does not hold even approximately over the whole of the range examined, the relation $F^N=\eta dv/dy$ appears to describe the flow of starch pastes better than any other two-constant equation and serves as a useful and accurate interpolation formula within the range usually covered by any one type of instrument. Results of measurements made in capillary tubes are expressed in terms of stress and strain, and therefore made independent of instrument dimensions and comparable with data obtained by the use of other forms of viscosimeter, by the use of a formula based on the above relation, viz., $(Pr/2l)^N=\eta(V/t)(N+3)/\pi r^3$, where r is the radius and l the length of the tube, P the driving pressure, and V the volume of liquid flowing in time t. The method is applied to results given by Freundlich and Schalek (A., 1925, ii, 112) for the flow of benzopurpurin sols in both capillary and rotating-cylinder viscosimeters, and it is shown that the discrepancy between the apparent viscosities as determined by the two methods then disappears. B. P. RIDGE.

Osmotic pressure of protein solutions containing salts. J. A. CHRISTIANSEN (Compt. rend. Trav. Lab. Carlsberg, 1928, **17**, No. 6, 1—17).—Theoretical. An attempt is made to derive general expressions applicable to the conditions existing in an osmometer of the type used by Sørensen and his co-workers (cf. A., 1919, i, 175). H. INGLESON.

Magnetic susceptibility and the supposed second isoelectric point of gelatin. M. FALLOT (Compt. rend., 1928, **186**, 1287—1288).—Between 3·69 and 8·20, the magnetic susceptibility curves of gelatin show a minimum value at p_H 4·7, and after a maximum at p_H 5·6, decrease regularly. The dispersions and refractive indices of gelatin solutions are independent of variations in the p_H value, and no evidence has been found of the supposed second isoelectric point at p_H 7·7. J. GRANT.

Isoelectric points of protamines. S. MIYAKE (Z. physiol. Chem., 1928, **172**, 225—229).—Different fractions of clupeine and salmine which have approximately equal arginine contents have the same isoelectric point. Arginine has the highest isoelectric point (p_H 10·5) of all amino-acids, and in twelve protamines examined the isoelectric point is higher or lower as the arginine content increases or decreases, the lowest being that of cyprinine. The precipitation of clupeine by alcohol shows an optimum at the isoelectric point (p_H 12·2). The mixture of amino-acids from the total hydrolysis of clupeine has an isoelectric point 9·37. The results show that the displacement of the isoelectric point towards the alkaline side by the imino-group is greater than that produced by the joint action of free carboxyl and amino-groups. C. HOLLINS.

Dependence of the viscosity of gelatin solutions on temperature. A. FODOR and K. MAYER (Kolloid-Z., 1928, **44**, 314—315).—Using the Ostwald viscosimeter, measurements were made of the viscosity of gelatin solutions with and without addition of acid or alkali between the temperatures 22° and 26°. The viscosity of an aqueous solution of gelatin has a higher temperature coefficient than that of a gelatin solution containing acid or alkali. It is inferred that solvation of the particles is not the primary cause of the increase in viscosity, and that the important feature is the formation of an adsorption compound between the gelatin and acid or alkali. E. S. HEDGES.

Turbidity phenomena in gelatin. K. MAYER (Kolloid-Z., 1928, **44**, 315—319).—The turbidity of solutions of electrodialysed gelatin was measured in an " extinctiometer " at various temperatures between 12·5° and 27·5°. For each temperature a maximum occurs at 1·8% of gelatin, and the turbidity is less at higher temperatures. The fall in turbidity with rising temperature is greatest for a 1% solution. Examination of the effect of hydrogen-ion concentration on the turbidity show that two maxima occur at p_H 5·2—5·4 and p_H 4·0—4·2. It is possible to purify gelatin by electrodialysis without previous dialysis by working with a small current density and

membranes with large pores, and maintaining a rapid flow of water in the anode and cathode chambers in order to remove the electrolytes. E. S. HEDGES.

Diffusion of silver ions [and dyes] in gels. K. YABUKI (J. Biochem. Japan, 1927, 8, 137—156).—The influence of the gel concentration, the concentration of the diffusing silver nitrate, and the chloride concentration on the velocity of diffusion of silver ions in gelatin and agar gels has been studied microscopically, employing a method in which the rate of advance of the silver chloride boundary is measured. An empirical relation $x=at^b$ was found, x being the distance travelled by the diffusing ions in time t, and a and b constants for the particular concentrations of gel, silver nitrate, and sodium chloride employed. The value of a may be taken as a measure of the velocity of diffusion. Up to 10% gelatin concentration, and 5% agar, the velocity of diffusion of the silver ion is inversely proportional to the gel concentration. With constant gel concentration the rate is greater for high than for low silver-ion concentration. Increase in sodium chloride concentration gives decreased rate of diffusion. A similar relation is observed for the diffusion of dyes in gelatin gels of 10—40% concentration. The fact that the change in rate of diffusion with gel concentration is continuous suggests that there is no essential difference in the structure of the gel within these concentration limits (Hardy, J. Physiol., 1899, 172).

W. A. RICHARDSON.

Conductivity of gel containing salt. K. YABUKI (J. Biochem. Japan, 1927, 8, 157—165).—The conductivity of potassium chloride (0·1—0·01N) in gelatin (2—28%) and agar (0·5—5%) gels has been measured, and it is found that the conductivity y due to the salt is a function of the concentration x of the colloid, the relation being of the form $y(ax+b)=1$, where a and b are constants. The decrease in conductivity produced by the colloid is attributed to the resistance offered by the colloid rather than to adsorption of the salt by the colloid particles. The rate of increase of resistance with concentration decreases with increasing concentration of the colloid. There appears to be no essential difference in the structure of gelatin and agar gels over the ranges examined. W. A. RICHARDSON.

Influence of slightly soluble substances on the thixotropy of ferric oxide sols. H. FREUNDLICH and K. SOELLNER (Kolloid-Z., 1928, 44, 309—313).—The accelerating influence of metals on the thixotropic change of ferric oxide sols containing sodium chloride is explained in the following way. Direct measurements have shown that the time of setting increases with increasing hydrogen-ion concentration, and it is considered that the metals dissolve in the weakly acid ferric oxide sol containing ferric chloride to a sufficient extent to diminish the hydrogen-ion concentration, and thus the time of setting. The ions of the metal are without influence. Pure gold and platinum are not sufficiently soluble in the acid solution to produce any effect. These results are confirmed by semi-quantitative experiments in which a large number of sparingly soluble substances (elements, oxides, sulphides, silicates, etc.) were added. A marked difference was found between the effects produced by a soluble and an insoluble steel. Substances such as graphite and sulphur were without influence, but a positive effect was produced by oxides of iron. In agreement with theory, a metal is effective when separated from the sol by a collodion membrane. E. S. HEDGES.

Electrokinetic potential of silicic acid gels. S. GLIXELLI and J. WIERTELAK (Rocz. Chem., 1928, 8, 10—21).—Measurements of the velocity of electro-osmosis of 0·001N-nitric acid solutions through silica gel diaphragms show that this is substantially the same when the concentration of the silica in the diaphragm changes from 1·8 to 5·3%, the mean electrokinetic potential ζ being $0{\cdot}211\times10^{-3}$ volt. The value of ζ rises with diminishing concentration of nitric acid, being $5{\cdot}42\times10^{-3}$ volt for pure water. This value of ζ is unusually low in comparison with other diaphragms; thus for powdered quartz and for ignited silicic acid ζ is respectively $12{\cdot}3\times10^{-3}$ and $23{\cdot}8\times10^{-3}$ volt. Previous shaking, concentration or dilution of the gel does not appear to affect the value of ζ obtained, which, however, diminishes rapidly with increase in the concentration of sodium silicate solution from which the original gel is precipitated. The above phenomena are explained on the basis of Eggert and Reitstötter's theory of the structure of gels (A., 1926, 1098).

R. TRUSZKOWSKI.

Coagulation of colloids by electrolytes. III. Potentiometric titration of the coagulation of ferric hydroxide sols. A. J. RABINOVITSCH and V. A. KARGIN (Z. physikal. Chem., 1928, 133, 203—232; cf. A., 1927, 654).—The chemical changes which occur during the coagulation of ferric hydroxide sols by electrolytes have been followed by potentiometric titration. The replacement of chlorine ions by ions from the colloidal particles and the adsorption of ions by the latter may be thus investigated. It is found that the adsorption and replacement of chlorine ions do not take place according to the usual adsorption isotherms, but partake more of the nature of a chemical reaction. Coagulation usually occurs only after the whole of the chlorine has been replaced by the anions, and in those cases in which it takes place previously, the replacement takes place from the precipitate. During the titration the chlorine ions are replaced by more than the equivalent quantity of other anions, the effect being greater the higher the concentration of the sol and of the coagulating electrolyte. Since there is no corresponding replacement of cations, the positive charge on the colloidal particles must be increased by the addition of electrolyte to the sol. This conclusion has been verified by cataphoretic measurements. H. F. GILLBE.

Electric charge and coagulation of colloids. H. MÜLLER (Kolloidchem. Beih., 1928, 26, 257—311).—Smoluchowski's theory of rapid coagulation for monodisperse systems is extended to polydisperse systems. Assuming that the effective radius of the attractive forces determining the coagulation between the single particles is small compared with the radii of the colloid particles, it is shown that coagulation takes place more rapidly between particles of different

sizes than between those of equal size. The view of Wiegner and Galecki, that in the coagulation of polydisperse sols the submicrons act as coagulation nuclei for the amicrons, receives theoretical confirmation. A mathematical theory is developed, which is applicable to any polydisperse system, and the following equation is deduced: $\Sigma\nu = N_0/(1+t/T)[\lambda n_0/\{(N_0\lambda+n_0)(1+t/T)^\lambda - n_0\}]$, where $\Sigma\nu$ is the total number of small particles at time t, N_0 and n_0 are the original numbers of large and small particles respectively, T is the coagulation time of the large particles, and $\lambda=(V_R^2+1)/2V_R$, where V_R is the ratio of the radii of the large and small particles, respectively. The equation has been experimentally confirmed by Tuorila (A., 1926, 1005) and Wiegner (*ibid.*, 242). The deviations shown by the results of Westgren and Reitstotter (A., 1918, ii, 301) from those demanded by Smoluchowski's theory can be explained by the polydispersivity of the initial colloid.

The influence of the concentration and valency of the added electrolyte on the electrokinetic potential (ζ) and stability of the colloid is discussed from the point of view of Gouy's theory of the diffuse double layer. A graphical method is given for determining the potential gradient in the diffuse double layer round a spherical particle. By means of the theory developed, the change of electric charge within the layer can be calculated from cataphoresis measurements, and a closer study is possible of the laws of ion adsorption on the colloid particles. The ζ–c curves (c=concentration of electrolyte) obtained by Freundlich and Zeh (A., 1925, ii, 115), who investigated the influence of valency on the cataphoresis and coagulation of an arsenious sulphide sol, can be explained simply by changes in the diffuse double layer, assuming a constant micelle charge. In most cases, however, the curves can be explained only on the assumption that a change in the particle charge, due to ion adsorption, takes place.

L. L. Bircumshaw.

Influence of temperature on the speed of coagulation of colloids. K. Jabłczynski and M. Knaster (Rocz. Chem., 1928, **8**, 36—39).—See this vol., 361.

Kinetics of the coagulation of colloids. K. Jabłczynski and M. Soroczynski (Rocz. Chem., 1928, **8**, 31—35).—See this vol., 360.

[Influence of] salt content on aggregation of hæmoglobin in solution. S. Kato, Y. Katsu, and K. Yabuki (J. Biochem. Japan, 1927, **8**, 133—136).—The relation deduced by Hill (J. Physiol., 1916, **40**, Proc. iv), $y=100Kx^n/(1+Kx^n)$, between the percentage saturation y of oxyhæmoglobin and x, the oxygen tension, where K is a constant, and n represents the average number of molecules which compose an aggregate particle, is confirmed for hæmoglobin solutions dialysed to different degrees, and it is shown that n decreases as the specific conductance and the chlorine-ion concentration decrease, but at a slower rate. W. A. Richardson.

Organic rhythmic structures. M. Copisarow (Kolloid-Z., 1928, **44**, 319—323).—Rhythmic precipitates were obtained in the diffusion of picric acid, tannic acid, lactic acid, phenol, phosphoric acid, and α-trinitrotoluene into gelatin. At low concentrations of the colloid, striated structures without definite ring formation were produced, the rings becoming definite at a certain higher concentration of colloid. The value of this concentration depends on the quality of the gelatin. The best qualities of gelatin, or those containing the smallest quantities of hydrolysis products, tend to form honeycomb structures, rather than stratified precipitates. The experiments with tannic acid indicated a tendency towards the formation of spirals in place of rings. Rhythmic precipitates were not produced in the diffusion of pyridine, benzaldehyde, oil of wintergreen, gallic acid, and *o*-nitrophenol into gelatin, isinglass, and agar. E. S. Hedges.

A physical factor in the Liesegang phenomenon. S. Ray (Kolloid-Z., 1928, **44**, 277—279).—An expression is derived which gives the relation between the density and the height of a colloidal suspension. According to this there are three possible heights for certain densities. This is considered to be the primary cause of the periodicity in Liesegang rings. E. S. Hedges.

"Acclimatisation phenomenon" in the coagulation of arsenious sulphide sols by barium chloride. V. N. Krestinskaja and V. S. Jakovleva (J. Russ. Phys. Chem. Soc., 1928, **60**, 295—310).—See this vol., 236.

Cataphoretic migration velocity of large particles in sols and gels. II. H. Freundlich and H. A. Abramson (Z. physikal. Chem., 1928, **133**, 51—68; cf. A., 1927, 931; this vol., 238).—The fact previously observed (*loc. cit.*), that the cataphoretic velocity of large particles is independent of their shape, has been confirmed by measurements on quartz particles in water, in aqueous sugar and salt solutions, and in serum, and also on glass and kaolin particles in water. The velocity of quartz particles in water (very dilute suspensions) is lowered by the addition of proteins such as gelatin, albumin, and hæmoglobin at very low concentrations (10^{-7} g. per litre); this effect is not found with other hydrophilic sols (starch, sodium oleate, etc.). At higher protein concentrations (10^{-4}—10^{-5} g. per litre) the cataphoretic velocity of quartz or glass particles is independent of the protein content, and it is assumed that the particles are now completely surrounded by a protein envelope and behave as protein particles. Measurements have been made of the cataphoresis of quartz particles in solutions of egg-albumin (10^{-3}—10^{-4} g. per litre) at constant p_H, and the results agree with those obtained by Svedberg and Tiselius (A., 1926, 1104) for the relation between the cataphoresis of egg albumin and the p_H of the medium. Exceptions are found to the behaviour shown by quartz particles, zinc oxide, air bubbles, etc. Thus, in spite of the high albumin content of serum, the mobility of the red corpuscles is about twice as great as that of the white. In mixtures of serum with gelatin, containing enough gelatin (about 0·7%) to cause it to set to a soft gel, the mobility of the red corpuscles is about twice that of quartz particles and leucocytes. With larger admixtures of gelatin (1·2—1·5%), so that the whole sets to a solid gel, the blood corpuscles

and suspended quartz particles move at first with the same velocity, but after a time, the red corpuscles again move with twice the velocity of the other particles. This behaviour is explained as being due to a thixotropic change in the gel, caused by the repeated to-and-fro motion of the particles.

L. L. BIRCUMSHAW.

Gaseous solutions. M. RANDALL and B. SOSNICK (J. Amer. Chem. Soc., 1928, **50**, 967—980).—The deviations of gaseous mixtures from the generalised Raoult law increase with the density of the gas, and are qualitatively the same as those of typical liquid pairs. In Hildebrand's simplified equation for log γ (cf. A., 1927, 936) the value of b will always be below the "critical mixing point," *i.e.*, the value necessary for the co-existence of two gaseous phases in equilibrium. The fugacity of a pure supercooled vapour cannot be calculated above the pressure corresponding with the maximum in the pv isotherm. Lewis and Randall's fugacity rule applies only to a limited extent to vapours below the critical point of the solute gas, although it holds approximately as a limiting law for all gaseous solutions above the critical temperature. The activity functions of certain solute gases below the critical temperature are tabulated; from these, the values for other mixtures and at other temperatures may be derived.

S. K. TWEEDY.

Thermodynamic deduction of Maxwell's distribution law. A. SCHUKAREV (Physikal. Z., 1928, **29**, 181—182).—Maxwell's deduction is open to criticism, although the law is in accord with experience. An attempt has therefore been made to deduce the law from thermodynamic principles.

R. A. MORTON.

Statistical series of the Charlier A type and Boltzmann's equation. U. WEGNER (Z. Physik, 1927, **45**, 539—547).—Mathematical. R. W. LUNT.

Deduction from two diffusion equations. W. HERZ (Z. anorg. Chem., 1928, **170**, 246).—Combining Gapon's relation $D\sqrt{n}$=constant (this vol., 134), where D is the diffusion coefficient of a substance, and n the number of atoms in the molecule, with the well-known equation $D\sqrt{M}$=constant, where M is the mol. wt., there results the relation
constant, which proves to be in satisfactory agreement with the experimental data. R. CUTHILL.

Equation of state for binary mixtures of methane and nitrogen. F. G. KEYES and H. G. BURKS (J. Amer. Chem. Soc., 1928, **50**, 1100—1106).—Compressibility data for three mixtures of nitrogen and methane between 0° and 200° and up to about 300 atm. are recorded. The equation of state for the mixtures is of the same form as that for the separate gases (cf. A., 1927, 507, 719), and the constants, provided the slight curvature of the isometrics is neglected, are linear functions of the weight percentage composition (W) of the mixtures and of the constants for the pure gases. Thus, $A=(A^{\frac{1}{2}}_{N_2}W \quad {}_{CH_4})^2$, $\beta=\beta_{N_2}W_{N_2}+\beta_{CH_4}W_{CH_4}$, etc. The relationships may not be so simple when the molecular "diameters" of the two constituents are less nearly equal than in the present case.

S. K. TWEEDY.

Brownian displacements and thermal diffusion of grains suspended in a non-uniform fluid. S. CHAPMAN (Proc. Roy. Soc., 1928, **A**, **119**, 34—54).—The distribution in magnitude and direction of the Brownian displacements, during any assigned interval, of small spherical grains suspended in a fluid (liquid or gaseous) is obtained for the general case of a non-uniform fluid. The non-uniformity may refer to temperature, composition, or any other property which affects the coefficient of diffusion (D) of the grains. The distribution function contains terms additional to that given by Einstein for the uniform case; some of these are definitely determined, but one term contains an undetermined constant which requires more detailed physical analysis for its evaluation. It is surmised that this coefficient vanishes in the case of Brownian particles which are large compared with the mean free path of the surrounding molecules. The steady distribution of grains in a fluid is considered for the case when the temperature (T) of the fluid is non-uniform. It is found that if the density of the grains is the same as that of the fluid, so that there is no tendency for them to settle in the lower strata, then the concentration n is inversely proportional to D, which varies with T more rapidly in liquids than in gases. In the case of a Maxwellian gas, D is independent of T, so that "Brownian" thermal diffusion, like true gaseous thermal diffusion, is not operative. In other fluids, the grains will tend towards the cooler regions. When the densities of the grains and fluid are unequal, it is shown that with a uniform temperature gradient nD is not constant, but varies as a power of T. The order of magnitude of the various effects is estimated, and it is shown how their accuracy might be experimentally tested. The present theory may be applicable to the Ludwig–Soret effect in liquid solutions for which the solute molecules are large and non-ionised.

L. L. BIRCUMSHAW.

Molecular displacements in diffusing gas mixtures. S. CHAPMAN (Proc. Roy. Soc., 1928, **A**, **119**, 55—60).—The arguments used in the consideration of the Brownian motion of grains suspended in a fluid (cf. preceding abstract) are applied to ordinary gas mixtures. For a perfect gas mixture in which the concentration of one kind of molecule is very small, it is shown that if the molecules are rigid elastic spheres, and if the rare molecules are much the lighter, the spreading of any particular cluster of molecules will be accompanied by a movement towards the hot region; on the other hand, if the rare molecules are much the heavier the spreading will be associated with a movement towards the colder regions, unless their diameter is small (less than half that of the other kind of molecule present). The spreading is not symmetrical relative to the mean motion. In gas mixtures of small concentration, the product (concentration)×(coefficient of diffusion) is not a constant.

L. L. BIRCUMSHAW.

Entropy and thermodynamic potentials of real gases and mixtures of real gases, and a mass action law for chemical reaction between real gases. I. General thermodynamic relations. J. A. BEATTIE (Physical Rev., 1928, [ii], **31**, 680—690).—Theoretical. General thermo-

dynamic equations are deduced for the energy, heat content, entropy, and thermodynamic potentials of gas mixtures, and the chemical potential of a gas in a mixture in terms of the independent variables p and T, and V and T. Two forms of the mass action law are deduced, p and T, or V and T, being chosen as the independent variables. A. A. ELDRIDGE.

Group theory of homopolar chemical combination. W. HEITLER (Z. Physik, 1928, **47**, 835—858).—Mathematical. An extension of the theory of Heitler and London (A., 1927, 923). J. W. SMITH.

Differential equations of a reacting mixture. R. D. KLEEMAN (Phil. Mag., 1928, [vii], 5, 620—629).—The results obtained from the generalised equations for a reacting mixture accord with that obtained previously (this vol., 239). The mass-action constant is usually a function of the temperature, volume, and masses of the constituents. In special cases the constant may be a function of the temperature alone. A. E. MITCHELL.

Decomposition of carbon dioxide at low pressure under the action of the electric current. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1928, **186**, 1119—1121; cf. this vol., 477).—The final equilibrium is independent of the intensity of the current between 0 and 2 milliamp., but is attained most rapidly with currents of high intensities. During the first moments of the passage of a current of medium intensity the rate of dissociation is proportional to the duration and intensity of the current. It decreases when the pressure is increased, and is less for a continuous current than for a spark discharge although the temperatures developed are approximately the same (2100—3000°). J. GRANT.

Theory of the decomposition of methane. O. K. RICE (Proc. Nat. Acad. Sci., 1928, **14**, 118—124; cf. this vol., 483).—The decomposition of azomethane is said to result from activation by collision, the chance of reaction of an activated molecule depending on the energy in the manner to be expected if reaction is due to energy which is localised in a particular centre. W. E. DOWNEY.

Dielectric constants of solutions of electrolytes. H. HELLMANN and H. ZAHN (Z. physikal. Chem., 1928, **132**, 399—400).—Polemical (cf. this vol., 14). H. F. GILLBE.

Formation and stability of metallic complexes in solution. P. JOB (Ann. Chim., 1928, [x], 9, 113—203).—An extended account of work already published (A., 1923, i, 307, 902; 1925, ii, 389, 471, 887; 1926, 571, 791; 1927, 205, 546). H. BURTON.

Cryoscopic measurements on aqueous solutions of resorcinol and pyrocatechol. F. BOURION and C. TUTTLE (Compt. rend., 1928, **186**, 1124—1126).—Solutions of resorcinol and pyrocatechol were examined at concentrations 0·75—3·0M and 0·375—1·25M, respectively. The f.-p. data suggest the existence of equilibria between simple and triple molecules, whilst at 100° the equilibria are between simple and double or triple molecules at low or high concentrations, respectively. The calculated heats of association of three simple molecules to form a triple molecule are +600 and −2400 g.-cal. (at constant volume) for resorcinol and pyrocatechol, respectively. J. GRANT.

Equilibrium between methoxide and hydroxyl ions in methyl alcohol–water mixtures. III. Calculation of the equilibrium constant from the dissociation constants of methyl alcohol and water. A. UNMACK (Z. physikal. Chem., 1928, **133**, 45—50; cf. this vol., 18).—The equilibrium constant for the process $OMe'+H_2O$ $OH'+MeOH$ may be calculated from the equation $K'-K_M(W)/K_M(M)$, where $K_M(W)$ is the dissociation constant of water in methyl alcohol and $K_M(M)$ that of methyl alcohol (in methyl alcohol?). $K_M(W)$ is given by $K_M(W)=K_W(W)\,.\,V_W^M(H)\times$ where $V_W^M(OH)$ is the partition coefficient of the hydroxyl ion, and $V_W(H)$ the partition coefficient of the hydrogen ion between methyl alcohol and water. From this, the equation $K'=[K_W(W)/K_M(M)][V_W^M(H)]^2\,.\,S(H)$ follows, $S(H)$ being the equilibrium constant for the solvation equilibrium of the hydrogen ion in mixtures of water and methyl alcohol. All the quantities in this equation are known. By taking values for $K_M(M)$ obtained by hydrolysis and potentiometric measurements, respectively, and values for $V_W(H)$ calculated by different methods, a number of values for K' are found ranging from 0·98 to 2·00. All these values are higher than those previously found. The reasons for this are discussed. L. L. BIRCUMSHAW.

Influence of neutral salts on acid–salt equilibria. II. Dissociation constants of citric acid. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1928, **47**, 558—575; cf. A., 1927, 829).—Measurements have been made of the p_H of mixtures of citric acid and its potassium salts at 18°, and the three dissociation constants of citric acid calculated. These are $K_1=8{\cdot}2\times10^{-4}$, $K_2=1{\cdot}77\times10^{-5}$, $K_3=3{\cdot}9\times10^{-7}$. The effect of neutral salts on the p_H of the solutions has been studied. Anions are relatively inactive, but there is a well-marked cation effect in the order (Cs, Rb)$<$K$=$$NH_4$$<Na<$Li. The influence of potassium chloride can be calculated approximately from the Debye–Hückel equation, but this does not give good results for sodium and lithium salts. The calculated average size of the ions in mixtures of di- and tri-citrate is $6{\cdot}2\times10^{-8}$, but a constant value is not obtained for the citric acid–monocitrate mixtures, and it seems that the activity coefficient of the undissociated acid is much larger than unity at moderate concentrations. It is proposed to replace for practical purposes the true dissociation constants quoted above, which refer to infinite dilution, by "acid strengths," which represent the true dissociation constants corrected for the activity coefficients of the components.

W. A. RICHARDSON.

Equilibrium law of electrolytes and their conductive power. K. JABŁCZYNSKI (Rocz. Chem., 1928, 8, 22—30).—The equation $\lambda_\infty=\lambda+d\lambda^{4/3}N^{1/3}$, connecting the conductivity and the concentration of an electrolyte (compare Jabłczynski and Wisniewski, A., 1922, ii, 190), is applied to measurements made by different authors, and shown to give better results than Debye and Huckel's equation. In some cases,

e.g., sodium and lithium chloride, the equation does not hold, but this is due to hydration of the ions, and on applying the necessary corrections the behaviour of these salts is found to be normal.

R. TRUSZKOWSKI.

Vapour equilibrium of aqueous glycerol solutions. D. F. STEDMAN (Trans. Faraday Soc., 1928, **24**, 289—298).—A distillation method which is described has been employed to determine the composition of vapour in equilibrium with aqueous solutions of glycerol at temperatures from 50° to 200° and pressures between 60 and 760 mm., with an accuracy of 0·1—0·5%. Values for the vapour pressure of anhydrous glycerol for the same temperature range have been determined with an accuracy of approximately 1%, and average values for the latent heat of evaporation over each 10° interval have been calculated.

M. S. BURR.

Condition of strong electrolytes in concentrated solution. I and II. Nitrates. H. VON HALBAN and J. EISENBRAND (Z. physikal. Chem., 1928, **132**, 401—432, 433—455).—I. The displacement of anion absorption bands in the presence of cations has been examined in detail for the nitrate ion band at 300 μμ, using concentrated solutions of alkali nitrates and also dilute solutions of the nitrates in concentrated solutions of other salts. All cations influence the absorption of the nitrate ion, which is in the same condition in a concentrated nitrate solution as in a dilute nitrate solution having a high cation concentration. The less easily deformed the cation, the greater is its influence on the anion, whilst the dielectric constant of the solvent is of considerable importance as regards the magnitude of the effect. The displacement of the band decreases on passing down a group of the periodic table, and in the case of the alkali metals changes sign. No influence is manifested by heavy metal cations such as the mercuric, cupric, and nickelous ions at the low concentrations at which the alkali metals are active. Schaler's observation, that Beer's law is not valid for these nitrates at even low concentrations, is not due to a change in the absorption of the nitrate ion, but is a cationic effect. Other anions present in the solution affect the extent, but not the nature, of the displacement. For a given concentrated nitrate solution there exists a dilute nitrate solution containing a different salt of the same cation, such that the two solutions possess at all wave-lengths identical absorption.

The displacement effect is discontinuous, and is due to the formation of a new type of absorbing molecule which contains both the nitrate ion and the cation.

II. Measurements have been made of the absorption spectrum of nitric acid in solutions of widely varying concentration in water and in aqueous solutions of perchloric, sulphuric, and phosphoric acids, and also in dilute ethyl ether, acetic acid, ethyl alcohol, and hexane solution. The spectra of the dilute aqueous solutions are identical with those of the corresponding nitrate solutions. At concentrations below about 10*N* the extinction-wave-length curves of all the aqueous solutions intersect at a common point. The extreme variations exhibited by the spectrum over this concentration range cannot be ascribed to the presence of undissociated molecules of nitric acid, and the possible formation of ionic pairs or of complex ions is suggested. In ether and in acetic acid solution, nitric acid exists to the extent of about 60% as associated ions; this is the case for concentrated aqueous solutions, the remainder consisting of undissociated molecules. The spectra of the solutions in hexane resemble those of the esters, the greater part of the acid being undissociated. Solutions in aqueous sulphuric acid have spectra which change from the first type to the second as the sulphuric acid concentration increases. The totally different spectrum exhibited by concentrated sulphuric acid solutions of nitric acid is ascribed to the presence of nitric anhydride.

H. F. GILLBE.

Graphical methods and empirical formulæ for the study of electrolytic dissociation. E. DENINA (Notiz. chim.-ind., 1927, **2**, 491—497; Chem. Zentr., 1927, ii, 2648).

p_H of buffered salt solutions. J. B. O'SULLIVAN (Trans. Faraday Soc., 1928, **24**, 198—300).—The effect of salt solutions on the p_H values of buffer solutions has been investigated. In most cases a lowering of the p_H of both buffer and salt solutions was observed. The results obtained are in agreement with Haynes' observations (Biochem. J., 1921, **15**, 440).

M. S. BURR.

Activity coefficients of small ions. H. MULLER (Physikal. Z., 1928, **29**, 78—82; cf. A., 1927, 626).—Theoretical.

W. E. DOWNEY.

Activity of hydrogen ions in aqueous solutions of beryllium sulphate. M. PRYTZ (Trans. Faraday Soc., 1928, **24**, 281—288).—The p_H values of solutions of beryllium sulphate of different concentrations, both in water and in aqueous sulphuric acid, have been determined electrometrically at different temperatures. Making certain assumptions, values for the "percentage hydrolysis," α, of beryllium sulphate have been calculated. For the more dilute solutions α apparently increases with temperature, but decreases in more concentrated solutions. As concentration increases the value of α falls to a minimum and then increases. This may be explained by the increase in the activity of the hydrogen ions due to increasing concentration of beryllium sulphate. By comparing solutions of beryllium sulphate with equivalent solutions of magnesium sulphate containing sufficient added sulphuric acid to yield the same values of p_H, an attempt has been made to ascertain the true degree of hydrolysis of solutions of beryllium sulphate. The curve of corrected values of α plotted against concentration, however, still shows a pronounced minimum.

M. S. BURR.

Activity coefficients of gases in aqueous salt solutions. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, **4**, 271—284).

Activity coefficients of non-electrolytes in aqueous salt solutions from solubility measurements. Salting-out order of the ions. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, **4**, 285—290).

Activity coefficients of the undissociated part of weak electrolytes. M. RANDALL and C. F. FAILEY (Chem. Reviews, 1927, 4, 291—318).

Activity coefficients of nitric acid in aqueous solution. E. ABEL, O. REDLICH, and B. VON LENGYEL (Z. physikal. Chem., 1928, 132, 189—207).—From measurements of the f.-p. depression of nitric acid solutions containing 0·00526—4·009 g.-mol. of acid/1000 g. of water the authors have calculated the activities and activity coefficients of both constituents of the solutions, and the free energies of dilution of the acid. The activity coefficient of the acid is minimal in an approximately 0·4*N*-solution.

R. CUTHILL.

Activity coefficients of aqueous solutions of lead chloride at 25°. A. J. ALLMAND and E. HUNTER (Trans. Faraday Soc., 1928, 24, 300—306; cf. A., 1927, 1030).—Electrometric measurements have been made on the cell Pb(amalgamated)|aqueous $PbCl_2$|AgCl(solid)|Ag, under air-free conditions at 25°, at concentrations between saturation and 0·00006*M*. By plotting the logarithm of the concentration against the *E.M.F.*, a curve is obtained which is convex to the axes at high concentrations and concave at low ones. The form of the latter part of the curve is due to the solubility of silver chloride. From the results the mean activity coefficients of the dissolved lead chloride have been calculated for concentrations down to 0·0003*M*. The results are in fairly good agreement with Lewis and Randall's deductions from some of Bronsted's earlier measurements (A., 1906, ii, 834). It is suggested, however, that their values for the activity coefficients of barium and cadmium chloride solutions may need revision.

M. S. BURR.

Concentrated solutions. V. Experimental determination of the thermodynamic activity of the constituents of binary mixtures of organic compounds. (MLLE.) M. ROLAND (Bull. Soc. chim. Belg., 1928, 37, 117—140).—The vapour pressures of binary mixtures of organic compounds have been determined at various temperatures and concentrations by Kohnstamm's method, one of the constituents in each case having a negligible vapour pressure at the temperature concerned. The experimental error, which is dependent on the pressure, varied from 0·15 to 4·0%. All the systems studied had vapour pressures higher than required by the law of ideal solutions, and mixtures of acetone with di*iso*amyl or with *sec.*-butyl*cyclo*hexane showed points of inflexion on the total pressure–concentration curves which gradually disappeared at temperatures removed from the critical solution temperature (−11·2° and −7·1°, respectively). The anomalies are less marked for mixtures of *sec.*-butyl alcohol with nitrobenzene, aniline, ethyl bromide, *iso*pentane, or carbon disulphide, and of *sec.*-butyl chloride with nitrobenzene, and the curves all tend towards those of ideal solutions at the higher temperatures. The thermodynamic activity coefficients, calculated by the method of Lewis and Randall, are shown to be greater than unity. Since the activity of one substance considered as solvent in a very concentrated solution of the other component equals that of the latter considered as a solute in a very dilute solution of the former, multiplied by a factor depending on the ratio of the states of reference chosen in each case, it is possible to calculate the activity of one component from that of the other.

J. GRANT.

Oxygen-, acid-, and base-combining properties of blood. III. Validity of hydrogen-ion activity determinations by the hydrogen electrode in systems containing carbonic acid, carbonates, hæmoglobin, carbon monoxidehæmoglobin, and methæmoglobin. IV. The apparent first dissociation constant, pK_1', of carbonic acid and the activity coefficient of the hydrogen carbonate ion in solutions of hæmoglobin, methæmoglobin, cyanhæmoglobin, and nitric oxide-hæmoglobin at varying ionic strengths. W. C. STADIE and E. R. HAWES (J. Biol. Chem., 1928, 77, 241—264, 265—302).—III. The values of the hydrogen-ion activity of these systems given by *E.M.F.* determinations with the hydrogen electrode differ by an indeterminate amount from the absolute values; the difference is due to faulty assumptions in regard to the hydrogen-ion activity of the reference solution and the liquid junction potentials which are involved. An approximate evaluation of the error due to liquid junction potentials is made. The junction potentials between saturated potassium chloride and solutions of the above substances of widely varying concentration are shown to be negligible when the Bjerrum extrapolation is made. The following evidence is advanced to show that the hydrogen electrode is a reversible source of *E.M.F.* in the above solutions. The *E.M.F.* is a function of the logarithm of the partial pressure of hydrogen over a wide range. Carbon monoxide is without effect on the *E.M.F.* of the electrode at partial pressures as great as 330 mm. The heats of ionisation of carbonic acid are identical in the presence and in the absence of hæmoglobin. There are no appreciable irreversible reactions in the presence of the electrode. Discrepancies are pointed out in the free energies and heats of ionisation of carbonic acid when calculated from *E.M.F.* data on the one hand and from conductivity and thermal data on the other. The hydration of the hydrogen ions in hæmoglobin solutions is discussed.

IV. Values of K_1' and $\gamma_{HCO_3^-}$ have been calculated from the hydrogen electrode determinations in solutions of varying ionic strength and varying concentration of the above derivatives of hæmoglobin. The results can be expressed in the equations, $pK_1'=pK_*-\beta\sqrt{\Gamma}$ and $\log\gamma_{HCO_3^-}=-\beta\sqrt{\Gamma}$, where $\beta=0{\cdot}54-\sigma[Hb]$ and $pK_*=6{\cdot}33-\rho[Hb]$. σ and ρ are constants characteristic of the hæmoglobin derivative present. It follows that $\gamma_{HCO_3^-}$ may be equated to two activity coefficients which measure respectively the effects of salts and of the hæmoglobin derivative on $\gamma_{HCO_3^-}$, and permit the calculation of pK_1' over a wide range of hæmoglobin and salt concentration. The pK_1' in the red blood-cell is calculated to be 5·98 and 5·87 for the oxidised and reduced states, respectively, and these values are confirmed by direct determinations in hæmolysed human, horse, and ox cells.

R. K. CANNAN.

Oxygen-, acid-, and base-combining properties of blood. V. Extension of the Debye-Hückel theory of ionic interaction to hæmoglobin, hydrogen carbonate-sodium chloride systems. W. C. STADIE (J. Biol. Chem., 1928, 77, 303—323; cf. preceding abstract).—Equations are developed on the basis of the Debye-Hückel theory which permit the calculation of the activity coefficients of the hydrogen carbonate ion in solutions of hæmoglobin varying from 0 to 20 millimols. and salt from 0 to 0·5 mol. per litre. The values calculated agree within experimental error with those observed. Theoretical and experimental reasons are given for assigning to the colloidal hæmoglobin ion an ionic strength valency of 1. The two activity coefficients of the hydrogen carbonate ion in hæmoglobin solutions are related to the ionic diameter of the ion and to the influence of hæmoglobin on the dielectric constant of water. Hæmoglobin and its derivatives appear to raise this constant.

R. K. CANNAN.

Internal equilibrium in liquid sulphur. I. D. L. HAMMICK, W. R. COUSINS, and E. J. LANGFORD (J.C.S., 1928, 797—802).—By chilling sulphur heated at 150—300° and analysing the product, the equilibrium between S_λ and in the molten state has been studied. The temperature-composition curve does not become vertical until the amount of S_μ exceeds about 40%, as against 33% in Smith and Holmes' experiments (A., 1906, ii, 157). This would seem to show that the method of chilling employed by these authors did not entirely prevent the reversion of S_μ to S_λ, and that the vertical part of the curve is not a true allelotropic line, but is merely a consequence of ineffective chilling. R. CUTHILL.

Influence of electric and magnetic fields on crystallisation of supercooled liquids. W. KONDOGURI (Z. Physik, 1928, 47, 589—601).—The number of crystallisation centres in supercooled piperine and salol increases considerably under the influence of electric and magnetic fields. The action of the fields is investigated by a microscopic method. For an electric field, the number of crystallisation centres varies directly as the strength of the field. For a given field strength the number of centres increases with the time of application of the field up to a limiting value. If the field strength is then increased, the number of centres again increases until a new boundary value is reached. Similar results were obtained with the radiation from radium bromide, as well as with a magnetic field, but the action of the radiation from radium on salol gives rise to some deviation from the results obtained by other methods. The explanation of this has not yet been reached. A. J. MEE.

Dissociation of formic acid vapour and the equilibrium between aqueous formic acid solutions and the vapour. M. S. VREVSKI and A. A. GLAGOLEVA (Z. physikal. Chem., 1928, 133, 370—376).—See this vol., 18.

Equilibrium between vapour and liquid in solutions of formic acid and benzene. M. S. VREVSKI, N. A. HELD, and S. A. SCHUKAREV (Z. physikal. Chem., 1928, 133, 377—389).—See this vol., 19.

Dissociation of acetic acid vapour and equilibrium between aqueous solutions and vapour of acetic acid. M. S. VREVSKI, K. P. MISCHTSCHENKO, and B. A. MUROMCEV (Z. physikal. Chem., 1928, 133, 362—369).—See this vol., 18.

Ice-point of the thermometer scale. A. MICHELS and F. COETERIER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 1017—1020).—The ice-point as usually determined is subject to inconstancy due to dissolved gases or impurities from the containing vessel. By preparing ice from supercooled gas-free water, out of contact with air, the variation obtained was less than 0·001° as measured by a mercury thermometer. When determined by electrical methods the temperature was constant to 0·00023°. The influence of dissolved silicates appears to be very small. It is suggested that the triple point of water should be made the first point on the temperature scale in place of the ice-point, 0° being defined as 0·007° below the triple point of water.

M. S. BURR.

M.-p. curve of helium and Nernst's heat theorem. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 952—956).—A reply to van Laar (A., 1927, 718). The variations in pressure for 0·1° intervals of temperature have been determined for the m.-p. curve of helium between 1·2° and 3·0° Abs. On plotting d^2p/dT^2 against T a sharp maximum is obtained at 1·85° Abs. Neither this curve, however, nor the p–T curve suggests that there should be a minimum of pressure in the neighbourhood of 1° Abs. as required by van Laar (*loc. cit.*). If dp/dT for the m.-p. curve approaches zero at $T=0$, the entropies for the solid and liquid phases should be equal at $T=0$. This is in accordance with Nernst's heat theorem, and, even if there is a slight inclination of the p–T curve to the T-axis at $T=0$, this is not necessarily a serious contradiction of the theorem. According to van Laar's view dp/dT must become infinite at absolute zero. M. S. BURR.

M.-p. line of helium and Nernst's heat theorem. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 957).—A reply to Keesom (cf. preceding abstract). Only further experiments can give with certainty the course of the m.-p. line at temperatures below 1° Abs. and determine whether or not the conclusions derived from Nernst's heat theorem are correct. M. S. BURR.

Accurate determination of the specific heats of salt solutions up to 80°; results for potassium nitrate and chloride solutions. F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1928, 50, 1005—1016).—An improved, compact twin adiabatic calorimeter, modelled after that developed by Richards and Gucker (A., 1925, ii, 848), is described. An improved method of water standardisation is also recorded. The specific heats of the above solutions, containing 1 mol. of salt to 25 mols. of water, are sensibly constant at 20°, 50°, and 80°, and do not exhibit the increase that Zwicky's theory requires (A., 1926, 462, 668). S. K. TWEEDY.

Heat of formation of the compound HCl,HBr. C. DEL FRESNO (Z. anorg. Chem., 1928, 170, 222—

224).—Using a cycle similar to that employed by Born (A., 1920, ii, 156), the calculated heat of formation of the solid compound HCl,HBr (Klemenc and Kohl, this vol., 130) (assumed to have the constitution $H_2Cl^{\bullet},Br'$) from the liquid halides is 27·2 kg.-cal. Since the heat of formation corresponding with the constitution $H_2Br^{\bullet},Cl'$ is less than this, the first formula is probably the correct one.

R. CUTHILL.

Heats of dissolution and dilution of salts between infinite dilution and saturation. IV. Lithium bromide. E. LANGE and E. SCHWARTZ (Z. physikal. Chem., 1928, **133**, 129—150).—The heats of dissolution and dilution of lithium bromide in aqueous solution have been measured at 25° up to the saturation concentration, viz., 32·26 mols./100 mols. of water. The specific heats of the solution over the whole concentration range have been calculated, and the temperature coefficient of the heat of dissolution has been determined. The concentration–heat of dissolution curve of lithium bromide resembles closely that of lithium chloride, although the slope of the differential heat of dissolution curve for the former is smaller at low concentrations and greater at high concentrations than for the latter. The difference between the initial and total heat of dissolution is +9105 g.-cal./mol., and is, despite the smaller molar saturation concentration, greater than the corresponding figure for the chloride, viz., +8100 g.-cal./mol.

H. F. GILLBE.

Thermal investigation of some important metallurgical reactions in a calorimeter working at high temperatures. W. A. ROTH and P. CHALL (Z. Elektrochem., 1928, **34**, 185—199).—A calorimeter is described for use at high temperatures with an accuracy of 1%. For the study of reactions in which gases are evolved a specially designed adjunct is used. The following data are given: Specific heats: $HCl+24{\cdot}65H_2O$ at 50° 0·8860, at 22·5—50° 0·8822; $HF+4{\cdot}181H_2O$ at 50° 0·8719, at 20—50° 0·8653; Thüringer glass, 10—50° 0·1923; platinum, 13—50° 0·03225; white marble, 18—50° 0·1994; quartz, 12—50° 0·1844; silica (ignited), 18—50° 0·1816. Heat of vaporisation of water at 50°, −570 g.-cal./g. Heats of dissolution in $HCl+24{\cdot}65H_2O$ at 50°: CaO, +46,150 g.-cal.; $Ca(OH)_2$, +30,710 g.-cal.; $CaSiO_3$, +23,040 g.-cal.; MgO, +34,750 g.-cal.; $Mg(OH)_2$, +26,560 g.-cal.; Zn, +27,225 g.-cal.; ZnO, +12,470 to +12,545 g.-cal.; $Zn(OH)_2$, +10,115 g.-cal.; zinc spar, −4,470 g.-cal.; data for different forms of calcium carbonate are also given; in $HF+4{\cdot}181H_2O$ at 50° of quartz, +31,040 g.-cal.; sand, +31,415 g.-cal.; silica (precip.), +34,465 g.-cal.; silica with 33% of water, +34,490 g.-cal. Heats of formation at 50°: $CaO+SiO_2=CaSiO_3$ +19,660 g.-cal.; $CaO+CO_2$=calcite+42,470 g.-cal.; $CaO+CO_2$=aragonite+42,520 g.-cal.; $CaO+H_2O=Ca(OH)_2$+15,440 g.-cal.; $MgO+H_2O=Mg(OH)_2$+8,190 g.-cal.; $ZnO+H_2O=Zn(OH)_2$+2360 to +-440 g.-cal.; $ZnO+CO_2$=zinc spar+16,940 to +17,020 g.-cal.: $Zn+\frac{1}{2}O_2=ZnO$+82,825 to +82,905 g.-cal. Heat of transformation: calcite ⟶ aragonite at 50° = +48 g.-cal.: amorphous to crystalline silica, +3425 g.-cal.

H. INGLESON.

Molecular structure of liquids and solids. G. ANTONOV (Bull. Soc. chim., 1928, [iv], **43**, 163—177; cf. A., 1907, ii, 334; 1918, ii, 437; 1919, ii, 392; 1925, ii, 865; 1926, 671, 786; 1927, 304).—The author postulates that when two phases, neither of which is solid, are in equilibrium with each other, they contain the same number of molecules per unit volume. Two methods of demonstrating the truth of this postulate are described, the first of which is based on general considerations, whilst the second depends on the use of expressions already obtained by the author for surface tension and pressure normal to the surface of the liquid as functions of the number of molecules per unit volume. The physical properties of liquids are discontinuous functions of the temperatures. The law of rectilinear diameters is shown to be incorrect, the so-called rectilinear diameter being in reality a broken line. The terms "normal" and "abnormal" liquid are misnomers since all liquids are associated. It is highly probable that at the m. p. of a solid the same number of molecules are present per unit volume in the solid and liquid phases.

H. INGLESON.

Anisotropy induced in photochloride by the Weigert effect. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, **132**, 303—312).—Under the influence of linearly polarised light, sensitive silver chloride similar to that examined by Weigert (A., 1921, ii, 289), but without any binding material such as gelatin, becomes dichroic and doubly refracting. Many of the other photosensitive systems do not undergo this change, but sensitive films of cuprous bromide have been prepared. In the case of silver, it seems probable that the anisotropy arises from the elongated form of the colloidal particles of metal.

R. CUTHILL.

Influence of grain size on the dissociation pressure of solids. II. Lead carbonate. M. CENTNERSZWER and J. KRUSTINSONS (Z. physikal. Chem., 1928, **132**, 185—188; cf. this vol., 10).—Lead carbonate prepared by passing a rapid current of carbon dioxide through a neutral solution of lead acetate at the ordinary temperature has grains of an average diameter 30 μ, whilst carbonate formed by the action of a slow current of carbon dioxide at 40° on an acetate solution acidified with acetic acid has grains only 15 in diameter, yet both preparations give the same values for the dissociation pressure, p, at 255—270°. The corresponding values for p are lower, on the other hand, for the product obtained by the action of a rapid stream of gas on an acidified solution at 40°, the grains here being 7·5 μ in diameter. In either case, however, the relation between p and the temperature, T, is of the form $\log p=a/T+b\log T+c$, where a, b, and c are constants. From the data obtained, the surface tension at the interface solid–gas is calculated to be about 63,000 dynes/cm.

R. CUTHILL.

Thermal dissociation of cadmium nitrate. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 249—250).—Anhydrous cadmium nitrate melts with decomposition at 325° instead of at 360° as stated in the literature. The decomposition which takes place according to the equation $2Cd(NO_3)_2$ $2CdO+$

$4NO_2+O_2$ is reversible, and the equilibrium pressures for the temperature range 200—315° are recorded. From these results the heat absorbed in the decomposition is found to be 55,881 g.-cal.

O. J. Walker.

Rubrene. VII. Dissociation pressure of rubrene peroxide at the ordinary temperature. C. Moureu, C. Dufraisse, and L. Girard (Compt. rend., 1928, **186**, 1166—1168).—The oxidation of rubrene in solution by free oxygen under the influence of light is a reversible phenomenon; formation or dissociation of the peroxide takes place according to the pressure of the oxygen on the liquid surface. The dissociation pressure is about 0·5 cm. of mercury at 16°. An analogy with the peroxidation of hæmoglobin is indicated. J. Grant.

System sodium–tin. W. Hume-Rothery (J.C.S., 1928, 947—963).—The study of cooling curves and microscopical examination have confirmed the existence of the compounds reported by Mathewson (A., 1905, ii, 634), and have demonstrated the existence of others. The liquidus curve has maxima corresponding with the compounds Na_2Sn (m. p. 478°) and NaSn (m. p. 578°), the latter compound undergoing a polymorphic transformation at 483°. Breaks on the curve show the existence of Na_4Sn (m. p. 408°) and Na_4Sn_3 (m. p. 479°), the latter of which decomposes into NaSn and Na_2Sn below 357°. The *compound* Na_3Sn exists only in the solid state, and above 377° decomposes into Na_4Sn and Na_2Sn. *Compounds* $NaSn_3$, $NaSn_4$, and $NaSn_6$, in addition to the compound $NaSn_2$, are formed by peritectic reactions. In no case has the formation of solid solutions been observed. R. Cuthill.

Two kinds of martensite. K. Honda and S. Sekito (Nature, 1928, **121**, 744).—The mechanism of the formation of α- and β-martensite is considered. It is concluded that in the outer layer of a quenched steel, where the cooling is rapid, the change austenite ⟶ α-martensite (body-centred tetragonal) is partly arrested, and the change α-martensite ⟶ β-martensite (body-centred cubic) is completely hindered, so that this layer contains α-martensite with a little austenite. In the inner portion, where the cooling is less rapid, both changes take place almost completely, so that this portion contains almost pure β-martensite.

A. A. Eldridge.

Equilibrium in the binary systems ethylenediamine–phenols. N. A. Pushin and L. Sladovich (J.C.S., 1928, 837—843).—By thermal analysis of binary mixtures of ethylenediamine with phenols, the formation of *compounds* has been detected, the numbers of mols. of phenol combining with 1 mol. of diamine being as follows (the respective m. p. are shown in parentheses): phenol, 2 (53·5°) or 4; *o*-cresol, 2 (48°); *p*-cresol, 2 (54°) or 6 (31°); pyrocatechol, 1 (73°), 2 (71°), or 3 (69·2°); guaiacol, 1 (51·5°), 2 (57·5°), or 6 (66·5°). R. Cuthill.

Systems hydrogen chloride–ethyl ether, and hydrogen chloride–acetone. D. McIntosh (Bull. Chem. Soc. Japan, 1928, **3**, 82—86).—Repetition of previous experiments on the above systems (A., 1913, i, 584) has confirmed the results then obtained; the divergent results of Hirai (A., 1926, 908) are therefore to be rejected. R. Cuthill.

System beryllium oxide–silicon dioxide. F. Machatschki (Z. physikal. Chem., 1928, **133**, 253—262).—Comparison of the Debye–Scherrer diagrams given by mixtures of beryllium oxide and silicon dioxide in proportions corresponding with the ortho- and meta-silicates indicates the existence, at temperatures between 1000° and the m. p., of the orthosilicate phenacite. Both molten phenacite and molten mixtures of the two oxides yield when cooled rapidly crystalline beryllium oxide and a glass containing beryllium oxide; beryllium metasilicate cannot be obtained by this method, and is probably not stable in the crystalline condition.

H. F. Gillbe.

Equilibria between metals and salts in the molten state. VII. Tin, lead, stannous bromide, and lead bromide. VIII. Tin, lead, stannous chloride, and lead chloride. IX. Zinc, cadmium, zinc chloride, and cadmium chloride. R. Lorenz and G. Schulz (Z. anorg. Chem., 1928, **170**, 247—256, 320—323, 324—326; cf. A., 1927, 518).—VII. The equilibrium $Sn+PbBr_2 \rightleftharpoons SnBr_2+Pb$ in the molten state has been studied. Since the two metals and also the two salts are completely miscible, the system consists of three phases. At 400° and 600° the results agree satisfactorily with the requirements of the new mass law (A., 1924, ii, 761), but the classical expression yields values of the equilibrium constant which vary considerably. If bismuth is added to the metallic phase, the equilibrium is displaced somewhat, and there is a rather closer approximation to the requirements of the ideal mass law. Dilution of the salt phase with lithium bromide, on the other hand, has no appreciable effect on the equilibrium.

VIII. The equilibrium $Sn+PbCl_2 \rightleftharpoons SnCl_2+Pb$ has been investigated at 500° and 600°, using methods more precise than those formerly employed (A., 1926, 799); the results are substantially the same.

IX. The equilibrium $Zn+CdCl_2 \rightleftharpoons Cd+ZnCl_2$ has been examined at 600°; the results are in satisfactory agreement with the new mass law, but not with the ideal law. R. Cuthill.

Equilibrium in the reactions of tin with water vapour and carbon dioxide. E. D. Eastman and P. Robinson (J. Amer. Chem. Soc., 1928, **50**, 1106—1114).—The equilibria $Sn(l)+2H_2O(g)=SnO_2(s)+2H_2$ and $Sn(l)+2CO_2=SnO_2(s)+2CO$ were investigated at 650—800° by a special dynamic and by static methods. The constants for the former reaction do not agree with those of Wohler and Balz (A., 1921, ii, 633). The values for the equilibrium constant of the water-gas reaction calculated from the present results indicate that the directly determined values for this reaction are erroneous. S. K. Tweedy.

Equilibrium in the reduction of tungsten disulphide by hydrogen. N. Parravano and G. Malquori (Atti R. Accad. Lincei, 1928, [vi], **7**, 189—192).—The equilibrium $WS_2+2H_2 \rightleftharpoons W+2H_2S$ was investigated by the method employed for the analogous molybdenum reaction (this vol., 480). The values of p_{H_2S}/p_{H_2} were measured for the range 795—1065°.

According to these results the heat of formation of tungsten disulphide is 73,400 g.-cal. Tungsten sulphide is more readily reduced than molybdenum sulphide.

O. J. WALKER.

Equilibrium (polarisation) composition of the liquid salt phase and the liquid alloy phase in a system composed of equiatomic quantities of sodium, potassium, and iodine. H. F. SILL (J. Physical Chem., 1928, **32**, 466—470).—The equilibrium atomic ratios Na : K in the alloy obtained from the reactions at 700° between potassium iodide and sodium, and sodium iodide and potassium, are 11 : 1 and 9 : 1, respectively.

L. S. THEOBALD.

Effect of manganese content and speed of cooling on the separation of ferrite. R. ZOJA (Notiz. chim.-ind., 1927, **2**, 559—560; Chem. Zentr., 1928, i, 248).—With constant manganese content the amount of ferrite is not a linear function of the carbon content; the deviation increases with increasing manganese content. With constant manganese content the quantity of ferrite which separates falls with increasing speed of cooling, and with constant speed of cooling it falls with increasing manganese content. The effect of the speed of cooling is the greater the higher is the manganese content.

A. A. ELDRIDGE.

Reciprocal salt pair $MgSO_4$–$Na_2(NO_3)_2$–H_2O. I. A. BENRATH [with H. BENRATH W. BEU, J. CLERMONT, N. ILIEFF, S. KOJITSCH, H. PITZLER, and A. SCHLOEMER] (Z. anorg. Chem., 1928, **170**, 257—287).—The above salt pair and the systems magnesium sulphate–magnesium nitrate–water, magnesium nitrate–sodium nitrate–water, sodium nitrate–sodium sulphate–water, and sodium sulphate–magnesium sulphate–water have been investigated at 15°, 25°, 50°, and 97°, and equilibrium diagrams constructed.

R. CUTHILL.

Systematic doctrine of affinity. XLVI. Measurement of oscillation of chemical affinity in crystalline dicarboxylic acids. W. BILTZ and G. BALZ (Z. anorg. Chem., 1928, **170**, 342—346; cf. A., 1927, 1157).—From measurements of the dissociation pressures of crystalline ammonium salts of the dibasic fatty acids, the heats of dissociation of the acid and normal salts have been calculated. Both quantities oscillate on ascending the series, particularly near its beginning, the acids with an even number of carbon atoms giving the higher values. With the normal salts, the heat of dissociation of the first ammonia molecule is less than that of the second.

R. CUTHILL.

Salt-like hydrides. IV. J. KASARNOVSKI (Z. anorg. Chem., 1928, **170**, 311—319; cf. A., 1927, 718).—From data for the heats of formation of the hydrides of lithium and the alkaline-earth metals and the electrode potentials of the metals, the normal potential at 25° of the negative hydrogen ion has been calculated to be −2·38 volts, by taking the solubilities of the hydrides to be equal to those of the corresponding fluorides. This figure leads to a value of 91·5 kg.-cal. for the energy of hydration.

R. CUTHILL.

Conductivity of electrolytes. I. Experimental and theoretical study of principles of design of the Wheatstone bridge for use with alternating currents and an improved form of direct-reading alternating-current bridge. G. JONES and R. C. JOSEPHS (J. Amer. Chem. Soc., 1928, **50**, 1049—1092).—The conditions essential for precision conductivity measurements are investigated. The best current source is a valve oscillator; a suitable circuit, giving 16 different frequencies between 500 and 2400 cycles, is given. Earthing at the mid-point of the bridge is inadmissible; an earthing system is described which maintains the telephone, when in null position, at earth potential and eliminates the variations in bridge reading observed when the current leads are reversed. Exterior disturbances should be shielded at the source. The cells should have a high constant, and the thermostat liquid must be oil. The relationship usually assumed between the resistances of the four arms of a balanced bridge is valid only if the phase angle between the voltage and the current is the same in two pairs of adjacent arms. Means of ensuring this are described. The capacity of the cell is balanced by a variable condenser in parallel with the adjacent resistance arm. The resistance of commercial resistance boxes at the frequencies used is a function of the frequency in the higher ranges and is not identical with the direct current resistance. The design and erection of boxes in which these errors are absent are considered. A direct-reading bridge is described, sensitive to 1 in 10^6, which can be used with either direct or alternating current. The non-reactive ratio arms are readily adjusted to exact equality of resistance and the third resistance may be adjusted to 0·001 ohm.

S. K. TWEEDY.

Electrical conductance of nickel sulphate solution and ionic conductance of nickel. K. MURATA (Bull. Chem. Soc. Japan, 1928, **3**, 47—53).—The conductance of aqueous solutions of nickel sulphate (0·0001—1*M*) was measured at 18° and 25°, and the equivalent conductance at infinite dilution calculated. The ionic conductance of nickel was found to be 45·1 at 18° and 53·0 at 25°, using Noyes and Falk's values for the sulphate ion. For 0·05*M*-nickel sulphate at 18° and 25° the relative viscosities are 1·0209 and 1·0175, and the degree of ionisation 0·3883 and 0·3939.

C. J. SMITHELLS.

Conductivity and catalytic action of trinitro-*m*-cresol in solution in ethyl alcohol. H. GOLDSCHMIDT, E. MARUM, and L. THOMAS (Z. physikal. Chem., 1928, **132**, 257—272; cf. A., 1927, 1143).—The conductivity of a solution of the sodium salt of 2 : 4 : 6-trinitro-*m*-cresol in aqueous ethyl alcohol is greater than that of a solution of the same concentration in absolute alcohol by an amount which increases with increase in the relative amount of water. Slight alcoholysis occurs with the aniline salt, but when this is repressed by addition of aniline the behaviour is closely similar to that of the sodium salt. From conductivity determinations with trinitrocresol in aqueous and absolute alcohol, the degrees of dissociation and affinity constants, K_0, have been calculated with the aid of Bjerrum's theory. The ratio of the values of K_0 for trinitrocresol and picric acid in solutions in which the proportion of alcohol to water is the same does not vary much with change in the relative amount of water present. Measurements

have also been made of the rate of esterification of acetic, phenylacetic, butyric, and *iso*valeric acids in aqueous and absolute alcohol in presence of trinitrocresol as catalyst. As the quotient of the velocity coefficient at zero time, k_0, by the hydrogen-ion concentration due to the catalyst has greater values than when picric acid is the catalyst, and also falls with decreasing concentration of catalyst, it appears that the catalytic action of an acid is not solely determined by the concentration of hydrogen ions or hydrogen-ion complexes. The depressing action of water on k_0 is greatest for phenylacetic and acetic acids, and least for *iso*valeric acid. R. CUTHILL.

Dispersion of conductivity and dielectric constant for strong electrolytes. P. DEBYE and H. FALKENHAGEN (Physikal. Z., 1928, **29**, 121—132).—A relaxation time exists for ionic movements in strong electrolytes, and this quantity is important for the dispersion of conductivity and dielectric constant. The conception of a relaxation time follows from the dissymmetry of the density of charge in an ionic atmosphere, and it can be shown that a " braking " force must operate with increasing effect as the velocity of an ion increases. The consequences of dissymmetrical ionic atmospheres and variable frequencies have been worked out theoretically, but the results are as yet only qualitative, because the forces tending to retard ionic movement include a cataphoretic action (brought about by a moving ion in a solvent containing ion). This latter effect will be worked out separately.

For very small frequencies the forces on the moving ion and the Stokes frictional force are in phase, but for very high frequencies this no longer holds. The absolute value of the force on the ion steadily decreases with increasing frequency until it becomes zero with very high frequencies. The " braking " force is now composed solely of the Stokes force, so that the molecular conductivity of strong electrolytes with increasing frequency approaches the value for infinite dilution, if the cataphoretic effect is neglected. The theory is applied to the numerical data for potassium chloride. R. A. MORTON.

Electrode potential of nickel. I. Measurements in an atmosphere of hydrogen with reduced nickel powder. K. MURATA (Bull. Chem. Soc. Japan, 1928, **3**, 57—69).—The potential of an electrode of powdered nickel in 0·05 and 0·005*M*-nickel sulphate solutions has been measured. By maintaining an atmosphere of hydrogen within the electrode vessel, and taking precautions to ensure the rigid exclusion of oxygen from the solution and electrode, definite and reproducible results were obtained. Calculating the ionic concentrations from the conductivity ratio, the electrode potential, in volts, for molar ionic concentration is —0·2508 at 18°, and —0·2496 at 25°. Using activities instead of concentrations, the corresponding values are —0·2492 and —0·2480, respectively. From these figures, the change in free energy involved in the reaction $Ni^{\cdot\cdot}+2\ominus=Ni$ has been computed. R. CUTHILL.

Calomel and silver chloride electrodes in acid and neutral solutions. Activity coefficient of aqueous hydrochloric acid and the single potential of the 0·1*M*-calomel electrode. M. RANDALL and (MISS) L. E. YOUNG (J. Amer. Chem. Soc., 1928, **50**, 989—1004).—The irregular, high potentials previously recorded for the calomel electrode with 0·1*M*-hydrochloric acid are due to the presence of air (cf. Güntelberg, A., 1926, 1207); the true value is 0·3976 volt. It is predicted that hydrochloric acid below 11·62*M* will not react with mercury in absence of oxygen. From a detailed consideration of all previous f.-p., vapour-pressure, and *E.M.F.* measurements, the most probable activity coefficients of hydrochloric acid are tabulated for 1·2—16*M*-solutions at 25°, as well as the water activity in the solutions. From these results new values for standard electrode potentials are derived. The free energies of formation of HCl from the gaseous elements are: HCl (*aq.*), —31345 g.-cal., HCl (*g.*), —22741 g.-cal. The 0·1*M*-calomel electrode has a potential at 25° of —0·3341 volt in vacuum, and about —0·3354 volt in air. The conditions for the preparation of reproducible Ag|AgCl electrodes are investigated. S. K. TWEEDY.

Physical interpretation of electrolytic solution potentials. A. VON HIPPEL (Z. Physik, 1927, **45**, 471—475).—The latent heat absorbed during the electrolytic transfer of 1 mol. of a metal from anode to cathode by a *N*-solution is shown to be the difference between the work associated with the chemical changes and the electrical energy. The former is equal to the difference between the difference of the heats of hydration of cations and anions and the corresponding difference of the work of removal of the positive ions. R. W. LUNT.

Potentials of manganese dioxides in electrolytes of various hydrogen-ion concentrations. T. J. MARTIN and A. J. HELFRECHT (Amer. Electrochem. Soc., April, 1928, **53**; advance copy, 4 pp.).—Solutions of p_H value ranging from 1·2 to 7·9 were prepared by adding hydrochloric acid or ammonia to a 20% ammonium chloride solution (p_H 5·48), and the potentials of dry-cell electrodes, prepared from graphite and seven different samples of manganese dioxide, were measured in these various solutions. The potential of a given electrode is nearly independent of the p_H value of the solution over the range 2—7, but rapidly becomes more positive or more negative at lower or higher p_H values, respectively. In the solution of p_H 5·48 the electrodes prepared from samples of pyrolusite exhibited potentials ranging from 0·33 to 0·42 volt more positive than the saturated calomel electrode, but the one electrode prepared from artificial manganese dioxide gave the value 0·56 volt. H. J. T. ELLINGHAM.

Electrolytic capacitance of platinum–sulphuric acid cells. W. M. PIERCE (Physical Rev., 1928, [ii], **31**, 470—475).—By recording the relation between current and time when a small, constant potential is impressed on the circuit containing the cell, it is found that the capacitance is not a function of the time constant. An empirical expression connects the capacitance with the frequency of the current flowing through it. A. A. ELDRIDGE.

Maxima on current–voltage curves. I. N. V. EMELIANOVA and J. HEYROVSKI. **II.** P. HERASY-

MENKO (Trans. Faraday Soc., 1928, **24**, 257—267, 267—272).—See this vol., 371, 372.

Overvoltage of alloys. M. G. RAEDER and J. BRUN (Z. physikal. Chem., 1928, **133**, 15—30).—From an examination of the current density–potential curves, the hydrogen overvoltage at alloy cathodes has been studied, with the object of determining the relative displacements which occur when the percentage composition of the alloy is changed, and particularly when new structural elements are formed as a result of the change in composition. The following systems were investigated: copper–nickel (homogeneous mixed crystals); silver–lead (simple eutectic system); lead–antimony and bismuth–tin (eutectic systems with incomplete mixed-crystal formation); silver–antimony (compound-forming system). In many cases, the course of the overvoltage differs from that previously assumed. In the mixed-crystal systems, the overvoltage may lie between the values for the pure components, but in some cases a pronounced rise occurs above the normal values for the components. The overvoltage of eutectic systems is not determined by the component of lowest overvoltage, but lies between the values for the components. The results for the lead–silver system are so unexpected that it is suggested that the structure of the system may be different from that usually accepted. The curves obtained for the system lead–antimony appear to confirm tho existence of the compound Pb_4Sb (cf. Dean, Hudson, and Fogler, B., 1926, 93). In the compound-forming system silver–antimony, the overvoltage of the compound is practically identical with that of the component of highest overvoltage (antimony). The further course of the curve is irregular, and suggests that the structure of the alloy in this region is not fully understood.

L. L. BIRCUMSHAW.

Electrolytic decomposition of glass. P. SELENYI (Ann. Physik, 1928, [iv], **85**, 643—644; cf. A., 1927, 1145).—In the electrolytic decomposition of glass, using a discharge tube with two copper electrodes, the whole being immersed in molten potassium nitrate, oxygen is liberated within the tube and is absorbed by the copper. The electrolysis proceeds quantitatively.

R. A. MORTON.

Electro-reduction of uranyl salts by means of the mercury dropping cathode. P. HERASYMENKO (Trans. Faraday Soc., 1928, **24**, 272—279).—See this vol., 372.

Becquerel effect. G. ATHANASIU (Z. physikal. Chem., 1928, **133**, 39—42).—A reply to the criticism of Lifschitz and Hooghoudt (A., 1927, 942) of the author's theoretical interpretation of Svensson's experimental results (cf. A., 1925, ii, 1067). It is stated that the author does not in general dispute Svensson's results, but emphasises the fact that the negative *E.M.F.* is not observed in the absence of polarisable electrodes.

L. L. BIRCUMSHAW.

[Becquerel effect.] J. LIFSCHITZ and S. B. HOOGHOUDT (Z. physikal. Chem., 1928, **133**, 43—44).—A reply to Athanasiu (cf. preceding abstract). It had been already observed by Schmidt (Ann. Phys. Chem., 1899, **67**, 563) that the Becquerel effect is not exhibited at reversible electrodes. Athanasiu's view that the negative effect at the beginning of the exposure has its origin in the electrode is strongly opposed.

L. L. BIRCUMSHAW.

Kinetics of the dissociation of diatomic molecules. J. FRENKEL and N. SEMENOFF (Z. Physik, 1928, **48**, 216—230).—The mechanism of the activation and deactivation of molecules and atoms is considered, and the relative part played by collisions and heat radiation is worked out on the basis of the "principle of detailed balancing." The several reactions which can take place when dissociation occurs through activation are considered, and by making use of the above principle, the relation between the velocity coefficients of the opposing reactions is obtained. The initial velocity of the whole reaction is calculated. The kinetics of the reaction without activation are then considered, as well as catalytic adsorption reactions, and the initial velocities are compared with each other and with that calculated for the reaction with activation.

A. J. MEE.

Autoxidation during slow combustion. E. W. J. MARDLES (J.C.S., 1928, 872—885; cf. B., 1926, 617).—Two experimental methods were employed. In the first the products of reaction of fuel–air mixtures passing through a suitably heated tube could be identified; in the second the mixtures were heated in a closed bulb to observe the rate of reaction as the temperature was slowly raised. Evidence was obtained of the formation of unstable peroxides of the fuels. Benzene and aniline are oxidised when added to hexane–air mixtures at temperatures below those at which they can be oxidised in the absence of the fuel. These effects are not due to the presence of hydrogen peroxide, since this substance when added to the fuel–air mixture exerts an effect similar to that shown by water. The hydrogen peroxide produced during combustion is a decomposition product of the very active unstable peroxides previously formed. Detonation in an engine using liquid fuel is due to the formation of organic peroxides which become concentrated in the nuclear drops during compression and ignite them when the temperature of detonation of the peroxide is reached. Detonation inducers, *e.g.*, nitrogen peroxide or amyl nitrite, lower the temperaature of spontaneous ignition, whilst organo-metallic compounds such as iron carbonyl and lead tetraethyl have the opposite effect. The last compound owes its effect to the formation of metallic lead by thermal decomposition.

H. INGLESON.

Burning of carbon disulphide. II. Velocity of uniform movement of flame in carbon disulphide–second combustible–air mixtures. A. G. WHITE (J.C.S., 1928, 751—763; cf. *ibid.*, 1922, **121**, 2561; A., 1927, 115, 317, 524).—It has been previously shown that the burning of carbon disulphide near the limits for the propagation of flame is markedly hindered by the presence of other combustibles and that the limit combustion is probably catalysed by one of the products of its combustion. This behaviour is now observed over the whole range of inflammability. The mixtures containing about 1% of water vapour were fired in a long, horizontal tube closed at one end, measurements of flame velocity

being made photographically. The maximum flame speed (123 cm./sec. in a tube of 2·5 cm. diam.) is given by a mixture containing 8 vol.-% of carbon disulphide. The flame speed can be varied as much as 500% by alteration in the means of ignition, more powerful ignition increasing it. Flame speeds in dilute carbon disulphide–air mixtures are far more sensitive to oxygen content than in similar mixtures of normal combustibles, *e.g.*, methane. The law of flame speeds of Payman and Wheeler (A., 1926, 689) breaks down for light petroleum–carbon disulphide–air mixtures, as values calculated from it are often more than 100% higher than the experimental ones. The reason for the failure of the law is probably that one combustible interferes with the burning of the other. H. INGLESON.

Velocity coefficient for bimolecular reactions in solution. L. S. KASSEL (Nature, 1928, **121**, 746—747).—Two factors, other than those mentioned by Norrish and Smith (this vol., 249), would lead to small and variable values of the probability coefficient P: the solvation and the complexity of the reactant molecules. A. A. ELDRIDGE.

Thermal decomposition of hydrogen peroxide in aqueous solutions. B. H. WILLIAMS (Trans. Faraday Soc., 1928, **24**, 245—255; cf. Rice and Reiff, A., 1927, 1035).—The decomposition is due to adsorption of molecules of hydrogen peroxide on the walls of reaction vessels and on dust present in solution. Glass that has been treated with cleaning agents possesses an activity comparable with that of dust. Preformed active points are present in silica vessels, and, with glass, active points in addition to those already present are formed by the action of the peroxide. An upper limit to the magnitude of the decomposition due to adsorption on the surface of the dust present has been determined by using a wax vessel. The decomposition in glass vessels is, for its first portion, a zero order reaction, which becomes unimolecular as the concentration of hydrogen peroxide in the bulk of the solution decreases. This can be explained from considerations of the relative rates of decomposition of molecules of hydrogen peroxide on the surface and that of their replacement. The decomposition of hydrogen peroxide in silica vessels follows a similar course except with high concentrations of hydrogen peroxide, when secondary effects probably come into action. L. F. GILBERT.

Oxidation of stannous hydroxide in sodium carbonate solution by means of air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 43—47).—The oxidation velocity of stannous hydroxide suspended in sodium carbonate solution is independent of the quantity of stannous hydroxide. Oxidation must therefore take place in solution and not in the solid phase. The effect of temperature and concentration of sodium carbonate on the reaction velocity is small. Sodium stannite is oxidised rapidly, whilst stannous hydroxide is oxidised very slowly by means of air. C. J. SMITHELLS.

Oxidation of sodium sulphite in sodium carbonate solution with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 76—82; cf. A., 1927, 525).—The rate of oxidation when a current of air is passed through a mixed solution of sodium sulphite and sodium carbonate at 20° is independent of the sulphite concentration, but decreases with increase in the carbonate concentration, the relation between the velocity coefficient and the carbonate concentration, when this exceeds about 0·02N, being approximately linear. It therefore appears that the velocity measured corresponds with the rate of dissolution of oxygen in the sodium carbonate solution. Raising the temperature to 30° or 40° has little effect. R. CUTHILL.

Hydrolysis of sucrose by hydrochloric acid in presence of alkali and alkaline-earth chlorides. C. F. KAUTZ and A. L. ROBINSON (J. Amer. Chem. Soc., 1928, **50**, 1022—1030).—The rate of inversion of sucrose at 25° in presence of 0·1N-hydrochloric acid and of chlorides of potassium, sodium, lithium, calcium, strontium, and barium at concentrations between 0·05 and 3N is investigated. The activity of the hydrogen ion is probably the most important factor in determining the rate of inversion, although there is no simple relationship between the increased inversion rate and the activity coefficients of the hydrogen ion in solutions of the same acid and salt concentration containing no sucrose. For salt concentrations above 0·5M the equation of Schmid and Olsen (A., 1927, 21), $\log K = \log K_0 + rc$, where K_0 and r are constants, applies fairly well. The equation may be derived with the aid of the Debye–Huckel interionic attraction theory in the form $\log f_{H^\cdot} - \log f_{H^\cdot_0} = B\mu_s + (a\sqrt{\mu_0})/(I+A\sqrt{\mu_0})$, where the symbols have their usual meanings. S. K. TWEEDY.

Mechanism of the hydrolysis of cellulose esters of the higher fatty acids. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 21—41).—An investigation has been made of the rate of hydrolysis of the cellulose esters of the higher fatty acids with alcoholic alkali. The reaction is bimolecular and may be represented, for the monoester, as follows: $R\cdot CO_2\cdot C_6H_9O_4 + KOH = R\cdot CO_2K + C_6H_{10}O_5$, or, for the polymerised ester or the di- and tri-esters, the ester must decompose in successive stages. Since the reaction is heterogeneous, the surface of contact of the ester must be proportional to the concentration. By shaking, the rate of hydrolysis was increased by 50%. The influence of temperature between 0° and 38° may be expressed by Arrhenius' equation $\log k = -A/T + C$. Dilution of the alcoholic alkali with water reduces the velocity coefficient to a remarkable extent, and the effect may be represented by the following equation: $\log k = mC + n$, where C is the concentration of alcohol. A neutral salt also diminishes the velocity, but its influence is not important. M. S. BURR.

Hydrolysis of cellulose acetate by alkali. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 42—53).—The rate of hydrolysis of cellulose acetate by aqueous alkali, to the extent of 50%, is in accordance with a unimolecular reaction. After this point the rate suddenly diminishes. If, however, the mixture is shaken, the unimolecular formula is valid until 90% has been hydrolysed, and the velocity, therefore, appears to be independent of the area of

the surface of contact. In alcoholic alkali of different concentrations, without shaking, the hydrolysis proceeds very rapidly for a short time and then the rate diminishes to a marked extent. When shaken with alkali of a rather high alcohol content the reaction is bimolecular, being proportional to the concentrations of alkali and ester. Since cellulose acetate of different origin has, under the same conditions, different rates of hydrolysis, this may be used as a test of the quality of the ester. M. S. BURR.

Hydrolysis of cellulose acetate during hydration. I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 54—61).—During the production of acetone-soluble cellulose acetate by hydration of the acetone-insoluble primary cellulose triacetate with acetic acid, water, and sulphuric acid, hydrolysis takes place. The mechanism of the reaction appears to be the same as for the hydrolysis by alkali. If the quantity of water is regarded as unchanged, the hydrolysis velocities of the tri-, di-, and mono-acetates may be expressed by the following equations, respectively: $dx_1/dt=3k(b-x_1)$; $dx_2/dt=2k(x_1-x_2)$; and $dx_3/dt=k(x_2-x_3)$, where b is the initial concentration of the triacetate and x_1, x_2, and x_3 are the quantities of tri-, di-, and mono-ester transformed after the time t. The concentrations of the different constituents after the time t are, $C_{\mathrm{Tri}}=be^{-3kt}$; $C_{\mathrm{Di}}=3b(1-e^{-kt})e^{-2kt}$; $C_{\mathrm{Mono}}=3b(1-e^{-kt})^2e^{-kt}$; and $C_{\mathrm{Cellulose}}=b(1-e^{-kt})^3$. The values calculated on the basis of these equations, and on the assumption that the mono-ester and the regenerated cellulose are acetone-insoluble, agree with the experimental results of Hess and others (A., 1925, i, 1245). M. S. BURR.

Chemical dynamics in a rigidly coherent plane. D. H. BANGHAM (Phil. Mag., 1928, [vii], 5, 737—749).—Equations of the form $S=\text{constant}\times t^{1/m}$ shown by Bangham and Burt (A., 1924, ii, 392) to represent the rate of sorption of gases on glass surfaces are of wide application to the variation with time of processes involving the disturbance of the inner equilibrium of solids provided that the solid after disturbance remains rigidly coherent. It is assumed that the condition for rearrangement is the momentary occupation, by the groups of atoms, of a volume considerably greater than the average, and calculations are made of the mode of variation, during the progress of the reaction, of the force restraining their thermal movements. An extension of Hooke's law to the conditions in the interior of a solid requires that the intensity of the stress set up by the partial occurrence of a reaction should be equal to the difference between the hydrostatic pressures with which the initial and actual states of the solid would be in equilibrium. It then follows that the index m (above) is the ratio of the difference of volume between the activated and final states of the atomic groups to the difference between their initial and final volumes. These ideas offer an explanation of the dependence of the activity of a sorbent on its past history. The sorbed molecules are regarded as distending the rigidly coherent structure of the sorbent, which thus becomes stressed. Such a distension may occur even if the structure is sufficiently open to allow easy penetration of the free gas molecules. A. E. MITCHELL.

Influence of pressure on reaction velocity and the function of the medium. A. L. T. MOESVELD and (MISS) W. A. T. DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 1039—1053).—Theoretical. The condition of substances in mixed media is considered; *e.g.*, dissolution of bornyl acetate in mixtures of alcohol and water may be expected to result in a non-homogeneous distribution of the components of the solvent, since alcohol will be attracted to the bornyl half of the molecule and water to the acid portion. The resultant force will cause a deformation of the ester molecule and have an influence on its reactivity. It may also be shown that the deformation should be greatest when there is only just sufficient of the better solvent present to keep the solute in solution. On account of the presence of associated molecules in pure solvent, similar if smaller effects may also be produced by the latter. When the external pressure is increased the molecules approach one another more closely, and all the effects depending on mutual forces are increased. This is borne out by experiment, and the pressure coefficient is greatest when the original effect may be expected to be greatest. The pressure coefficient also increases with pressure. It is shown, further, that rise of temperature, because of increased solubility in the medium, should cause a diminution in the pressure coefficient which can be compensated by increase in the concentration of soluble reactant or by the addition of another substance which so influences the medium that the reactant again approaches its critical solubility. These predictions have been verified experimentally for the hydrolysis of bornyl acetate by sodium hydroxide in 30% alcohol. The views put forward are independent of the mechanism of the activation process considered. M. S. BURR.

Relationship between velocity of hydrolysis by alkali and structure of esters. H. OLSSON (Z. physikal. Chem., 1928, 133, 233—252).—A number of esters have been prepared in a pure state and their rates of hydrolysis in presence of alkali measured. The velocity coefficients of the hydrolysis of some eighty-five typical esters, given in the literature, have been reduced to the same units and the results compared from the same point of view of structure. The velocity coefficient is mainly influenced by the strength of the acid component of the ester, but in other cases steric hindrance influences the velocity in the opposite sense. It may be that these two influences are manifestations of one fundamental property, viz., the force of dissociation of the separate components.
H. F. GILLBE.

Corrosion of iron and its anodic polarisation. H. J. DONKER and R. A. DENGG (Korrosion u. Metallschutz, 1927, 3, 217—222; Chem. Zentr., 1928, i, 251).—In dilute alkaline solutions (containing chloride), the surface of iron is uniformly attacked, but in more concentrated solutions point-corrosion predominates. Alkali hydroxide is more protective than carbonate. Sulphate solutions attack iron less than chloride solutions. Iron is not markedly attacked by neutral solutions containing dichromate, or dichromate and chloride, but it is vigorously attacked if the solution is not neutralised. A. A. ELDRIDGE.

Passivity of metals. E. S. HEDGES (J.C.S., 1928, 969—978; cf. A., 1926, 581; 1927, 25).—The lowest concentration of nitric acid which can passivate iron at 30° was repeatedly found to be 86 vol.-% of the acid *d* 1·42. To obtain reproducible results, it is necessary to pass the metal rapidly through the surface of the acid. Iron previously rendered passive by nitric acid becomes active when whirled at 3000 r.p.m. after a short induction period representing the time for removal of the film of oxide which causes the passivity. These facts are not explained on Smits' theory. When passive iron is heated in concentrated nitric acid, it dissolves at 74·5—75·5° independently of the concentration of the acid. Freshly ignited ferric oxide does not dissolve appreciably until this temperature is reached. This temperature does not correspond with an allotropic change in the iron. At −11° copper becomes passive in concentrated nitric acid, being covered by a visible film of oxide. Passivity produced by anodic polarisation and by chemical means is the same phenomenon and is the result of the formation of a film of oxidised material. A theory of anodic polarisation is advanced.

H. INGLESON.

Practical problems of corrosion. III. Formation of rust and its consequences. IV. Corrosion of wrought iron in relation to that of steel. V. Corrosion and protection at the contacts of dissimilar metals. U. R. EVANS.—See B., 1928, 300.

Action of hydrochloric acid on extra-pure aluminium. J. CALVET.—See B., 1928, 302.

Corrosion of aluminium. W. GUERTLER.—See B., 1928, 302.

[Catalytic] synthesis of methyl alcohol from carbon monoxide and hydrogen. W. K. LEWIS and P. K. FROLICH.—See B., 1928, 359.

Induction of reaction between chromic acid and a manganous salt by arsenious acid. R. LANG and J. ZWEŘINA (Z. anorg. Chem., 1928, 170, 389—396).—Reaction may be induced in a mixed solution of a chromate and a manganous salt in a 0·5—1*N*-solution of sulphuric or hydrochloric acid by addition of arsenite (cf. this vol., 605), the manganous salt being oxidised to the manganic state, and the chromate reduced by the arsenite. The chromic acid is thus the actor, and the manganous salt the acceptor. At the start, the induction factor has the value 0·5, independent of the concentration of the acceptor, which is most readily accounted for by supposing the main stages in the reaction to be $Cr^{VI}+As^{III}=Cr^{IV}+As^{V}$, and $Cr^{IV}+Mn^{II}=Cr^{III}+Mn^{III}$. As the reaction proceeds, the value of the induction factor falls, owing to reaction of the arsenious acid with manganic salt; this reaction may be catalytically accelerated by addition of iodine. R. CUTHILL.

Catalytic action of mineral waters. F. C. GAISSER (Z. angew. Chem., 1928, 41, 401—407).—The benzidine reaction has been investigated for a number of naturally occurring waters. Those showing a positive reaction invariably contain ferrous and/or manganous ions, but the converse does not hold. Further, waters containing iron and manganese are the most active catalysts of the decomposition of hydrogen peroxide. The explanation of these relationships, however, remains obscure. Experiments have also been made on the catalytic activity of the waters during the hydrolysis of starch.

H. F. GILLBE.

Preparation of a catalyst by the electrolytic corrosion of nickel. S. IKI (Ind. Eng. Chem., 1928, 20, 472—473).—See this vol., 377.

Catalytic action of platinum and the law of mass action. B. BATSCHA (Z. physikal. chem. Unterr., 1927, 40, 258—261; Chem. Zentr., 1928, i, 285).—Lecture experiments are described.

A. A. ELDRIDGE.

Platinic oxide catalyst for reductions. R. ADAMS, V. VOORHEES, and R. L. SHRINER (Org. Syntheses, 1928, 8, 92—99).—Chloroplatinic acid is fused with sodium nitrate at 500—550°, the platinic oxide formed being washed with water until practically free from nitrates. The material can be re-activated by shaking with air or oxygen, but repeated re-preparation appears to result in an accumulation of poison, and to necessitate purification. A. A. ELDRIDGE.

Catalytic synthesis of ammonia. H. VALENTIN (Z. physikal. chem. Unterr., 1927, 40, 271—272; Chem. Zentr., 1928, i, 285).—In Florke's demonstration method (*ibid.*, 1926, 39, 283) the formation of water is observed even when dry nitrogen and ammonia are used; hence the ammonia is apparently formed from combined nitrogen and hydrogen.

A. A. ELDRIDGE.

Catalytic reduction of nitro-organic compounds in the liquid system. O. W. BROWN, G. ETZEL, and C. O. HENKE (J. Physical Chem., 1928, 32, 631—635).—The catalytic reduction of nitrobenzene, 1-nitronaphthalene, *p*-nitrotoluene, *o*-nitrophenol, *p*-nitrophenol, and dinitrotoluene in the liquid phase by hydrogen under pressure with nickel as catalyst has been studied. Quantitative reduction to the amine was obtained at 215° for the first three cases and at 226° for the last and at a pressure of 500 lb./in.^{2} 0·52 g. of catalyst was required per g. of nitro-compound reduced. With nitrobenzene dissolved in benzene, the yield of amine increased with an increase in pressure up to 500 lb./in.^{2}, and reduction was then quantitative with or without the solvents benzene and absolute alcohol. With 1-nitronaphthalene (cf. Parrett and Lowy, A., 1926, 512), benzene was a better solvent than ethyl alcohol or ethylene glycol.

L. S. THEOBALD.

Catalytic reduction of nitrobenzene to aniline in the gaseous phase. G. B. SEMERIA and M. MILONE.—See B., 1928, 327.

First report of the committee on photochemistry. Division of Chemistry and Chemical Technology, National Research Council. H. S. TAYLOR (J. Physical Chem., 1928, 32, 481).—Introductory to the following abstracts. L. S. THEOBALD.

Experimental technique for quantitative study of photochemical reactions. G. S. FORBES (J. Physical Chem., 1928, 32, 482—502).—A selective summary in which light sources, the quantitative measurement of radiation intensity, light filters,

monochromators, analytical methods, and reaction vessels are the chief topics of discussion.

L. S. THEOBALD.

Excited systems formed by the absorption of light. L. A. TURNER (J. Physical Chem., 1928, **32**, 507—515).—The possible stages in the processes of the absorption of light by atoms and molecules, and the properties of the resultant excited systems are discussed in relation to their bearing on photochemical reactions. L. S. THEOBALD.

Quantum processes in photochemistry. H. S. TAYLOR (J. Physical Chem., 1928, **32**, 516—528; cf. following abstract).—Photochemical processes are discussed in the light of the quantum theory with especial consideration of depolarisers, the systems hydrogen–halogen, photosensitised processes, inhibition, and more complex processes such as the oxidation of quinine and the reduction of Fehling's solution. The quantum theory gives a clearer and more comprehensive view of photochemical processes than does an analogy between these and electrochemical processes. Experimental work has not widely confirmed the idea of equivalence suggested by Einstein's law, and it is now preferable to distinguish the Grotthus–Draper absorption law as the first law of photochemistry, and the second as " The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption."

L. S. THEOBALD.

Displacement of equilibrium by light. W. D. BANCROFT (J. Physical Chem., 1928, **32**, 529—572; cf. preceding abstract).—A review of photochemical processes on the theory of the displacement of equilibrium by light. When confined to reversible equilibrium, the theory provides the simplest interpretation of the facts. Conditions must be such that the rate of photochemical change shall be greater than the sum of the rates of the reversible reaction in the dark and in the light. The functions of depolarisers and optical sensitisers are emphasised.

L. S. THEOBALD.

Relation between photochemical and ionisation reactions. S. C. LIND (J. Physical Chem., 1928, **32**, 573—575).—Certain photochemical and ionisation reaction mechanisms with their similarities and differences are discussed, but further experimental examination, under identical conditions, is necessary to establish a relation between the respective yields.

L. S. THEOBALD

Photochemistry of chlorine. G. KORNFELD (Z. physikal. Chem., 1928, **132**, 460—461).—Cf. this vol., 253). H. F. GILLBE.

Reaction mechanism of photochemical decomposition of hydrogen iodide. K. F. BONHOEFFER and L. FARKAS (Z. physikal. Chem., 1928, **132**, 235—236).—If the first stage in the photochemical decomposition of hydrogen iodide were a molecular excitation, it would be expected that at low pressures fluorescence instead of chemical reaction would occur. Not only is this not the case, however, but the law of equivalence is valid down to low pressures. Consequently, it must be assumed that the first stage in the process is a direct dissociation of the molecule into atoms, $HI=H+I$. This view finds confirmation in the observation that when the iodide is exposed to light there is a fall in pressure which can be attributed only to adsorption of free atoms on the walls of the containing vessel. The same experiments also indicate that the iodine molecules formed impede the reaction. Adsorption of free atoms also occurs when hydrogen bromide or iodine vapour is illuminated. Under the influence of light, it appears that hydrogen atoms may become detached from the surface of solid hydrogen iodide. R. CUTHILL.

[Decomposition of nitrogen oxides.] I. Effect of radiation on the decomposition of ozone and nitrous oxide. II. Low-pressure decomposition of nitrogen pentoxide and nitrous oxide. J. H. HIBBEN (J. Amer. Chem. Soc., 1928, **50**, 937—940, 940—950).—I. The homogeneous decomposition of nitrous oxide at 610° and the heterogeneous decomposition of ozone at 0° are uninfluenced by infra-red radiation. Molecular activation is probably not caused through the absorption of single or multiple frequencies.

II. The observed decomposition velocity of nitrous oxide at very low pressures is 1000 times as great as that calculated with the aid of Hinshelwood and Burk's equation (A., 1924, ii, 751). The reaction changes from bimolecular to unimolecular, and probably is entirely heterogeneous at very low pressures (0·01 mm.). The velocity coefficients for the decomposition of nitrogen pentoxide between 0·186 and 0·0018 mm. are in agreement with the values found at higher pressures by Daniels and Johnston (A., 1921, ii, 249), and are practically independent of pressure (cf. Hirst and Rideal, A., 1926, 32). There is no evidence of initial transition between unimolecular and bimolecular reactions as required by Lindemann's theory. The assumption of 30 degrees of freedom in the molecule will not account for the observed activation rate. S. K. TWEEDY.

Photochemical clustering. B. LEWIS (Nature, 1928, **121**, 792).—Macdonald's views of the mechanism of the photochemical decomposition of nitrous oxide (this vol., 254, and private communication) are discussed; the agreement between the value for $M/h\nu$ and that for M/N in the α-ray reaction (Lind, above) suggests clustering, but a general theory of photochemical clustering is not proposed. The view is, however, more acceptable for reactions involving association or polymerisation.

A. A. ELDRIDGE.

Decomposition of azoimide in ultra-violet light. K. SLEU (Ber., 1928, **61**, [*B*], 702—707).—Exposure of solutions of azoimide acidified with sulphuric acid to ultra-violet light results in rapid evolution of almost pure nitrogen and formation of hydroxylamine accompanied by a very small proportion of ammonia which is not derived by secondary photolysis of hydroxylamine; the course of the change is largely independent of the concentration of the sulphuric acid. It is suggested that the reactions involved are: $HN_3=NH+N_2$ and $NH+H_2O=NH_2{\cdot}OH$. Support for this hypothesis is found in the observation that in hydrochloric acid solution the

process of reaction is considerably affected by the concentration of mineral acid. Increase in the latter favours the production of ammonia to a remarkable extent and the change induced in the ratio N : H suggests the simultaneous formation of nitrous oxide. The reaction is represented : $N_3H=NH+N_2$; $NH+HCl=NH_2Cl$; $NH_2Cl+2HCl=NH_4Cl+Cl_2$. Production of nitrous oxide is ascribed to slow oxidation of hydroxylamine by chlorine. If aqueous solutions of azoimide, free from mineral acid, are illuminated to such an extent that the residual azoimide is more than sufficient to neutralise the basic nitrogen compounds obtained, nitrogen and hydroxylamine are the predominating products but ammonia and small quantities of hydrazine are also obtained; other substances are not formed. Solutions of pure sodium azide become alkaline when illuminated and contain large amounts of hydrazine in addition to ammonia and hydroxylamine; the evolved gases contain nitrogen and hydrogen. Pre-addition of sodium hydroxide does not influence appreciably the course of the reaction. H. Wren.

Light-sensitivity of dyes. A. Steigmann (Kolloid-Z., 1928, **44**, 326—329).—A summary and discussion of a series of papers by the author on the light-sensitivity of dyes. E. S. Hedges.

Laws of photographic blackening when the luminous source is a series of electric sparks. (Mlle.) M. Hanot and H. Guillemet (Compt. rend., 1928, **186**, 1048—1050).—Although the densities of plates exposed for the same time to continuous and spark sources of light are known to differ, their blackening curves (density plotted against log. time of exposure or number of sparks) are exactly parallel for measurements between 0·415 and 0·537 μ, the relative error in measurement being 0·04%. The Schwarzschild exponent (p—0·87) is of the same order in the two cases, and the brightness of the spark approaches a maximum when the energy expended is increased. J. Grant.

Chemical action of Röntgen rays on dilute ferrous sulphate solutions as a measure of dose. H. Fricke and S. Morse (Amer. J. Roentgenol. Rad. Therapy, 1927, **18**, 430—432).—The oxidation of a dilute solution of ferrous sulphate satisfies the essential conditions. Chemical Abstracts.

Lithium chlorate and its hydrates. L. Berg (J. Russ. Phys. Chem. Soc., 1927, **59**, 1093—1103).—See A., 1927, 1042.

Composition of crystals obtained from solutions containing sodium sulphate and iodides. II. (Signa.) E. Fabris (Annali Chim. Appl., 1928, **18**, 115—122).—Crystallisation at 16—25·5° of solutions containing sodium sulphate and either potassium, sodium, or ammonium iodide (cf. A., 1927, 939) shows that the content of iodine in the crystals separating increases progressively with the amount of iodide present. Curves are given which show the conditions necessary to obtain a definite proportion of iodine in sodium sulphate. T. H. Pope.

Action of sodium hydroxide on carbon disulphide. J. G. Weeldenburg (Rec. trav. chim., 1928, **47**, 496—512).—When carbon disulphide is shaken with excess of 20% sodium hydroxide solution a deep red solution is obtained. Reaction proceeds slowly at the ordinary temperature, is more rapid at 80°, and still more rapid in presence of emulsifying agents. In freshly-prepared solutions sodium sulphide, polysulphides, and thiosulphate are not present. The diluted reaction product can be titrated with hydrochloric acid towards phenolphthalein without decomposition of the sodium trithiocarbonate produced, but not towards methyl-red. Titration with iodine gives a neutral reaction mixture. The red solution is oxidised by hydrogen peroxide, chlorine, and bromine, forming sulphates, whilst salts of the heavy metals yield coloured precipitates which when moist are unstable, giving carbon disulphide and the metallic sulphide.

Determination of the constituents of the red reaction mixture by detailed methods shows that no dithiocarbonate is present, whilst the amount of carbonate and trithiocarbonate satisfies the equation $3CS_2+6NaOH=2Na_2CS_3+Na_2CO_3+3H_2O$. When carbon oxysulphide is kept over sulphuric acid very slight decomposition occurs. Reaction with aqueous alkali hydroxides is slow, but rapid with alcoholic potassium hydroxide, and the resulting product can be titrated with iodine, one atom of iodine being equivalent to 1 mol. of carbon oxysulphide. There is no reaction between carbon oxysulphide and iodine, neutral or acid copper sulphate solutions, cadmium acetate and acetic acid, or ethereal triethylphosphine. H. Burton.

Alteration of concentrated solutions of sodium hydrogen sulphate. E. Isnard.—See B., 1928, 296.

Action of copper on sulphuric acid. G. Fowles (Chem. News, 1928, **136**, 257—259; cf. Druce, this vol., 378).—A critical discussion of previous work. The following series of reactions is suggested : $Cu+H_2SO_4=SO_2+H_2O+CuO(CuSO_4)$, followed by two simultaneous reductions : $4Cu+SO_2=Cu_2S+2CuO(2CuSO_4)$; $Cu+CuSO_4=Cu_2SO_4$. Sulphuric acid is then reduced by cuprous sulphide, $Cu_2S+H_2SO_4=Cu_2SO_4+H_2S$; $H_2S+H_2SO_4=2H_2O+SO_2+S$; $S+2H_2SO_4=2H_2O+3SO_2$, and simultaneously by cuprous sulphate, $Cu_2SO_4+2H_2SO_4=2CuSO_4+SO_2+2H_2O$. The result of combining these equations is $Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$. C. W. Gibby.

Hydrogen content of metals and alloys containing a trace of oxide. Guichard, Clausmann, and Billon (Compt. rend., 1928, **186**, 1121—1123). —The phenomena observed when copper or one of its silver alloys (containing a trace of oxide) is fused in a current of hydrogen are due to the reduction of the crystals of copper oxide, with the formation of water vapour. This forms bubbles which diffuse out slowly, and at the point of fusion escape violently and scatter particles of the metal. Below the fusion point there is a gradual loss in weight and increase in volume of the alloy, but in the absence of the oxide these phenomena do not occur. J. Grant.

Production of tenorite and crystalline oligist and cobaltous oxide. Duboin (Compt. rend., 1928, **186**, 1133—1135; cf. this vol., 257).—Large

crystals of tenorite (d^0 6·3) were produced by the addition of potassium chloride to a fused mixture of potassium hydrogen fluoride and copper oxide or chloride. After 2—3 days at red heat the mass was cooled and extracted with water. Crystals of cobaltous oxide (d^0 6·05) and of oligist (d^0 5·16) were obtained analogously from pure crystalline potassium cobalt fluoride and from ferrous chloride, respectively. The oxides are readily reduced by hydrogen.

J. GRANT

Hexabromostannates of rubidium, cæsium, and beryllium. G. I. COSTEANU (Bul. Chim. Soc. Romane Chim., 1927, **30**, 31—34).—See A., 1927, 741.

Decomposition of alkaline-earth sulphates. L. E. BHATT and H. E. WATSON.—See B., 1928, 296.

Behaviour of metals towards dry salts at high temperatures. B. GARRE (Korrosion u. Metallschutz, 1927, **3**, 194—200; Chem. Zentr., 1927, ii, 2657).—When a polished zinc rod is heated in powdered cupric oxide at 400°, the boundaries of the zinc crystallites are strongly attacked; when a piece of tin is similarly heated at 220°, it becomes covered with a thick layer of copper, and the grain boundaries are specially attacked. Silver powder does not react with copper oxide. In other experiments magnesium and aluminium were heated with sodium, potassium, or lithium carbonate, lithium hydroxide, copper, cadmium, zinc, or iron oxide; zinc with copper oxide or lead oxide; lead with copper oxide; tin with lead oxide; nickel with copper oxide.

A. A. ELDRIDGE.

Preparation of mercurammonium iodide in the crystalline state. M. FRANÇOIS (Compt. rend., 1928, **186**, 1205—1207).—On the analogy of his early experiments on dimercurammonium iodide (A., 1900, ii, 346) the author has found that in the presence of a suitable quantity of a 10% solution of pure ammonia at 21°, a 10% solution of the white additive compound, $3HgI_2,4NH_3$ (produced from the action of an excess of ammonia on the compound $HgI_2,2NH_3$), deposits spherical groups of dark purple, short, hexagonal microscopical prisms of the compound $Hg_9N_4I_6$. The reaction is: $3(3HgI_2,4NH_3)+nNH_3 \rightleftharpoons Hg_9N_4I_6+12NH_4I+(n-4)NH_3$. J. GRANT.

Mercury-thallium molecule. R. K. WARING (Nature, 1928, **121**, 675).—Volatilisation and absorption spectral observations indicate that when mercury and thallium vapours are mixed, mercury-thallium molecules are produced. A. A. ELDRIDGE.

Rare earths. XXVII. I. Fractional precipitation of the cerium group earths by electrolysis. II. Solubility of rare-earth oxalates in nitric acid. J. W. NECKERS with H. C. KREMERS (J. Amer. Chem. Soc., 1928, **50**, 950—954).—Lanthanum, in the form of hydroxide, may be separated from the other cerium-group metals by electrolysis of a neutral solution, preferably containing 5% of sodium chloride. Samarium and yttrium-group metals concentrate in the first cathodic deposits. The solubilities at 90° of some rare-earth oxalates in nitric acid solutions, both pure and containing oxalic acid, are recorded. The results are of the same order as at 25°.

S. K. TWEEDY.

Rare earths. XXVIII. Separation of cerium. J. W. NECKERS with H. C. KREMERS (J. Amer. Chem. Soc., 1928, **50**, 955—958).—Addition of sodium phosphate solution to a ceric nitrate solution containing 5% of nitric acid, followed by slow addition of potassium permanganate and more sodium phosphate, causes complete precipitation of insoluble ceric phosphate. Thorium, if present, is also precipitated, but the other rare-earth phosphates are soluble. Anodic oxidation of cerium in sulphate and nitrate solutions proceeds to 90% completion with no precipitation, and in presence of the phosphate ion to 99% completion with precipitation.

S. K. TWEEDY.

Rare earths. XXIX. Preparation and properties of some anhydrous rare-earth chlorides. J. H. KLEINHEKSEL with H. C. KREMERS (J. Amer. Chem. Soc., 1928, **50**, 959—967).—By dehydrating at 100—200° the chloride hexahydrates in a stream of hydrogen chloride under reduced pressure the anhydrous chlorides of lanthanum, cerous cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium, and thulium were prepared. The respective m. p. were: 872°, 822°, 823°, 761°, 682°, 655°, 624°, 696°, 866°, and d^{25} for coarsely-powdered material: 3·82, 3·97, 4·15, 4·17, 4·30, 3·60, 2·81, 4·25, and 4·34. The p_H values of solutions of the anhydrous chlorides are recorded; the values place the elements almost in the order of basicity given by Hopkins, except in the case of dysprosium, which appears to be more basic than was previously supposed. The salts will probably be completely hydrolysed at infinite dilution.

S. K. TWEEDY.

Influence of carbon dioxide under pressure on glass. O. K. BOTVINKIN.—See B., 1928, 334.

Constitution of ultramarine. E. GRUNER (Z. angew. Chem., 1928, **41**, 446—450).—A review of the various theories of the constitution and of the cause of the colour of ultramarine. A. R. POWELL.

Stannic dichloride diacetate. F. FICHTER and S. HERSZBEIN (Helv. Chim. Acta, 1928, **11**, 562—567).—The properties of stannic dichloride diacetate previously isolated by Fichter and Reichart (A., 1925, ii, 193) are described. It reacts with pyridine to form stannic dipyridine chloride. *Stannic dichloride dipropionate* and *dibutyrate* were also prepared. The corresponding compounds of *iso*valeric acid and aromatic acids could not be isolated.

F. J. WILKINS.

Displacement of metals or their oxides from solutions by hydrogen under pressure. Displacement of lead or its oxides. Crystalline modifications of lead oxide. V. IPATIEV and V. IPATIEV, jun. (Ber., 1928, **61**, [*B*], 624—630).—The action of hydrogen under pressure on solutions of lead nitrate in water commences at 130—150° and at 250—300° a series of basic salts is produced in which the proportion of lead oxide increases with rising temperature. At 270—300° under a definite pressure crystalline lead oxide is the main product, whereas at higher temperatures metallic lead is formed. Hydrolysis of the salt causes liberation of nitric acid which does not accumulate in the solution since it is reduced by hydrogen to nitrogen. Addition

of nitric acid to the solution merely delays hydrolysis, the usual basic salts being produced after the added acid has been reduced. Water in the absence of hydrogen has no appreciable action on the precipitates, which are slowly affected by hydrogen, particularly at high temperatures. The effect of the addition of acetic acid to solutions of lead acetate is closely similar to that of nitric acid to solutions of lead nitrate; whereas lead oxide is precipitated from neutral solution, little change is effected in acidified solution after the same interval of time. The acetic acid is partly converted into ethyl acetate. The rate of change depends to some extent on the material (gold, quartz, glass) of which the tubes are composed, since reduction of nitric acid is accelerated by gold surfaces. In gold tubes at 250° and 80 atm. initial pressure, crystalline, blood-red lead oxide, d 8·59—8·79, is produced, whereas in quartz tubes under similar conditions the requisite temperature is 300° or more. At 260—270° in quartz tubes *yellow lead oxide* is formed in thin, crystalline leaflets, whereas at 300° and 200 atm. initial pressure *colourless lead oxide* results. Separation of metallic lead occurs at 250—275° and upwards, according to the pressure.

H. Wren.

Production of active nitrogen. J. Kaplan (Proc. Nat. Acad. Sci., 1928, **14**, 258—260).—Experiments are described in which active nitrogen has been obtained in discharge tubes containing air. The usual apparatus was used, the discharge being condensed and a spark-gap connected in series with the tube and condenser. The glow observed was blue and changed to the ordinary yellowish-green glow when the spark gap was excluded. The spectrum was photographed by means of a small Hilger quartz-spectrograph, and also with a nitrogen-filled spectrograph, covering together the region 1800—4500 Å. Many of the bands could not be identified accurately owing to their large number and the relatively small dispersion of the spectrograph. Second positive bands of N_2 were found at 2815, 2953, and 3341 Å., as well as several members of the fourth positive group of N_2. No members of the Lyman–Birge–Hopfield bands or the predicted A—X bands were found on the plates from the nitrogen-filled spectrograph. There is therefore no evidence for transitions to the normal state of the molecule. The results of Strutt on the difference between the condensed discharge and the uncondensed discharge are confirmed. Experiments at somewhat lower voltages showed that the blue active nitrogen afterglow could be obtained when the potential at the spark-gap was only 10,000 volts.

A. J. Mee.

Formation of ammonia in the preparation of phosphorus. E. Urbain and V. Henri (Compt. rend., 1928, **186**, 1207—1208).—In the preparation of phosphoric acid by the action of steam on natural phosphates in the presence of active carbon, the addition of a halogen acid, normally required to produce a lowering of the reaction temperature, has no effect above 600°, but in the presence of nitrogen an unstable phosphorus nitride is probably formed, which is decomposed by the steam with the formation of ammonia. A yield of 0·46 g. of ammonia (representing 2·95 g. of monoammonium phosphate) was obtained at 900° from 5 g. of phosphorus in the form of phosphoric acid impregnated on carbon.

J. Grant.

Production of ammonium phosphates from secondary and tertiary calcium phosphates. C. Mückenberger.—See B., 1928, 297.

Allotropic modifications of phosphorus obtained under high temperatures and pressures. V. Ipatiev and V. Nikolajev (Ber., 1928, **61**, [*B*], 630—634).—Colourless, crystalline phosphorus is obtained by heating phosphorus in benzene at a temperature not exceeding 200° at 70—80 atm. pressure in an indifferent gas or by heating violet-red phosphorus at 400°/10—15 mm.; it has m. p. 44·5°, d 1·82. Crystalline, purple phosphorus (cf. A., 1926, 487) is prepared by heating yellow phosphorus in nitrogen at 260—280° and 100—150 atm. Treatment of yellow phosphorus with lead in nitrogen at 335° and 165 atm. affords violet-red phosphorus, d_1^{16} 2·11; determinations of density by the flotation method in potassium mercury iodide solution are untrustworthy, since the material becomes amalgamated. A ruby-red phosphorus, d_4^{20} 2·10, is prepared from iron powder and yellow phosphorus in nitrogen at 350° and 110 atm., and a similar product, d_{15}^{15} 2·10, from magnesium powder and yellow phosphorus at 350° and 116 atm. Black phosphorus, d_{16}^{1} 2·70, ignition temperature 481—490°, is conveniently prepared by heating yellow or technical red phosphorus for 4—5 days in nitrogen at 350° and 150—250 atm.

H. Wren.

Salt of hexafluorophosphoric acid, HPF_6. W. Lange (Ber., 1928, **61**, [*B*], 799—801).—If the solution obtained by dissolving phosphoric oxide in 40% hydrofluoric acid is preserved at the ordinary temperature, the difluorophosphoric acid, HPO_2F_2 (cf. A., 1927, 532), becomes hydrolysed and the residual solution yields the *nitron* salt of hexafluorophosphoric acid, $C_{20}H_{16}N_4,HPF_6$, m. p. 233° after softening at 228°, which does not depress the m. p. of nitron difluorophosphate. The *potassium* salt and the free *acid* are described. Solutions of the former do not yield precipitates with salts of the heavy metals or alkaline earths. The PF_6' ions are very stable towards boiling water and alkali hydroxides, but are slowly decomposed by concentrated acids. The PF_6' ion is also produced by dissolving phosphorus pentafluoride in cold water. Nitrosyl fluoride and phosphorus pentafluoride appear to yield the crystalline *compound* NOF_6.

H. Wren.

Perphosphoric acids and perphosphates. S. Husain and J. R. Partington (Trans. Faraday Soc., 1928, **24**, 235—245).—The action of hydrogen peroxide on phosphates (alkali, alkaline earth, ammonium, and thallium) has been investigated. Acid-reacting phosphates, such as primary phosphates, do not react with hydrogen peroxide or else give very unstable compounds. Alkaline phosphates, *e.g.*, secondary phosphates or pyrophosphates of alkali metals, give rather stable compounds, whilst strongly alkaline phosphates, *e.g.*, tertiary potassium phosphate, decompose hydrogen peroxide. The compounds formed by the action of hydrogen peroxide

are in no case true perphosphates, but appear to be phosphates combined with hydrogen peroxide of crystallisation. Electrolysis of orthophosphoric acid or of phosphates of lithium, sodium, and thallium does not give rise to perphosphates, whilst secondary phosphates of potassium, rubidium, cæsium, and ammonium produce on electrolysis two perphosphates in solution, namely, permonophosphate and perphosphate. In contradiction to Siebold's statement (G.P. 279,306), perphosphoric acids are not obtained by the action of 30% hydrogen peroxide at 0° on phosphorus oxychloride. Doubt is thrown also on the results of many other investigators in this field. True perphosphates do not give any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether, or titanic acid, as do the phosphates containing hydrogen peroxide of crystallisation. On the other hand, they oxidise acidified manganous salt solutions to permanganic acid, acidified aniline solution to nitrosobenzene, which is then slowly oxidised to nitrobenzene, and silver nitrate solution to a black precipitate, which gradually turns yellow.

L. F. GILBERT.

Chloro-complex salts of bismuth. H. REMY and L. PELLENS (Ber., 1928, **61**, [*B*], 862—868; cf. A., 1926, 94).—Calculations based on Coulomb's law and Goldschmidt's ionic radii (A., 1927, 611) indicate the particular stability of bismuth compounds in which the metal is co-ordinatively quinquevalent. The prediction is experimentally confirmed. The following compounds are described: methylammonium enneachlorodibismuthate, $[NH_3Me]_3[Bi_2Cl_9]$, m. p. 302°, *hendecachlorodibismuthate*, decomp. above 240°; and *heptachlorobismuthate*, m. p. above 210° (decomp.); *dimethylammonium pentachlorobismuthate*, m. p. 228°, and *heptachlorobismuthate*, m. p. 208°; *trimethylammonium enneachlorodibismuthate*, m. p. about 284° after softening at 260°, and *hexachlorobismuthate*, m. p. (indef.) 272°; *tetramethylammonium tetradecachlorotribismuthate*, m. p. 286° (decomp.); *ethylammonium tetrachlorobismuthate*, m. p. 158°, *pentachlorobismuthate*, m. p. 268°, *hexachlorobismuthate*, m. p. 239°, and *heptachlorobismuthate*, m. p. 199°; *propylammonium tetrachlorobismuthate*, m. p. (indef.) 157°, *pentachlorobismuthate*, m. p. 243°, and *heptachlorobismuthate*, m. p. (indef.) 170°; *butylammonium pentachlorobismuthate*, m. p. 225°, and *enneachlorobismuthate*, m. p. 180°. The salts are prepared by mixing the hydrochlorides of the ammonium bases and bismuth chloride in the requisite molecular proportions in water or dilute hydrochloric acid.

H. WREN.

Reaction between chromic acid and manganous salts. R. LANG (Z. anorg. Chem., 1928, **107**, 387—388; cf. following abstract).—No reaction occurs between potassium dichromate and manganous sulphate in a *N*-solution of sulphuric acid, either in the cold or on boiling, or even when the sulphate is present in excess. If, however, an alkali fluoride or metaphosphoric acid is added to form complexes with the manganic ions, the manganous salt is oxidised with a measurable velocity, even at the ordinary temperature; if metaphosphoric acid is used, the reaction may be reversed by the subsequent addition of hydrochloric acid.

R. CUTHILL.

Action of dichromate ions on manganous ions. S. ORLOVSKI (Z. anorg. Chem., 1928, **170**, 184—190).—Potassium dichromate in a solution made slightly alkaline with ammonia is reduced on boiling with manganous salts, chiefly in accordance with the equation $K_2Cr_2O_7+6MnSO_4+10NH_4OH+7H_2O=2Cr(OH)_3+6Mn(OH)_3+K_2SO_4+5(NH_4)_2SO_4$. The whole of the manganese may be precipitated in this way, but the reaction is not suitable as a method of determination, as the precipitate appears to contain unoxidised manganous compounds. If a stronger base is used instead of ammonia, the oxidising action of the dichromate is diminished.

R. CUTHILL.

Formation and decomposition of ferrite. C. E. SWARTZ and F. C. KRAUSKOPF (Amer. Inst. Min. Met. Eng. Tech. Pub., 1927, No. 40. 19 pp.).—Zinc ferrite, $Zn(FeO_2)_2$, is formed by heating zinc oxide with ferric oxide above 650°, and is decomposed by heating with calcium or magnesium oxide at 850°. Magnesium and calcium ferrites are formed similarly. The compounds are non-magnetic.

CHEMICAL ABSTRACTS.

***X*-Ray studies on the "nitrides" of iron.** G. HAGG (Nature, 1928, **121**, 826—827).—*X*-Ray examination of the products obtained by heating iron at 450° in a current of ammonia show that they are solid solutions of nitrogen in iron, and not definite chemical compounds. The structure of the products is dependent only on the nitrogen content. The -phase (a solid solution of nitrogen in γ-iron) lies etween 5·7 and 6·1% N, corresponding approximately with Fe_4N; the lower limit of the homogeneous ε-phase (a solid solution of nitrogen in a hexagonal close-packed form of iron) lies between 7·5 and 8% N, corresponding with Fe_3N, and the upper limit of attainable concentration (slightly above 11% N) corresponds with Fe_2N. It is possible that these coincidences may be related to certain concentrations of valency electrons. The catalytic effect of iron in the Haber process for combining nitrogen and hydrogen may be ascribed to the dissolved nitrogen being in the monatomic condition.

A. A. ELDRIDGE.

Thermal decomposition of complex cyanides of iron in relation to the catalytic synthesis of ammonia. A. MITTASCH, E. KUSS, and O. EMERT (Z. anorg. Chem., 1928, **170**, 193—212).—When ammonium ferrocyanide is heated in a vacuum, decomposition starts at about 110°, ammonium cyanide being evolved gradually until the temperature reaches 320°, when ferrous cyanide remains. It thus appears that there are in the decomposition stages intermediate between the ferrocyanide and the two simple cyanides. On heating further, decomposition starts again above 430°, nitrogen being evolved, and at 700° 95% of it has come off, the residue consisting principally of iron, along with iron carbide, carbon, and a little nitride; the formation of carbide is favoured by a low decomposition temperature and a short period of heating. When the ferrocyanide is heated in a current of hydrogen and nitrogen prepared by decomposing ammonia, the

course of the reaction up to 320° is the same as it is in a vacuum. At 320°, however, the ferrous cyanide formed is reduced to nearly pure iron, with formation of ammonia, and methane and other hydrocarbons, at a rate which increases with the pressure. Ferrous cyanide itself begins to be reduced by the mixture of nitrogen and hydrogen above 210°. At 230°, the carbon and nitrogen of the cyanide radical are reduced at approximately equal speeds, so that metallic iron only is formed. At 400°, on the other hand, the nitrogen is reduced much more rapidly than the carbon, so that the solid residue when most of the nitrogen has been removed contains iron, iron carbide, and carbon; in no case, at any temperature, is carbide unaccompanied by the metal. The fact that this mixture is not formed at 230° may be explained by supposing that the carbide FeC_2 is formed as an intermediate product, and at 400° decomposes into carbon and the carbide Fe_3C, whereas at 230° it is directly reduced. It also appears that metallic iron must be formed from the very start of the reduction. The mixture of carbide and carbon obtained at 400° is readily reduced completely by the mixture of nitrogen and hydrogen, but if the mixture is first heated in a vacuum at 400° or 500° for some time, reduction of the carbon in particular becomes much more difficult. The decomposition of the cyanide $KAlFe(CN)_6$ in the nitrogen–hydrogen mixture at 450—500° under 1 atm. pressure is similar to that of ferrous cyanide at the same temperature, whilst at 360° and 95 atm. there is complete reduction to the metal; ferrous cyanide and carbide–metal mixtures must thus be intermediate products here also. This cyanide does not in itself bring about the decomposition of ammonia below 400°, or its synthesis at 360° under 95 atm. It is therefore to be concluded that the actual catalyst is the metallic iron produced in the decomposition, and activated by the substances which accompany it. R. CUTHILL.

Reaction between monohydrated ferric oxide and hydrogen sulphide at 100°. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1928, 814—823).—The black product obtained in this reaction contains free sulphur extractable by carbon disulphide. The ratio of "sulphide" produced to oxide taken corresponds very nearly with that required for complete conversion into ferric sulphide. The course of the reaction varies considerably, but the mean composition of the product is as follows: free sulphur 2·44%, iron disulphide, 7·83%, ferric sulphide, 69·4%, ferrous sulphide, 9·76%, unchanged ferric oxide, 7·48%, moisture, 1·55%. The ferrous sulphide and disulphide are formed by the decomposition of ferric sulphide. The free sulphur results from the oxidation of the hydrogen sulphide by oxygen adsorbed on the oxide surface. H. INGLESON.

Ruthenium. F. KRAUSS (Z. angew. Chem., 1928, 41, 413—418).—From a comprehensive review of the literature and from his own researches the author concludes that in the solution obtained by treating ruthenium tetroxide with hydrochloric acid the metal is almost entirely in the tervalent state and that by evaporation of this solution and addition of alkali chlorides derivatives of pentachlororuthenic acid are obtained. The light yellowish-brown or colourless solution obtained as the first stage in the reduction of ruthenium trichloride in solution contains bivalent, and the blue solution obtained by more vigorous reduction univalent ruthenium. A. R. POWELL.

Application of the photo-electric cell to automatic titrations. R. H. MULLER and H. M. PARTRIDGE (Ind. Eng. Chem., 1928, 20, 423—425).—A circuit containing a photo-electric cell and one vacuum tube is described. Light passes through the solution being titrated and falls on the cell; the change in colour during the titration varies the intensity of the light sufficiently to actuate the cell, and through the vacuum tube operates a relay and burette release. The relay contacts may be reversed as required, and by a proper selection of indicators all cases of acidimetry and alkalimetry can be covered. Permanganate and dichromate titrations may be made by using *m*-phenylenediamine as indicator, and iodometric titrations are also possible. Certain precipitation reactions may also be followed by using reflected light. The apparatus is well adapted to precise determinations of p_H values, and automatic titrations were found to be more accurate than visual determinations. D. G. HEWER.

Spectroscopic control of the end-point of indicators of the phthalein and sulphonephthalein groups. P. BRUERE (Bull. Soc. Chim. biol., 1928, 10, 283—290).—By spectroscopic control of the titration of coloured solutions it is possible to obtain accurate results with the usual indicators.
G. A. C. GOUGH.

Stable colorimetric standards for simple and mixed indicators. P. BRUERE (Bull. Soc. Chim. biol., 1928, 10, 291—293).—Permanent colorimetric standards for mixtures of indicators such as methyl-red, bromothymol-blue, and phenol-red may be prepared from mixtures of (*a*) potassium and cobalt dichromates (yellow), (*b*) cobalt and copper sulphates (blue), (*c*) an acetic acid solution of cobalt chloride.
G. A. C. GOUGH.

Colorimetry. H. ECKSTEIN (Chem.-Ztg., 1928, 52, 317).—The suggestion is made that the changes in colour of many of the comparison solutions used in colorimetric determinations might be avoided either by the use of suitably coloured stable dyes or of coloured glasses as comparison standards when such materials can be obtained. H. INGLESON.

Detection of small differences in the hydrogen-ion concentration of solutions. W. KESTING (Z. angew. Chem., 1928, 41, 358—360).—Malononitrile reacts with α-naphthaquinone in solutions of $p_H>2{\cdot}5$ with the formation of an intensely blue solution, and the speed of the reaction increases with an increase in the p_H value. To compare the p_H of two solutions, 5 c.c. of each are placed in two test-tubes and 5 drops of a 0·2% alcoholic solution of malononitrile added to each, followed by 5 drops of a 0·3% alcoholic solution of α-naphthaquinone. After shaking, the intensities of the colours are compared; differences of only 0·2 in the p_H value are readily apparent after a little practice. In solutions with the addition of the above reagents produces a green colour and the test is no longer of value; in this case

β-naphthaquinone is used instead of the α-compound and the intensities of the red colour produced in standard and test are compared. For solutions with relatively low p_H values benzoquinone gives more delicate colour changes than either of the naphthol derivatives. A. R. POWELL.

Non-gas electrodes for p_H determinations. A. J. DE LA CRUZ (Philippine Agric., 1927, **16**, 307—322).—An electrode combination of aluminium and barium dioxide gave reproducible results for *E.M.F.* when used in ordinary acid-base titrations or in buffer solutions containing no protein, the optimal range being p_H 7—10, but not in determinations of the p_H value of sugar juices. The quinhydrone electrode can be used for this purpose for p_H values up to 10, provided the *E.M.F.* is read exactly 1 min. after addition of the quinhydrone.

CHEMICAL ABSTRACTS.

New iodoso-(iodoso-iodyl-)benzene electrode and its application to the determination of p_{OH} or p_H. F. GROSSMAN (Rocz. Chem., 1927, **7**, 567—578).—Two new electrodes, iodosobenzene and a mixture of iodoso- and iodyl-benzene, are applied to the measurement of p_{OH} or of p_H between the limits 1 and 13. An iodylbenzene electrode does not appear to be applicable to the determination of p_H.

R. TRUSZKOWSKI.

Differential potentiometric titration. I. Simple method. II. Refined methods. B. CAVANAGH (J.C.S., 1928, 843—855, 855—872; cf. A., 1927, 1045).—The three methods described are applicable to the titration of univalent ions, *e.g.*, $Ag^{\cdot}$, $H^{\cdot}$, Cl', to which a corresponding reversible electrode can be found. All the methods depend on the changes of the potential of the indicator electrode and not on particular values of the potential. The first method is applicable in cases where an absolute uncertainty of the order of one fifth or one seventh of the solubility of silver chloride (or the corresponding constant) is permissible. A first addition of the reagent is made and from the resulting potential change an approximate estimate of the amount still required is obtained by reference to a table. Nearly this amount is added and the small deficiency can then be estimated accurately by the same means. The second and third methods are used for dilute solutions where higher absolute accuracy is required. The second method is an extension of the first up to and beyond the end-point. The third method is independent of a knowledge of solubility, the end-point being deduced from two successive potential measurements by reference to a table and the use of a set of curves. Numerical examples illustrating the use of the methods are given. H. INGLESON.

Colorimetric p_H determination [of water] in a neutral atmosphere. H. F. MUER and F. E. HALE.—See B., 1928, 318.

Fellenberg's method for the determination of iodine. E. JOCHMANN (Biochem. Z., 1928, **194**, 454—460).—Fellenberg's method for the determination of minute amounts of iodine does not always give results as consistent as claimed.

P. W. CLUTTERBUCK.

Determination of traces of iodine. I. J. F. MCCLENDON (J. Amer. Chem. Soc., 1928, **50**, 1093—1099).—The sample, containing more than 0·01 mg. of iodine, is ashed in oxygen, by atomising if necessary, in a heated silica tube; the vapours are sucked through sodium hydroxide solution and a Cottrell precipitator. To the former solution the washings of the ash are added; after neutralising with phosphoric acid containing sulphurous acid the solution is boiled and on cooling the iodine is extracted with carbon tetrachloride. The latter solution is examined in a micro-colorimeter. The limit of error is 1% on samples containing more than 1 mg. of iodine and 5% on samples containing less than this.

S. K. TWEEDY.

Testing for iodine in potable waters. P. DRAWE.—See B., 1928, 350.

Determination of fluorine in zinc blende. L. FRESENIUS, K. SCHRODER, and M. FROMMES.—See B., 1928, 302.

Determination of dissolved oxygen in water. V. G. ANDERSON and J. R. DICKSON.—See B., 1928, 390.

Determination of sulphuric acid by the benzidine method. O. NYDEGGER (Chem.-Ztg., 1928, **52**, 318—319; cf. A., 1907, ii, 196).—The chief sources of error in the method arise from the relatively large solubility of benzidine sulphate in water and from the adsorption of benzidine hydrochloride by the precipitated sulphate. Experimental details of the method are given. Results obtained are accurate, duplicate determinations agreeing to within 0·5% absolute. The presence of moderate amounts of other salts and acids is without influence on the accuracy of the determinations. H. INGLESON.

Examination of sulphuric acid for selenium. R. C. WELLS.—See B., 1928, 332.

Changes in the titre of thiosulphate solutions. C. MAYR and E. KERSCHBAUM (Z. anal. Chem., 1928, **73**, 321—352).—Although carbon dioxide decomposes thiosulphate solutions with the deposition of colloidal sulphur and with the production of traces of hydrogen sulphide, this action has very little to do with the changes in the titre that take place during storage of thiosulphate solutions. Oxygen alone and exposure to direct sunlight have no action when the solution is kept in glass vessels, but photochemical decomposition takes place rapidly in quartz vessels. The principal cause of the instability of thiosulphate solutions is the presence of bacteria, of which there are three active kinds. The first type causes decomposition as follows: $2Na_2S_2O_3+H_2O+O=Na_2S_4O_6+2NaOH$; the second, according to the equations $Na_2S_2O_3=Na_2SO_3+S$ and $Na_2SO_3+O=Na_2SO_4$, and the third, according to the first equation and to $S+3O+H_2O=H_2SO_4$ The presence of copper accelerates decomposition only when bacteria are also present. The protective action of alkalinity is ascribed to the restraining effect of alkalis on the growth of bacteria; a p_H value of 9—10 affords the greatest protection. Practically complete sterility may be produced by the addition to thiosulphate solutions of 1 vol.-% of amyl alcohol. A. R. POWELL.

Apparatus for micro-analytical determination of [ammoniacal] nitrogen. H. Leopold (Chem.-Ztg., 1928, **31**, 309).—A round-bottomed distillation flask, 150—200 c.c. capacity, carries a dropping funnel (containing 30% sodium hydroxide solution) and an inclined spray trap. The latter is connected with a bent tube, the vertical portion of which is enclosed by a condenser and dips into 4—6 c.c. of 0·0143*N*-hydrochloric acid. 0·002—0·005 g. of the substance is used; the distillation is carried on for 20 min., the delivery tube raised above the acid, the boiling continued for 5 min. longer, and the excess of acid titrated with 0·0143*N*-sodium hydroxide solution. D. Woodroffe.

Hypophosphoric acid. W. D. Treadwell and G. Schwarzenbach (Helv. Chim. Acta, 1928, **11**, 405—416).—An electrometric precipitation method for the analysis of hypophosphoric acid is based on the very slight solubility of the uranous salt. Electrometric neutralisation curves with sodium hydroxide indicate the successive formation of disodium dihydrogen hypophosphate, trisodium monohydrogen hypophosphate, and normal sodium hypophosphate, and give values for the dissociation constants of the acid of ($\geq 10^{-2 \cdot 2}$), $10^{-2 \cdot 81}$, $10^{-7 \cdot 27}$, $10^{-10 \cdot 02}$.

F. J. Wilkins.

Determination of small amounts of carbon monoxide in air. G. M. Edell.—See B., 1928, 365.

Determination of carbon monoxide in mines. G. S. McCaa and J. A. Davis (U.S. Bureau Mines Circ., 1928, No. 6057, 5 pp.).—The gas, previously passed over activated charcoal, is passed through a small glass tube containing granulated pumice saturated with a mixture of iodine and fuming sulphuric acid ("hoolamite"). The liberated iodine is determined colorimetrically, the standards being contained in a tube as part of the apparatus.

Chemical Abstracts.

Determination of free alkali in hypohalite solutions. E. Rupp and F. Lewy.—See B., 1928, 365.

Rapid determination of zinc. G. Spacu and J. Dick (Z. anal. Chem., 1928, **73**, 356—359).—Addition of pyridine and ammonium thiocyanate to neutral solutions of zinc salts produces quantitative precipitation of white, crystalline $Zn(SCN)_2,2C_5H_5N$, which contains 19·25% Zn. The details of precipitating, washing, and drying the compound are similar to those described for the precipitation of cadmium by the same reagents (cf. this vol., 499).

A. R. Powell.

Nephelometric determination of small quantities of lead in presence of zinc by means of potassium chromate. L. S. van der Vlugt.—See B., 1928, 336.

Detection and colorimetric determination of aluminium. I. M. Kolthoff (J. Amer. Pharm. Assoc., 1928, **17**, 360—361).—For the detection and determination of traces of aluminium (0·5—0·02 mg. per litre), 1 : 2 : 5 : 8-tetrahydroxyanthraquinone in presence of a buffer solution is employed. Most metals are without influence on the reaction.

E. H. Sharples.

Determination of iron and sulphur in sulphides of iron. P. L. Robinson, L. A. Sayce, and J. Stevenson (J.C.S., 1928, 813—814).—The method of analysis of iron sulphide (Weyman, B., 1920, 219a) in which the solid is treated with warm aqueous copper sulphate, iron being determined in the filtrate and sulphur indirectly determined by dissolving the residue in nitric acid and precipitating the copper electrolytically, gives very untrustworthy results, especially in the presence of even small quantities of free acid. H. Ingleson.

Colorimetric determination of iron in water. P. Lehmann and A. Reuss.—See B., 1928, 390.

Detection of cobalt in steel. J. Moir.—See B., 1928, 301.

Gravimetric determination of titanium in iron alloys. J. Ciochina.—See B., 1928, 301.

Determination of antimony in bronze, brass, and similar alloys. S. A. Tschernichof.—See B., 1928, 371.

Analytical chemistry of tantalum, niobium, and their mineral associates. X. Separation of silica from earth acids. XI. Precipitation of titanium by tannin. W. R. Schoeller and A. R. Powell (Analyst, 1928, **53**, 258—267).—X. Volatilisation of the fluorides of tantalum and niobium is discussed and a method of separation of small quantities of silica from much earth acid by a reagent other than hydrofluoric acid is given, which involves the use of an acid flux. The mixed oxides are fused with potassium hydrogen sulphate, the cooled mass is digested with oxalic or tartaric acid, the solution (containing nearly the whole of the earth acids) filtered, and the residue (more or less pure silica) washed with hot water, ignited, and weighed. It is then evaporated with hydrofluoric acid and sulphuric acid and again ignited and weighed. The small residue is once more fused with hydrogen sulphate, the mass dissolved in the organic solvent, and the solution added to the first filtrate.

XI. Titanium may be quantitatively precipitated by tannin from oxalic or tartaric acid solution if the solution be neutralised and boiled with excess of tannin. Tantalum cannot be separated from niobium in the presence of more than an insignificant amount of titanium, *i.e.*, 1% of the tantalic oxide to be determined, as a discoloration of the yellow tantalum precipitate occurs. Thus the method may usually be used for tantalites, but in most columbites titania must first be separated from the earth acids.

D. G. Hewer.

[Analysis of platinum ores.] S. F. Shemtschushni and others.—See B., 1928, 302.

Micro-analytical filtration. G. Fontès and L. Thivolle (Bull. Soc. Chim. biol., 1928, **10**, 495—500).—An apparatus for this operation, based on that of Pregl, is described and its application to modified determinations of potassium and sodium is detailed. G. A. C. Gough.

Platinum–tungsten welding. J. H. Hibben (J. Amer. Chem. Soc., 1928, **50**, 1118).—The tungsten is cleaned with sodium nitrite and several coats of platinum are burned into it from a solution of lavender

oil and platinic chloride. It is then rapidly welded in an oxygen flame to platinum coated with borax. If cleaned tungsten is covered with borax, heated, and plunged into molten gold, it may then easily be welded to gold. Gold is an excellent flux for platinum welding. S. K. TWEEDY.

Electrolytic gas apparatus. R. MAND (Z. physikal. chem. Unterr., 1927, **40**, 305; Chem. Zentr., 1928, i, 285).—A demonstration apparatus is described. A. A. ELDRIDGE.

Apparatus for the determination of gas densities. M. NIKIEL (Metan, 1925, **9**, 203—210; Chem. Zentr., 1928, i, 227—228).—The density of a gas is compared with that of air by a determination of the time taken for a liquid to flow out of a vessel attached to a gas supply, and then opened to the air. The apparatus is described and figured.

A. A. ELDRIDGE.

Registering photodensitometer. E. A. HARRINGTON (J. Opt. Soc. Amer., 1928, **16**, 211—222).—A direct-reading, self-recording densitometer with single thermo-couple and low-resistance D'Arsonval galvanometer, which can be used for measuring the relative opacities of photographic images of line spectra and powder photographs, is described. Quick action and small lag result from the small heat capacity of the thermo-couple and special arrangement of the galvanometer. Applications to *X*-ray work and ordinary spectroscopy are discussed.

C. J. SMITHELLS.

Colour glass standardisation. D. B. JUDD and G. K. WALKER (Oil and Fat Ind., 1928, **5**, 16—26).—A large number of red Lovibond glasses for grading vegetable oils were compared with a standard glass and graded by means of a Martens photometer. The engraved numerals were found to be only an approximate index of colour, previous findings as to inaccuracies in the region 7·0—8·0 being confirmed (samples engraved 7·6 covering a range of 1·1 red units). Results indicated that the Priest and Gibson scale departed by about 0·1 from the average Lovibond red glass of the order 7·0—8·0 used in the United States. A. COUSEN.

Spectrocomparator. F. STANLEY (J. Opt. Soc. Amer., 1928, **16**, 208—210).—A comparator, which enables two spectra taken on different scales to be compared directly, is described. The optical system is arranged to give different magnifications in the two fields, and the eyepiece carries a micrometer.

C. J. SMITHELLS.

Selenium cell. R. E. MARTIN (J. Opt. Soc. Amer., 1928, **16**, 279—281).—A cell in which the selenium is in the form of a cylinder, and a method for making the latter by pouring viscous selenium are described. C. W. GIBBY.

Spectroscopic demonstrator for the exhibition of emission, continuous, and absorption spectra. H. T. STETSON and H. W. GEROMANOS (J. Opt. Soc. Amer., 1928, **16**, 293—294).—The continuous spectrum is produced by an incandescence electric lamp supported 1 ft. from a direct-vision spectroscope. The interposition of a sodium flame gives rise to an absorption spectrum, and the latter flame alone to the two sodium lines. C. W. GIBBY.

Light filters for the isolation of narrow spectral regions. L. A. JONES (J. Opt. Soc. Amer., 1928, **16**, 259—271).—Spectral absorption curves are shown for distilled water, for aqueous solutions of copper sulphate and of nickel sulphate, for Corning glasses G 986A, G 586, and G 980A, and for Wratten filters 88A, 25, 61, and 49 and combinations thereof.

C. W. GIBBY.

Refracto-dispersometer. C. CHEVENEAU and VAURABOURG (Bull. Soc. chim., 1928, [iv], **43**, 374—384).—A simple adaptation of the Fery refractometer to the measurement of dispersion is described. Two lines in the spectrum of the mercury vapour lamp are employed, and a disc attached to the eyepiece tube can be rotated so that suitable screens can be brought into the eyepiece in turn, and only monochromatic light of the desired wave-length transmitted. The relation between the true index of refraction n_λ and the apparent index (the scale reading) is given by $n_\lambda - Cn_\lambda - D$, and the method of deriving the constants C and D is given, whence the dispersion, $\Delta n = n_\lambda \quad n_{\lambda_2}$, is determined.

W. A. RICHARDSON.

Chamber for the study of ions and electrons in gases. L. B. LOEB and A. M. CRAVATH (J. Opt. Soc. Amer., 1928, **16**, 191—196).—A detailed description is given of a metal ionisation chamber suitable for use in research on the mobilities and saturation currents of ions and electrons in gases. The apparatus has been employed successfully with hydrogen sulphide. C. J. SMITHELLS.

Devices for increasing accuracy in weighing. F. C. GUTHRIE (Nature, 1928, **121**, 745—746).—The rider is in contact with the beam of the balance at one point only, and is moved, if possible, without raising the beam knife-edge; otherwise, the mean of several zero observations, the knife-edge being raised between each pair, is taken. Swinging is set up by a puff of air through a glass tube bent under the pan from an external bulb. A. A. ELDRIDGE.

Laboratory thermostat. M. COPPOLA (Annali Chim. Appl., 1928, **18**, 97—98).—A convenient form of insulated, electrically heated thermostat with pulley-driven stirring gear is described. T. H. POPE.

Micro-calorimeter. S. G. LIPSETT, F. M. G. JOHNSON, and O. MAASS (J. Amer. Chem. Soc., 1928, **50**, 1030—1033).—The construction of an adiabatic platinum micro-calorimeter on the lines of the large calorimeter previously used (A., 1927, 520), and having a thermal capacity of 1 g.-cal., is described. With its aid heats of dissolution in 4 c.c. of solvent may be determined. S. K. TWEEDY.

Simplified manometer for vacuum distillations. G. B. HEISIG (Ind. Eng. Chem., 1928, **20**, 382—383).—The Pyrex glass manometer is so constructed that the long (150 mm.) capillary tubing arm dips into a mercury pool (the mercury of which rises only about 0·5 mm. when the whole tube is emptied into it) on the other side of which the short arm (50 mm.) rises, bent at right angles at the top and tapering, for attachment to the distilling system. The manometer is read directly by means of a scale behind the long arm; any distillate coming over

will enter the large chamber and not interfere with the reading, and no stop-cock is necessary for attachment. The maximum error, which would be at very low pressure, is 0·5 mm. D. G. HEWER.

Glass manometer. F. DANIELS (J. Amer. Chem. Soc., 1928, **50**, 1115—1117).—The gas pressure is measured, with an accuracy of about 0·2 mm., by balancing it against a known air pressure through a glass diaphragm, the point of balance being determined electrically. The device, which is totally enclosed in glass, is claimed to be more trustworthy and easier to construct than previous, similar, devices. S. K. TWEEDY.

Laboratory evaporator. P. OERTEL (Chem.-Ztg., 1928, **52**, 302).—A steam-heated evaporating bath is described which may be worked at pressures from about 0·2 to 0·5 atm. The mean temperature is 85° and the maximum 95°, so that spurting or overheating of the material is avoided. The apparatus is so designed that little corrosion takes place and that the solution which is being evaporated cannot be contaminated with products of the corrosion of the bath. H. F. GILLBE.

Micro-fractionating column for analytical purposes. C. M. COOPER and E. V. FASCE (Ind. Eng. Chem., 1928, **20**, 420—421).—The active part of the column consists of a Pyrex tube 36×0·7 cm., constricted by projections, and vacuum-jacketed, the jacket being maintained electrically at 20° below the b. p. of the material inside, and a condenser returns reflux to the column. The Fisher organic thermometer indicates the temperature of the vapour product, which, when condensed, drops into a 5-c.c. water-jacketed burette. Permanent gases escape by a side-tube. The material remaining in the column after distillation is about 0·4 c.c. and the time required for fractionating a 10 c.c. sample is between 30 and 90 min. D. G. HEWER.

Clamp for rubber tubing. H. W. BATCHELOR (Ind. Eng. Chem., 1928, **20**, 366).—Rubber tubing is secured to glass tubing by a short glass tube of slightly larger diameter slipped over the rubber and then worked back over the junction by stretching the rubber tube. With slight modification a mercury seal may be arranged. C. IRWIN.

Constant-volume pyknometer. H. V. ELLSWORTH (Min. Mag., 1928, **21**, 431—435).—The pyknometer of 10 c.c. capacity is made of silica-glass, thus possessing several advantages over one made of ordinary glass. The stopper is perforated by a capillary and is continued into a graduated side-tube, which dips under water while the apparatus is cooling. The volume of the contained water to the graduations on the side-tube can be readily and accurately determined to 0·0002 c.c. L. J. SPENCER.

Measuring bomb for very volatile substances. K. H. SLOTTA (Chem.-Ztg., 1928, **52**, 291).—An apparatus suitable for the storage and delivery of small measured amounts of substances such as hydrogen cyanide, carbonyl chloride, methyl bromide, etc. is described. H. INGLESON.

Rapid ashing furnace. A. FORNET (Chem.-Ztg., 1928, **52**, 319).—In this apparatus, in which four ash determinations can be made simultaneously, the design brings about an intimate contact of air with the substance treated and renders stirring or addition of oxidising agents unnecessary. H. INGLESON.

Steam still for volatile acids. D. H. CAMERON. —See B., 1928, 287.

Drying vessel. A. OPPE (Chem. Fabr., 1928, 241).—A vacuum-tight drying vessel capable of being weighed consists of a cap making an external joint on to the vessel, the vessel itself, an upright cylinder, and top and bottom gas connexions, the latter forming a spiral on which the vessel rests. The vessel is particularly intended for bulky hygroscopic substances and is adapted for use in a heating bath. C. IRWIN.

Electromagnetic vacuum cut-off. J. H. HIBBEN (J. Amer. Chem. Soc., 1928, **50**, 1117—1118).—A piece of soft iron enclosed in glass is suspended by means of a solenoid at the top of the sealed limb of a U-tube containing mercury. Interruption of the current causes the iron to fall; the mercury level in the other limb then rises and seals the vacuum lead from the apparatus. S. K. TWEEDY.

Apparatus for catalytic reduction. R. ADAMS and V. VOORHEES (Org. Syntheses, 1928, **8**, 10—16).—The apparatus, which is fully described, is suitable for catalytic reductions with hydrogen at 2—3 atm., the reaction vessel being continuously shaken. A. A. ELDRIDGE.

Danger of mercury vapour. W. KRONER.—See B., 1928, 350.

Nomography. II. O. LIESCHE (Chem. Fabr., 1928, 228—230, 241—243; cf. this vol., 501).—The construction of charts for the reading of analytical results of the type corresponding with the relation $y=f(x)$ is developed. In the determination of barium sulphate by sedimentation the original curve is parabolic. If the relation is linear as in the iodometric determination of antimony, sulphites, etc. the chart takes the form of two scales at an angle. A more complicated linear relationship is found in the conversion of wt.-% into at.-% in alloys, *e.g.*, of magnesium copper. The direct construction method cannot be used directly for non-linear relationships, but by breaking up the equation it may be partly applied. The method may be equally applied to empirical data as in the distillation of a mixture of water and benzene. C. IRWIN.

Geochemistry.

Measurements of the ozone in the higher atmosphere during 1927. H. BUISSON (Compt. rend., 1928, **186**, 1229—1230).—The ozone content of the higher atmosphere was determined from the absorption of rays of several wave-lengths for different heights of the sun, expressed as a function of the thickness of air traversed, and from the absorption coefficients of ozone for these wave-lengths. Expressed in mm. of pure ozone directly overhead at midday under normal conditions of temperature and pressure, it varies from 4 in spring to 2 in autumn, with minor irregular variations depending (in an inverse sense) on the atmospheric pressure. The results confirm those of Dobson and Harrison (A., 1926, 140, 493) and others. J. GRANT.

Composition of the thermal waters from Bareges. R. MASSY and P. CAZAUX (J. Pharm. Chim., 1928, [viii], **7**, 340—345).—The hydrogen sulphide, total sulphur, and temperature of eighteen of these waters have been determined. The results do not agree with those obtained by Robine and Dejussieu (this vol., 267) and the reasons for the differences are discussed. E. H. SHARPLES.

Sulphate : chloride ratio of the waters of the North Pacific. T. G. THOMPSON, J. W. LANG, and L. ANDERSON (Pub. Puget Sound Biol. Sta., 1927, **5**, 277—292).—The ratio was constant at 0·1396 for samples from the coasts of Alaska and Washington, from Puget Sound and Gray's Harbour.

CHEMICAL ABSTRACTS.

Occurrence of iodine in nature. XII. Geochemistry of iodine. III. Atmophile character of iodine. T. VON FELLENBERG (Biochem. Z., 1928, **193**, 384—389; cf. A., 1926, 1022; 1927, 955).—Gases escaping from various mineral springs are shown to contain iodine in spite of the alkaline nature of the fluid from which they escape. The iodine content runs parallel with the chlorine, bromine, and ammonium contents. The springs from which most gas escapes are richest in iodine, and it appears that their content of iodine is derived for the most part from the volcanic gases as they escape.

P. W. CLUTTERBUCK.

Physical factors on the sandy beach. II. Chemical changes: carbon dioxide concentration and sulphides. J. R. BRUCE (J. Marine Biol. Assoc., 1928, **15**, 553—565).—The observations were made at Port Erin from 1923 to 1927. The gaseous exchanges of animals and plants cause changes in the p_H of the interstitial waters of the beach, but the calcareous matter present in the sand acts as an alkali reserve preventing undue rise in acidity and widening the potential range of carbon assimilation by surface flora. The black layer observed at varying depths below the surface of the sandy beach is associated with the decay of organic matter under conditions of stagnation and oxygen deficiency brought about either through gross obstruction or through the fineness of grade of the sand. Since moist ferrous sulphide to which the layer owes its dark colour oxidises very rapidly on exposure to the air, a special iodometric method was devised for its examination. The following scheme is suggested as representing the sulphur cycle in the sea-bed and in the sandy beach: S RSO$_3$ RSO$_4$+organic matter —— RS H$_2$S $\xrightarrow[\text{Thio-bac}]{}$ S and simultaneously H$_2$S+ Fe$_2$O$_3$,nH$_2$O $\longrightarrow$ FeS+Fe$_2$S$_3$ —— Fe$_2$O$_3$,nH$_2$O+S.

H. INGLESON.

X-Ray study of fluoride micas. C. MAUGUIN and L. GRABER (Compt. rend., 1928, **186**, 1131—1133; cf. this vol., 463).—Fluorine atoms may replace oxygen atoms in the crystal lattice of micas, the sum of the two sets of electronegative atoms always being 12. This involves the loss of a positive and a negative elementary charge due to the departure of a hydrogen atom if the fluorine replaces a hydroxyl group, and explains the low hydrogen content of the fluoride micas. The analogy between oxygen and fluorine in geochemistry is discussed. J. GRANT.

Composition of basaltic lavas of Indo-China. A. LACROIX (Compt. rend., 1928, **186**, 985—991; cf. this vol., 207).—The composition of these lavas is of importance since a fertile "red earth" is produced as the result of their decomposition. In general, they fall into a series ranging from those containing up to 8·7% of free silica (α-basalts) to those in which there is a deficit of silica sufficient to cause the appearance of nepheline (β-basalts). In the former, the pyroxene is an augite containing a relatively large amount of magnesium (pigeonite), and having a very small or zero angle between the optical axes, whilst in the latter the augite is titaniferous. The β-basalts predominate and are rich in olivine. They fall into two groups in which the silica deficit affects only the bivalent metals and the mode of combination of the alkali metals, respectively The basalts are poor in coloured minerals, and bronzite is rare, but ilmenite is abundant. The structure is doleritic with a variable grain, which is sometimes truly holocrystalline. Glomeroporphyric associations of phenocrystals of olivine augite and bronzite were also observed. The analyses show that the volcanic glasses are poorer in ferric iron than the crystalline lavas derived from them. J. GRANT.

Crystalline carnotite from Utah. F. L. HESS and W. F. FOSHAG (Proc. U.S. Nat. Mus., 1927, **71**, Art. 21, 1—6).—The specimen contained UO$_3$ 65·62, V$_2$O$_5$ 21·12, Al$_2$O$_3$ 0·16, Fe$_2$O$_3$ 0·04, CaO 0·64, MgO 0·22, K$_2$O 9·58, Na$_2$O 0·35, H$_2$O 1·35, CuO, PbO, and P$_2$O$_5$ traces, insol. 0·32, total 99·40%, corresponding with the formula K$_2$O,2UO$_3$,V$_2$O$_5$,0·67H$_2$O; $2V$ 50±2°, n_β 2·06—2·04, n_γ 2·08—2·06. The radium : uranium ratio is discussed.

CHEMICAL ABSTRACTS.

Composition of chevkinite. L. E. KAUFMAN (Bull. Acad. Sci. Russ., 1924, **18**, 315—320).—The composition of chevkinite corresponds with the formula 0·5(H.K,Na)$_2$O,2(Fe,Ca,Mn)O,2(La,Ce,Fe)$_2$O$_3$, 6(Si,Ti)O$_2$.

CHEMICAL ABSTRACTS.

Bauxite. T. V. M. RAO (Min. Mag., 1928, **21**, 407—430).—Detailed analyses are given of "laterites" from India, British Guiana, Gold Coast, etc.

The material consists of a mixture of minerals resulting from the decomposition of rocks, the principal constituent being bauxite. It is concluded that bauxite is a definite mineral species with the formula $Al_2O_3,2H_2O$. Experiments were made of the action on granulated basalt of dilute solutions of sodium carbonate at 30—50° during several months. Analyses of the partly decomposed products show a decrease in silica and an increase in alumina, and it is concluded that bauxite has been formed by such action.
L. J. SPENCER.

Potarite, a new mineral from British Guiana. L. J. SPENCER (Min. Mag., 1928, **21**, 397—406).—The palladium mercuride described by Harrison (A., 1925, ii, 592, 593) has been found very sparingly as small nuggets and grains in the diamond-washings on the Potaro river. It is silver-white and brittle, and shows a crystalline structure with the form of cubic octahedra. The mineral has the composition PdHg, and it has since been named potarite. The supposed hexagonal modification of palladium, "allopalladium," is perhaps potarite or simply the cubic modification of palladium.
L. J. SPENCER.

Radium and thorium content of volcanic rocks of the Hegau. H. LEDERER (Ber. naturforsch. Ges. Freiburg i. Br., 1927, **27**, No. 2, 20 pp.; Chem. Zentr., 1927, ii, 2273).—The rocks of the Hegau may be classified in three groups; phonolite, basalt, and tufa, having a radium ($\times 10^{-12}$) and thorium ($\times 10^{-5}$) content as follows: 8·03—4·1, 6·18; 2·33—1·01, 0·57; 1·05—0, 1·01 g. per g.
A. A. ELDRIDGE.

Radium and thorium content of phonolite of the Kaiserstuhl. W. SEITH (Ber. naturforsch. Ges. Freiburg i. Br., 1927, **27**, No. 2, 4 pp.; Chem. Zentr., 1927, ii, 2273).—Phonolite and tephrite of the Kaiserstuhl contain, respectively, 4·83 and $6·62\times 10^{-12}$ g. per g. of radium, and 4·25 and $4·33\times 10^{-5}$ g. per g. of thorium, corresponding with a uranium content of $1·55—2·10\times 10^{-5}$ g. per g.
A. A. ELDRIDGE.

Fresh-water lime-manganese rocks and lime-magnesia fresh-waters. H. KLAHN (Chem. Erde, 1928, **3**, 453—587).—A detailed account of travertine deposits (fresh-water limestones and dolomites), with a discussion of the conditions for their formation and the composition of the waters from which they are deposited.
L. J. SPENCER.

"Cone-in-cone" marl. G. LINCK and W. NOLL (Chem. Erde, 1928, **3**, 699—721).—A discussion of "cone-in-cone" structure in marls, including "nail limestone," with descriptions of material from Thuringia and Romania. Analyses show that calcium carbonate is the main constituent, with considerable and variable amounts of clayey matter and free silica. The structure is attributed to the crystallisation of a calcium carbonate gel in the presence of much foreign matter. Comparisons are made with a similar structure in fibrous celestine pseudomorphous after gypsum from Jena.
L. J. SPENCER.

Constituents and genesis of a few minerals produced from hot springs and their vicinities in Japan. I. Akita hokutolite. II. Composition and genesis of soluble sulphates produced near a sulphur spring. I. SUGANUMA (Bull. Chem. Soc. Japan, 1928, **3**, 69—73, 73—76).—I. A deposit found near a sulphur spring in Akita-ken, Japan, resembles hokutolite (Hayakawa and Nakano, A., 1912, ii, 1123) in general composition, but contains radioactive elements of the thorium series as well as of the radium series. It is probable that the mineral owes its origin to the coagulation of colloidal silicic acid in the water of the spring by substances produced by species of *Cyanophyceæ* growing in the water. Depending on the acidity and temperature of the water, the substances adsorbed by the silica vary, and the mineral has accordingly a zonal structure.

II. Specimens of halotrichite, alunogen, and melanterite found near sulphur springs have been analysed.
R. CUTHILL.

Salt formation in the Chilean desert. W. WETZER (Chem. Erde, 1928, **3**, 375—436).—Microscopical examination of thin sections of Chile saltpetre (caliche) showed the presence of halite, nitratine, darapskite, gypsum, anhydrite, thenardite, glauberite, bloedite, "Chile-loeweite" [minute trigonal crystals with ε 1·434, ω 1·470, *d* 2·153, and, after deducting impurities, the composition $K_2Na_4Mg_2(SO_4)_5,5H_2O$], "chromloeweite" (?), and leonite (?). Potassium perchlorate, although a product of extraction, could not be detected as crystals in the raw caliche. The distribution and relative ages of formation of each of these salts are discussed in detail. It is considered that the nitrates were formed by the action of atmospheric nitric acid on the alkali silicates of the rocks of the region.
L. J. SPENCER.

Comparative study of the weathering of rocks under different climatic conditions. E. BLANCK and A. RIESER (Chem. Erde, 1928, **3**, 437—452).—Fragments of sandstone and of limestone were exposed to the weather during a period of five years at Gottingen and on the summit of the Brocken (1142 m.), where, owing to the difference in altitude, there are marked differences in the temperature, rainfall, and humidity. Detailed analyses of the rocks and of the portions extracted by hydrochloric acid, both before and after the experiment, showed no appreciable differences in composition.
L. J. SPENCER.

Soils [and rock weathering] in Spitzbergen. E. BLANCK and A. RIESER [with H. MORTENSEN] (Chem. Erde, 1928, **3**, 588—698).—A study of rock weathering under arctic conditions. Numerous detailed analyses are given of various rocks (sandstone, quartzite, clay-slate, phyllite, diabase, and calcareous shale) and of their disintegration products, including soils and muds; analyses are also given of the portions extracted by hydrochloric acid and by sulphuric acid from the débris. Chemical action in weathering is here retarded owing to deficient water circulation, and the action of frost is of more importance in breaking down the rocks.
L. J. SPENCER.

Coals as colloid systems. L. L. FERMOR (Nature, 1928, **121**, 705—706).—Evidence is adduced in support of the author's view that coals are to be regarded as colloid systems; the data refer to certain Indian coals.
A. A. ELDRIDGE.

Base exchange and the formation of coal. E. McK. TAYLOR (Nature, 1928, **121**, 789—790).—

Bituminous coal appears always to occur under a roof which has undergone base exchange and containing sodium as the chief replaceable base; the "drift" and "*in situ*" theories may thereby be reconciled. Base exchange between the material covering the petroleum-bearing strata and solutions of sodium chloride must also have taken place. Experiments on the bacterial decomposition of fats under a roof which has undergone base exchange and hydrolysis indicate that the fat is hydrolysed, the resulting glycerol being converted into methane and the fatty acid being reduced to a corresponding paraffin. Hence both coal and petroleum may have resulted from the bacterial decomposition of animal or vegetable fats under alkaline anaerobic conditions.

A. A. ELDRIDGE.

J. L. Smith method for the analysis of samarskite. R. C. WELLS (J. Amer. Chem. Soc., 1928, **50**, 1017—1022).—Observations on the above analysis are recorded. The mineral contained helium; d^{25} 5·67—5·656; μ 2·18—2·20; it had an average age of 1040×10^6 years. The mineral is isotropic.

S. K. TWEEDY.

Minerals. H. COLLINS (Chem. News, 1928, **136**, 305—306).—The author's characteristic data for atoms are applied to minerals.

A. A. ELDRIDGE.

Organic Chemistry.

Catalytic hydrogenation of different types of unsaturated compounds. II. Hydrogenation of conjugated systems. S. V. LEBEDEV and A. O. YAKUBCHIK (J.C.S., 1928, 823—837, and J. Russ. Phys. Chem. Soc., 1927, **59**, 981—1011; cf. A., 1925, i, 350).—The process of hydrogenation of conjugated compounds of butadiene structure in presence of platinum-black may be of four types: (I) In the first phase hydrogen adds on exclusively in the αδ-position. In the second phase, proceeding at a different rate, there occurs addition to the βγ-position of the ethylenic derivative formed in the first phase. The point at which the original conjugated system is consumed, the "critical point of hydrogenation," is at 50% hydrogenation. (II) In the first phase there occurs simultaneous hydrogenation of the conjugated system in the αβ-, βγ-, and γδ-positions of the ethylenic products. The "critical point" is then found at 68—77% hydrogenation. In the second phase, the remainder of the ethylenic compounds formed in the first phase are hydrogenated. (III) It is theoretically possible, although not actually observed, that the addition of 2 mols. of hydrogen might take place simultaneously, giving a saturated compound directly. (IV) Addition of hydrogen occurs exclusively in the αβ- and γδ-positions. The double linkings of the formally conjugated system are hydrogenated independently, either consecutively at different rates, or concurrently, according to the type of substitution. The position of the "critical point of hydrogenation" is characteristic of the type of reaction.

The hydrogenation of isoprene was studied, using the methods previously described (*loc. cit.*). The process is of type (II). The hydrogenation curve, depicting rate of addition of hydrogen, is a horizontal line up to the "critical point" at 70% hydrogenation; after this, it shows three sections corresponding with the successive hydrogenation, at different rates, of the ethylenic products formed before the "critical point," viz., β-methyl-Δ^{γ}-butene, β-methyl-Δ^{α}-butene, and β-methyl-Δ^{β}-butene. *iso*Pentane is formed in the first phase, probably from β-methyl-Δ^{γ}-butene. The total concentration of methylbutenes increases regularly with time, but excess of β-methyl-Δ^{β}-butene was found in the first part of the curve, probably owing to its formation from the other products by isomerisation under the influence of the sulphur dioxide used to separate the isoprene for analysis. In the second phase of the hydrogenation the reactions are no longer "conjugated" by the isoprene, and the methylbutenes are successively hydrogenated in the order given above, which agrees with the rules previously formulated (*loc. cit.*). This was confirmed by the behaviour in the presence of added β-methyl-Δ^{γ}-butene or β-methyl-Δ^{β}-butene. When isoprene is hydrogenated in admixture with various ethylenic compounds, the "critical point" retains its position, although ill-defined with β-methyl-Δ^{β}-butene.

R. K. CALLOW.

***cis–trans*-Isomerism and homologous series.** B. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 19—46).—The physical properties of paraffin hydrocarbon chains in homologous series are reviewed, with the conclusion that the chains are zig-zag in shape, the angle not necessarily being the tetrahedral angle, but depending on the nature of the terminal groups, which are in the *cis*-position if the number of atoms forming the chain is even, and in the *trans*-position if it is odd. The m. p., solubilities, surface tensions, dielectric constants, ionic mobilities, molecular magnetic rotations, molecular volumes, and heats of combustion and fusion of the two types are compared with the same properties of corresponding *cis*- and *trans*-isomerides of the ethylene series, and shown to have the same effect relative to their respective series. The external fields of force of isomerides are shown to vary inversely as their intramolecular tension. Similar terminal groups at both ends of the chain cause mutual repulsion, whilst other combinations cause mutual attraction. Both these factors may result in a twisting of the paraffin chain in "pseudo-*cis*" and "pseudo-*trans*" forms. It is suggested that some compounds in the liquid state are equilibrium mixtures of the true and pseudo-forms, and an explanation offered why certain monobasic fatty acids with an odd number of carbon atoms crystallise in two forms.

Attempts are made to extend these considerations so as to include the *cyclo*paraffins.

M. ZVEGINTZOV.

Erythrene and its dibromides. C. PRÉVOST (Compt. rend., 1928, **186**, 1209—1211).—Erythrene from the dehydration of methylvinylcarbinol had b. p.

$-4{\cdot}75°$, d_4^{-8} 0·650, n_D^{-8} 1·4222, and when brominated at $-20°$ in chloroform or at $-90°$ in methyl chloride, gave the *trans*-αδ-dibromide; no *cis*-form was obtained, and only a small amount of the αβ-dibromide was formed. The two products are desmotropic, and the former when maintained at 85°/10 mm. gives rise to the latter, which has b. p. 52°/10 mm., d_4^{21} 1·865, n_D^{21} 1·541. At 20°, the αβ-dibromide changes slowly to the αδ-form, the change at 100° being more rapid and reversible. The desmotropic nature is confirmed by the tautomerism of the αδ-dibromide, which gives rise to αβ- or αδ-derivatives in quantities different from those of the bromides originally present. At 100°, sodium acetate gives almost entirely the diacetate of Δ^{β}-butene-αδ-diol, and traces of the diacetate of the αβ-diol, whilst hydrolysis of the former furnishes the αβ-diol in 40% yield. Tautomerism and desmotropy are distinct, the latter usually including the former, whilst the reverse is not true (cf. A., 1926, 131; 1927, 851; this vol., 152). Hydrolysis of the above acetates with water alone gives rise to crotonaldehyde (not isolated).

J. D. FULTON.

Derivatives of βγ-dimethylbutadiene. A. D. MACALLUM and G. S. WHITBY (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 33—38).—The action of sulphur chloride on βγ-dimethylbutadiene in carbon disulphide yielded an oily *additive product*, $(CH_2Cl{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}S)_2$, d_4^{26} 1·1172, n_D^{26} 1·5400. There occurred no formation of a thiophen derivative on treatment of the diene with sulphur or reaction with antimony trichloride. Bromination yielded the two dibromides, solid, b. p. 105—110°/18·5 mm., d_4^{30} 1·6912, n_D^{0} 1·5470, and liquid, b. p. 105—110°/18·5 mm., d_4^{30} 1·6502, n^{30} 1·5390. Ozonolysis of the solid dibromide yielded bromoacetone, and it is, therefore, an αγ-compound (cf. Kondakov, A., 1901, i, 62). The solid dibromide is highly reactive. With sodium methoxide and ethoxide at 100° *αδ-dimethoxy-βγ-dimethyl-Δ^β-butene*, b. p. 81—84°/33·5 mm., and *αδ-diethoxy-βγ-dimethyl-Δ^β-butene*, b. p. 90—95°/25 mm., respectively, were obtained. Dimethylamine and diethylamine yielded both open-chain ditertiary bases and cyclic quaternary compounds which may be either pyrrolinium compounds or have a constitution of double mol. wt. with a ten-membered ring. *αδ-Di(dimethylamino)-βγ-dimethyl-Δ^β-butene chloroaurate*, m. p. 188—189°; *αδ-di(diethylamino)-βγ-dimethyl-Δ^β-butene chloroaurate*, m. p. 177—179°; *1 : 1 : 3 : 4-tetramethyl-Δ³-pyrrolinium chloroplatinate* (?), decomp. 199°, and *3 : 4-dimethyl-1 : 1 diethyl-Δ³-pyrrolinium bromoaurate* (?), m. p. 52·8°, were isolated. Methylaniline gave *αδ-di(phenylmethylamino)-βγ-dimethyl-Δ^β-butene*, m. p. 76—77°. Pyridine gave *βγ-dimethyl-Δ^β-butene-αδ-dipyridinium dibromide*, m. p. 124° (*chloroplatinate*, decomp. 229°). An attempt was made to allot *cis*- and *trans*-constitutions to the two dibromides. The liquid is probably the *cis*-form, for it gave with diethylamine a higher yield of a cyclic product, *3 : 4-dimethyl-1 : 1-diethyl-Δ³-pyrrolinium bromoaurate* (?), m. p. 106—107°, than the solid dibromide, although the quaternary products were not identical. Analogy with butadiene dibromides, refractivities, and m. p., but not molecular volumes, support this conclusion. The liquid dibromide showed no tendency to isomerise to the solid when heated or treated with acids. The solid could be isomerised to the liquid, wholly by treatment with magnesium, partly by heating with the original diene. The solid dibromide and magnesium methyl iodide yielded the diene and two *dimerides*, $C_{12}H_{20}$, one, b. p. 50°/20 mm., and the other the distillation residue.

R. K. CALLOW.

Tetramethylbutadiene [γδ-dimethyl-Δ^βδ-hexadiene]. A. D. MACALLUM and G. S. WHITBY (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 39—44).—A review of the published data leads to the conclusion that the ease of polymerisation of butadienes is diminished by increase in the number of substituent methyl groups, and more by substitution in the αδ- than in the βγ-positions.

The most satisfactory of numerous methods tried for the reduction of methyl ethyl ketone to γδ-dimethylhexane-γδ-diol was to heat with magnesium and mercuric chloride in benzene solution. Distillation of this pinacol with a little dilute sulphuric acid yielded *γδ-dimethyl-Δ^βδ-hexadiene*, b. p. 132—134°, 71—73°/100 mm., $d_4^{19\cdot2}$ 0·7832, n_D^{25} 1·4630, not identical with the by-product obtained by Herschmann (A., 1893, i, 547). An unstable *dibromide* was formed with bromine at 0°. Oxidation by 3% aqueous permanganate solution yielded acetic acid alone, confirming the constitution. It showed no tendency to polymerise on heating under conditions which cause formation of caoutchouc from isoprene. The action of sulphuric acid yielded an impure *dimeride*, b. p. 170—200°, n_D^{25} 1·4915. Air, which brought about autoxidation, caused some polymerisation. An attempt was made to synthesise γδ-dimethyl-Δ^βδ-hexadiene by another method. Bromination of *n*-butyl bromide was tried under various conditions; the desired βγ-dibromobutane was obtained by using iron wire as a catalyst in Reboul's method (A., 1892, i, 127). Excess of methyl-alcoholic potash yielded γ-bromo-Δ^β-butene, which, on treatment with magnesium, yielded only a *substance*, $C_{16}H_{31}O$, b. p. about 160°, n_D^{25} 1·4735.

R. K. CALLOW.

Law of periodicity. III. P. PETRENKO-KRITSCHENKO [with A. RAVIKOVITSCH, V. OPOTZKI, E. PUTJATA, and M. DIAKOVA] (Ber., 1928, **61**, [*B*], 845—854; cf. A., 1927, 713).—Periodicity is observed in the action of potassium, tetramethylammonium, tetraethylammonium, barium, and thallous hydroxides, sodium ethoxide, and silver on the chloro-derivatives of methane, but not with its bromo- or iodo-derivatives or with the halogen derivatives of toluene or acetic acid. Ammonia, piperidine, water, alcohol, silver nitrate, potassium acetate, and potassium thiocyanate behave less consistently; the reagents of this group can behave differently according to conditions and to the compound on which they act. Under equivalent conditions, the following substances are hydrolysed to the indicated extent by acetic acid in benzene at 95°: $CH_2(OEt)_2$, 13·6%; $CH(OEt)_3$, 18%, $C(OEt)_4$, 9·7%; $CH(OEt)_2{\cdot}CH(OEt)_2$, 3%. The mutual relationship of the data is the same as that recorded by Skrabal (A., 1926, 1010), but his attribution of minimum activity to maximal symmetry of structure can scarcely be maintained. Duplication of functions does not invariably lead to a strengthening

of all the influences which distinguish the simple molecules. Thus tetraphenylethylene glycol is less readily etherified than triphenylcarbinol and ethyl tartrate less easily than ethyl lactate. Diminution of activity may also be caused by accumulation of similar but not identical groups. Among carbonyl compounds duplication of function results in enhanced activity. With halogen derivatives of methane and ethane the following results are obtained by the use of potassium hydroxide as reagent: $CH_3X>[CH_2X]_2$ for chloro- and bromo-compounds, whereas the reverse holds for iodo-derivatives; $CH_2X_2<[CHX_2]_2$ and $CHX_3>[CX_3]_3$—reversal is caused by accumulation of halogen; the slightly active CH_2X_2 is converted by duplication into the active $[CHX_2]_2$, whereas the active CHX_3 yields the slightly active $[CX_3]_2$. The results are considered from the point of view of Thiele's theory of conjugated double linkings. H. WREN.

Action of cuprous cyanide on methyl iodide. E. G. J. HARTLEY (J.C.S., 1928, 780—781; cf. *ibid.*, 1916, **109**, 1296).—Cuprous cyanide and methyl iodide at 100° yielded a *compound*, $(CuNC)_3$,MeI, stable in air, but losing all the methyl iodide on heating or dissolution in potassium cyanide. At 100°, in excess of acetonitrile the reaction yielded the stable *compound*, 3(CuNC,MeI), which was also formed in small amount at 135° in absence of the nitrile. The action of potassium cyanide on this compound yielded methylcarbylamine, whilst aqueous solutions of silver salts yielded silver iodide, silver, cupric salts, and probably compounds of the type $Cu(NCMe)_2SO_4$, which, however, could not be isolated. Cuprous cyanide and certain other insoluble cyanides combine with acetonitrile to give unstable compounds, *e.g.*, the *compound* CuNC,MeCN. R. K. CALLOW.

[Preparation of] *tert.*-butyl chloride. J. F. NORRIS and W. OLMSTED (Org. Syntheses, 1928, 8, 50—51).

[Preparation of] trimethylene chlorohydrin. C. S. MARVEL and H. O. CALVERY (Org. Syntheses, 1928, 8, 112—115).

Mechanism of the action of oxidising agents on alcohols. B. V. TRONOV and M. A. LUKANIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 181—191).—The reactions of oxidising agents with alcohols are discussed from the point of view of the relative strength of the carbon–hydrogen and hydrogen–oxygen linkings (cf. Tronov and others, this vol., 44).

The rates of reaction of primary and secondary alcohols, both saturated and unsaturated, with bromine, nitric and chromic acids, and potassium permanganate (both in acid and alkaline solution) were investigated.

It is probable that an intermediate compound, of the nature of an ester, is first formed, which then decomposes into the final product. The molecules of the inorganic oxidising agents appear to form the ester-like compounds in the non-ionised state.

M. ZVEGINTZOV.

Determination of alcohols. A. VERLEY (Bull. Soc. chim., 1928, [iv], **43**, 469—472).—The method previously described (A., 1902, ii, 54) for the determination of phenols gives satisfactory results with primary alcohols and most secondary alcohols if 5% of acetyl chloride is added to the acetic anhydride before mixing with 2 parts of pyridine. For the determination, 10 c.c. of this mixture are used and about 2—3 g. of the alcohols. Complete acetylation is obtained by heating for 1—2 hrs. with most primary alcohols and for 2—3 hrs. with secondary alcohols: the recommended periods for the determination are 3 hrs. and 4 hrs., respectively. Accurate results cannot be obtained with very volatile alcohols or if the mixture contains a tertiary alcohol, phenol, primary or secondary amines, or an aldehyde. Small amounts of aldehydes, however, do not affect the accuracy of the results, as acetylation of aldehydes under these conditions never exceeds 14—15%. On account of their volatility alcohols lower than the pentanols give results varying from 53·85% with methyl alcohol, 66·5% with ethyl alcohol, to 97·3% for *sec.*-butyl alcohol and 99·9% for *n*-butyl alcohol. R. BRIGHTMAN.

Liberation of hydrogen from carbon compounds. Interaction with fused alkali hydroxides of: III. Monohydric alcohols and esters; IV. [with E. L. SCHULZE.] **Glycol and glycerol; V. Dextrose, lævulose, sucrose, and cellulose.** H. S. FRY and E. OTTO (J. Amer. Chem. Soc., 1928, **50**, 1122—1131, 1131—1138, 1138—1144).—III. The mechanism proposed for the action of fused alkali hydroxides on methyl alcohol (A., 1924, i, 1277) has been confirmed by further experiments with a eutectic mixture, m. p. 185°, of sodium and potassium hydroxides at 250—450°. At temperatures below 370° the reaction residue contains methoxide, and below 300°, formate. At 370°, 85% of the methyl alcohol is converted into carbonate and hydrogen, at 450°, 100%, and using sodium or potassium hydroxide alone at 450°, 95%. Ethyl alcohol gives no acetate or ethylene at 530° (cf. A., 1926, 710), the reaction, $EtOH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4$, predominating. Similarly, the amounts of carbonate, hydrogen, and methane formed when (*a*) propyl alcohol, (*b*) *iso*propyl alcohol, and (*c*) *tert.*-butyl alcohol are oxidised by fused alkali hydroxide at 500° agree well with the schemes: (*a*) $Pr^{a}OH+6NaOH \longrightarrow Na_2CO_3+Na_4CO_4+CH_4+5H_2$, (*b*) $CHMe_2{\cdot}OH+2NaOH \longrightarrow Na_2CO_3+H_2+2CH_4$, (*c*) $CMe_3{\cdot}OH+2NaOH \longrightarrow Na_2CO_3+3CH_4$. Carbonisation is (*a*) slight, (*b*) very slight, (*c*) nil, but with *iso*butyl alcohol it is extensive, even at 350°. Esters are first hydrolysed by the fused alkali, then oxidised in the normal way. Thus, the oxidation of methyl formate at 475° conforms to the extent of 70% to the scheme $H{\cdot}CO_2Me+4NaOH \longrightarrow 2Na_2CO_3+4H_2$ (slight carbonisation), and that of methyl acetate to the extent of 88% to the scheme $CH_3{\cdot}CO_2Me+4NaOH \longrightarrow 2Na_2CO_3+CH_4+3H_2$. Ammonia, methyl-, dimethyl- and trimethyl-amines, and dimethyl and diethyl ethers are not attacked. These results are in accordance with the general type reactions previously developed.

IV. The general reaction mechanism accounts for the formation of the compounds obtained by Würtz (Ann. Chim. phys., 1859, [3], **55**, 417) and Nef (A., 1905, i, 3) from glycol and fused alkali hydroxides. Using the author's method, reaction is complete in 20 hrs. at 250° and a little oxalate is formed, whilst at

350°, 5—7 hrs. are required and oxalate is absent. In either case at least 80% of the glycol reacts as follows : $C_2H_6O_2+4NaOH \longrightarrow 2Na_2CO_3+5H_2$. The complex results obtained by Nef with glycerol were due to a deficiency of alkali hydroxide. When glycerol is added to the fused alkali at 345—360° and the reaction completed by heating to 400° and finally to 450°, 78% is oxidised according to Buisine's equation (A., 1903, i, 455), $C_3H_8O_3+4NaOH \longrightarrow 2Na_2CO_3+3H_2+CH_4+H_2O$, and 21% according to the equation $C_3H_8O_3+6NaOH \longrightarrow 7H_2+3Na_2CO_3$.

V. When dextrose or lævulose is fused with alkali at 185° and the product gradually heated during about 15 hrs. to 550°, it is oxidised to the extent of 90—95%. Of this 90% is due to the reaction $C_6H_{12}O_6+8NaOH \longrightarrow 4Na_2CO_3+2H_2O+2CH_4+4H_2$, which involves intermediate formation of lactic acid or ethyl alcohol, and the remainder to the direct oxidation, $C_6H_{12}O_6+12NaOH \longrightarrow 6Na_2CO_3+12H_2$. Quantitative results could not be obtained with sucrose, owing to carbonisation. Cellulose is completely oxidised without carbonisation when made into a paste with water and alkali and heated during 8 hrs. to 550° ; 95% reacts according to the equation $C_6H_{10}O_5+14NaOH \longrightarrow 5Na_2CO_3+Na_4CO_4+12H_2$, and 5% according to $C_6H_{10}O_5+8NaOH \longrightarrow 4Na_2CO_3+2CH_4+4H_2+H_2O$. H. E. F. NOTTON.

Chlorine dioxide explosions. E. C. WAGNER (J. Amer. Chem. Soc., 1928, 50, 1233—1234).—The use of potassium chlorate in the oxidation of *n*-butyl alcohol by the method of Milas (this vol., 392) may lead to explosions unless the temperature is kept below 80° until some time after the final addition of acid has been made. H. E. F. NOTTON.

Kessyl alcohol. IV. Y. ASAHINA and S. NAKANISHI (J. Pharm. Soc. Japan, 1928, [551], 1—20).—It was previously shown (*ibid.*, [544], 485) that deoxykessyl ketone dichloride gave with alcoholic potassium hydroxide deoxy-α-kessylene ketone, a compound with two double linkings, which was converted into deoxy-α-kessvlanone by catalytic reduction. It is now found that the analogous deoxidation takes place simply on heating with palladised charcoal (1 : 10) or with charcoal only : α-kessyl ketone gives on treatment with the palladised charcoal iso*deoxy-α-kessylene ketone*, b. p. 153—155°/7 mm., d_4^1 1·0031, n^1, 1·52005, $[\alpha]_D^{18}$ +42·60° (*semicarbazone*, m. p. 182°), which decolorises permanganate in acetone and is converted into iso*deoxy-α-kessylanone*, b. p. 134—136°/5 mm., d_4^{18} 0·9498, 1·48072, $[\alpha]_D^{17}$ +32·54° (*semicarbazone*, m. p. 220—223°), by catalytic reduction. The latter compound is stable to permanganate, turns cherry-red with vanillin and hydrochloric acid, reddish-violet-blue with bromine in glacial acetic acid. Kessyl alcohol, when heated with the palladised charcoal, affords a deep blue oil, which by treatment with phosphoric acid (Ruzicka and Rudolph, A., 1926, 299) is separated into a deep blue oil, *kessazulene*, b. p. 153°/7 mm., d_4^{2x} 0·9717, soluble in phosphoric acid, and a colourless oil, *kessylene*, b. p. 109—111°/9 mm., 0·9115, 1·48905, insoluble in acid. The absorption spectrum of kessazulene closely resembles those of Kremer's azulene (A., 1923, i, 594) and of the azulenes of Ruzicka and Rudolph (*loc. cit.*). Analysis of the *picrate*, m. p. 123°, and *styphnate*, m. p. 106°, of kessazulene, and of many other kessyl alcohol derivatives indicates C_{15}-formulæ, not C_{14} (cf. Bertram and Gildemeister, A., 1891, 238). Kessazulene, $C_{15}H_{18}$, absorbs catalytically 3 mols. of hydrogen at the ordinary temperature, and one more molecule at 70°, giving the *octahydro*-derivative, $C_{15}H_{26}$, b. p. 112—115°/7 mm., d_4^{18} 0·8930, 1·47141, which is stable to permanganate, showing its tricyclic constitution, and gives with bromine first a violet and then a blue colour. Kessylene, $C_{15}H_{22}$, similarly gives a saturated *hydrocarbon*, $C_{15}H_{26}$, b. p. 105—108°/5 mm., 0·8931, n_D^{18} 1·47289, which is stable to permanganate, and shows the same coloration as octahydrokessazulene.

Unsaponifiable matter from the oils of elasmobranch fish. IV. Establishment of the structure of selachyl and batyl alcohols as monoglyceryl ethers. I. M. HEILBRON and W. M. OWENS (J.C.S., 1928, 942—947).—Batyl alcohol was prepared from the liver oil of *Centrophorus granulosus* (cf. Tsujimoto and Toyama, A., 1922, i, 297 ; Toyama, A., 1924, i, 604) by an improved method. The *phenylurethane*, m. p. 98°, and p-*nitrobenzoate*, m. p. 53—54°, are described. The presence of an ether oxygen atom was confirmed, but, contrary to Weidemann's statement (A., 1926, 980), no methoxyl is present. Treatment with hydriodic acid yielded octadecyl iodide, m. p. 33°, the identification of which was confirmed by the preparation from it of octadecane, methyl octadecyl ether, octadecyl alcohol, and its phenylurethane. The constitution of batyl alcohol is represented by $C_{18}H_{37}\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, (I), or $C_{18}H_{37}\cdot O\cdot CH(CH_2\cdot OH)_2$, (II), of which (II) is preferred. It follows that selachyl alcohol, $C_{21}H_{42}O_3$, is the corresponding monoglyceryl oleyl ether, whilst chimyl alcohol, $C_{19}H_{40}O_3$, will correspond with the monoglyceryl cetyl ether. R. K. CALLOW.

Configuration of pentaerythritol. J. BOESEKEN and B. B. C. FELIX (Ber., 1928, 61, [*B*], 787—790).—If pentaerythritol has the tetrahedral configuration, the products, $C(C_2H_4O_2{>}CRR')_2$, derived from it by condensation with 2 mols. of an aldehyde, ketone, or ketonic acid must be asymmetric and hence capable of resolution into enantiomorphous isomerides. If, however, the pyramidal structure of the solid persists in the solution, *cis–trans*-isomerides must be capable of existence. In several cases examined, the latter possibility has not been realised, but an isolated instance of the isolation of an optically active derivative is recorded. It is suggested that both forms may be present in solution and that the central carbon atom oscillates between positions within and without the tetrahedron.

Pentaerythritol and benzaldehydediethylacetal afford dibenzylidenepentaerythritol, which, apparently by spontaneous resolution, afforded the dextrorotatory *compound*, m. p. 188—189°, $[\alpha]_D$ +30° in chloroform; the active material is rapidly racemised by hydrogen chloride in chloroform to the ordinary racemate, m. p. 160°. Attempts to repeat the resolution failed. *Ditrichloroethylidenepentaerythritol*, $C(C_2H_4O_2{:}CH\cdot CCl_3)_2$, from pentaerythritol, chloral hydrate, and concentrated sulphuric acid, has m. p. 275°. The *com-*

pound $C(C_2H_4O_2{:}CMe{\cdot}CH_2{\cdot}CO_2Et)_2$, b. p. 145—150°/4 mm., prepared from pentaerythritol, ethyl acetoacetate, and alcoholic hydrogen chloride, is hydrolysed to the corresponding *acid*, which could not be resolved by means of strychnine, brucine, codeine, or *l*-phenylethylamine; at about 100°, the acid loses carbon dioxide and affords pentaerythritol di*iso*propylidene ether, m. p. 115—116°. From ethyl pyruvate the *substances* $C(C_2H_4O_2{:}CMe{\cdot}CO_2Et)_2$, m. p. 145°/0 mm., and $(CH_2{\cdot}OH)_2C{:}C_2H_4O_2{:}CMe{\cdot}CO_2Et$, m. p. 95°, are derived, the former of which yields the corresponding *acid*, m. p. 238° (sodium salt). The condensation *products* of pentaerythritol with 2 mols. of the following substances have been prepared: lævulic acid, m. p. 186—188°; terephthalaldehydic acid; benzaldehyde-*m*-sulphonic acid; *m*-dimethylaminobenzaldehyde. H. WREN.

Sodium ethylene thiosulphate, $Na_2C_2H_4S_4O_6$. O. MAGIDSON [with W. KROL] (Trans. sci. chem.-pharm. inst., Moscow, 1923, **6**, 21—28; Chem. Zentr., 1927, ii, 2542).—When ethylene dibromide and saturated aqueous sodium thiosulphate are stirred for 10—15 days at 40°, plates of *sodium ethylene thiosulphate*, $Na_2C_2H_4S_4O_6$, decomposing when heated, are obtained. A. A. ELDRIDGE.

Preparation of aliphatic and aromatic sulphones with sodium hypochlorite. A. E. WOOD and E. C. TRAVIS (J. Amer. Chem. Soc., 1928, **50**, 1226—1228; cf. B., 1926, 811; Birch and Norris, A., 1925, i, 1229).—(*a*) Ethyl, (*b*) propyl, (*c*) *n*-butyl, (*d*) *n*-heptyl, (*e*) phenyl, and (*f*) benzyl sulphides have been oxidised by sodium hypochlorite (2·3—9·3% of available chlorine) at the ordinary temperature. Solutions containing 2% of free sodium hydroxide attacked only (*a*) and (*b*); those with 0·2—0·1% oxidised all except (*d*) within 3 hrs., and those with 0·12—0·61% of sodium carbonate gave sulphones instantly with all except (*d*), which gave mainly sulphoxide. H. E. F. NOTTON.

Electrolysis of anhydrous formic acid. G. BAUR [with F. SOMLO and H. W. MACKINNEY].—See this vol., 489.

Determination of formic acid in acetic acid. F. G. GERMUTH (Chemist-Analyst, 1928, **17**, 7).—Mercuric chloride solution (4%, 20 c.c.), potassium acetate solution (15%, 20 c.c.), and hydroxylamine hydrochloride solution (2%, 1 c.c.) are added to 2 g. of the acetic acid, and the precipitate of mercurous chloride is collected, dried, and weighed. CHEMICAL ABSTRACTS.

Determination of small quantities of acetic acid in air in presence of carbon dioxide. V. KUNI and S. NIKOLSKI (Gigiena truda, 1927, 41—43; Chem. Zentr., 1927, ii, 2329).—The air is drawn through 0·1*N*-sodium hydroxide solution, the change in alkalinity is determined, and the carbonate precipitated as barium carbonate; the latter is determined titrimetrically or as barium sulphate. A. A. ELDRIDGE.

[Preparation of] trimethylacetic acid. S. V. PUNTAMBEKER and E. A. ZOELLNER (Org. Syntheses, 1928, **8**, 104—106).

[Preparation of] trimethylacetic acid. L. T. SANDBORN and E. W. BOUSQUET (Org. Syntheses, 1928, **8**, 108—110).

[Preparation of] β-chloropropionic acid. C. MOUREU and R. CHAUX (Org. Syntheses, 1928, **8**, 54—56).

[Preparation of] β-chloropropionic acid. S. G. POWELL (Org. Syntheses, 1928, **8**, 58—59).

Mechanism of the transformation undergone by ricinoleic acid. Pyrogenic decomposition of methyl ricinoleate. P. S. PANIUTIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 1—6).—The position and behaviour under the influence of heat of the double linking in ricinoleic acid were investigated. Pure ricinoleic acid was prepared (in a 75% yield) from castor oil by hydrolysis and precipitation as the lead salt with lead acetate. As the free acid polymerised under the action of heat, the behaviour of the methyl ester was investigated. On distillation it gave a 62% yield of heptaldehyde. By regulating the distillation rate and introducing lumps of pumice saturated with anhydrous borax as an anti-polymerising agent, 92·7% of the aldehyde and 87% of methyl undecenoate were obtained. There was no evidence of either racemisation or migration of the double linking. M. ZVEGINTZOV.

Condensation of hydroxy-acids by the simultaneous action of several catalysts in the presence of hydrogen under high pressure; α-hydroxy-*n*-butyric and α-hydroxy*iso*valeric acids. V. IPATIEV and G. RASUVAJEV (Ber., 1928, **61**, [*B*], 634—637; cf. A., 1926, 1124; 1927, 1053, 1054).—The production of dibasic acids by heating the salts of α-hydroxy-acids in aqueous solution at 250—270° under high hydrogen pressure in the presence of the oxides of nickel and aluminium becomes less marked as the carbon chain of the hydroxy-acid is lengthened. Thus, sodium α-hydroxy-*n*-butyrate affords α-methyl-β-ethylsuccinic acid in 10% yield together with about 25% of *n*-butyric acid, higher monobasic acids probably derived from dicarboxylic acids by loss of carbon dioxide, and methane. Sodium α-hydroxy*iso*valerate does not give a dicarboxylic acid. The main products are carbon dioxide, formic acid, *iso*butyl alcohol, saturated acids among which propionic acid is identified, and methane; *iso*valeric acid could not be isolated. H. WREN.

Condensations of hydroxy- and keto-acids; β- and γ-hydroxy- or -keto-acids and acids with a tertiary hydroxyl group. G. RASUVAJEV (Ber., 1928, **61**, [*B*], 637—640; cf. A., 1926, 1124; 1927, 1053, 1054, and preceding abstract).—The production of dibasic acids is not observed with the acids named in the title. Thus sodium β-hydroxybutyrate in aqueous solution at 245—250° in presence of nickel and aluminium oxides and hydrogen under 56 atm. gives *n*-butyric acid in about 35% yield accompanied by carbon dioxide, formic and acetic acids, methane, and a non-homogeneous liquid. Sodium lævulate, at a temperature not exceeding 230°, affords successively γ-hydroxyvaleric acid and valeric acid in yield not exceeding 20%. About 20% of the acid suffers conversion into methane, carbon dioxide, and un-

identified products; at 250°, this type of decomposition becomes more marked, and the resulting solution, when acidified, deposits a tar. Sodium α-hydroxy*iso*butyrate yields 60% of *iso*butyric acid in addition to methane, carbon dioxide, formic acid, and unidentified products. H. Wren.

Influence of groups and associated rings on the stability of certain heterocyclic systems. IV. Substituted butyro- and valero-lactones. S. S. G. Sircar (J.C.S., 1928, 898—903; cf. A., 1927, 756).—The observed rates of hydrolysis of the series of butyro- and valero-lactones substituted in the β-position by the groups H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane, and *cyclo*hexane show that there is a general increase in stability in the order given, but in the series of butyrolactones the Me,H member is more stable than the Et,H member, and there is a maximum of stability at the Me,Et and Et,Et members, whilst in the valerolactones the Me,H member is least stable and the *cyclo*pentane member shows maximum stability. It is concluded that there is an "optimum condition" of stability peculiar to each ring-system, its exact position being difficult to predict on the Thorpe–Ingold modified strain theory alone. This indicates the existence of other factors in deciding ease of ring-formation and ring-stability.

The butyrolactones were prepared by heating the silver salt of the glutaric acid with iodine (cf. Windaus and Klanhart, A., 1921, i, 392), and the valerolactones by reduction of the glutaric anhydrides with sodium and alcohol. The following are new: β-*methylbutyrolactone*, b. p. 88°/12 mm., β-*ethylbutyrolactone*, b. p. 99°/12 mm.; β-*methyl*-β-*ethylbutyrolactone*, b. p. 98°/10 mm.; ββ-*diethylbutyrolactone*, b. p. 117°/12 mm; β-cyclo*pentane*spiro*butyrolactone*, b. p. 120—121°/11 mm.; β-cyclo*hexane*spiro*butyrolactone*, b. p. 138°/11 mm.; β-*methylvalerolactone*, b. p. 90°/12 mm.; β-*ethylvalerolactone*, b. p. 104°/13 mm.; β-*methyl*-β-*ethylvalerolactone*, b. p. 122°/10 mm.; ββ-*diethylvalerolactone*, b. p. 143—144°/15 mm.; β-cyclo*pentane*spiro*valerolactone*, b. p. 146°/12 mm.; and β-cyclo*hexane*spiro*valerolactone*, b. p. 158—159°/10 mm. The *silver* salts of the corresponding acids were prepared. R. K. Callow.

Porphyrins. XVI. γ-Chloro-αγ-dimethylitaconic acid. W. Kuster, H. Maurer, and K. Packendorff (Z. physiol. Chem., 1928, 172, 244—250; cf. Kuster, Maurer, and Palm, A., 1926, 713, 1024).—Ethyl α-acetyl-αβ-dimethylsuccinate (hydrolysis product of the imide, $C_8H_{11}O_3N$, from hæmatoporphyrin dimethyl ether) gives with phosphorus pentachloride an acid chloride, from which by treatment with sodium ethoxide and then with acid is obtained in small yield γ-chloro-αγ-dimethylitaconic acid, m. p. 127° (decomp.). Distillation in a vacuum converts this into the *anhydride*, m. p. 145°, b. p. 125°/15 mm., of γ-chloroaticonic acid, $CH_2{:}CCl{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CO_2H$; at ordinary pressure there is also formed the isomeric oily *anhydride*, b. p. 210—225°, of α-methyl-β-(α′-chloroethyl)maleic acid. The crystalline and the oily anhydrides are converted by sodium and barium hydroxide, respectively, into trans-γ-*chloroaticonic acid*, m. p. 152°. The *ammonium* salt of this acid and the products of addition of 2 mols. of ammonia to the two anhydrides all give on distillation an *imide*, m. p. 166°. C. Hollins.

Methyl-β-hydroxyethylmaleic anhydride and the hydrolysis of α-hydroxynitriles with sulphuric acid. III. W. Küster [with K. May, R. Wolf, A. Eberle, and G. Mandry] (Z. physiol. Chem., 1928, 172, 230—243; cf. A., 1925, i, 922).—Ethyl 1-acetyl*cyclo*propane-1-carboxylate (*thiosemicarbazone*, m. p. 160°; p-*bromophenylhydrazone*, m. p. 131°) is converted into its cyanohydrin, which, when heated with hydriodic acid (*d* 1·7) at 140—150°, gives a less impure methyl-β-iodoethylmaleic anhydride (cf. *loc. cit.*), from which the *barium* salt and thence the *silver*, *copper*, and *calcium* salts of methyl-β-hydroxyethylmaleic acid are obtained pure. Hydrolysis of the cyanohydrin with concentrated sulphuric acid water-cooled below 40° gives oily *methyl*-β-*hydroxyethylmaleic anhydride* (*copper* salt), which is converted by boiling 10% sodium hydroxide into a dibasic *acid*, $C_7H_{10}O_5$, subliming at 200°; the anhydride is accompanied by an oxidation product, γ-*hydroxy*-β-*carbethoxy*-γ-*carbamyl*-n-*valeric acid*, m. p. 127°. Ice-cooling during hydrolysis prevents formation of this product.

The *cyanohydrin*, b. p. 114—117°/3 mm., of ethyl ethylacetoacetate yields with 70% sulphuric acid an amide-ester, α-*hydroxy*-β-*carbethoxy*-α-*methyl*-n-*valeramide*, m. p. 121—122°, and a *by-product*, m. p. 116°. From the cyanohydrin of ethyl acetylglutarate is similarly obtained the corresponding di-ester-amide, *ethyl* δ-*hydroxy*-γ-*carbethoxy*-δ-*carbamyl*-δ-*methyl*-n-*hexoate*, m. p. 101°, from which by hydrolysis with 40% sodium hydroxide a small amount of hæmatic acid results; under other conditions, the γ-carbethoxy-group is also hydrolysed by sulphuric acid, giving *ethyl* δ-*hydroxy*-γ-*carboxy*-δ-*carbamyl*-δ-*methyl*-n-*hexoate*, m. p. 186°. Hydrolysis of ethyl cyanomethylsuccinate (Küster and Hugel, A., 1923, i, 1207) with 85% sulphuric acid yields a *compound*, $C_{10}H_{17}O_5N$, m. p. 146—147°, which loses no ammonia when heated with 0·5—20% potassium hydroxide. Ethyl γ-cyanopentane-αγδ-tricarboxylate (*ibid.*) is converted by 85% sulphuric acid into *ethyl pentane*-γδ-*dicarboxylimide*-αγ-*dicarboxylate* [αγ-dicarbethoxypentane-γδ-dicarboxylimide]. C. Hollins.

Reducing power of chemically pure glycuronic acid. G. Scheff (Biochem. Z., 1928, 194, 96—104).—A method is described for determining the reducing power of pure glycuronic acid and of the ammonium salt of its menthol derivative, and comparison is made with the reducing power of arabinose and dextrose. No simple relationship, calculable from the mol. wt., exists between the reducing powers of dextrose and glycuronic acid (cf. A., 1927, 551). P. W. Clutterbuck.

Resolution of r-α-sulphodi-n-butyric acid. R. Ahlberg (Ber., 1928, 61, [*B*], 811—817; cf. A., 1924, i, 832).—The preparation of *barium* r-α-*sulphodi*-n-*butyrate* (*octa*-, *tri*-, and *semi*-*hydrates*) is best effected by dissolving the acid in barium hydroxide followed by addition of an excess of the latter and preservation of the solution for a few days. The

salt is the most sparingly soluble of the possible isomerides. To avoid isomerisation during crystallisation, sulphodibutyric or acetic acid must be added to the salt until alkalinity completely disappears. The *r*-acid can be resolved into its optical antipodes by brucine, cinchonine, or cinchonidine. The alkaloidal salts are derived from 2 mols. of base and 1 mol. of acid. With the two alkaloids first named, the (+)-acid gives the most sparingly soluble salts, whereas with cinchonidine the salt of the (−)-acid separates. The homogeneous (−)-acid is, however, isolated more conveniently and in better yield from the mother-liquors of the precipitated brucine salt. On account of the readiness with which the active α-sulphodi-*n*-butyric acids undergo isomerisation their isolation is a matter of considerable difficulty, and the success of the operations depends on their sufficient insolubility in comparison with that of the other forms and their relative stability in anhydrous ether. (+)-*α-Sulphodi*-n-*butyric acid* has m. p. about 156—160° (indefinite by reason of isomerisation), $[\alpha]^{13}_{D}$ +107·9° in ether, +88·6° in acetone, $[\alpha]^{25}$ +84·4° in absolute alcohol. For the (−)-*acid*, $[\alpha]^{14}_{D}$ −106·7° in ether, is recorded. (+)-Sulphodi-*n*-butyric acid undergoes slow racemisation in moist ether.

H. WREN.

Kinetics of the transformation of the active α-sulphodi-*n*-butyric acids. R. AHLBERG (Ber., 1928, **61**, [*B*], 817—826; cf. preceding abstract).—The rate of racemisation of α-sulphodi-*n*-butyric acid in aqueous solution increases with the dilution to a well-defined maximum for 0·1*M*-solutions, after which it diminishes sharply. In solutions which are 0·1*M* with respect to the organic acid but also contain 0·01—2·01 mols. of hydrogen chloride per litre, an ill-defined maximum rate of racemisation is observed in presence of 0·01 mol. of hydrogen chloride; with higher concentrations of mineral acid the rate of inactivation falls steadily. 0·1*M*-Solutions of the acid partly neutralised by sodium hydroxide show an indistinct maximal rate of racemisation if about 20% of the acid is neutralised; with further addition of alkali hydroxide the rate of racemisation falls almost linearly with the decrease of free acid until the completely neutral solutions are nearly stable. If a portion of the α-sulphodi-*n*-butyric acid in aqueous solution is replaced by the corresponding molecular amount of orthophosphoric acid, the velocity of racemisation remains unchanged or is very slightly increased. H. WREN.

α-Ethyl-αα′-sulphodipropionic acid. R. AHLBERG (Ber., 1927, **61**, [*B*], 827—829).—A mixture of the *r*-α-ethyl-αα′-thiodipropionic acids is oxidised to a mixture of *r*-α-ethyl-αα′-sulphodipropionic acids one of which can be isolated by means of its sparingly soluble barium salt. This acid can be resolved into its optical isomerides by brucine or quinine, thus giving two of the four possible active acids. The rate of racemisation of the acids in aqueous solution has been studied. Among the sulphonic acids, increasing mol. wt. causes rapid diminution in the rate of inactivation. The following half-periods in hours for approximately 0·2*M*-solutions at about 25° are recorded: α-sulphodipropionic acid, 1·3; α-ethyl-αα′-sulphodipropionic acid, 2·3; α-sulphodi-*n*-butyric acid, 2·75; α-sulphodi*iso*valeric acid, 50.

H. WREN.

Determination of acetaldehyde by different methods. J. WAGNER (Biochem. Z., 1928, **194**, 441—452).—Acetaldehyde, present in standard dilute aqueous solutions or liberated from known amounts of its hydrogen sulphite compound, its thiosemicarbazone, and from *dl*-lactic acid, is comparatively determined by the usual iodine titration, by the mercuric oxide, and hydroxylamine sulphate methods. The sulphite titration method may also be used for very small concentrations of aldehyde.

P. W. CLUTTERBUCK.

Acraldehyde. J. PRITZKER (Helv. Chim. Acta, 1928, **11**, 445—448).—A criticism of the structure assigned to the colouring matter forming the product of interaction of acraldehyde, hydrogen peroxide, and phloroglucinol (Powick, A., 1924, i, 487).

H. BURTON.

Pyrogenic decomposition of mixed magnesium carbonates. Preparation of ketones. D. IVANOV (Bull. Soc. chim., 1928, [iv], **43**, 441—447).—The carbonated magnesium compounds obtained by the action of carbon dioxide on magnesium aralkyl or *n*-primary alkyl compounds at −20° (cf. A., 1925, i, 503) after removal of the ether by distillation afford (1) the hydrocarbon resulting from the decomposition $2RX+Mg=R{\cdot}R+MgX_2$ with (2) the ketone from the secondary decomposition $R{\cdot}CO{\cdot}O{\cdot}MgX+R{\cdot}MgX=R{\cdot}CO{\cdot}R{\cdot}MgX_2+MgO$; and (3), mainly, the ketone resulting from the decomposition $2R{\cdot}CO{\cdot}O{\cdot}MgX=R{\cdot}CO{\cdot}R+MgX_2+MgCO_3$, the commencement of the third stage being usually marked by the liberation of carbon dioxide. With magnesium *sec.*-alkyl or aryl or hydroaryl compounds the yields of ketone are poor and the decomposition affords mainly the corresponding ethylenic hydrocarbon, water, carbon monoxide and dioxide. In the case of the carbonated magnesium aryl compounds the corresponding hydrocarbon is the chief product, and dry distillation of the corresponding calcium or barium salts affords the same products. Since decomposition of the corresponding magnesium salts at similar temperatures affords practically the same yield of ketone, the mixed magnesium carbonates are regarded as true salts of magnesium and probably possess the symmetrical structure suggested by Jolibois (A., 1912, i, 753) at high as well as at low temperatures (cf. A., 1927, 961), and the decomposition is to be represented: $(R{\cdot}CO_2)_2Mg,MgX_2=R{\cdot}CO{\cdot}R+MgX_2+MgO+CO_2$. The stability of the carbonated compound is also dependent on the nature of the halide, the temperature of decomposition being lowest with the iodides and highest with the chlorides. The reaction is, however, best effected with the chlorides or bromides, these affording crystalline carbonates, whereas those derived from *sec.*-bromides or iodides are oily products. The following ketones have been prepared in this way, the yields and temperature of decomposition being indicated: acetone, 330—360°, 157% (59% from magnesium acetate); diethyl ketone, 340—360°, 70% (74% from the propionate); di-*n*-propyl ketone, 330—340°, 70%; di-*n*-butyl ketone, 360—380°, 63%

(from the chloride), 50% from the bromide at 330—340°; di*iso*amyl ketone, 390—400°, 43% from the chloride, 35% at 370—390° from the bromide; di-*iso*propyl ketone, 380—390°, 35%, di*iso*butyl ketone, 360°, 28%; di-*sec.*-butyl ketone, 340—350°, traces; dibenzyl ketone, 370°, 57% (60% from magnesium phenyl acetate at 370—380°); dihexyl ketone, 390—410°, traces; benzophenone, 460—500°, 6% (30% from magnesium benzoate); di-*p*-tolyl ketone, 450°, traces. The following m. p. are recorded for the anhydrous (probably basic) magnesium salts: *acetate*, 357°; n-*propionate*, 286°, n-*butyrate*, 275°; n-*valerate*, 258°, iso*valerate*, 224°, *benzoate*, 320°, *hexahydrobenzoate*, 492°. R. BRIGHTMAN.

Dioximes. XLVIII. I. DE PAOLINI and A. IMBERTI (Gazzetta, 1928, **58**, 196—202).—The method of preparing hydroxyglyoximes previously described (cf. A., 1926, 850; 1927, 135) is extended to the preparation of aminohydroxytrioxime, $NH_2\cdot C(N\cdot OH)\cdot C(N\cdot OH)\cdot C(N\cdot OH)\cdot OH$ (described by Wieland and Hess, A., 1909, i, 370, as *iso*nitrosomalonohydroxamic acid amine-oxime). Ethyl oximinocyanoacetate, prepared by treating a mixture of ethyl cyanoacetate and aqueous sodium nitrite solution with dilute hydrochloric acid, when treated in methyl-alcoholic solution with hydroxylamine and alcoholic ammonia solution, yields the *ammonium* salt of aminohydroxytrioxime, of which the hydrochloride has new m. p. 156° (decomp.), and the tetra-acetyl derivative, m. p. 179°. The above ammonium salt when heated in dilute sulphuric acid yields 3-amino-4-oximino-1 : 2 : 5-*iso*oxazolone (cf. Wieland and co-workers, A., 1909, i, 370, 610; 1912, i, 838), which forms a *monobenzoyl* derivative, m. p. 193° (decomp.). The aminoglyoximecarboxylic acid, obtained by Wieland and Hess (*loc. cit.*) by the action of barium hydroxide on the amino-oximino*iso*-oxazolone, is synthesised by the action of hydroxylamine on oximinocyanoacetic acid, and has m. p. 170° (decomp.). Its *ammonium* salt, m. p. [$+H_2O$] 114—115°, and *silver* salt are described; it is converted by acetic anhydride into acetoximinocyanoformamide (Wieland and Gmelin, A., 1909, i, 610). E. W. WIGNALL.

Structure of carbohydrates. W. N. HAWORTH (Helv. Chim. Acta, 1928, **11**, 534—548).—A lecture delivered to the Swiss Chemical Society. H. BURTON.

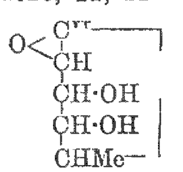
Ultra-violet spectrograms of carbohydrates. V. HENRI and S. A. SCHOU (Z. physiol. Chem., 1928, **174**, 295—299).—Absorption experiments with dextrose solutions show that the absorption is less with purer dextrose preparations, and preparations which give much less absorption than that recorded by Niederhoff (A., 1927, 396, 724) are readily obtained. With the purest dextrose used, there is no detectable absorption at 2800 Å. and the absorption can be measured only below 2210 Å. In the solutions where the absorption at 2800 Å. can be measured, the values are less than one twentieth of those obtained by Niederhoff, and a comparison with the absorption coefficients of acetone leads to the conclusion that less than 1 in 300 of the molecules present in the dextrose solution have the carbonyl form. The formation of an absorption band at 2800 Å. in dextrose solutions is dependent on the p_H, temperature, and time; the band can be detected at p_H values as low as 7·0 in phosphate-buffered solutions. A. WORMALL.

Ultra-violet absorption of carbohydrates. P. NIEDERHOFF (Z. physiol. Chem., 1928, **174**, 300—301).—The absorption band at 2800 Å. of reducing sugars in aqueous, especially alkaline, solution is not due to impurities as suggested by Kwiecinski and Marchlewski (A., 1927, 1056) and by Henri and Schou (preceding abstract). The decrease in the selective absorptive power of dextrose or galactose on recrystallisation from alcohol is not due to the removal of impurities, since the mother-liquors show no selective absorption. Also, reducing sugars show a selective absorption, whereas sucrose does not. A. WORMALL.

Reactions between sugars and amino-acids. G. QUAGLIARIELLO and P. DE LUCIA (Boll. soc. ital. biol. sperim., 1927, **2**, 26—30; Chem. Zentr., 1927, ii, 2179).—A study of the effect of glycine on the rotation of aldehydic sugars, with which it forms compounds. The largest reduction (50%) is observed with mannose. With dextrose, the maximal fall of rotation varies with p_H: 0% at p_H 8·46, 37% at 8·95, 17·57% at 9·1, 50% at 9·5, 99% at 10·4. Simultaneously, the f. p. is changed. A. A. ELDRIDGE.

[Preparation of] *l*-arabinose. E. ANDERSON and L. SANDS (Org. Syntheses, 1928, **8**, 18—21).—The authors' method (B., 1926, 169) for the preparation of *l*-arabinose from mesquite gum is modified. A. A. ELDRIDGE.

Rhamnosan. H. VOGEL (Helv. Chim. Acta, 1928, **11**, 442—444).—When rhamnose is heated at 150—155°/15—16 mm., there is formed a *rhamnosan* (annexed formula), m. p. 90°, $[\alpha]_D$ +2·5° in water (*diacetate*, m. p. 102—105°, $[\alpha]_D$ + 30·47° in chloroform), which when boiled in aqueous solution regenerates rhamnose. This rhamnosan differs from that described by von Lippmann (A., 1925, i, 366). H. BURTON.



Oxidation of dextrose in alkaline solution by air or oxygen with formation of carbon monoxide. M. NICLOUX (Compt. rend., 1928, **186**, 1218—1220).—A measured volume of oxygen or air was passed into an evacuated flask containing dextrose in dilute alkaline solution at the required temperature. Carbon monoxide and dioxide were formed in amounts varying with temperature, alkalinity, and time of contact of the solution with oxygen. J. D. FULTON.

Oxidation of lævulose in absence of oxygen. F. AUBEL and L. GENEVOIS (XII Int. Cong. Physiol., 1926, 11—12; Chem. Zentr., 1927, i, 2724—2725).—In anaerobiosis, lævulose reduces certain dyes, the rate of reduction of 10^{-3}—$10^{-6}N$-methylene-blue solution being independent of the dye concentration, but increasing with increased p_H value and lævulose concentration. A. A. ELDRIDGE.

Ketonic nature of α-glucoheptulose. G. BERTRAND and G. NITZBERG (Compt. rend., 1928, **186**,

1172—1175).—Sorbose bacteria grown on yeast with addition of α-glucoheptitol give rise to a crystalline reducing sugar, $C_7H_{14}O_7$, named *α-glucoheptulose.* The sugar when heated with dilute hydrochloric acid in presence of orcinol, phloroglucinol, or resorcinol gives definite colour reactions, a characteristic of some ketonic sugars. The reducing power of the sugar is unaffected by treatment with bromine in aqueous solution. A further proof of its ketonic nature is given on reduction with 2·5% sodium amalgam in faintly acid solution, to prevent isomerisation at a temperature not above 35°, two products, *glucoheptulitol*, m. p. 144°, and α-glucoheptitol, being obtained. J. D. Fulton.

Thiocellobiose and thiocellobiosides. F. Wrede and O. Hettche (Z. physiol. Chem., 1928, **172**, 169—178).—Cellobiose bromide hepta-acetate in hot alcohol reacts with methyl-alcoholic potassium disulphide to give *dicellobiosyl disulphide tetradeca-acetate*, m. p. 271—273°, $[\alpha]_D^{18}$ −79°, which is hydrolysed by methyl-alcoholic ammonia to *dicellobiosyl disulphide*, decomp. 165—170°, $[\alpha]^{20}$ −90·8°, or is reduced and acetylated by zinc dust and acetic anhydride to *thiocellobiose octa-acetate*, m. p. 205°, $[\alpha]_D^{20}$ −13°. *Thiocellobiose hepta-acetate*, m. p. 197° (clear at 220°), $[\alpha]^{20}$ −12·6°, obtained by reduction of the disulphide tetradeca-acetate in phenol by aluminium amalgam and aqueous-alcoholic acetic acid, gives by methylation with diazomethane the *methyl ether hepta-acetate*, m. p. 200°, $[\alpha]^{20}$ −20·2°, from which *methylthiocellobioside*, m. p. 220°, $[\alpha]^{20}$ −31°, is prepared by hydrolysis; the *ethyl ether hepta-acetate*, m. p. 193°, $[\alpha]_D^{20}$ −26·7°, and *ethylthiocellobioside*, m. p. 219°, $[\alpha]^{20}$ −37·7°, are similarly obtained. *Thiocellobiose*, $C_{12}H_{22}O_{10}S$, prepared from the octa-acetate and methyl-alcoholic ammonia, sinters about 110°, and in 50% alcohol shows $[\alpha]^{20}$ −33·3°, changing to +14·8° in 6 days; the *silver* salt gives, by treatment with methyl iodide followed by acetylation, the above methyl ether hepta-acetate. C. Hollins.

Quantitative hydrolysis of starch by buffered taka-diastase. [Determination of starch.] I. D. Collins (Science, 1927, **66**, 430—431).—When 50 c.c. of 0·3% starch solution are kept at 40° for 36 hrs. with 1 c.c. of 10% taka-diastase and 5 c.c. of acetate buffer (p_H 5·0), dextrose values representing 98·5—101·1% hydrolysis are obtained. Reduction of the concentration of taka-diastase to 0·75 did not decrease the amount of dextrose formed; with 0·5 the dextrose value was 95·6—99·0. A phosphate buffer at p_H 4·5 gave 100·1% of dextrose. A. A. Eldridge.

Structure of the crystalline component of cellulose. K. H. Meyer and H. Mark (Ber., 1928, 61, [B], 593—614).—The determination of the structure is based on the following considerations: (1) Cellobiose can be obtained in 60% yield from cellulose under conditions which do not permit the formation of cellobiose from dextrose; (2) cellobiose has the constitution assigned to it by Haworth and co-workers; (3) the crystalline component of cellulose has an elementary cell of which the edge in the direction of the fibre axis is 10·3 Å. long, whereas the length of the other edges is 7·9 and 8·7 Å.; the smallest possible elementary cell contains four glucose residues. From these considerations it is deduced that the cellobiose residues are oriented in the direction of the fibre axis and are united to one another by glucosidic oxygen bridges. In the space-groups C^2, V^3, and V^4, a configuration can be elucidated which explains the axial ratios and the most important intensity effects. The conclusion is reached that about forty dextrose residues in the amylene-oxide ring form are united by β-glucosidic linkings in the 1 : 4-position to a straight, extended, main-valency chain. About forty to sixty of such chains are arranged parallel to one another and united by "micellary forces" to a cellulose particle. This conception is shown not only to be compatible with the established facts of cellulose chemistry and its Röntgen analysis, but also to afford a ready explanation of the processes of esterification, swelling, and dissolution. H. Wren.

Sulphuric esters of cellulose. W. Traube, B. Blaser, and C. Grunert (Ber., 1928, **61**, [*B*], 754—767).—Cellulose, in the form of filter-paper dried at 100° in a high vacuum until constant in weight, absorbs sulphur trioxide vapour with avidity from a mixture of the latter with air. If the cellulose has absorbed only 50—75% of its weight of sulphur trioxide, the product is directly converted into its potassium salt by cautious neutralisation with potassium hydroxide. If greater absorption has occurred, the product is treated with water, followed by lead hydroxide or carbonate in amount slightly greater than is required to neutralise the free sulphuric acid. The slight excess of lead is removed as lead sulphide and the clear solution is neutralised with potassium hydroxide. *Potassium cellulose trisulphate*-A crystallises readily from the solution in yield of about 65%. It is amorphous and yields colloidal solutions in water. The copper number is 2·5—4·0. In aqueous solution it has $[\alpha]_D$ −5·5° to −6·5°. The neutral, aqueous solutions are very stable when boiled; addition of hydrochloric acid causes gradual, quantitative elimination of sulphuric acid and the solution acquires strong reducing power compatible with the quantitative production of dextrose. Towards alkali hydroxides the salt *A* is very stable. Regeneration of cellulose from it has therefore not been accomplished. Solutions of the salt do not give a precipitate with silver nitrate, only a turbidity with lead acetate, and marked precipitates with basic lead acetate, nitron, and barium chloride. If the mother-liquors from the preparation of the salt *A*, which has every sign of homogeneity, are concentrated, *potassium cellulose trisulphate*-B, $C_6H_7O_5(SO_3K)_3$, separates in very varying amount; it has $[\alpha]_D$ +1° to +7° in aqueous solution, copper number 8—9, and probably contains a varying proportion of the salt *A*.

Pre-addition of cellulose sulphate to solutions of sulphates acidified with hydrochloric acid inhibits completely the separation of barium sulphate after addition of barium chloride within certain limits; inhibition appears to be due to the formation of colloidal barium sulphate rather than to the production of complexes. Similar observations are recorded for

lead iodide, silver chromate, and mercurous chromate. In the case of sparingly soluble salts, such as potassium perchlorate, the habit of the precipitate is frequently greatly modified by the presence of potassium cellulose trisulphate.

If preparations of cellulose which have absorbed considerably more than 3 mols. of sulphur trioxide are preserved, a homogeneous, transparent, brown, viscous mass is obtained which dissolves without residue in water or alcohol. Such products when treated with water and neutralised with potassium hydroxide afford little or no potassium cellulose trisulphate-*A*, and the solutions when evaporated deposit a material containing much *potassium cellulose tetrasulphate*, $C_6H_6O_5(SO_3K)_4$, probably usually admixed with a little salt *B*. The tetrasulphate is not a derivative of cellulose, since in its formation a ring of the anhydro-sugar is necessarily ruptured.

Wood is also converted by sulphur trioxide into potassium cellulose trisulphate-*A* if the product is worked up immediately; if, however, it is preserved and a large excess of sulphur trioxide is used, the product is almost completely soluble in water, the lignin also appearing to be converted into water-soluble substances. H. WREN.

Constitution of pine lignin. VII. β-Lignosulphonic acid. P. KLASON (Ber., 1928, **61**, [*B*], 614—615; cf. A., 1920, i, 821).—α-Lignosulphonic acid is removed from the liquors by β-naphthylamine hydrochloride and the filtrate is treated with lead acetate; the precipitate is decomposed by hydrogen sulphide. The β-lignosulphonic acid thus obtained is treated with a further portion of naphthylamine to remove residual α-lignosulphonic acid and then successively with barium hydroxide and sulphuric acid. It is probable that the β-acid contains a combination of coniferaldehyde and coniferyl alcohol of the type, R·CH(OH)·O·CH_2R and formula $C_{19}H_{18}O_6$; it is impossible for the corresponding hydrosulphonic acid to yield an internal naphthylamine salt. The naphthylamine salt of the β-acid to which the structure $C_{19}H_{18}O_7,H_2SO_3,2C_{10}H_7{\cdot}NH_2$ has been ascribed (A., 1923, i, 187) probably has the composition $C_{19}H_{18}O_6,H_2SO_3,2C_{10}H_7{\cdot}NH_2,H_2O$.
H. WREN.

Primary amines from Grignard reagents and monochloroamine. G. H. COLEMAN and C. R. HAUSER (J. Amer. Chem. Soc., 1928, **50**, 1193—1196).—When monochloroamine (cf. Marckwald and Wille, A., 1923, ii, 558) is treated in ethereal solution at 0° with excess of Grignard reagent, RMgX (R being methyl, ethyl, *n*-propyl, *n*-butyl, *iso*amyl, phenyl, benzyl, or β-phenylethyl and X, chlorine, bromine, or iodine), 80—90% of it is converted into primary amine and ammonia. The yield of primary amine, which increases as that of ammonia decreases, is greatest for the same radical R when X is chlorine and least when X is iodine. Magnesium benzyl chloride gives 85% of benzylamine, whilst magnesium phenyl iodide gives 95·6% of ammonia with benzene, chloro- and iodo-benzene, and diphenyl.
H. E. F. NOTTON.

Derivatives of tetramethylenediamine, pyrrolidine, and γ-aminobutyric acid. W. KIEL (Z. physiol Chem., 1927, **171**, 242—251).—Whereas αδ-dibromobutane and δ-iodo-*n*-butylamine react with primary and secondary amines to form pyrrolidine ring systems, and with tertiary amines, forming the corresponding substituted tetramethylenediamine, γ-chloro(or -bromo)-*n*-butyronitrile reacts equally characteristically with ammonia, and with mono-, di-, and tri-methylamine, without ring formation in all cases. The following substances are described: *γ-amino*-n-*butyronitrile* [*chloroaurate*, m. p. 154° (decomp.)]; *γ-methylamino*-n-*butyronitrile*, b. p. 173° [*hydrochloride*, m. p. 162°; *chloroaurate* (+H_2O); *picrate*]; *γ-dimethylamino*-n-*butyronitrile* (*chloroaurate*, m. p. 129°; *picrate*, m. p. 120°); *trimethyl-γ-cyanopropylammonium picrate*, m. p. 126°, and *chloroaurate*. Hydrolysis of γ-dimethylamino-*n*-butyronitrile with hydrochloric acid affords the hydrochloride of *γ-dimethylamino*-n-*butyric acid*, isolated as the *chloroaurate*, m. p. 142°. The latter is also obtained by heating γ-iodo-*n*-butyric acid with alcoholic dimethylamine, treating the resulting iodide with thallium hydroxide and the latter with hydrochloric acid and auric chloride. Reduction of γ-methylamino-*n*-butyronitrile with sodium and alcohol gives the known δ-methylamino-*n*-butylamine, analysed as the chloroaurate. The similarly obtained δ-dimethylamino-*n*-butylamine gives a *chloroaurate*, m. p. 175°, a *chloroplatinate*, decomp. 216°, and a *picrate*. *NN'*-Dimethylputrescine (methyl-δ-methylamino-*n*-butylamine) is conveniently prepared from tetramethylenediamine hydrochloride and formaldehyde in presence of aqueous calcium chloride. It was identified as the *chloroplatinate*, m. p. 237°. *Trimethyl-δ-amino*-n-*butylammonium chloroaurate*, *chloroplatinate*, and *picrate* were obtained from trimethylamine and δ-iodo-*n*-butylamine hydriodide.

Rapid dry distillation of *NN*-dimethylputrescine hydrochloride gives 1-methylpyrrolidine. The methiodide of the latter is obtained from δ-iodo-*n*-butylamine hydriodide and cold alcoholic dimethylamine.
J. STEWART.

Complex salts of bivalent platinum with αβγ-triaminopropane. F. G. MANN (J.C.S., 1928, 890—898; cf. A., 1927, 754).—When potassium chloroplatinite was treated with αβγ-triaminopropane trihydrochloride, co-ordination occurred between the metal and the α- and β-amino-groups of the amine, giving *dichloro(triaminopropane-γ-monohydrochloride)-platinum monohydrate*, $[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl]H_2O$, m. p. 290—291° (decomp., darkening at 280°). This compound is similar in type to the platinic compound previously described (*loc. cit.*), and its constitution was verified by resolution into optically active forms by fractional crystallisation of the bromocamphorsulphonates, which were then reconverted into the hydrochlorides. d-*Dichloro(triaminopropane-mono-*d-*bromocamphor-*-*sulphonate)platinum monohydrate*, +522°, the l-*base* l-*sulphonate*, $[M]^{15}_{5461}$ −524°, d-*dichloro(triaminopropane-monohydrochloride)platinum*, +195°, and the l-*monohydrochloride*, −192°, were prepared. *Dichloro(triaminopropane-mono-*d-*camphor-β-sulphonate)platinum*, $[M]^{15}_{5461}$ +61°, gave no satisfactory resolution. The monohydrochloride yielded with oxalic acid *dichloro-*

(triaminopropane-γ-monohydrogen oxalate)platinum, m. p. 216—217° (decomp., darkening), and with ammonia *monochlorotriaminopropaneplatinous monochloride*, $[ClPtNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2]Cl$, m. p. 282—283° (decomp.). When potassium chloroplatinite was treated with free triaminopropane, co-ordination occurred, and two new types of complex salts were separated. Treatment of the solution with acetic acid and potassium thiocyanate yielded *bis(triaminopropane-γ-monothiocyanate)platinous dithiocyanate*, $[Pt\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCNS\}_2](SCN)_2$, m. p. 177—178°, of the same type as the cupric compound previously described (A., 1926, 1234). This should exist in racemic and *meso*-forms by virtue of two asymmetric carbon atoms, and probably the *meso*-form should be resolvable by virtue of the tetrahedral configuration about the platinum, but recrystallisation of *bis(triaminopropane-γ-mono-*d-*bromocamphorsulphonate)platinous di-*d-*bromocamphorsulphonate trihydrate*, +1340°, gave no evidence of resolution. If the solution obtained from potassium chloroplatinite and triaminopropane was treated with potassium iodide, *bis(triaminopropane)platinous diiodide*, $[Pt\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2]I_2$, m. p. 266—267° (decomp.), was formed. The *dibromide*, m. p. 270—271° (decomp.), was also prepared, and from this the *dipicrate*, which deflagrated when heated. These compounds appear to be a new type in which bivalent platinum has a co-ordination number of 6. The constitution is discussed. Ammonium chloropalladite and triaminopropane trihydrochloride yielded *dichloro(triaminopropane-γ-monohydrochloride)palladium*, m. p. 279—280° (decomp.), unstable in hot water. *Triaminopropane trihydrogen trioxalate monohydrate*, m. p. 173—174° (decomp.), is described.

R. K. CALLOW.

Oxidation of amino-acids. I. Effect of temperature on the oxidation of amino-acids by animal charcoal. II. Effect of amines. S. TOYODA (J. Biochem. Japan, 1927, **7**, 209—216, 217—225).—The greatest oxidation of glycine in the Warburg charcoal model occurs at the body-temperature. Amines retard the rate of oxidation of amino-acids on charcoal to an extent dependent in homologous series on the length of the chain.

CHEMICAL ABSTRACTS.

Isomeric glycylglycine-*N*-carboxylic acids. F. WESSELY and E. KOMM (Z. physiol. Chem., 1928, **174**, 306—318).—Hydrolysis of hydantoin-3-acetic acid with *N*-sodium hydroxide yields glycylglycine-*N*-carboxylic acid, m. p. 204—206° (decomp.), for which the formula $CO(NH\cdot CH_2\cdot CO_2H)_2$ (I) is suggested in contrast to $CO_2H\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ (II) and $CO_2H\cdot NH\cdot CH_2\cdot C(OH){:}N\cdot CH_2\cdot CO_2H$ (III), given by Fischer and Fourneau (A., 1901, i, 675) and by Leuchs and co-workers (A., 1907, i, 770; 1908, i, 723; 1925, i, 1248), respectively. Support for this hypothesis is given by the fact that hydantoin-3-acetic acid under the influence of ammonia yields a diamide identical with that formed from ammonia and carbonylbisglycine ester; also the ester of the glycylglycine-*N*-carboxylic acid is identical with that synthesised from carbonyl chloride and glycine ester. The carbonylbisglycine ester obtained from the acid formed by the alkali hydrolysis of hydantoin-3-acetic acid has m. p. 147°, but after recrystallisation from water the m. p. falls considerably (even as low as 129°). This alteration in m. p. is not due to differences in the size of the crystals, and the analytical values show no alteration. Similar changes occur on recrystallisation from alcohol and ether or from benzene. Treatment of the crude product of carbonylbisglycine ester (m. p. 147°), or a recrystallised product with lower m. p., with hydrochloric acid in alcohol or ether yields a substance, m. p. 148—149°, which undergoes no change on recrystallisation. It is considered improbable that a change occurs on recrystallisation corresponding with a conversion of the ester of (I) into that of (II) or (III).

A. WORMALL.

Formation of guaninido-compounds by the action of guanidine on amino-esters. II. Formation of creatinine from sarcosine ethyl ester and guanidine or cyanamide, and of *dl*-2-imino-4-keto-5-*p*-hydroxybenzyltetrahydroglyoxaline from *dl*-tyrosine ethyl ester and guanidine. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1928, **175**, 68—74; cf. this vol., 511).—Guanidine (and less easily cyanamide) reacts with sarcosine ethyl ester [ethyl methylaminoacetate] to give creatinine. From *dl*-tyrosine ethyl ester and guanidine there is obtained *2-imino-4-keto-*ɔ-p-*hydroxybenzyltetrahydroglyoxaline*, m. p. 257—263°. The mechanism of the reaction is discussed.

C. HOLLINS.

Benzylidenecreatinine and related compounds. B. H. NICOLET and E. D. CAMPBELL (J. Amer. Chem. Soc., 1928, **50**, 1155—1160).—Acetyl-5-benzylidenecreatinine (cf. Erlenmeyer, A., 1895, i, 310), prepared by an improved method, is hydrolysed by acids to ɔ-benzylidenecreatinine (*dihydrochloride*), which is reduced by hydriodic acid to 5-benzylcreatinine (cf. Hennig, A., 1913, i, 1106; Greenwald, A., 1925, i, 839). This is hydrolysed by barium hydroxide, first to *5-benzyl-1-methylhydantoin*, m. p. 106°, then to α-methylamino-β-phenylpropionic acid (Fischer and Lipschitz, A., 1915, i, 242), the yield of which from creatinine is 22% of the theoretical. Benzylidenecreatinine (I) is similarly hydrolysed to *1-methyl-5-benzylidenehydantoin*, m. p. 193—194°, which is also formed from benzaldehyde and 1-methylhydantoin, and is methylated by sodium hydroxide and methyl iodide to *1 : 3-dimethyl-5-benzylidenehydantoin*, m. p. 92°. Methylation of (I) affords *methyl-ɔ-benzylidenecreatinine*, $\begin{matrix} CO\cdot C{:}CHPh \\ | \\ NH\cdot C{:}NMe \end{matrix}\!\!>\!NMe$, m. p. 129°, which is hydrolysed to 1-methyl-5-benzylidenehydantoin. Attempts to condense methylcreatinine, or an (?) isomerised product obtained from this by ring opening and reclosure, with benzaldehyde were unsuccessful (cf. Kunze, A., 1911, i, 21).

H. E. F. NOTTON.

Compound of carbon monoxide with "ferrocysteine" and its decomposition by light. W. CREMER (Biochem. Z., 1928, **194**, 231—232).—The compound obtained by the reaction of carbon monoxide with a mixture of ferrous sulphate and cysteine in which 1 atom of iron combines with 2 mols. of carbon monoxide (cf. this vol., 315) is decomposed by

light, but it may be distinguished from the corresponding compound of carbon monoxide and hæmin, which is similarly decomposed, by its absorption spectrum. P. W. CLUTTERBUCK.

[Preparation of] ethyl cyanoacetate. J. K. H. INGLIS (Org. Syntheses, 1928, **8**, 74—76).

Action of organo-magnesium derivatives on some oxamides. R. BARRE (Ann. Chim., 1928, [x], **9**, 204—275).—Partly an account of work already published (A., 1927, 447). The following is new. The α-form, m. p. 140—141°, of propionylformdiethylamide semicarbazone is converted by hydrochloric acid into the stable β-*form*, m. p. 170—171°. *Propionylformdiethylamide phenylhydrazone* and p-*nitrophenylhydrazone* have m. p. 101—102° and 124—125°, respectively. Magnesium butyl bromide and ethyl diethyloxamate react at −15° to form n-*valerylformdiethylamide* (90%), b. p. 120—122°/11 mm. (*semicarbazone*, m. p. 163°), hydrolysed by hydrochloric acid to α-*ketohexoic acid*, b. p. 93—94°/14 mm. (*oxime*, m. p. 140°; *phenylhydrazone*, m. p. 89°; *semicarbazone*, m. p. 200°). Ethyl diethyloxamate and magnesium phenyl bromide (1·6 mols.) at −15° give benzildiethylamide (63%), m. p. 95—96° (cf. McKenzie and Duff, A., 1927, 755), and *benzoylformdiethylamide* (15%), b. p. 183—185°/18 mm. (*semicarbazone*, m. p. 204—205°). When 2 mols. of the Grignard reagent are used 63% of the keto-diethylamide is obtained. Magnesium benzyl chloride and ethyl diethyloxamate furnish α-*hydroxy*-β-*phenyl*-α-*benzylpropiondiethylamide* (15%), m. p. 119°, and *phenylacetylformdiethylamide* (70%), b. p. 155—157°/7 mm. (*semicarbazone*, m. p. 211—212°), hydrolysed to phenylpyruvic acid, m. p. 155°.

The product of the action of diethylamine on magnesium ethyl bromide converts ethyl oxalate into tetraethyloxamide, b. p. 142°/4 mm., m. p. 31—32°. This reacts with magnesium ethyl bromide (3 mols.) in ether to form α-*diethylaminobutyrdiethylamide* (20%), b. p. 98—99°/3 mm. (*picrate*, m. p. 114—115°), also obtained from diethylamine and α-bromobutyrdiethylamide, together with propionylformdiethylamide (70%). In benzene the corresponding amounts are 36% and 55%, together with 1% of dipropionyl [*disemicarbazone*, m. p. 285° (decomp.)], whilst in toluene, with mechanical agitation, the percentages are 60 and 28. With magnesium ethyl iodide in benzene, the product is mainly the keto-diethylamide. Tetraethyloxamide and magnesium phenyl bromide (4 mols.) in toluene give *diethylaminodiphenylacetdiethylamide* (75%), b. p. 182—184°/3 mm. [*perchlorate*, m. p. 177° (decomp.)], easily hydrolysed by acid or alkali to benzildiethylamide.

The reaction between magnesium alkyl and aryl halides and the iminochloride from oxanilide yields mainly resinous products. H. BURTON.

[Preparation of] acetamidine hydrochloride. A. W. DOX (Org. Syntheses, 1928, **8**, 1—3).

[Preparation of] allyl cyanide. J. V. SUPNIEWSKI and P. L. SALZBERG (Org. Syntheses, 1928, **8**, 4—6).

[Preparation of] γ-chlorobutyronitrile. C. F. H. ALLEN (Org. Syntheses, 1928, **8**, 52—53).

Oxidation of alkali cyanides by permanganate. H. GALL and G. LEHMANN (Ber., 1928, **61**, [*B*], 670—675).—During the direct oxidation of potassium cyanide by potassium permanganate in strongly alkaline solution, approximately two equivalents of oxygen are used for each molecule of cyanide; the reaction is very tedious and is accompanied by many side changes, so that it is useless for analytical purposes. Addition of copper sulphate greatly accelerates the oxidation, so that alkali cyanide may be oxidimetrically determined as follows. The solution of the cyanide is treated successively with potassium hydroxide (about 30%, 20 c.c.) and copper sulphate (5%, 20 c.c.). After addition of permanganate it is warmed for 5 min. at 60°, after which excess of the oxidising agent is determined by oxalic acid. It is essential that the cold and hot solution should exhibit the pure green colour of the manganate. If the latter disappears when the solution is warmed, more permanganate may be added. If, however, permanganate remains (shown by the blue colour of the solution), the following "cold titration" method must be used. The cyanide is treated with alkali hydroxide and copper sulphate as described above and then with so much permanganate that the solution has a pure blue colour; excess of permanganate is immediately titrated with oxalic–sulphuric acid solution. In place of oxalic acid, acidified ferrous sulphate solution may be employed. The successful use of permanganate in this connexion depends on its immediate conversion into manganate; if reaction occurs slowly, apparent consumption of permanganate ensues, due to its decomposition in alkaline solution. Manganate is used in the determination of cyanide by adding potassium hydroxide (about 30%, 20 c.c.) and copper sulphate (5%, 20 c.c.) to the solution of the cyanide followed by an excess of manganate solution. The mixture is heated nearly to boiling over a free flame, whereby the green colour must persist. Excess of manganate is titrated by ferrous sulphate or oxalic acid. The preparation of pure potassium cyanate is described in detail. H. WREN.

Grignard's reaction. J. MEISENHEIMER (Ber., 1928, **61**, [*B*], 708—720).—The magnesium alkyl halide produced by the action of magnesium on alkyl halide may be determined by decomposing a measured volume of the ethereal solution with water and a known excess of standard nitric acid and titrating the unused acid (cf. Gilman and others, A., 1923, ii, 272). The ionic halogen is also determined by Volhard's method. In the case of the exclusive formation of magnesium alkyl halide, the ratio nitric acid : silver nitrate is 1 : 1. The method is trustworthy only if moisture and atmospheric oxygen are excluded as far as possible during the preparation of the reagent. For some unexplained reason, great dilution of solutions of magnesium methyl or ethyl iodide with ether previously to titration causes a very marked alteration in the ratio I′ : OH′, although the sum, I′+OH′, is influenced but little if at all.

The composition generally assigned to magnesium alkyl halides is deduced from Tschelinzev's colorimetric measurements and not previously controlled by analyses. Magnesium α-naphthyl bromide has been

isolated as a crystalline *trietherate*, $MgC_{10}H_7 \cdot Br,3Et_2O$, which readily loses 1 mol. of ether, forming the non-crystalline *dietherate*.

Ethereal solutions of magnesium ethyl iodide, when preserved, slowly deposit crystals of *magnesium ethoxyiodide monoetherate* owing to oxidation by the atmosphere; if moisture is also present, the deposit is mixed with magnesium iodide dihydrate. If a current of air is rapidly passed through the solution, the precipitate consists of more highly basic magnesium salts. Magnesium ethoxyiodide is readily obtained crystalline by addition of the calculated amount of anhydrous ethyl alcohol to an ethereal solution of magnesium methyl or ethyl iodide, methane or ethane being vigorously evolved. Auto-oxidation of magnesium methyl iodide solutions proceeds less smoothly, whilst magnesium ethyl bromide affords *magnesium hydroxybromide etherate* instead of the expected ethoxybromide.

The crystalline precipitates obtained by Zerewitinov from solutions of magnesium methyl iodide in amyl ether evolve little methane when treated with water and appear to consist mainly of magnesium iodide diamyletherate with varying amounts of magnesium methyl iodide (?diamyletherate) and decomposition products. If dry air is passed through the solution, crystals are gradually formed which have approximately the composition of magnesium methoxyiodide monoamyletherate and correspond most closely with Zerewitinov's magnesium methyl iodide monoamyletherate in properties. When magnesium reacts with methyl bromide in presence of a regulated amount of amyl ether, the precipitate formed appears to consist of 80·5% of magnesium methyl bromide semiamyletherate, 23·3% of magnesium bromide semiamyletherate, and 1·7% of magnesium oxide.

o-Chloro-γ-chloro-*n*-propylbenzene could not be caused to react with magnesium in ethyl ether under any conditions. Since *p*-dibromo- and *p*-di-iodobenzene are active, whereas *p*-dichlorobenzene is indifferent, it is remarkable that *o*-iodo-γ-chloro-*n*-propyl-, *o*-chloro-γ-iodo-*n*-propyl-, and *o*-iodo-γ-iodo-*n*-propyl-benzenes are indifferent. Replacement of ethyl ether by benzene induces activity in the case of the di-iodo-compound only, whereas all four halides react in boiling *iso*amyl ether; under these conditions, however, the tendency to side reactions is so pronounced that the actions do not promise usefulness in syntheses. The failure of the aliphatic halogen atom to react is unexplained, since γ-iodo-*n*-propylbenzene, *o*-iodopropylbenzene, and *o*-bromobenzyl bromide are readily active. With other reagents, the halogen atoms behave normally. o-*Chloro*-γ-*chloro*-n-*propylbenzene*, b. p. 112°/20 mm., prepared from γ-chloro-*n*-propylaniline, o-*chloro*-γ-*iodo*-n-*propylbenzene*, b. p. 142°/20 mm., from the dichloride and sodium iodide in boiling absolute alcohol, o-*iodo*-γ-*chloro*-n-*propylbenzene*, b. p. 102°/high vacuum, and o-*iodo*-γ-*iodo*-n-*propylbenzene*, b. p. 132—134°/high vacuum, do not appear to have been described previously.

Under all conditions magnesium and ethylene bromide in ether yield ethylene and homogeneous magnesium bromide dietherate. Bischoff's observation (A., 1905, i, 589), that benzil is reduced to benzoin by the product of the action of magnesium and ethylene bromide, could not be confirmed, but may be due to reduction by metallic magnesium in the presence of magnesium bromide (cf. Gomberg and Bachmann, A., 1927, 1190). H. WREN.

Mol. wt. and constitution of Grignard's magnesium compounds. J. MEISENHEIMER and W. SCHLICHENMAIER (Ber., 1928, 61, [*B*], 720—729).—The structure $Mg[Alk_2MgI_2,2Et_2O]$ for magnesium alkyl halides has been suggested by Terentiev (A., 1926, 1130) in place of the constitution $Alk.MgI—(OEt_2)_2$ advocated by Meisenheimer and Casper (A., 1921, i, 654) mainly on grounds of determination of the mol. wt. of magnesium methyl iodide in boiling ether. Repetition of Terentiev's experiments shows that the Grignard reagent is strongly associated in solution, but that, at sufficiently great dilution, the values for the mol. wt. approximate to those of the unimolecular compound. The experiments are not completely satisfactory, partly due to inconstancy in the b. p. of the solvent which can be avoided by using a large volume of it, but mainly owing to the ultimate formation of a precipitate in the solution. Terentiev's method of isolating the Grignard compound by evaporation of its ethereal solution and subsequent heating of the residue at 75° in a vacuum for 2 hrs. causes extensive decomposition. Magnesium ethyl bromide and magnesium methyl iodide, dried at 25° in a vacuum during 1 hr., give almost clear solutions in ether, and their mol. wt. increases with increasing concentration in a regular manner. Protracted ebullition causes some alteration in the composition of magnesium methyl iodide, as shown by alteration in the ratio I′ : OH′ (cf. preceding abstract). Magnesium phenyl bromide is more strongly associated in ethereal solution, in which it appears to undergo little alteration when heated. The results indicate that magnesium alkyl halides are not bimolecular in solution as postulated by Terentiev. In dilute ethereal solution it is considered that magnesium ethyl bromide exists mainly as the complex $Et \cdot MgBr—(OEt_2)_2$; a very small proportion is dissociated ionically and a somewhat larger amount is doubly or more highly polymerised. Precisely similar observations are made with magnesium iodide dietherate. The interpretation placed by Ivanov on the course of the action of carbon dioxide on magnesium ethyl bromide (A., 1927, 961) and on that between magnesium methyl iodide and water or carbon disulphide by Kierzek (*ibid.*, 1176) is arbitrary and the assumption of the existence of bimolecular compounds is unnecessary. Unfortunately, the magnesium alkoxyhalides which are readily prepared pure (cf. preceding abstract) are unsuitable for mol. wt. determination, since they readily decompose when heated, but their relationship to the unimolecular Grignard compounds and unimolecular magnesium iodide renders a bimolecular structure highly improbable. H. WREN.

Condensation of *cyclo*hexene with aromatic hydrocarbons in presence of aluminium chloride. D. BODROUX (Compt. rend., 1928, 186, 1005—1006).—*cyclo*Hexene was added to half its weight of aluminium chloride in an excess of an aromatic hydrocarbon, sometimes diluted with carbon disulphide, and the

monosubstituted product, which might be accompanied by small quantities of disubstituted product, separated by steam distillation or distillation. The following compounds were obtained: *cyclo*hexyltoluene (mixture of two isomerides), b. p. 255—261°/758 mm., d^{16} 0·938, 1·527; 2-cyclo*hexyl*-p-*xylene*, b. p. 261—262°/760 mm., d^{18} 0·936, n_D^{18} 1·529; *di*cyclo*hexyl*-p-*xylene*, m. p. 156—157°; 5-*cyclo*hexyl-*m*-xylene, b. p. 266—268°/763 mm., d^{18} 0·931, n_D^{18} 1·525 2-cyclo*hexyl*-1 : 3 : 5-*trimethylbenzene*, b. p. 283—284·5°/740 mm., d^{9} 0·946, n_D^{9} 1·535; cyclo*hexyl*-4-iso*propyl*-*toluene*, b. p. 279—283°/739 mm., d^{24} 0·916, n_D^{24} 1·517; *di*cyclo*hexyl*-4-iso*propyltoluene*, b. p. 210—220°/22 mm.

R. K. CALLOW.

Phenylpropinenes. M. BOURGUEL (Compt. rend., 1928, **186**, 1211—1213).—γ-Phenylpropinene (A., 1923, i, 429) had an anomalous value for density and refractive index when compared with its higher and lower homologues. On preparing the hydrocarbon by different methods (A., 1920, i, 603; 1925, i, 770; 1927, 47), the physical constants were in agreement amongst themselves and with those of the homologues, whilst the original values were never obtained. γ-Phenylpropinene has b. p. 68°/16 mm., d^{14} 0·935, n_D^{14} 1·536, and yields a silver derivative. Fractionation with cuprous chloride and sodamide shows that the product is homogeneous. Hydration gives rise to methyl benzyl ketone and oxidation with permanganate to benzoic acid. With sodamide a hydrogen atom of the methylene group is replaced by sodium to give a red derivative. α-Phenylpropinene has b. p. 73°/13 mm., d^{15} 0·942, n^{15} 1·563.

J. D. FULTON.

Halogenation of aromatic compounds in aqueous solutions. D. TISCHENKO (J. Russ. Phys. Chem. Soc., 1928, **60**, 153—162).—A *résume* of the behaviour of aromatic compounds towards chlorine water and bromine water, and of the mechanisms suggested for the reactions.

The action of a solution of bromine in aqueous sodium carbonate was investigated. Bromine reacts with sodium carbonate in solution according to the equations $Na_2CO_3+H_2O+Br_2 \rightleftharpoons NaBr+NaHCO_3+HBrO$, and finally $6Na_2CO_3+3H_2O+6Br_2=6NaHCO_3+3NaBr_3+2NaBr+NaBrO_3$. The solution gives all the reactions of free bromine, and hypobromous acid cannot be detected in the presence of an excess greater than 10% of free carbonate.

The sodium hydrogen carbonate formed maintained a constant hydrogen-ion concentration during the reactions with aromatic compounds, which were carried out in 0·1*N*-solutions. Benzene, toluene, and the xylenes did not react, but naphthalene gave an 80% yield of very pure bromonaphthalene. Phenol gave a 70% yield of *p*-bromophenol. Resorcinol was partly oxidised, and partly yielded a dibromoresorcinol, m. p. 111°. β-Naphthol, *o*-, *m*-, and *p*-cresols gave, respectively, 1-bromo-β-naphthol, m. p. 84°, 6-bromo-*o*-cresol, m. p. 63—64°, 6-bromo-*m*-cresol, m. p. 54—55°, and a liquid monobromocresol, b. p. 110—114°/19 mm. Pyrogallol and quinol were resinified, anthraquinone and alizarin were unaffected, whilst indigotin was oxidised to indoxyl. Sodium benzoate and phthalate did not react, but the salicylate yielded a bromotrihydroxybenzoic acid. The probable brominating agent in acid solutions was free bromine, in alkaline solutions hypobromous acid.

Chlorine under similar conditions gave with phenol *o*- and *p*-chlorophenols; with *o*-cresol a mixture of 4-chloro-*o*-cresol and impure 6-chloro-*o*-cresol; with *m*-cresol 6- and 4-chloro-*m*-cresol, m. p. 66°; with thymol *p*-chlorothymol, m. p. 59—60°.

Resorcinol was oxidised; β-naphthol gave a mixture of 8-chloro-β-naphthol, m. p. 101°, and $\beta\beta'$-dinaphthol. Aniline was oxidised, acetanilide, the acetotoluidides, acetonaphthalides, α-aminoanthraquinone, and diphenylamine were unaffected, whilst dimethylaniline yielded a mixture of *o*- and *p*-chlorodimethylanilines.

Salts of carboxylic or sulphonic acids which do not contain reactive groups, such as amino- or hydroxyl groups, were not chlorinated, but sodium sulphanilate gave the sodium salt of azobenzene-4 : 4'-disulphonic acid.

Sodium salicylate yielded sodium chlorosalicylate, and sodium *p*-hydroxybenzoate furnished sodium 3-chloro-*p*-hydroxybenzoate.

In general, the oxidising effect in solution of chlorine is much greater than that of bromine, due to the much greater concentration of free hypochlorous acid.

M. ZVEGINTZOV.

Nitration of chlorobenzene. O. MAGIDSON [with L. KALISCHEVSKI] (Trans. sci. chem.-pharm. inst., Moscow, 1923, **6**, 17—20; Chem. Zentr., 1927, ii, 2542).—Chlorobenzene and nitrating acid afford chiefly *p*-chloronitrobenzene, whilst sodium nitrate and sulphuric acid afford chiefly the *o*-compound. The latter reagent readily gives 1-chloro-2 : 4-dinitrobenzene at a higher temperature.

A. A. ELDRIDGE.

[Preparation of] *m*-bromonitrobenzene. J. R. JOHNSON and C. G. GAUERKE (Org. Syntheses, 1928, **8**, 46).

Dinitroethylbenzenes. O. L. BRADY, J. N. E. DAY, and P. S. ALLAM (J.C.S., 1928, 978—982).—2 : 4 : 6-Trinitroethylbenzene (Schultz and Sander, A., 1909, i, 639) was reduced by ammonium sulphide to 2 : 6-dinitro-4-aminoethylbenzene, m. p. 175° (lit. 110°), which, on removal of the amino-group by diazotisation and treatment with alcohol, yielded 2 : 6-*dinitroethylbenzene*, m. p. 57·5°. 2-Nitro-4-acetamidoethylbenzene, m. p. 111° (cf. Cline and Reid, this vol., 162), on nitration in nitric and sulphuric acids yielded 2 : 3-*dinitro-4-acetamidoethylbenzene*, m. p. 143°, and a smaller proportion of 2 : 5-*dinitro-4-aminoethylbenzene*, m. p. 125°, was separated by hydrolysing the solid separated from the mother-liquors of the 2 : 3-compound. 2 : 3-*Dinitro-4-aminoethylbenzene*, m. p. 121·6°, obtained by hydrolysis, yielded, by removal of the amino-group, 2 : 3-*dinitroethylbenzene*, m. p. 58·5°. 2 : 5-*Dinitroethylbenzene*, m. p. 59·5°, was obtained similarly. 3 : 5-Dinitro-4-aminoethylbenzene (Pauksch, A., 1884, 1142), on removal of the amino-group, yielded 3 : 5-*dinitroethylbenzene*, m. p. 41°. The dinitroethylbenzenes were oriented by oxidation to the dinitrobenzoic acids, the methyl esters of which were also prepared. *Methyl* 2 : 3-*dinitrobenzoate* had m. p. 134°.

R. K. CALLOW.

Michler's "sulphones." F. BERGEL and H. DORING (Ber., 1927, **61**, [*B*], 844—845; cf. Doring,

Diss., Freiburg, 1928).—The "sulphone" obtained by Michler by the action of *p*-toluenesulphonyl chloride on dimethylaniline is identified as *p*-toluenesulphonmethylanilide. A methyl group appears to be removed during the change and forms the methane carbon atom of methyl-violet and tetramethyldiaminodiphenylmethane formed as by-products.

H. WREN.

[Preparation of] *p*-bromodiphenyl. M. GOMBERG and W. E. BACHMANN (Org. Syntheses, 1928, **8**, 42—44).

Polymerisation of indene, cinnamylidenefluorene, and some indene derivatives. G. S. WHITBY and M. KATZ (J. Amer. Chem. Soc., 1928, **50**, 1160—1171).—Determination of the mol. wt., bromine absorption, and m. p. of indene polymerised by heating or treatment with stannic chloride or antimony pentachloride shows that (*a*) the products are complex mixtures, (*b*) the lower the temperature of production, the greater is the complexity of the product, (*c*) the polymerides, whether formed by physical or chemical means, form an unbroken series showing a smooth relation between m. p. and mol. wt. (cf. Bruson, A., 1927, 654; Stobbe and Färber, A., 1925, i, 19), (*d*) the polyindene molecule always combines with 2 atoms of bromine and therefore contains one double linking. Polymerisation is probably accompanied by migration of hydrogen giving a product of the general

$$\begin{array}{l} CH_2\cdot C_6H_4 \left[\; CH_2\cdot C_6H_4 \; \right] CH_2\cdot C_6H_4 \\ CH_2\cdot CH-\left[-CH\cdot CH-\right]_n-C{=}CH \end{array}$$

. Cinnamylidenefluorene is converted by heating or the usual catalysts into red, amorphous, non-elastic polymerides. At 200° it gives a *product* $(C_{22}H_{16})_2$, m. p. 168—170°, and at 240—250°, $(C_{22}H_{16})_9$, m. p. 356—370°, whilst antimony pentachloride gives a series of *products* from $(C_{22}H_{16})_4$, m. p. 286—290°, to $(C_{22}H_{26})_{12}$, m. p. 365—368°, the m. p. of which show a linear relationship to the mol. wts. A similar series, m. p. 245—246° to 273—275°, is obtained by thermopolymerisation of cinnamylideneindene, which gives a quadrimolecular *product*, m. p. 238—242°, with stannic chloride. Benzylideneindene is converted by heat into a *tetrameride*, m. p. 238—242°, and by antimony pentachloride into a *hexameride*, m. p. 252—255°, whilst hydroxybenzylbenzylideneindene gives a *hexameride*, m. p. 297—300°, when heated and a lower *polymeride*, m. p. 195—200°, with stannic chloride.

H. E. F. NOTTON.

α-Chloronaphthalene. I. Chlorination of naphthalene in the gaseous phase. P. FERRERO and R. WUNENBURGER (Helv. Chim. Acta, 1928, **11**, 425).—An apparatus is described in which naphthalene is chlorinated in the gaseous phase either in absence or presence of a catalyst at 250—400°. Without catalyst, the maximum yield (about 60%) of α-chloronaphthalene using 1·5 mols. of chlorine at a flow of 15 litres per hr. is at 350°. At 400°, the reaction products are destroyed. In presence of 0·5% of iodine the formation of mono-substituted derivatives is favoured, whilst ferric chloride, porous earthenware, or wood charcoal activates the production of both mono- and poly-chlorinated products. The α-chloronaphthalene obtained is technically pure.

H. BURTON.

Extension of Witt's colour theory on a basis of chemical co-ordination. W. DILTHEY and R. WIZINGER (J. pr. Chem., 1928, [ii], **118**, 321—348).—The colour of triphenylmethyl is ascribed to the chromophoric effect of the tervalent carbon atom. An ethylenic linking is regarded as comprising a pair of tervalent carbon atoms, and an extension of Witt's colour theory is developed from this starting-point. The weak chromophoric effect of such a pair of tervalent carbon atoms is strengthened by conversion, whilst maintaining the co-ordinative deficiency, into the heteropolar (ionic) condition. These central atoms are not to be considered as necessarily the sole or chief source of electronic vibrations (cf. Madelung and Oberwegner, this vol., 171); as ionic centres they probably give off electrons, but the further history of these is left indefinite. The co-ordination number of carbon and of nitrogen is 4; that of oxygen may be 3 or 4, but a singly-bound oxygen atom is certainly unsaturated. Thus a triply-bound carbon atom is co-ordinatively unsaturated, a distinction being drawn between co-ordination unsaturation and valency unsaturation. Thus, in crystal-violet base the central carbon atom is tervalent and hence shows valency (and also co-ordination) unsaturation, but in the colour salt this carbon atom is quadrivalent, and therefore saturated, yet there remains a co-ordination deficiency, since the negative radical occupies the second sphere and is not connected directly with the central atom. Such a condition of co-ordinative unsaturation at a heteropolar central atom in a colour salt is conveniently indicated by a dot above the atom in the formula. The introduction of auxochromes such as amino- and hydroxyl groups into a coloured substance is not in itself sufficient to endow it with dyeing properties, but in general leads to only a comparatively slight change of colour. The necessary condition for dye formation is the production of a salt. Thus, whilst triphenylmethyl is yellow and its hexamethyltriamino-derivative is orange, neither is a dye; but the salt $[(NMe_2\cdot C_6H_4)_2{:}\dot{C}\cdot C_6H_4\cdot NMe_2]^+Cl^-$ is deep violet and possesses dyeing properties. A similar effect is observed with the introduction of the antiauxochromes NO_2, NO, CN, etc.; whilst azobenzene is yellow and hexanitroazobenzene is orange, the salt $[(NO_2)_3C_6H_2\cdot N\cdot N\cdot C_6H_2(NO_2)_3]^{--}K^{++}$ is a dark blue dye. The effect of auxochromes and antiauxochromes in dye formation is not entirely due, however, to their salt-forming capacity, but also indirectly to their stabilising effect on the salts, which in some cases could be formed in their absence. The hydroxyl group, *e.g.*, usually figures in the negative ions of dyes in which it is present, and in these cases alkylation destroys its effect. But it may also figure in the positive ions, thus taking no direct part in salt formation, as in *p*-hydroxytriphenylpyrylium perchlorate. Here its favourable effect lies in the increased stability of this salt to water compared with the non-hydroxylated perchlorate. In such cases alkylation does not destroy the auxochromic effect of the hydroxyl group. Since auxochromes favour formation of positive, and antiauxochromes of negative ions, in binuclear systems containing two co-ordinatively unsaturated atoms an intramolecular ionoid condition may be approached if on the one nucleus

auxochromes, and on the other antiauxochromes, are accumulated. Such a dipolar condition should show the depth and intensity of colour of a true colour salt, a deepening of colour in ionising solvents. Examples of these phenomena are given. C. HOLLINS.

Rubrene peroxide. C. MOUREU, C. DUFRAISSE, and L. GIRARD (Compt. rend., 1928, **186**, 1027—1031).—The m. p. and crystalline form of rubrene peroxide (cf. A., 1926, 945) vary according to the solvent used, the following m. p. being observed: ether, 192—193°; acetone, 186—188°; ethyl acetate, 196—197°; ethyl bromide, 186—187°; ethyl iodide, 181—182°; benzene, 192—193°; toluene or chloroform, 187—188°; and bromobenzene, 165—167°. Cryoscopic measurements show that the solvent is combined only as solvent of crystallisation and that each mol. of the peroxide retains 1 mol. of bromobenzene and 0·5 mol. of benzene or ether. These proportions are confirmed by analysis and by the dissociation of the peroxide in a high vacuum, the liberated solvent being condensed in a freezing mixture of acetone and solid carbon dioxide. The gas obtained by the thermal decomposition of the peroxide consists only of oxygen and carbon dioxide, the proportion of the latter varying from 4·4 to 6·7% of the total volume of gas. Below 140°, the gas evolved is almost pure oxygen, whilst at about 180° only carbon dioxide is obtained, the two gases seemingly being the products of two different reactions. In the case of the peroxide containing benzene of crystallisation, 74—79·5% of the theoretical proportion of the oxygen is liberated as such, 4·2—6·1% as carbon dioxide, whilst 15—21% remains combined in the residue, which has a distinct phenolic odour. Similar results are obtained with a sample containing bromobenzene of crystallisation, the proportion of oxygen liberated being 72·1—74·6% of the theoretical.

J. W. BAKER.

Electrometric titration of phenols in alcoholic solution. W. D. TREADWELL and G. SCHWARZENBACH (Helv. Chim. Acta, 1928, **11**, 386—405).—The dissociation constants of a number of phenols in alcoholic solution have been measured electrometrically with the following results. In absolute-alcoholic solution: phenol, $10^{-12\cdot8}$; pyrocatechol, $10^{-12\cdot0}$; resorcinol, $10^{-12\cdot3}$; quinol, $10^{-12\cdot6}$; *o*-nitrophenol, $10^{-10\cdot7}$; *p*-nitrophenol, $10^{-10\cdot1}$; picric acid, $10^{-5\cdot7}$; 2:4-dinitronaphthol, $10^{-9\cdot0}$. In 96% alcoholic solution: *p*-nitrosophenol, $10^{-8\cdot1}$; 1-nitroso-β-naphthol, $10^{-8\cdot7}$; and the following anthraquinone derivatives, α-hydroxy-, $10^{-8\cdot8}$; β-hydroxy-, $10^{-5\cdot7}$; 1:4-dihydroxy-, $10^{-8\cdot8}$; 1:8-dihydroxy-, $10^{-6\cdot9}$; 1:2-dihydroxy-, $10^{-5\cdot4}$; 1:3-dihydroxy-, $10^{-5\cdot3}$; 2:3-dihydroxy-, $10^{-5\cdot7}$; 2:6-dihydroxy-, $10^{-5\cdot6}$ and $10^{-7\cdot4}$; 1:2:4-trihydroxy-, $10^{-3\cdot9}$; 1:2:5-trihydroxy-, $10^{-5\cdot7}$; 1:2:6-trihydroxy-, $10^{-4\cdot8}$; 1:2:7-trihydroxy-, $10^{-5\cdot2}$; 1-2:3-trihydroxy-, $10^{-4\cdot8}$; 1:2:3:4-tetrahydroxy-, $10^{-3\cdot1}$; also eriochrome-yellow G, $10^{-3\cdot6}$; eriochrome-blue-black R, $10^{-5\cdot6}$. Only in the case of 2:5-dihydroxyanthraquinone were dissociation constants obtained for more than one hydroxyl group. F. J. WILKINS.

Catalytic reduction of nitro-organic compounds in the liquid system. O. W. BROWN, G. ETZEL, and C. O. HENKE.—See this vol., 600.

Reduction of aromatic nitro-derivatives by means of iron in the presence of magnesium chloride. S. MICEWICZ (Rocz. Chem., 1928, **8**, 50—53).—Iron filings in the presence of magnesium chloride constitute a satisfactory reducing agent for the preparation of aromatic amines, no intermediate products being isolated from the reaction mixture.

R. TRUSZKOWSKI.

Chlorination of anilides. III. *N*-Chlorination and *C*-chlorination as simultaneous side-reactions. K. J. P. ORTON, F. G. SOPER, and G. WILLIAMS (J.C.S., 1928, 998—1005).—Measurements have been made of the velocities of both *N*-chlorination and *C*-chlorination in 40% acetic acid at 18°, in the reaction between chlorine and seven acetanilides which is represented by the scheme $Ar{\cdot}NHAc+Cl_2 \longrightarrow Cl{\cdot}ArNHAc+HCl$ or $\rightleftharpoons Ar{\cdot}NClAc+HCl$ (cf. Orton and Jones, J.C.S., 1909, **95**, 1456). The reaction mixture is poured alternatively into (*a*) potassium iodide solution, the titre of the liberated iodine representing chlorine+chloroamine concentration, and (*b*) aqueous *p*-cresol which removes chlorine, the chloroamine then being determined as in (*a*). The ratio of the amounts of chloroamine and chloroanilide formed at any given instant is independent of time, and chloroamine formation and nuclear chlorination are therefore simultaneous side-reactions. The values of the velocity coefficients for *o*-, *m*-, and *p*-chloro- and *p*-bromo-acetanilides, aceto-*o*-, and aceto-*p*-toluidide, and acetanilide are, respectively: k_N 286, 172, 115, 123, 140, 2540, and 96; k_C 27·5, 3140, 135, 116, 1390, 18500, and 11000, the values of the ratio k_N/k_C being, 10·4, 0·0548, 0·848, 1·06, 0·102, 0·137, and 0·00873, respectively. J. W. BAKER.

Chlorination of anilides. IV. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFIELD and B. JONES (J.C.S., 1928, 1006—1012).—A quantitative study has been made of the velocities of chlorination in 99% acetic acid of a series of 21 phenolic ethers of the type $RO{\cdot}C_6H_4{\cdot}X$ (*o* or *p*), in which X=Cl, CO_2H, or NO_2, and R=Me, Et, Pr^{α}, Pr^{β}, Bu^{α}, CH_2Ph, (*p*) $C_6H_4Cl{\cdot}CH_2$, *p*- and *m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$. The velocity of chlorination increases rapidly with increasing water content of the medium. An application of the concept of kinetic activation is applied to the problem of benzene substitution and, with certain assumptions, the expression $\log_{10}(r_1/2)/\log_{10}(r_2/2)=T_2/T_1$, where r_1 and r_2 are the ratios of the total *ortho*- to total *para*-compound produced at the temperatures T_1 and T_2, respectively, is deduced. By means of this and similar expressions the ratio $o:m:p$ can be calculated at any one temperature from the known values of the ratio at another temperature. Very good quantitative agreement is found with existing data. The extension of this principle to the introduction of a third substituent into a disubstituted benzene derivative is tentatively considered, and it is shown that the relative directive powers of OR and OR′ as measured by the ratio of the chlorination velocity coefficients in the derivatives $RO{\cdot}C_6H_4{\cdot}X$ (*o* and *p*) should be independent of the group X, a prediction which is verified experimentally. Similarly, the relative directive power of the group X is independent of the nature of R.

J. W. BAKER.

Chloroamines as halogenating agents. Iodination by a chloroamine and an iodide. A. E. BRADFIELD, K. J. P. ORTON, and I. C. ROBERTS (J.C.S., 1928, 782—785).—The method of chlorination based on the interaction of hydrogen chloride and a chloroamine (Orton and King, J.C.S., 1911, **99**, 1185; Orton and Bradfield, A., 1927, 655) has been extended to the preparation of a solution of iodine chloride and the iodination of various aniline derivatives. Finely-powdered sodium iodide is added in small amounts, with shaking, to a solution of "dichloramine-T" in glacial acetic acid. Little or no liberation of iodine occurs and the reduction in acidity consequent on the presence of sodium ions affects favourably the rate of iodination of anilines. Aniline with 1 equivalent of this reagent yields *p*-iodoaniline, and with 3 equivalents, tri-iodoaniline, and by similar methods the following iodoanilines are obtained from the appropriate aniline derivative: 2 : 4-dichloro-6-iodoaniline (*acetyl* derivative, m. p. 198—199°); *2-chloro-4-bromo-6-iodoaniline*, m. p. 95—96° (*acetyl* derivative, m. p. 213°); *p*-iodoacetanilide, which by treatment with 2 mols. of bromine in 70% acetic acid at 70° yields *2-bromo-4-iodoacetanilide*, m. p. 143°, hydrolysed to *2-bromo-4-iodoaniline*, m. p. 75—76°. The last is chlorinated with "dichloramine-T" and hydrochloric acid forming *2-chloro-6-bromo-4-iodoaniline*, m. p. 113—114° (*acetyl* derivative, m. p. 221°). By heating *o*-nitroaniline with 50% excess of the iodinating agent for 20—30 min., an 80% yield of 4-iodo-2-nitroaniline is obtained, whilst with excess of the reagent the 4 : 6-di-iodo-derivative is obtained. Chlorination and bromination of the former yields, respectively, *2-chloro-*, m. p. 124° (*acetyl* derivative, m. p. 227°), and *2-bromo-*, m. p. 117—118° (*acetyl* derivative, m. p. 222°) *-4-iodo-6-nitroaniline*. 4-Chloro- and 4-bromo-2-nitroanilines yield respectively, *4-chloro-*, m. p. 137—138° (*acetyl* derivative, m. p. 207°), and *4-bromo-*, m. p. 146—147° (*acetyl* derivative, m. p. 215°), *-2-iodo-6-nitroaniline*, which by diazotisation with amyl nitrite in alcoholic solution yield, respectively, 3-chloro- and 3-bromo-5-iodo-1-nitrobenzene (Körner and Contardi, A., 1913, i, 963). J. W. BAKER.

[Preparation of] benzylaniline. F. G. WILLSON and T. S. WHEELER (Org. Syntheses, 1928, **8**, 38—40).

[Preparation of] benzylideneaniline. L. A. BIGELOW and H. EATNOUGH (Org. Syntheses, 1928, **8**, 22—23).

Doebner reaction. VI. R. CIUSA and A. CREMONINI (Gazzetta, 1928, **58**, 153—159).—*N*-Benzyl-β-naphthylamine, m. p. 67·5°, b. p. 405°, is obtained as a by-product in the Doebner reaction (cf. Ciusa and Zerbini, A., 1921, i, 195); it forms a *benzoyl* derivative, m. p. 115° (of which a dose of 1 g. per kg. causes a rise of about 1° in the body temperature of the rabbit—A. BALDONI), a *picrate*, m. p. 140—141°, and a *hydrochloride*, m. p. 219°. The nitroso-derivative (Koehler, A., 1888, 49) is reduced by zinc and acid α-*benzyl*-α-*2-naphthylhydrazine*, m p. ,9 (*hydrochloride*, m. p. 177°; *picrate*, m. p. 152°), from which the *acetone-*, m. p. 104°, *benzaldehyde-*, m. p. ° and p- *robenzaldehyde-*, m. p. 137°, 166°, and 168°, respectively, *vanillin-*, m. p. 170°; *piperonal-*, m. p. 156°, *anisaldehyde-*, m. p. 150°, and *cinnamaldehyde-*, m. p. 214°, *-benzyl-β-naphthylhydrazones* are prepared.

1-Benzeneazo-2-benzylnaphthylamine, m. p. 138—139°, *sodium 2-benzylamino-1-naphthaleneazobenzene-p-sulphonate* [$+3{\cdot}5H_2O$], 1-p-*nitrobenzeneazo-*, m. p. 199°, and 1-o-*nitrobenzeneazo-2-benzylnaphthylamine*, m. p. 165°, and 1-α-*naphthaleneazo-2-benzylnaphthylamine*, m. p. 168°, are described. E. W. WIGNALL.

Cyclic thiocarbamides derived from fluorene. L. GUGLIALMELLI and A. NOVELLI (Anal. Asoc. Quím. Argentina, 1927, **15**, 287—307; cf. A., 1926, 720).—The mechanism of formation of aromatic thiocarbamides from amines and carbon disulphide in the presence of various catalysts is discussed. The ease of formation may be influenced by the solvent and by the presence of substituents in the aromatic nucleus; thus no thiocarbamide could be obtained from *o*- and *p*-nitroanilines and carbon disulphide, even using potassium xanthate as a catalyst. Neither a dithiocarbamate nor a thiocarbamide could be obtained from 2-aminofluorene and carbon disulphide except by the method of treating the mixture containing excess of the latter with pyridine (2 mols.) and adding iodine (1 mol.). In this way, *di-2-fluorenylthiocarbamide*, m. p. 245°, was obtained. Distillation with phosphorus pentoxide yielded *2-fluorenylthiocarbimide*, m. p. 70—80°. The difficulty of formation of the thiocarbamide is attributed to the effect of the methylene group. R. K. CALLOW.

Action of sodium triphenylmethyl on methoxytrimethylammonium iodide, and of triphenylmethyl halides on trimethylamine. L. W. JONES and M. W. SEYMOUR (J. Amer. Chem. Soc., 1928, **50**, 1150—1154).—When sodium triphenylmethyl and methoxytrimethylammonium iodide are shaken together in dry ether, sodium iodide, trimethylamine, triphenylmethane, and βββ-triphenylethyl alcohol are formed, probably as decomposition products of the desired triphenylmethyltrimethylammonium methoxide. Although triphenylmethyltriethylammonium iodide appears to exist (Schlubach and Miedel, A., 1923, i, 1068), attempts to prepare triphenylmethyltrimethylammonium salts from triphenylmethyl chloride or bromide and trimethylamine were unsuccessful, whilst triphenylmethyldimethylamine and methyl iodide gave only tetramethylammonium iodide and impure triphenylmethyl iodide.

H. E. F. NOTTON.

[Preparation of] triphenylamine. F. D. HAGER (Org. Syntheses, 1928, **8**, 116—119).

Derivatives of benzyl-*p*-phenylenediamine. J. REILLY and J. J. MOORE (J.S.C.I., 1928, **47**, 116T).—Benzyl-*p*-phenylenediamine prepared from benzylaniline and diazotised sulphanilic acid had m. p. 37° (lit. 30°). On diazotisation with excess of nitrous acid a nitrosodiazonium salt, $CH_2Ph{\cdot}N(NO){\cdot}C_6H_4{\cdot}N{:}NCl$, is formed, which couples with β-naphthol to give *p-benzylnitrosoaminobenzeneazo-β-naphthol*, m. p. 169—170°, and forms an azo *dye* with chromotropic acid.

Attempted synthesis of β-*m*-aminophenylethylamine. A. K. DE (J. Indian Chem. Soc., 1928, **5**, 29—31).—*m*-Aminocinnamic acid, m. p. 180°,

prepared from *m*-nitrocinnamic acid, m. p. 200—201° (colourless), yields *m-acetamidocinnamic acid*, m. p. 235°, which in turn affords β-m-*acetamidophenylpropionic acid*, m. p. 162°, on reduction with sodium amalgam. The failure of the preparation of the amide of the last-named precluded the synthesis of β-*m*-aminophenylethylamine by this method. It was also not found possible to reduce m-ω-*dinitrostyrene*, m. p. 123—124°, prepared from *m*-nitrobenzaldehyde and nitromethane, to the amine. G. A. C. GOUGH.

Orientation effects in the diphenyl series. VI. Supposed isomerism of the dinitrotolidines. R. J. W. LE FEVRE and E. E. TURNER (J.C.S., 1928, 963—969).—Nitration and subsequent hydrolysis of diacetyl-*o*-tolidine yields a mixture of 5 : 5'- and 6 : 6'-dinitro-*o*-tolidine. The former by bisdiazotisation and treatment with bromine yields a perbromide, which is decomposed by boiling glacial acetic acid to yield 4 : 4'-*dibromo*-5 : 5'-*dinitro*-3 : 3'-*dimethyldiphenyl*, m. p. 271—272°. This by heating with piperidine is converted into 4 : 4'-*dipiperidino*-5 : 5'-*dinitro*-3 : 3'-*dimethyldiphenyl*, m. p. 226—227°. The 6 : 6'-dinitro-compound similarly yields 4 : 4'-*dibromo*-6 : 6'-*dinitro*-3 : 3'-*dimethyldiphenyl* (I), m. p. 230—233° (softening at 225°), which does not react with boiling piperidine. Cain and Micklethwait's *o*-dinitrotolidine II, m. p. 202—203° (J.C.S., 1914, **105**, 1442), is thus proved to be a mixture of 5 : 5'- and 6 : 6'-dinitrotolidines, thus explaining its supposed conversion into *o*-dinitrotolidine I and the production of the same quinoxaline (by reduction followed by condensation with benzil) from both the I and II compounds. Nitration of 6-nitrodiacetyltolidine yields the 6 : 6'-dinitro-compound, since the product is converted into (I) on treatment by the perbromide method. Nitration of 4 : 4'-dichloro- (Schultz, Rohde, and Vicari, A., 1907, i, 244) and 4 : 4'-dibromo-3 : 3'-dimethyldiphenyl, m. p. 63—64° (Stolle, A., 1888, 699, gives 58—59°), yields, respectively, mainly 4 : 4'-*dichloro*-, m. p. 211—212°, identical with the compound obtained from 6 : 6'-dinitrotolidine by replacement of the amino-group by chlorine, and 4 : 4'-dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl, identical with (I) (above). The four isomeric dinitrotolidines of the *meta* series described by Cain and Micklethwait are probably position and not space isomerides, the positions of the nitro-groups being, respectively, 6 : 6', 2 : 2', 2 : 6', and 6 : 5'. J. W. BAKER.

α- and β-Substituted semicarbazides. α-Benzylsemicarbazide and β-benzylsemicarbazide. J. BOUGAULT and J. LEBOUCQ (Compt. rend., 1928, **186**, 957—960).—The benzylsemicarbazide, m. p. 235°, obtained by the method of Curtius (A., 1900, i, 610) is not 1-benzylsemicarbazide but 2-*benzylsemicarbazide*, $NH_2\cdot N(CH_2Ph)\cdot CO\cdot NH_2$, since it reacts with benzaldehyde to yield *benzaldehydebenzylsemicarbazide*, $CHPh:N\cdot N(CH_2Ph)\cdot CO\cdot NH_2$, m. p. 159·5—160°, and with excess of potassium cyanate to yield *benzylhydrazodicarboxylamide*, $CH_2Ph\cdot N(CO\cdot NH_2)\cdot NH\cdot CO\cdot NH_2$, m. p. 256°. Thus hydrazines containing a negative substituent react with potassium cyanate to yield 1-substituted semicarbazides, whilst those containing a less negative substituent yield the corresponding 2-compounds (cf. Young and Oates, J.C.S., 1901, **79**, 659). J. W. BAKER.

Bivalent triazenes. H. KLEINFELLER (J. pr. Chem., 1928, [ii], **119**, 61—73).—*m*-Phenylenediazide reacts with magnesium ethyl and phenyl bromides to form m-*bisethyltriazenobenzene*, $C_6H_4(NH\cdot N:NEt)_2$, m. p. 104°, and m-*bisphenyltriazenobenzene*, m. p. 161° (*silver* derivative, *phenylcarbimide* derivative, m. p. 230°). These compounds explode when heated rapidly and are decomposed by acetic or sulphuric acid.

Magnesium acetylenyl bromide and phenyl azide react yielding *bisphenyltriazenoacetylene*, $(NHPh\cdot N:N\cdot C:)_2$, m. p. 170° (*silver* compound; *phenylcarbimide* derivative, m. p. 197°), together with an isomeric *compound*, $C_{14}H_{12}N_6$, m. p. 156°, which is converted into the triazeno-derivative by treatment of its chloroform solution with alkali. When the triazeno-derivative is warmed with 20% sulphuric acid there is formed 2-*phenyl*-1 : 2-*dihydro*-1 : 2 : 3 : 4-*tetrazole*(?), m. p. 107°, whilst similar treatment of the isomeride gives a *compound*, $C_8H_8N_4$, m. p. 172°. *p*-Bromophenyl azide and magnesium acetylenyl bromide yield *bis*-p-*bromophenyltriazenoacetylene*, m. p. 215° (*silver* compound, m. p. 153°), and an isomeric *compound*, m. p. 198°. Bromine converts the triazene in chloroform solution into a *compound*, $C_{14}H_{11}N_6Br_5$, which when crystallised from alcohol passes into the *substance*, $C_{14}H_{11}ON_6Br_3$, m. p. 204°. Similar treatment of the isomeric substance gives a *compound*, $C_{14}H_{11}N_6Br_5$, m. p. 176°, unchanged by crystallisation from anhydrous solvent, but passing into the *substance*, $C_{14}H_{10}N_6Br_3\cdot OH$, m. p. 186°, when crystallised from 96% alcohol. *m*-Phenylenediazide and magnesium acetylenyl bromide react to give small amounts of reddish-violet and yellow substances. H. BURTON.

Migration of acyl from nitrogen to oxygen. L. C. RAIFORD and F. C. MORTENSEN (J. Amer. Chem. Soc., 1928, **50**, 1201—1204).—The acyl radicals in monoacyl derivatives of 2-amino*cyclo*hexanol and 1-α-aminobenzyl-2-naphthol, unlike those in the corresponding derivatives of *o*-aminophenols (cf. A., 1925, i, 809), do not migrate during further acylation. 2-Amino*cyclo*hexanol, m. p. 65° (cf. Brunel, A., 1903, i, 680), benzoyl chloride, and aqueous alkali give 2-*benzamido*cyclo*hexanol*, m. p. 168—169°, also formed by hydrolysing its *benzoate*, m. p. 204—205°, or *acetate*, m. p. 143—144°. Similarly, 2-*acetamido*cyclo*hexyl acetate*, m. p. 117—118°, and *benzoate*, m. p. 198—199°, are both hydrolysed to 2-acetamido*cyclo*hexanol. Benzoylation of 1-α-acetamidobenzyl-2-naphthol (Betti, A., 1903, i, 480) in pyridine gives 1-α-*acetamidobenzyl-2-naphthyl benzoate*, m. p. 176—177°, which is hydrolysed to the *N*-acetyl derivative. 1-α-*Benzamidobenzyl-2-naphthyl benzoate*, m. p. 118—119°, and *acetate*, m. p. 118—119°, are hydrolysed to 1-α-benzamidobenzyl-2-naphthol, m. p. 240—241° (Betti, *loc. cit.*, gives m. p. 224°). H. E. F. NOTTON.

Aluminium powder as a synthetic reagent. A. C. RAY and S. DUTT (J. Indian Chem. Soc., 1928, **5**, 103—110; cf. J.C.S., 1920, **117**, 1335).—Aluminium powder may be activated for synthetic purposes by heating it in a current of dry hydrogen at 500°. The

activation is apparently not due to the formation of a hydride nor to the removal of a film of aluminium sesquioxide, since that oxide is not reduced under the conditions employed. It is suggested that a film of a suboxide is removed in the activation. Dry distillation of phenol with the activated aluminium affords benzene and diphenyl; nitrophenols yield aminophenols, ammonia, and benzene. The powder may also be used in typical Ullmann, Freidel–Crafts, and Reformatsky reactions. When used in the reduction of a suspension of nitrobenzene in aqueous ammonium chloride, it affords β-phenylhydroxylamine at 0° and aniline at the ordinary temperature. Under the latter conditions it may be employed in the reduction of benzophenone to benzhydrol and in the reduction of azo dyes. G. A. C. GOUGH.

Sodium and potassium phenoxides. A. N. MELDRUM and M. M. PATEL (J. Indian Chem. Soc., 1928, **5**, 91—94).—These compounds may be obtained in a state of purity by precipitation of solutions of the phenol in 20% alkali hydroxide with concentrated alkali solution (100—200 g. in 100 g. of water). In this way the following are prepared: sodium phenoxide, m. p. 59—60°; potassium phenoxide, m. p. 103—104°; sodium *o*-, *m*-, and *p*-tolyloxides, m. p. below 0°, and 92—94°, and 123—125°, respectively; potassium *o*-, *m*-, and *p*-tolyloxides, crystalline, m. p. about 36° and 92°, respectively; sodium *m*-xylyloxide, m. p. 41—43°; potassium *m*-xylyloxide, liquid; sodium *p*-xylyloxide, m. p. 83°; potassium *p*-xylyloxide, m. p. 35°; sodium guaiacoxide, m. p. 120°; potassium guaiacoxide, m. p. 168°; sodium eugenoxide, m. p. 115°; potassium eugenoxide, m. p. 128°; sodium α- and β-naphthoxides, m. p. 44—45° and 120°, respectively; potassium α-naphthoxide, liquid; potassium β-naphthoxide, m. p. 38—40°.
G. A. C. GOUGH.

Action of hydrogen peroxide on phenol and anisole. O. MAGIDSON and N. PREOBRASHENSKI (Trans. sci. chem.-pharm. Inst., [Moscow], 1926, **16**, 65—67; Chem. Zentr., 1928, i, 35).—From phenol (31 g.), ferrous sulphate (0·1—0·2 g. in 100 c.c. of water), and 2% hydrogen peroxide are obtained, according to the temperature, 6—8 g. of pyrocatechol and 4—7 g. of quinol (with resin and excess of phenol). Anisole (36 g.) similarly yields guaiacol (1·5—2·5 g.).
A. A. ELDRIDGE.

Preparation of *p*-iodoanisole. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1928, **50**, 1229—1231).—A modification of the method of Brenans (Bull. Soc. chim., 1901, [iii], **25**, 819) gives 73% of the theoretical yield at 50—60°, and 57% at the ordinary temperature, whilst *p*-anisidine by the diazo reaction gives 75—80%. Iodination of anisole by way of its mercuration products or directly using iodine monochloride gives complex mixtures.
H. E. F. NOTTON.

Bromoiodophenols produced from 5-bromo- and 3 : 5-dibromo-salicylic acids. P. BRENANS and C. GIROD (Compt. rend., 1928, **186**, 1128—1130). Iodine reacts with 5-bromosalicylic acid (Hewitt, Kenner, and Silk, J.C.S., 1904, **85**, 1228; also produced from 5-aminosalicylic acid by the diazo-reaction) in the presence of sodium hydroxide or carbonate to afford 4-*bromo*-2 : 6-*di-iodophenol*, m. p. 128° (*ethyl ether*, m. p. 75°), which, when heated with aqueous sodium carbonate, is converted into an amorphous red *compound* of unknown constitution. 3 : 5-Dibromosalicylic acid, when treated with less than 1 mol. of iodine under similar conditions, yields 2 : 4-*dibromo*-6-*iodophenol*, m. p. 104° (*ethyl ether*, m. p. 54°), which is transformed into a red compound when treated with an excess of iodine in aqueous sodium carbonate. G. A. C. GOUGH.

[Preparation of] *m*-nitrophenol. R. H. F. MANSKE (Org. Syntheses, 1928, **8**, 80—82).

[Preparation of] di-*o*-nitrophenyl disulphide. M. T. BOGERT and A. STULL (Org. Syntheses, 1928, **8**, 64—65).

Derivatives of phenolmonosulphonyl chlorides. E. G. FULNEGG and A. SCHLESINGER (Ber., 1928, **61**, [*B*], 781—784).—Derivatives of phenolmonosulphonyl chlorides are obtained directly by the action of chlorosulphonic acid on the requisite ethylcarbonato-compounds. Since other groups which protect the phenolic hydroxyl group do not exert a similar effect, a specific action must be attributed to the carbethoxy-group, probably due to its negative nature. *m*-Ethylcarbonatotoluene gives (?) 5-*ethylcarbonatotoluene*-2-*sulphonyl chloride*, converted into the corresponding *anilide*, m. p. 149°. α-Ethylcarbonatonaphthalene affords α-ethylcarbonatonaphthalene-4-sulphonyl chloride, m. p. 83° (cf. Zincke and Ruppersberg, A., 1915, i, 135), transformed by treatment with the requisite base and subsequent hydrolysis of the product into α-naphthol-4-sulphonanilide, m. p. 198° (cf. Zincke, *loc. cit.*), α-*naphtholsulphondiphenylamide*, m. p. 176°, and α-*naphtholsulphon*-β-*naphthylamide*, m. p. 204°. β-Ethylcarbonatonaphthalene yields β-*ethylcarbonatonaphthalene*-8-*sulphonyl chloride*, m. p. 118°, identical with the product derived from β-naphthol-8-sulphonic acid by carbethoxylation and treatment with phosphorus pentachloride (Pollak and Halward, unpublished work); the corresponding *anilide* has m. p. 195°. Reduction of the sulphonyl chloride by zinc dust and sulphuric acid in presence of acetone gives 8-thiol-β-naphthol, isolated as the *lead* salt, $(C_{10}H_7OS)_2Pb$. H. WREN.

Synthetic musks. II. Elimination of side-chains during the nitration of aromatic compounds. R. DE CAPELLER (Helv. Chim. Acta, 1928, **11**, 426—427).—The dinitro-*m*-tolyl methyl ether, m. p. 101°, formed during the nitration of 2-*iso*butyl-*m*-tolyl methyl ether (Barbier, this vol., 280) is 4 : 6-dinitro-*m*-tolyl methyl ether, the *iso*butyl group having been replaced by hydrogen. When heated with ammonia at 100° under pressure this yields 4 : 6-dinitro-*m*-toluidine. Nitration of butyl-*m*-xylene (prepared from *m*-xylene and α-butylene in presence of aluminium chloride), dibutyl-*m*-xylene, and amyl-*m*-xylene gives in each case appreciable amounts of trinitro-*m*-xylene. H. BURTON.

Sulphonylides of cresol- and chlorophenol-disulphonic acids. C. S. SCHOEPFLE, F. J. VAN NATTA, and R. G. CLARKSON (J. Amer. Chem. Soc., 1928, **50**, 1171—1178).—These are obtained in high yield by heating the phenol for 6—8 hrs. at 100° with

sulphuric acid containing 20% of sulphur trioxide. In this way *p*-cresol yields tolylene-4 : 5-sulphonylide-3 : 3′-disulphonic acid (I),

$$SO_3H\cdot C_7H_5<\begin{matrix}O\cdot SO_2\\O_2\cdot O\end{matrix}>C_7H_5\cdot SO_3H \quad (+4H_2O)$$

(cf. Anschutz, A., 1918, i, 424); *o*-cresol, tolylene-2 : 3-sulphonylide-5 : 5′-disulphonic acid (II) $(+6H_2O)$ (cf. Pollak, A., 1926, 514); *p*-chlorophenol, 4 : 4′-*dichlorobenzene*-1 : 2-*sulphonylide*-6 : 6′-*disulphonic acid* $(+4H_2O)$; *o*-chlorophenol, 6 : 6′-*dichlorobenzene*-1 : 2-*sulphonylide*-4 : 4′-*disulphonic acid* $(+6H_2O)$; and *m*-chlorophenol, 5 : 5′-*dichlorobenzene*-1 : 2-*sulphonylide*-4 : 4′-*disulphonic acid* $(+8H_2O)$, whilst *m*-cresol does not react. The approximate solubility of the sodium salt of each acid has been measured. The sulphonylide (I) is converted through its acid chloride into its *diamide*, decomp. above 300°, *diethyl* ester, decomp. 90° (also +2MeOH), and *dimethyl* ester (+2MeOH), decomp. above 250°, which had half the correct mol. wt. in methyl alcohol. (II) also gives a *diamide*, decomp. above 300°, and *methyl* ester (+2MeOH), decomp. above 250°, which like the free acid (II) and *methyl* 4-*hydroxytoluene*-3 : 5-*disulphonate*, m. p. 148—149°, gives normal mol. wt. results in solvents other than methyl alcohol. Tolylene-4 : 5-sulphonylide (Anschütz, *loc. cit.*) and fuming sulphuric acid at the ordinary temperature yield *tolylene*-4 : 5-*sulphonylide*-*o*-*sulphonic acid* $(+2H_2O)$, m. p. 220—222°.

H. E. F. NOTTON.

Reaction between phenacetin and acetaldehyde. O. CARLETTI (Giorn. Chim. Ind. Appl., 1928, 10, 66).—If a small quantity of phenacetin, moistened with acetaldehyde in a porcelain dish, is stirred with 2—3 c.c. of concentrated sulphuric acid, the latter assumes a red colour, which intensifies gradually in the cold or more rapidly on a water-bath. Dilution of the liquid results in the separation of a bluish-brown substance, which gives the red coloration when dissolved in concentrated sulphuric acid. This reaction is given also by paraldehyde and metaldehyde, but not by formaldehyde, trioxymethylene, or hexamethylenetetramine.

T. H. POPE.

Condensation of chloral with substituted phenols. F. D. CHATTAWAY and F. CALVET (Anal. Fis. Quím., 1928, 26, 75—91; cf. A., 1927, 458, 967).—The condensation of chloral with *p*-aminophenol in excess of concentrated sulphuric acid yielded anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I), previously obtained by reduction of the 5-nitro-compound (A., 1926, 1242). Boiling alcoholic potassium hydroxide converted (I) into *anhydro*-5-*amino*-2-ββ-*dichloro*-α-*hydroxyethenoxy*-1-ββ-*dichloro*-α-*hydroxyethenylbenzene*, m. p. 113—117° (*acetyl* derivative, m. p. 191—196°). *p*-Tolueneazophenol and 4-nitro-*m*-cresol reacted similarly with chloral, giving the 5-p-*tolueneazo*-compound (II), m. p. 153°, and the 5-*nitro*-4-*methyl* compound (III), m. p. 148—150°, respectively. Reduction of (II) by stannous chloride yielded (I) and *p*-toluidine. The action of alcoholic potassium hydroxide on (III) yielded 5-*nitro*-2-*ethoxy*-p-*tolylglycollic acid*, m. p. 155°, which was oxidised by alkaline permanganate solution to 5-*nitro*-2-*ethoxy*-p-*toluic acid* (IV), m. p. 166°, and 5-*nitro*-2-*ethoxy*-p-*tolylglyoxylic acid*, m. p. 194° (*phenylhydrazone*, m. p. 199°). By sulphuric acid, (IV) was converted into 6-nitro-3-hydroxy-*p*-toluic acid, m. p. 225°, identical with the product of nitration of 3-hydroxy-*p*-toluic acid with fuming nitric acid in glacial acetic acid.

The formation of (III) shows that a substituent in the *m*-position to the hydroxyl group does not prevent the normal reaction. Substituents in the *o*-position, however, interfere, and 4-nitro-*o*-cresol, 5-nitrosalicylic acid, and 2 : 4-dinitrophenol do not condense under these conditions, probably owing to steric hindrance of the primary addition to the hydroxyl group. When the *p*-position is unoccupied, the chloral residue may enter in this position, as in the case of *m*-hydroxybenzoic acid, which yielded 5-*hydroxytrichloromethylphthalide*, m. p. 199—200° (cf. Fritsch, A., 1897, i, 568). Condensation of chloral with salicylic acid and *o*- and *m*-nitrophenols probably takes place in this way, but the products are resinous.

R. K. CALLOW.

Photo-oxidation of certain organic substances in presence of fluorescent dyes. C. W. CARTER (Biochem. J., 1928, 22, 575—582).—None of the aliphatic compounds employed was found to undergo photo-oxidation. Of the benzene derivatives only those containing a nuclear amino- or hydroxyl group were oxidised. Side-chains in which the groups $\cdot NH_2$ and ·CH:CH· occur are oxidised. The other side-chain compounds investigated were inactive. Certain other ring compounds, α-naphthol, tryptophan, thiophen, and to a marked degree the purine derivatives are oxidised. The carbon dioxide evolved during the oxidation was determined in a Barcroft apparatus.

S. S. ZILVA.

Derivatives of quinitol. L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1928, 186, 1007—1008; cf. this vol., 518).—The action of acetyl chloride or acetic anhydride in pyridine and chloroform at −5° on *cis*-quinitol yielded a mixture of the stereoisomeric diacetates, but *trans*-quinitol underwent no appreciable isomerisation. The monoacetates could not be isolated. As a by-product of the action of acetyl chloride, *trans*-quinitol yielded 4 : 4′-*dihydroxydicyclohexyl ether*, b. p. 132—133°/16 mm., d_4^{19} 1·0920, n_D^{19} 1·4574. Benzoyl chloride under similar conditions yielded cis-*quinitol dibenzoate*, m. p. 116—117°, and trans-*quinitol dibenzoate*, m. p. 151°, isomerisation during reaction of the *cis*-compound occurring only on rise of temperature. Acetic acid caused acetylation and isomerisation of *cis*-quinitol at 150°.

R. K. CALLOW.

Dyes resembling orcein. F. HENRICH and W. HEROLD (Ber., 1928, 61, [*B*], 767—770).—2-Aminoorcinol is not affected by dry air if dissolved in ether, benzene, or xylene; in methyl or ethyl alcohol it becomes oxidised, slowly in cold, more rapidly in hot solution, with loss of ammonia to a red *dye*, $C_{21}H_{18}O_6N_2$, regarded provisionally as a complex indophenol,

$$O:C_6H_2Me(OH):N\cdot C_6HMe(OH)_2\cdot N:C_6H_2Me(OH):O.$$

Oxidation appears to follow a different course in amyl alcohol. The possibility of the production of indophenols by this method is established by the formation of 4 : 6 : 6′-trihydroxy-3 : 3′-dimethylindo-

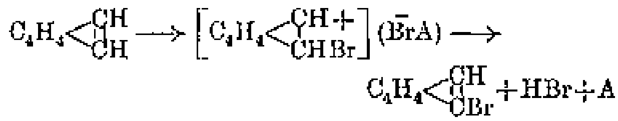
phenol from o-amino-2 : 4-dihydroxytoluene (cf. Henrich and Gotz, A., 1925, i, 913) and of a compound giving the indophenol reaction from a dilute alcoholic solution of phenol, *p*-aminophenol, and sodium. The dye is transformed by treatment with concentrated hydrochloric acid and stannous chloride at 180—200° mainly into a dark mass, which rapidly becomes oxidised and then ceases to give the reactions of the dye, but yields also about 10% of amino-orcinol hydrochloride and a little ammonium chloride. Diamino-orcinol, a possible product from the dye, yields ammonium chloride, but not amino-orcinol hydrochloride under analogous conditions. Similarly, orcein yields a product resembling that from the dye, which, however, contains much ammonium chloride and only a trace of substance which gives the same coloration as amino-orcinol with ferric chloride.

H. WREN.

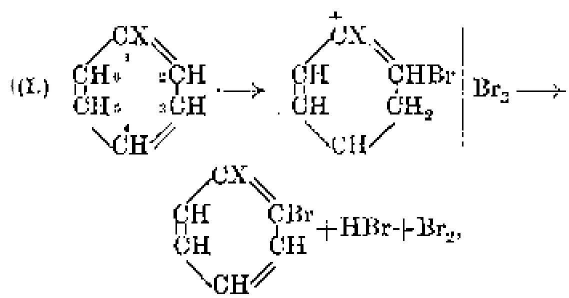
Synthesis of 3 : 5-dihydroxyethylbenzene. Y. ASAHINA and S. IHARA (J. Pharm. Soc. Japan, 1928, [551], 28—31).—Ethyl 3 : 5-dimethoxybenzoylacetate is boiled with dilute sulphuric acid for 10 hrs., and 3 : 5-dimethoxyphenyl methyl ketone is obtained. This ketone is reduced by zinc amalgam and hydrochloric acid to 3 : 5-dimethoxyethylbenzene, which yields on boiling with hydriodic and glacial acetic acids, 3 : 5-dihydroxyethylbenzene, m. p. 72—73°, with benzene of crystallisation. Unlike orcinol and divarinol, it develops no coloration with ferric chloride, but with vanillin and hydrochloric acid turns red and exhibits greenish fluorescence on boiling with alkali hydroxide and chloroform.

Theory of halogen substitution. P. PFEIFFER and R. WIZINGER (Annalen, 1928, 461, 132—154).—It was stated by Gattermann (A., 1889, 862) that certain αα-dianisylethylenes gave a violet colour with bromine vapour, but that this colour rapidly disappeared, the original compounds being recovered unchanged. This statement is correct as regards the colour change, but otherwise incorrect, for the compounds undergo bromination. The bromo-derivatives behave towards bromine like the parent substances until the limit is reached when no further bromination can occur. The colours observed intermediately are apparently those of unstable bromo-perbromides; one of the latter, that of 4 : 4′-bis-dimethylamino-αα-diphenylethylene, is isolable as a deep blue solid (the corresponding iodoperiodide, also isolated, is a stable blue solid). The constitution of the coloured intermediate compounds is deduced from the fact that the depth of colour given by a compound with bromine corresponds with that given with concentrated sulphuric acid or with perchloric acid. Thus, αα-diphenylethylene gives no colour with bromine and a greenish-yellow with the two acids, whilst αα-di-*p*-anisylethylene, which affords a deep bluish-violet with bromine, gives deep orange colours with both acids. If the perchlorate formed in this case is represented as $[(OMe\cdot C_6H_4\cdot)_2C-CH_3]\bar{C}lO_4$, then the coloured bromine compound will be $[(OMe\cdot C_6H_4)_2C-CH_2Br]Br_3$, undergoing decomposition into $(OMe\cdot C_6H_4)_2C{:}CHBr+HBr+Br_2$.

It is suggested by analogy that the bromination of benzene in presence of a bromine carrier A (in absence of which ordinary addition occurs) may be expressed :



When pyridine is used as a bromine carrier, the compound $\left[C_6H_4<^{CH\cdot C_5H_5N}_{CHBr}\right]Br$ (cf. Meerwein, Z. angew. Chem., 1925, 38, 816) is the intermediate formed. Again, the *ortho–para*-directive effect of certain groups X (OH, OMe, NH_2, etc.) receives explanation if it be assumed that in formula (I) the ethylenic linking 5 : 6 and the group X confer polar properties on the attached carbon atom (number 1) as similar groups are known to do in the case of the types : $[R_2C-R]X$; $[R_2C-OH]X$; $[R_2C-OMe]X$; $[R_2C-NH_2]X$; and $[(NH_2)_2C-NH_2]X$. The bromination of C_6H_5X can thus be written :



p-substitution depending on a 1 : 4-conjugation-additive process. When $X=NO_2$, the "negative" effect of this group is to cause the appearance of the positive charge in the 4-position, viz., the position farthest from X. As a result, *m*-substitution occurs (position 3).

αα-Di-*p*-anisylethylene, prepared either from di-anisyl ketone and magnesium methyl iodide or from ethyl acetate and magnesium *p*-anisyl bromide, is converted by bromine (1 mol.), in benzene or carbon tetrachloride solution, into *β-bromo-αα-di-*p*-anisylethylene*, m. p. 84°, the constitution of which follows from its oxidation to di-*p*-anisyl ketone. This bromo-compound is converted by bromine in carbon tetrachloride into *ββ-dibromo-αα-di-*p*-anisylethylene*, m. p. 93—94°, also obtained by the action of methyl-alcoholic potassium hydroxide on *βββ-tribromo-αα-di-*p*-anisylethane*, m. p. 114°, which is in turn obtained by condensing bromal and anisole in presence of concentrated sulphuric acid. Dianisylethylene and the above dibromodianisylethylene are quantitatively converted by excess of bromine in glacial acetic acid solution into ββ-3 : *-tetrabromo-4 : 4′-dimethoxy-αα-diphenylethylene*, m. p. 150°, oxidised to 3 : 3′-dibromo-4 : 4′-dimethoxybenzophenone.

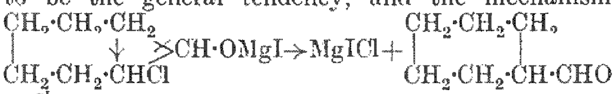
The following substances are described as being obtained by processes mostly similar to the above : αα-di-*p*-anisyl-β-methylethylene (dianisylpropylene); *αα-di-*p*-anisyl-ββ-dimethylethylene* (*dianisylmethylpropylene*), m. p. 64°; αα-di-*p*-tolylethylene, from toluene

and bromoacetal in presence of concentrated sulphuric acid; αα-di-*m*-xylylethylene, similarly obtained, b. p. 197—200°/17 mm.; β-*bromo-αα-di*-p-*anisyl-β-methylethylene*, m. p. 57°; β-3 : -*tribromo*-4 : 4′-*dimethoxy-αα-diphenyl-β-methylethylene*, m. p. 131°; 4 : 4′-bisdimethylamino-αα-diphenylethylene, from Michler's ketone and magnesium methyl iodide; *bromoperchlorate*, deep blue, from the above bromoperbromide and sodium perchlorate, or, better, from the ethylene and ferric bromide, followed, after isolation of the ferribromide, by sodium perchlorate.

A table is given of the colours shown when bromine, concentrated sulphuric acid, or perchloric acid acts on a number of αα-diarylethylenes of the type CAr_2:CXY, where X or Y=H, Me, Br, or Cl.

E. E. TURNER.

Molecular transpositions in the *cyclo*heptane series. M. GODCHOT and G. CAUQUIL (Compt. rend., 1928, **186**, 955—957; cf. this vol., 410; Vavon and Mitchovitch, this vol., 516).—The action of magnesium phenyl bromide on 2-chloro*cyclo*heptanol yields phenyl*cyclo*hexylcarbinol, m. p. 48—49° (*hydrogen phthalate*, m. p. 163°; *phenylurethane*, m. p. 146—147°), identical with a specimen prepared by Sabatier and Mailhe's method (A., 1904, i, 809) together with an ethylenic hydrocarbon, $C_{13}H_{16}$, b. p. 140—141°/15 mm. (cf. Auwers and Treppmann, A., 1915, i, 789). The formation, by this reaction, of a ring containing one less carbon atom would thus appear to be the general tendency, and the mechanism



$\xrightarrow{\text{gI}}$ C_6H_{11}·CHR·OH, suggested by Tiffeneau, is probably correct.

J. W. BAKER.

Mobile-anion tautomerism. I. Conditions of activation of the three-carbon system, and modes of addition to conjugated systems. H. BURTON and C. K. INGOLD (J.C.S., 1928, 904—921).—An examination has been made of the relative mobility of X (=OH, OAc, Br) and its facilitation by R (=Me, Ph, *p*-Me·C_6H_4, *p*-Cl·C_6H_4) in R·CHX·CH:CH_2R′ R·CH:CH·CHX·R′, and of the effect of R on equilibrium. The order of increasing mobility is as indicated in each series, and hence corresponds with the anionic stability of X and the power of R to take up the cationic charge. The analogy with aromatic substitution and the bearing of the results on 1 : 4-addition to conjugated systems and related topics are discussed. Contrary to the observations of Valeur and Luce (Bull. Soc. chim., 1920, [iv], **27**, 611), the conversion of α-phenylallyl alcohol (p-*nitrobenzoate*, m. p. 45—46°) into cinnamyl alcohol could not be effected, but on heating with acetic anhydride, smooth conversion into cinnamyl acetate occurs. The action of an acetic acid solution of hydrogen bromide on either alcohol yields cinnamyl bromide (Moureu and Gallacher, A., 1922, i, 34), the structure of which is proved by ozonolysis. α-p-*Tolylethyl alcohol*, b. p. 120—122°/10 mm. (p-*nitrobenzoate*, m. p. 82°), prepared by the action of magnesium *p*-tolyl bromide on acraldehyde, is readily converted by the action of acetic anhydride and subsequent hydrolysis into 4-*methylcinnamyl alcohol*, m. p. 51—52° (p-*nitrobenzoate*, m. p. 131—132°), and on bromination yields 4-*methylcinnamyl bromide*, m. p. 64—65°. In the investigation of αγ-diarylated systems the structures of the various alcohols were established by ozonolysis, and by conversion under the influence of alcoholic alkali, into the isomeric ketones, R·CH(OH)·CH:CHR′ ⟶ R·CO·CH_2·CH_2R′ Tiffeneau, Bull. Soc. chim., 1907, [iv], **1**, 1209; Nomura, A., 1927, 770). αγ-Diphenylallyl acetate when treated with bromine in cold carbon tetrachloride deposits a *bromide*, m. p. 176—177°, a second *bromide*, m. p. 122°, being obtained from the mother-liquors. γ-*Phenyl*-α-p-*tolylallyl alcohol*, m. p. 78—79°, obtained by the action of magnesium *p*-tolyl bromide on cinnamaldehyde, is converted by boiling 20% alcoholic potassium hydroxide into p-*tolyl* β-*phenylethyl ketone* (I), m. p. 70° (*oxime*, m. p. 101—102°), and on acetylation yields a mixture of γ-phenyl-α-*p*-tolyl and α-phenyl-γ-*p*-tolyl acetates with a constant b. p. 210—212°/11 mm. The action of cinnamaldehyde on magnesium *p*-chlorophenyl iodide yields a mixture of the isomeric phenylchlorophenylallyl alcohols, the mixed acetates of which, b. p. 225—226°/13 mm., on treatment with bromine yield two isomeric *bromides*, m. p. 193—194° and 180°, respectively. Treatment of the mixed acetates with 20% alcoholic potassium hydroxide solution yields a mixture of *phenyl* β-p-*chlorophenylethyl ketone* (II), m. p. 58°, and p-*chlorophenyl* β-*phenylethyl ketone* (III), m. p. 78°, which were isolated as their *oximes*, m. p. 117—118° and 111—112°, respectively (below). The various reference ketones are synthesised as follows : *ethyl* p-*chlorobenzylbenzoylacetate*, b. p. 240°/12 mm., m. p. 54—55°, is obtained by the action of *p*-chlorobenzyl bromide on ethyl sodiobenzoylacetate, and hydrolysis with dilute sulphuric acid or barium hydroxide yields (II). *Ethyl* p-*chlorobenzoylacetate*, b. p. 181—182°/18 mm., m. p. 36°, obtained by the action of *p*-chlorobenzoyl chloride on ethyl sodioacetoacetate, is similarly converted into *ethyl benzyl*-p-*chlorobenzoylacetate*, b. p. 228—233°/14 mm., m. p. 65°, which on hydrolysis yields (III). Ethyl *p*-toluoylacetate, b. p. 172—173°/14 mm. (Marguery, A., 1905, i, 527, gives b. p. 170°/30 mm.), is similarly converted into *ethyl benzyl*-p-*toluoylacetate*, b. p. 232—233°/11 mm., which by hydrolysis yields (I). *Ethyl* p-*methylbenzylbenzoylacetate*, b. p. 223—225°/10 mm., on hydrolysis yields *phenyl* β-p-*tolylethyl ketone*, low m. p., a waxy solid (*oxime*, m. p. 85—86°).

J. W. BAKER.

[Preparation of] benzhydrol. C. S. MARVEL and N. A. HANSEN (Org. Syntheses, 1928, **8**, 24—25).—Benzophenone is reduced with technical zinc dust (85% purity), 95% alcohol, and sodium hydroxide; the benzophenone must first be heated with the alcoholic alkali.

A. A. ELDRIDGE.

Preparation of crystal-violet from oxalyl chloride and dimethylaniline. I. N. POSTOVSKI (J. Chem. Ind. [Moscow], 1927, **4**, 552—553).—Powdered aluminium chloride (1 part) is added to dimethylaniline (10 parts), and oxalyl chloride (7 parts) is added gradually; the hot, green mixture is cooled with water while the remainder of the oxalyl chloride is added. The reaction is complete in 5 min. The crude mass is converted into the

carbinol with sodium hydroxide, the excess of dimethylaniline removed with steam, and the carbinol dissolved in acidified water, filtered, and recrystallised. The yield is 92—95% of the dimethylaniline taken (cf. G.P. 34,607). CHEMICAL ABSTRACTS.

Amino-alcohols of the naphthalene series. E. FOURNEAU, TREFOUEL, and (Mme.) TREFOUEL (Bull. Soc. chim., 1928, [iv], **43**, 454—458).—A number of amino-alcohols of mol. wt. approaching that of quinine and of amino-alcohols of the benzene series containing a methoxy-group or a piperidine ring have been prepared. The following are described: *α-dimethylamino-γ-*1*-naphthyl-*, b. p. 216—217°/28 mm. (*hydrochloride*, m. p. 134°); *α-diethylamino-γ-*1*-naphthyl-*, b. p. 214°/19 mm. (*hydrochloride*, m. p. 138°); *α-diamylamino-γ-*1*-naphthyl-*, b. p. 240°/22 mm. (*hydrochloride*, m. p. 114°); and *α-piperidino-γ-*1*-naphthyl-*iso*propyl alcohol*, b. p. 228°/10 mm. (*hydrochloride*, m. p. 145°). The foregoing compounds were all obtained from *α-chloro-γ-*1*-naphthyl*iso*propyl alcohol*, b. p. 210°/25 mm. (from magnesium α-naphthyl bromide and epichlorohydrin), or from *γ-*1*-naphthylpropylene αβ-oxide*, b. p. 186°/15 mm., obtained by the action of sodium hydroxide on the chlorohydrin in alcoholic solution. *γ-*4*-Methoxy-*1*-naphthylpropylene αβ-oxide*, b. p. 225°/25 mm., *α-chloro-γ-*4*-methoxy-*1*-naphthyl-*, b. p. 180°/0·2 mm., and *α-piperidino-γ-*4*-methoxy-*1*-naphthyl-*iso*propyl alcohol*, b. p. 200°/0·1 mm. (*hydrochloride*, m. p. 193—194°), are similarly prepared. 1*-Bromo-*4*-methoxynaphthalene*, b. p. 178°/15 mm., is obtained by brominating α-methoxynaphthalene in acetic acid. *γ-Chloro-α-phenyl*iso*propyl alcohol*, b. p. 135—155°/20 mm., *γ-phenyl-αβ-propylene oxide*, b. p. 113°/39 mm., *α-piperidino-γ-phenyl*iso*propyl alcohol*, b. p. 172°/12 mm. (*hydrochloride*, m. p. 178—179°); *γ-chloro-α-*p*-methoxyphenyl*iso*propyl alcohol*, b. p. 188—190°/24 mm., *γ-*p*-methoxyphenyl-αβ-propylene oxide*, b. p. 145—150°, and *α-piperidino-γ-*p*-methoxyphenyl*iso*propyl alcohol*, b. p. 213°/18 mm. (*hydrochloride*, m. p. 164°), are described. α-Naphthol condensed with epichlorohydrin in presence of sodium hydroxide affords *γ-*1*-naphthoxy-αβ-propylene oxide*, 194°/16 mm., from which *α-piperidino-γ-*1*-naphthoxy-*, b. p. 196°/0·2 mm. (*hydrochloride*, m. p. 177—178°), and *α-diethylamino-γ-*1*-naphthoxy-*iso*propyl alcohol*, b. p. 176°/0·2 mm. (*hydrochloride*, m. p. 125°), are obtained. *γ-*2*-Naphthoxy-αβ-propylene oxide*, b. p. 200°/16 mm., *α-piperidino-γ-*2*-naphthoxy*iso*propyl alcohol*, b. p. 200°/0·15 mm. (*hydrochloride*, m. p. 172—173°), and *α-diethylamino-γ-*2*-naphthoxy*iso*propyl alcohol*, b. p 190°/0·6 mm. (*hydrochloride*, m. p. 162°), are also described. R. BRIGHTMAN.

Action of magnesium *cyclo*hexyl bromide on oxalic acid derivatives. C. G. GAUERKE and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 1178—1182).—Ethyl oxalate and magnesium *cyclo*hexyl bromide give the *ethyl* ester (I) (20% of the theoretical yield), m. p. 69° (corr.), of *hydroxydi*cyclo*hexylacetic acid*, m. p. 171—172°, also some di*cyclo*hexyl, but only a small amount of *tetra*cyclo*hexylethylene glycol*, m. p. 151—152°, even when the Grignard reagent is in excess. Similarly, methyl and *iso*propyl oxalates give *methyl*, m. p. 48·5°, and iso*propyl*, m. p. 80°, *hydroxydi*cyclo*hexylacetates*. Magnesium *cyclo*hexyl bromide does not react further with the ester (I); with methyl benzilate in di-*n*-butyl ether it gives cyclo*hexoyldiphenylcarbinol*, m. p. 112·5°, which is hydrolysed by alcoholic potassium hydroxide to potassium hexahydrobenzoate and diphenylcarbinol, and with benzil, s-*diphenyldi*cyclo*hexylethylene glycol*, m. p. 150—151°. Attempts to reduce di*cyclo*hexyl ketone to tetra*cyclo*hexylethylene glycol, using magnesium with iodine or mercury (cf. Gomberg, A., 1927, 245, 1190), were unsuccessful. H. E. F. NOTTON.

Tetraphenylethylene oxide (α-benzpinacol). (MLLE.) J. LEVY and R. LAGRAVE (Bull. Soc. chim., 1928, [iv], **43**, 437—441).—The reactivity of arylated ethylenic hydrocarbons towards perbenzoic acid depends partly on the mol. wt. and partly on the symmetrical or unsymmetrical nature of the molecule. Hydrocarbons such as stilbene, which possess a symmetrical molecule, are less easily oxidised than unsymmetrical triaryl-hydrocarbons (cf. A., 1926, 818; 1927, 872; Boeseken, A., 1927, 39; Lagrave, *ibid.*, 872). Tetraphenylethylene oxide, m. p. 193—194° in mercury, 198—199° in acid bath, prepared by oxidation of tetraphenylethylene with perbenzoic acid in chloroform solution, is identical with α-benzpinacolin. Tetraphenylethylene is best prepared from β-benzpinacolin, obtained by reduction of benzophenone with zinc and excess of acetyl chloride (cf. Paal, A., 1884, 1167), which with 2¼ mols. of magnesium ethyl bromide affords a theoretical yield of αααβ-tetraphenylethan-β-ol, converted by acetyl chloride into ααββ-tetraphenylethylene. Yields of oxide up to 43% can be obtained by Thorner and Zincke's process (A., 1878, 425, 874), but replacement of the hydrochloric acid by dilute sulphuric acid leads to benzpinacol. No benzhydrol is isolated in these reactions, but 1—2% of tetraphenylethylene is formed. R. BRIGHTMAN.

Ether corresponding with *iso*safrole bromohydrin. C. MANNICH and F. SCHMITT (Arch. Pharm., 1928, **266**, 84—86).—In preparing *iso*safrole bromohydrin from *iso*safrole dibromide by the action of aqueous acetone (cf. Mannich, A., 1910, i, 411) there is formed as a by-product *β-bromo-α-*3 : 4*-methylenedioxyphenyl* n*-propyl ether*, m. p. 134°, evidently produced by interaction of unchanged dibromide with the bromohydrin, since it can be produced in quantity by allowing these compounds to remain in contact for 10 weeks. The bromine atoms are not readily replaced (cf. the methyl ether of the bromohydrin, *loc. cit.*): thus, palladium and hydrogen, and organic bases, have no action on the compound. Hot alcoholic potassium hydroxide removes the bromine, giving what is apparently a diethylenic ether, a viscous oil, which is converted by hot 20% hydrochloric acid into 3 : 4-methylenedioxyphenyl ethyl ketone. The ether is also debrominated by the action of silver acetate in glacial acetic acid. The product here appears to be the diacetate of the corresponding dihydroxy-compound; when distilled it decomposes into acetic acid and *iso*safrole oxide. A cold 15% solution of hydrogen bromide in glacial acetic acid converts the ether into *iso*safrole bromohydrin. W. A. SILVESTER.

Synthesis of amino-alcohols from *iso*safrole, *iso*eugenol, and anethole. C. MANNICH and F. SCHMITT (Arch. Pharm., 1928, **266**, 73—84).—The benzoate of γ-dimethylamino-γ-3 : 4-methylenedioxyphenylpropan-β-ol (Mannich, A., 1910, i, 411) is a powerful but only weakly toxic anæsthetic. The following compounds were prepared in fruitless efforts to obtain a pharmacologically superior product. Dimethylaminomethylenedioxyphenylpropan-β-ol is now obtained in better yield (70%) and has m. p. 66—68°, b. p. 178—182°/16 mm. When the *methiodide*, m. p. 176°, is heated with potassium hydroxide it breaks up into trimethylamine and *iso*safrole oxide. This formation of *iso*safrole oxide is an instance of a readiness to decompose which is exhibited also in other reactions, *e.g.*, acylation. Thus, the *benzoate* (m. p. 80—83°; *hydrochloride*, m. p. 202—208°), obtained by heating the hydrochloride of the base with benzoyl chloride at 115—125°, is accompanied by about 10% of a *by-product*, m. p. 164—165°, apparently the benzoate of γ-chloro-γ-3 : 4-methylenedioxyphenylpropan-β-ol, as it is decomposed by the action of alcoholic potassium hydroxide into *iso*safrole oxide and benzoic acid. Similarly, when the hydrochloride of the base is heated with *o*-carbomethoxybenzoyl chloride, the *o-carbomethoxybenzoate* (*hydrochloride*, m. p. 125—126°, anæsthetic) is obtained, but when the base is similarly treated, part is simply converted into its hydrochloride, part is converted into 3 : 4-dimethoxybenzyl methyl ketone apparently by way of *iso*safrole oxide, and the third product is *o*-carbomethoxybenzdimethylamide. The p-*nitrobenzoate* of the dimethylaminomethylenedioxyphenylpropanol has m. p. 223° and is reduced in dilute hydrochloric acid solution by the action of metallic copper and hydrogen sulphide to the corresponding *aminobenzoate*, m. p. 120°, which also is an anæsthetic. γ-*Diethylamino*-γ-3 : 4-*methylenedioxyphenylpropan*-β-*ol*, b. p. 175°/14 mm. (*hydrochloride*, m. p. 196°), is obtained when a cold solution of isosafrole bromohydrin and diethylamine in alcohol is kept for a month. The *benzoate*, m. p. 185°, is a potent anæsthetic. The p-*nitrobenzoate*, m. p. 220°, is also described. When the amino-alcohol is oxidised in warm glacial acetic acid solution by chromic acid, 3 : 4-methylenedioxybenzyl methyl ketone is obtained. γ-*Piperidino*-γ-3 : 4-*methylenedioxyphenylpropan*-β-*ol*, m. p. 77°, b. p. 235—240°/15 mm., yields a *hydrochloride*, m. p. 204°, and a *benzoate* [*hydrochloride*, m. p. 204°, (decomp.)] which is a powerful anæsthetic. γ-Dimethylamino-γ-3 : 4-dimethoxyphenylpropan-β-ol (Mannich, *loc. cit.*) is now found to have m. p. 51°. Its p-*nitrobenzoate* (*hydrochloride*, m. p. 198°) is obtained in mediocre yield. γ-*Diethylamino*-γ-3 : 4-*dimethoxyphenylpropan*-β-*ol*, b. p. 197—199°/14 mm., is obtained by the usual procedure in 70% yield. γ-*Piperidino*-γ-3 : 4-*dimethoxyphenylpropan*-β-*ol* cannot satisfactorily be isolated; when the syrupy crude base is distilled (b. p. 212—220°/14 mm.) it breaks up into piperidine and 3 : 4-dimethoxybenzyl methyl ketone. γ-*Dimethylamino*-γ-p-*anisylpropan*-β-*ol*, obtained from anethole by way of the bromohydrin in the usual way, has m. p. 39°, b. p. 162°/17 mm. The *hydrochloride*, m. p. 195°, and p-*nitrobenzoate* [*hydrochloride*, m. p. 205° (decomp.)] are described. The latter is reduced by tin and hydrochloric acid to the p-*aminobenzoate*, m. p. 159°, which is an anæsthetic. γ-*Diethylamino*-γ-p-*anisylpropan*-β-*ol*, b. p. 210°/30 mm., yields a very hygroscopic *hydrochloride*. γ-*Piperidino*-γ-p-*anisylpropan*-β-*ol*, b. p. 203—205°/14 mm. (*hydrochloride*, m. p. 180°), yields a p-*nitrobenzoate*, m. p. 213°, (decomp.). Although the bases described above should consist of a mixture of stereoisomerides, it appears doubtful whether they really do so, those that are obtained in a crystalline form being evidently not mixtures.

W. A. SILVESTER.

Benzoic esters and electronic affinities of radicals. I. A. ZAKI (J.C.S., 1928, 983—989).—The nitration at 0° and 25° of a series of alkyl benzoates has been studied. The percentage of the *meta*-isomeride produced in the various cases is as follows: methyl, 72·6; ethyl, 69·9; *n*-propyl, 71·8; *n*-butyl, 67·9; *n*-amyl, 68·3; *n*-hexyl, 63·7; *n*-heptyl, 62·8; *n*-octyl, 60·2; *n*-cetyl, 52 (ca.); *iso*propyl, 64·1; *iso*butyl, 69·4; *sec.*-butyl, 65·2; *tert.*-butyl, 59·4; *sec.*-octyl, 59·4% at 0°, the values for the first four of the series at 25° being, 69·7, 66·3, 68·6, and 65·1%, respectively Branching of the carbon chains decreases the proportion of the *meta*-isomeride produced, but with the normal alkyl benzoates, alternation between the odd and even series is found. This alternation decreases as the length of the chain is increased, and it is suggested that a direct effect through space of the carbonyl oxygen atom on the more proximate odd carbon atoms of the zigzag alkyl chain is superimposed on the general inductive effect (Allan and others, A., 1926, 397) transmitted through the chain. A modification of Holleman's titration method for the determination of the percentage of *meta*-isomeride (A., 1899, i, 757; cf. Baker, A., 1927, 454) is described, an accuracy of 0·3% being claimed.

J. W. BAKER.

Carboxyphenylcarbamide derivatives. S. WEIL and (MLLE.) J. ROZENTAL (Rocz. Chem., 1928, **8**, 44—49).—The following compounds of the "anæsthesine" group have been prepared: p-*carbethoxyphenylcarbamide*, m. p. 95°; N-*acetyl*-N′-p-*carbethoxyphenylcarbamide*, m. p. 139—140°; N-*isovaleryl*-N′-p-*carbethoxyphenylcarbamide*, m. p. 237°, and N-α-*bromoisovaleryl*-N′-p-*carbethoxyphenylcarbamide*, m. p. 134—135°. The last substance is a more powerful anæsthetic agent than "bromural."

R. TRUSZKOWSKI.

[Preparation of] perbenzoic acid. M. TIFFENEAU (Org. Syntheses, 1928, **8**, 30—34).

[Preparation of] ethyl *p*-aminobenzoate. R. ADAMS and F. L. COHEN (Org. Syntheses, 1928, **8**, 66).—Ethyl *p*-nitrobenzoate is catalytically reduced by hydrogen in presence of platinum oxide.

A. A. ELDRIDGE.

State of aggregation of phenylbromoacetonitrile. A. NEKRASSOV (J. pr. Chem., 1928, [ii], **119**, 108).—Phenylbromoacetonitrile has b. p. 137—139°/15 mm., m. p. 25·4° (cf. Steinkopf, A., 1920, i, 590; Schotz, "Synthetic Organic Compounds," 310).

H. BURTON.

Dioximes. XLVII. L. AVOGADRO (Gazzetta, 1928, **58**, 191—196; cf. A., 1927, 470).—Oximino-*p*-tolylacetonitrile oxide (cf. A., 1924, i, 294) is converted by benzoyl chloride or bromide into 3-*chloro*- or 3-*bromo*-5-p-*tolyl*-1 : 2 : 4-*oxadiazole*, m. p. 42—43° and 27—28°, respectively. It is suggested that the structures $C_6H_4Me{\cdot}C(OH){:}N{\cdot}C{:}N{:}O$ and $C_6H_4Me{\cdot}C(OBz){:}N{\cdot}CCl{:}N{\cdot}OH$ are intermediately formed. Either halogen compound on prolonged heating with methyl-alcoholic potassium hydroxide yields 3-*hydroxy*-5-p-*tolyl*-1 : 2 : 4-*oxadiazole*, m. p. 199—200° (with partial sublimation), which is decomposed by nitric acid, and with *m*-4-xylidine yields s-*di*-m-4-*xylylcarbamide*. The hydroxy-compound yields a *sodium* salt, explodes 204°, a *silver* double salt, $C_{18}H_{15}O_4N_4Ag$, m. p. 258° (exploding), and a *cupric* salt which decomposes to a basic compound; it is alkylated by the appropriate alkyl sulphate to the 3-*methoxy*-, m. p. 47—48°, or 3-*ethoxy*-compound, m. p. 45°, also obtained by the action of an alkali ethoxide on the chloro- or bromo-compound.

The action of an aqueous sodium hydroxide solution on oximino-*p*-tolylacetonitrile oxide, followed by passage of carbon dioxide and acidification, yields 3-hydroxy-5-*p*-tolyl- and 5-hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazoles, separated by means of the copper salt of the former (cf. Ponzio and Zanardi-Lamberti, A., 1924, i, 324); by means of its *nickel* salt is also isolated p-*tolylmetazonic acid*, m. p. 176—177°, decomp. to *p*-toluonitrile and 5-hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole. E. W. WIGNALL.

Racemisation of amino-acid derivatives. P. KARRER and M. DALLA VEDOVA (Helv. Chim. Acta, 1928, **11**, 368).—When acylated amino-acids, *e.g.*, *N*-benzoyl-*l*-leucine and *N*-benzoyl-*d*-alanine, are converted into the acid chlorides by treatment with phosphorus pentachloride in acetyl chloride at 0°, complete racemisation occurs. This must be due to the intermediate formation of a compound with a symmetrical structure, such as $NHBz{\cdot}CR{:}CCl{\cdot}OH$. R. K. CALLOW.

Resin acids of *Coniferæ*. P. LEVY [with H. BRUNOTTE and H. RAALF] (Ber., 1928, **61**, [*B*], 616—623; cf. Aschan and Levy, A., 1927, 1067).—The acid, $C_{20}H_{32}O_4$, regarded by Levy and Brunotte (*loc. cit.*) as dihydroxyabietic acid, is shown to be identical with the dihydroxydihydro-*d*-pimaric acid of Ruzicka and Balas (this vol., 297); it is also obtained by oxidation of abietic acid prepared according to G.P. 221,889 and of crude American colophony. Abietic acid, previously regarded as homogeneous, must therefore contain isomeric resin acids (cf. Dupont, A., 1924, i, 640). This conception is confirmed by the isolation of dihydro-*d*-pimaric acid, $C_{20}H_{32}O_2$ (cf. Tschugaev and Tearu, A., 1913, i, 726), from the products of the catalytic hydrogenation of abietic acid derived from American turpentine. The production of the dihydroxy-acid and the tetrahydroxy-acid of higher m. p. or of the two tetrahydroxy-acids during the oxidation of abietic acid is closely connected with the amount of permanganate used. All three acids are shown to be homogeneous. The preparation of uniform hydroxylated acids thus affords a certain method of establishing the number of double linkings in resin acids (contrast Jonas, A., 1922, i, 326), whereas this cannot safely be determined by catalytic hydrogenation, since the volume of hydrogen absorbed is dependent on solvent, catalyst, and temperature. H. WREN.

Derivatives of acenaphthene[-5-carboxylic acid]. I. G. FARBENIND. A.-G.—See B., 1928, 293.

Esterification in presence of silica gel. A. KOROLEV (J. Chem. Ind. [Moscow], 1927, **4**, 547).—Silica gel is an efficient catalyst for the esterification of salicylic acid. Salicylic acid (50 g.), methyl alcohol (120 g.), and silica gel (4 g.) are heated on a water-bath for 6—8 hrs.; the yield is 75—80% of the theoretical. CHEMICAL ABSTRACTS.

Preparation of phenyl salicylate. O. MAGIDSON and W. KROL (Trans. sci. chem.-pharm. Inst., 1926, **16**, 54—63; Chem. Zentr., 1928, i, 40).—Optimally, phosphorus oxychloride (56 g.) is gradually added to a mixture of salicylic acid (138 g.) and phenol (94 g.) which is heated for 2·5 hrs., first at 60—65°, and then at 120°; the yield is 90% of the salicylic acid consumed. There is also formed an oil which on distillation in a vacuum yields 57% of phenyl salicylate. A. A. ELDRIDGE.

Derivatives of salicylic acid. I. 3-Nitro- and 5-nitro-salicylic acids. A. N. MELDRUM and N. W. HIRVE (J. Indian Chem. Soc., 1928, **5**, 95—101). —Nitration of salicylic acid by the method of Meldola, Foster, and Brightman (A., 1917, i, 453) yields a mixture of 3-nitrosalicylic acid, m. p. 148—149° ($+H_2O$, m. p. 128—129°), and 5-nitrosalicylic acid, m. p. 228° (22·5 g. and 50 g., respectively, from 100 g. of salicylic acid), which is best separated by crystallisation of the potassium salts. A neutral solution of the mixture in potassium hydroxide deposits the *monopotassium* salt of the 3-nitro-acid (yellow; corresponding *sodium* salt, crimson), whilst treatment of the mother-liquors with excess of potassium hydroxide yields the *dipotassium* salt of the 5-nitro-acid (yellow: corresponding sodium salt, yellow). Methyl 3-nitrosalicylate, m. p. 132° [the ester, described by Keller (A., 1908, i, 285) is probably a mixture of the isomeric esters; corresponding ethyl ester, m. p. 48·5°; corresponding amide, m. p. 155° (potassium salt, $+H_2O$, described)], and methyl 5-nitrosalicylate, m. p. 119° [corresponding ethyl ester, m. p. 102°; corresponding amide, m. p. 225° (potassium salt, $+H_2O$, described)], are prepared in the usual ways. G. A. C. GOUGH.

Derivatives of salicoylsalicylic acid. E. LEWICKA (Bull. Acad. Sci. Cracovie, 1927, *A*, 4 pp.; Chem. Zentr., 1928, i, 190).—The following compounds are described: acetylsalicoyl chloride; *methyl* (m. p. 82—84°) and *ethyl* (m. p. 72—73°) *acetylsalicoylsalicylates*; *methyl methylsalicoylsalicylate*, m. p. 102—104°. A. A. ELDRIDGE.

Fission of the dioxymethylene ring. F. MAUTHNER (J. pr. Chem., 1928, [ii], **119**, 74—76).—When acetopiperone is treated with aluminium chloride in boiling chlorobenzene there is formed acetopyrocatechol. Similarly, piperonylic and

guaiacol-*o*-carboxylic acids afford protocatechuic and *o*-catechuic acids. H. BURTON.

Stereochemistry of tervalent nitrogen. J. G. JACKSON and J. KENNER (J.C.S., 1928, 573—581).—The possibility that the configuration of compounds of tervalent nitrogen is plane had been inferred from the general failure to detect the isomerism demanded by a non-planar configuration. A method of obtaining positive evidence on this point is suggested, and in this connexion experiments have been carried out on the internal condensation of β-phenylglutaric and anthranilodiacetic acids. The results in the former case directly refute Sachse's benzene formula and accord with the conception of a plane formula such as Kekulé's. If this be accepted, it is pointed out that compounds of tervalent nitrogen are described in the literature for which a plane configuration seems very probable. β-Phenylglutaric acid is readily converted, under the influence of sulphuric acid, into 1-*ketohydrindene-3-acetic acid* (I), m. p. 151° {*semicarbazone*, m. p. 268° (decomp.); *methyl* ester, m. p. 65° [*semicarbazone*, m. p. 152; 2-*oximino*-derivative, m. p. 167° (decomp.)]; *ethyl* ester, b. p. 194—200°/13 mm. [*semicarbazone*, m. p. 131—132°; 2-*oximino*-derivative, m. p. 193° (decomp.)]}, but no tricyclic, non-acidic, ketonic product could be isolated. Similarly, β-*phenylglutaryl chloride*, m. p. 46°, undergoes only partial internal condensation under the influence of aluminium chloride, yielding the compound (I). When condensation takes place in light petroleum containing aromatic components, ω-3-*hydrindonylacetophenone*, m. p. 78° [*disemicarbazone*, m. p. 233° (decomp.); *dioxime*, m. p. 179°], is also obtained. Anthranilodiacetic acid, m. p. 216° (decomp.) (*lit.* 212°), condenses under the influence of sodium hydroxide, giving *indoxylacetic acid*, m. p. 165° (decomp.) [o-*methoxy*-derivative, m. p. 141—142° (*monohydrate*)]. When sodamide is used as condensing agent, and the crude product is treated with methyl sulphate, a small yield of a *compound*, $C_{10}H_{10}O_2N_2$, m. p. 163°, results. M. CLARK.

[Preparation of] ethyl benzoylformate. B. B. CORSON, R. A. DODGE, S. A. HARRIS, and K. K. HAZEN (Org. Syntheses, 1928, 8, 68—72).

Condensation products of diethyl succinylsuccinate with primary arylamines. D. MIGLIACCI and R. GARGIULO (Gazzetta, 1928, 58, 110—121; cf. Liebermann, A., 1914, i, 658; Migliacci, this vol., 289).—The interaction of diethyl succinylsuccinate with excess of primary arylamines at 125—130° yields a diethyl 2:5-diarylaminoterephthalate; at 180—200° the main product is a *NN'*-diarylcarbamide; as the proportion of ester is increased, these products are mixed with increasing amounts of a yellow substance of unknown composition. The following are described: *ethyl* 2:5-*di*-o-*phenetidinoterephthalate*, m. p. 152° (*dibenzoyl* derivative, m. p. 249—251°); 2:5-*di*-o-*phenetidinoterephthalic acid*, m. p. 273° (decomp.); *NN'-di-o-phenetylcarbamide*, m. p. 222°, and *p*-phenetyl- and *p*-anisylcarbamides; yellow *substances* from *o*- and *p*-phenetidine and from *p*-anisidine, m. p. 180—181°, 163—168°, and 182—187°, respectively; *ethyl* 2:5-*di*-o-*phenetidino*-$\Delta^{1:4}$-*dihydroterephthalate*, m. p. 201°, prepared at low temperature in the absence of air. E. W. WIGNALL.

β-Phenylalanine derivatives. W. M. RODIONOV and A. M. FEDOROVA (Arch. Pharm., 1928, 266, 116—121; cf. A., 1927, 137, 451).—Continuing the investigation of pharmacologically interesting β-phenylalanine derivatives the following methoxy-compounds have been prepared. Both vanillin and protocatechualdehyde are smoothly converted into veratraldehyde by treatment with phenyltrimethylammonium hydroxide (Rodionov, A., 1926, 532), the yields being 86% and 58·3%, respectively. 2:4-Dimethoxybenzaldehyde is similarly obtained from resorcaldehyde (yield, 41·7%) and *o*-, *m*-, and *p*-methoxybenzaldehydes from salicylaldehyde, *m*-hydroxy- and *p*-hydroxy-benzaldehydes, respectively (yield, 72·8%, 88%, and 66·6%). By interaction of veratraldehyde, malonic acid, and ammonia in alcoholic solution β-*amino*-β-3:4-*dimethoxyphenylpropionic acid* (*hydrochloride*, m. p. 207—208°) is obtained (yield, 59%). The 2:4-*dimethoxy*-isomeride was also prepared in poor yield from 2:4-dimethoxybenzaldehyde. The three monomethoxy-analogues were similarly obtained, being accompanied in each case by the corresponding methoxycinnamic acid. β-*Amino*-β-o-*anisylpropionic acid* (yield, 33%) (*hydrochloride*, m. p. 208—210°), β-*amino*-β-m-*anisylpropionic acid* (yield, 39%) (*hydrochloride*, m. p. 190°), and β-*amino*-β-p-*anisylpropionic acid* (yield, 59%) [*hydrochloride*, m. p. 205° (decomp.)], are described. W. A. SILVESTER.

Synthesis of 3:4-dihydroxyphenylalanine. C. R. HARINGTON (Biochem. J., 1928, 22, 407).—A simplified method of preparation of ethyl benzamido-3-methoxy-4-hydroxycinnamate which is employed in the synthesis of the above compound (Harington and McCartney, A., 1927, 961) is described. The azlactone obtained by the condensation of vanillin with hippuric acid is dissolved in alcohol and boiled with sulphuric acid under a reflux condenser. After distilling off the greater part of the alcohol, the reaction mixture is treated with sodium hydrogen carbonate until slightly alkaline. The ester is then extracted with ethyl acetate and the solvent removed. The ester which crystallises from the residue is recrystallised from dilute alcohol. S. S. ZILVA.

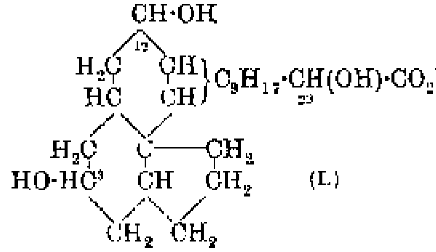
[Preparation of] phenylsuccinic acid. A. LAPWORTH and W. BAKER (Org. Syntheses, 1928, 8, 88—90).

Synthesis of methyl phenylethylmalonate. M. M. RISING and T.-W. ZEE (J. Amer. Chem. Soc., 1928, 50, 1208—1213).—The overall yield of ester (43·1% of the theoretical, from phenylacetonitrile) is the highest yet attained. α-Phenylbutyronitrile is converted by absolute methyl alcohol and hydrogen chloride at −5° to −10° into the *imide hydrochloride*, m. p. 92°, of methyl α-phenylbutyrate. The free ester, m. p. 77—78° (cf. Neure, A., 1889, 597), yields a tautomeric *sodio*-derivative (cf. A., 1927, 359) which condenses with ethyl chloroformate in ether, giving methyl phenylethylmalonate. H. E. F. NOTTON.

Indicators. XI. Phenolphthalein and derivatives. A. Thiel and R. Diehl (Sitzungsber. Ges. Naturwiss. Marburg, 1927, **62**, No. 15, 472—546; Chem. Zentr., 1927, ii, 2669—2672).—Acree's view of the mechanism of the colour change of phenolphthalein (A., 1908, i, 423) is preferred, together with Pfeiffer's theory (1922) of halochromic compounds. In the chloro- and amino-phenolphthalein series the influence of the substituents on the position of the absorption maximum is additive. Phthaleins in which the hydrogen atom *ortho* to the phenolic hydroxyl group is replaced by chlorine, bromine, or an amino-group readily form oximes; 3-nitro- and 3 : 5-dinitrophenolphthalein yield oximes, but not 3 : 3-dinitro-, 3 : 5 : 3′-trinitro-, or 3 : 5 : 3′ : 5′-tetranitro-phenolphthalein; hence hydroxylamine does not attack the lactone ring, or act on the carbinol–carboxylic acid form. The oxime must thus be derived from the *p*-quinonoid form, it being supposed that one phenolic residue is free from, but that the two others contain, nitro-groups. The view is supported by the fact that the quinonoid ester of 3 : 5 : 3′ : 5′-tetrabromophenolphthalein forms an oxime, as is shown by measurements of the extinction coefficient in admixture with hydroxylamine. Further, etherification of the second hydroxyl group of 3-nitrophenolphthalein prevents oxime formation, but the reduction product of the ether gives an oxime. Apparently the formation of a quinone produces a yellow colour (*e.g.*, pure phenolphthalein monomethyl ether is yellow in slightly alkaline solution), the deep colours of the phthaleins being due to the joint effect of both phenolic residues. Substitution in the phthalic acid nucleus of phthaleins also influences the absorption curves; hence the whole complex is to be regarded as a chromophore. The effect of the substitution of chlorine in the phenolic and phthalic acid portions of the molecule is discussed in terms of the tautomeric equilibrium of the indicator system. Isochromatism, optical analogy, and optical similarity of dyes are considered.

The following substances were prepared (all m. p. are corr.): 3-chlorophenolphthalein, m. p. 228—230°; 3 : 3′-dichlorophenolphthalein, m. p. 181°; 2-chloro-4-aminophenyl dibenzoate, m. p. 204·5—205°; 3 : 5-dichlorophenolphthalein, m. p. 227—229°; 3 : 5 : 3′ : 5′-tetrabromophenolphthaleinoxime, m. p. 120°; 3-nitrophenolphthalein, m. p. 178—179°; *o*-(3-nitro-4-hydroxybenzoyl)benzoic acid, m. p. 180—181°; 3 : 5-dinitrophenolphthalein, m. p. 186—187°; *o*-(3 : 5-dinitro-4-hydroxybenzoyl)benzoic acid, m. p. 200°; 3 : 5 : 3′-trinitrophenolphthalein, m. p. 133°; 3′-aminophenolphthalein; 3 : 3′-diaminophenolphthalein, m. p. 262—263°; 3 : 5-diamino-, 3 : 5 : 3′-triamino-, and 3 : 5 : 3′ : 5′-tetra-amino-phenolphthalein; 3-nitrophenolphthalein 4′-methyl ether, m. p. 140·5—141°; 3-aminophenolphthalein 4′-methyl ether, m. p. 125° (oxime, m. p. 228°); 3-nitro- and 3 : 5-dinitro-phenolphthaleinoxime; 3 : 5 : 3′ : 5′-tetrabromophenolphthalein ethyl ester oxime. A. A. Eldridge.

β-Phocæcholic acid. A. Windaus and A. van Schoor (Z. physiol. Chem., 1928, **173**, 312—320).—β-Phocæcholic acid (*iso*cholic acid), present in the bile of seals and the walrus (cf. Hammarsten, A., 1909, ii, 819; 1910, ii, 879), has the same skeleton structure as cholanic acid, but differs from the other bile acids in having a hydroxyl group in the side-chain (I). It is suggested that the other two hydroxyl groups are attached to carbon atoms 3 and 12, since β-phocæcholic acid on oxidation with sodium hypobromite behaves exactly like chenodeoxycholic acid (cf. A., 1927, 56), which is 3 : 12-dihydroxycholanic acid. In this oxidation, β-phocæcholic acid yields a hydroxylactonedicarboxylic acid, which on further oxidation yields nordeoxybiliobanic acid (II). Hare and antelope bile have also been examined, and in the former, *acids* having m. p. 125°, 151°, 185°, and 222° have been found; the analytical figures for the acid having m. p. 185° suggest a tetrahydroxycholanic acid. The preparation of β-phocæcholic acid from seal bile is described and the preparation and properties of the following compounds are given: an *acid*, $C_{23}H_{38}O_4$ (III), m. p. 197°, formed by oxidation of β-phocæcholic acid with potassium permanganate (*methyl* ester, m. p. 78°); an *acid*, $C_{23}H_{34}O_4$ (IV), m. p. 200°, formed by the oxidation of (III) with chromic acid,



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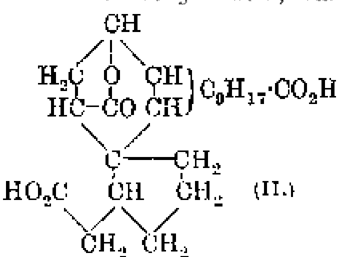

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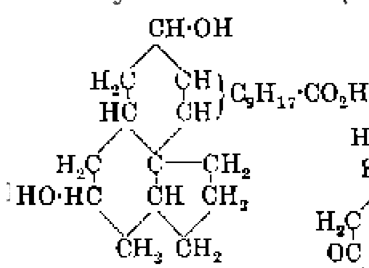

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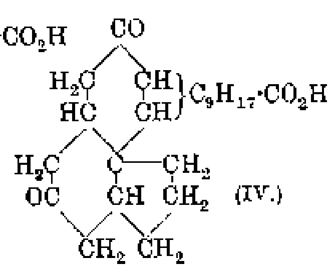

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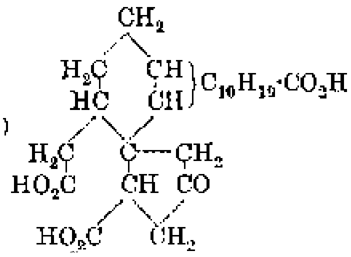
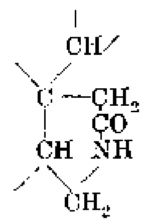
yielding on reduction with zinc amalgam and hydrochloric acid an acid identical with Wieland's norcholanic acid (A., 1927, 247); a *hydroxylactonedicarboxylic acid*, $C_{21}H_{30}O_7$, m. p. 170°; *nordeoxybiliobanic acid*, m. p. 256° (*dimethyl* ester, m. p. 125°); a *hexacarboxylic acid*, $C_{22}H_{32}O_{12}$ (decomp. 225—233° with charring), formed by the action of fuming nitric acid on β-phocæcholic acid; a nitrogenous *acid*, m. p. 205°, is formed when this oxidation with fuming nitric acid is carried out at −10°. A. Wormall.

Bile acids. XVIII. M. Schenck and H. Kirchhof (Z. physiol. Chem., 1928, **172**, 159—168).—Experiments similar to those with the oxime of deoxybilianic acid (cf. A., 1927, 665) have been carried

out with nitrogenous derivatives of *iso*deoxybilianic acid (I).

The *oxime* of *iso*deoxybilianic acid is converted by heating with sulphuric acid into the iso*oxime*, m. p. (after sintering) 262—264°, which is hydrolysed by heating with 20% hydrochloric acid to the corresponding *amino-acid*, $C_{24}H_{39}O_8N$ (II); the last named is reconverted, when heated at 210° for 15 min. or if warmed in acetic acid solution, into the *iso*oxime or lactam [(III) or (IV), or possibly a mixture of the two].

(I.) 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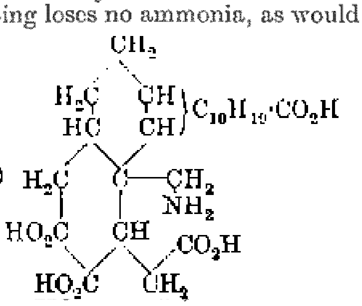
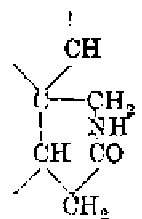
Only one *iso*oxime has so far been isolated and this is believed to have the structure (IV), a supposition supported by the fact that the amino-acid (II) on heating loses no ammonia, as would be expected from

(II.) 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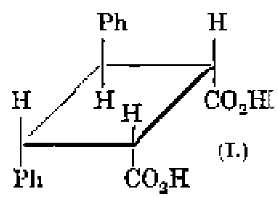
a β-amino-acid derived from (III), but this evidence is not conclusive. The *dioxime* of *iso*bilianic acid, m. p. 263° (not sharp), heated with concentrated sulphuric acid yields the *di*iso*oxime* (decomp. with frothing and darkening at 239—240°), which when heated with 20—25% hydrochloric acid yields a crystalline mass which has not been investigated further.

A. WORMALL.

Fish bile. I. *Serola quinqueradiata*. S. IKONIA (J. Biochem. Japan, 1927, 7, 205—208).—The bile acid, $C_{24}H_{40}O_5$, has m. p. 196—197°, [α] in alcohol +37°, and is similar to the cholic acid from ox, sheep, or human bile. CHEMICAL ABSTRACTS.

Synthesis of cyclic compounds. II. Ethyl and *meso*-βγ-diphenylbutane-ααδδ-tetracarboxylates. Synthesis of a truxinic acid. I. VOGEL (J.C.S., 1928, 1013—1022; cf. A., 1927, 959).—Reduction of ethyl benzylidenemalonate, b. p. 180°/14 mm., $d_4^{18\cdot4}$ 1·1048, 1·53795, with moist aluminium amalgam (cf. A., 1927, 449) yielded 50—55% of ethyl benzylmalonate, b. p. 163°/14 mm., d_4^{20} 1·0750, n_D^{20} 1·4872, and 35—40% of a mixture, b. p. 255—270°/3 mm., which was separated completely by fractional crystallisation from alcohol into 40% of solid *ethyl* r-*βγ-diphenylbutane-ααδδ-tetracarboxylate*, m. p. 88°, and 60% of the liquid *meso*-ester. Hydrolysis by alcoholic potassium hydroxide gave the corresponding *r*- and *meso*-acids, m. p. 219—220° and 182—183° (softening at 172°), respectively. The *disodio*-derivative of the *r*-ester, obtained by treatment with sodium methoxide, reacted with 2 mols. bromine to give only *ethyl* r-*αδ-dibromo-βγ-diphenylbutane-ααδδ-tetracarboxylate*, m. p. 180°, whereas the *disodio*-derivative of the *meso*-ester reacted with only 1 mol. of bromine to give an oil, presumably *ethyl* 2 : 3-*diphenyl*-1 : 1 : 4 : 4-cyclo*butanetetracarboxylate*, which was not purified. On hydrolysis with alcoholic potassium hydroxide this product gave a solid which, on heating at 280° until effervescence ceased, gave less than 1% yield of an acid, m. p. 239°, which could also be separated in the form of its dimethyl ester, m. p. 117°. The properties of these substances agree with those of ζ-truxinic acid (2 : 3-diphenyl*cyclo*butane-1 : 4-dicarboxylic acid), m. p. 239° (I), and its dimethyl ester, m. p. 116° (Stoermer and Bacher, A., 1922, i, 830). The mixed disodio-derivatives of the mixture of ethyl βγ-diphenylbutane-ααδδ-tetracarboxylates reacted with the amount of bromine required by a mixture of 45% of the solid form with 55% of the liquid form, and the dibromo-compound and the dimethyl ester could be isolated by suitable treatment. There is thus no inversion during ring formation such as occurs with ethyl *r*- and *meso*-dimethylbutanetetracarboxylates (Part I, *loc. cit.*). As the acid now synthesised has the configuration (I), it is considered probable that the *cis*-2 : 3-dimethyl acid described previously (*loc. cit.*) has an analogous structure, and not that then assigned to it.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R. K. CALLOW.

Aldehydes from acetylenic carbinols. I. *cyclo*Hexylideneacetaldehyde. H. RUPE, W. MESSNER, and E. KAMBLI (Helv. Chim. Acta, 1928, 11, 449—462).—The action of acetylene on sodium *cyclo*hexanone is to furnish 1-*ethinyl*cyclo*hexan*-1-*ol* (I), b. p. 74—76°/12 mm. (*acetate*, b. p. 87°/10 mm.), together with the *glycol*, $[C_5H_{10}{>}C(OH)\cdot C{:}]_2$, m. p. 109—110° (*diacetate*, m. p. 46—47°). When (I) is heated with 86% formic acid (9 parts) for 2·5 hrs., it is converted into cyclo*hexylideneacetaldehyde* (92·3%), b. p. 84—85°/12 mm., d_4^{20} 0·9694, n_D 1·49081 (*semicarbazone*, m. p. 214—215°; *oxime*, m. p. 61—62°; *phenylhydrazone*). Reduction of this aldehyde with hydrogen and a nickel catalyst or zinc dust and acetic acid gives cyclo*hexylacetaldehyde*, b. p. 69°/12 mm., d_4^{20} 0·9187, n_D 1·45273 (*semicarbazone*, m. p. 171—172°). Oxidation experiments with the aldehyde and ozone, potassium permanganate, chromic acid, and hydrogen peroxide yield adipic acid, formed through the intermediate *cyclo*hexanone. Treatment of the above oxime with excess of acetic anhydride gives cyclo*hexylideneacetaldoxime acetate*, b. p. 145—147°/12 mm.

Magnesium ethyl bromide and *cyclo*hexylideneacetaldehyde react yielding 1-*ethyl*cyclo*hexyl*-1-*acetaldehyde*, b. p. 84—85°/10—11 mm., when regenerated from the *semicarbazone*, m. p. 171—172°, together with cyclo*hexylidenemethylethylcarbinol* (II), $C_5H_{10}{>}C{:}CH\cdot CHEt\cdot OH$, b. p. 96—97°/12 mm. (*benzoate*). The saturated aldehyde is formed by a 1 : 4-addition of the Grignard reagent with subsequent rearrangement of the substituted vinyl alcoholic grouping. When (II) is heated with acetic anhydride

and sodium acetate, elimination of water takes place, yielding α-cyclo*hexylidene*-Δ^{β}-*butylene*, C_5H_{10}>C:C:CHEt, b. p. 77—78°/12 mm.

*cyclo*Hexanone and 30% hydrogen peroxide solution yield a crystalline additive *compound*, $C_6H_{10}O,H_2O_2$.

H. BURTON.

Stability of benzaldehydecyanohydrin. G. BUMMING (Arch Pharm., 1928, **266**, 231—232).—Benzaldehydecyanohydrin undergoes changes on keeping, the hydrocyanic acid content decreasing, whilst resinous and insoluble oily matters make their appearance. The aqueous solution may be clarified by shaking with talc and filtering, a satisfactory pharmaceutical product being thereby obtained.

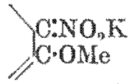
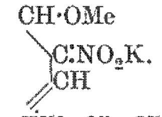
S. COFFEY.

Isomerisation of hydroxyaldehydes. S. DANILOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1105—1124).—See this vol., 64.

Behaviour of cyclic ketones when heated. W. TREIBS (Ber., 1928, **61**, [*B*], 683—687).—*cyclo*Hexanone is only slowly affected at 250°; at 300°, polymerised products, chiefly *cyclo*hexylidene*cyclo*hexanone, result together with dodecahydrotriphenylene. Hydrocarbons of low b. p., from which *cyclo*hexene is isolated, are formed in small amount. Carbon monoxide is formed in considerable quantity at 350°; if the action is prolonged at this temperature, the production of carbon monoxide diminishes, and mainly saturated hydrocarbons (presumably *cyclo*hexane) result. Methyl*cyclo*hexanone (mixture of the three isomerides) is more resistant to heat than *cyclo*hexanone. Carbon monoxide is not eliminated at 300—350°, at which temperature a bimolecular, unsaturated ketone, $C_{14}H_{22}O$, b. p. 160—164°/20 mm., d^{20} 0·9771, and methyl*cyclo*hexane are produced. At 375—400°, carbon monoxide is lost and (mainly) saturated hydrocarbons of low b. p. are produced. Piperitone, b. p. 236°, d^{20} 0·934, passed over porous earthenware at 450° gives a blue distillate and loses the *iso*propyl group. At 400° in an autoclave, it loses carbon monoxide and yields phenols among which *m*-cresol and thymol are identified. When passed over porous earthenware at 500°, thymol yields *m*-cresol and propylene; carvacrol decomposes analogously, but with greater difficulty, whilst cymene gives benzene only slowly at 600°. Carvone at 450° yields phenols containing carvacrol. Small amounts of cymene and phenols are derived from citronellal at 420°. Fenchone is much more stable towards heat than is camphor and remains unchanged to a considerable extent after 6 hrs. at 450°; carbon monoxide is lost above 400°, but elimination of water is irregular. Phenols from which carvacrol is isolated are formed in relatively small and varying amounts. From the hydrocarbon mixture, *m*-cymene and an unsaturated hydrocarbon, C_9H_{14}, are isolated. Camphor affords carbon monoxide, phenols (*m*-cresol and carvacrol), *m*- and *p*-cymene, and fenchone; the polymerised, unsaturated products from camphor and fenchone are ill-defined.

H. WREN.

Cyclic α-nitroketones. H. WIELAND, P. GARBSCH, and J. J. CHAVAN [with A. SCHAFER] (Annalen, 1928, **461**, 295—308).—1-Nitro-Δ^1-*cyclo*hexene forms a *dibromide*, m. p. 100—101°, which when treated with cold methyl-alcoholic potassium hydroxide affords the *potassium* salt:

 or, less probably,  This reacts with sodium nitrite to give an oximino-compound, $C_7H_{10}O_4N_2$, decomp. 122—125°, and with hydroxylamine hydrochloride to give a *substance*, m. p. 122°.

*cyclo*Hexene-ψ-nitrosite reacts (1) with alcoholic ammonia to give some 2 : 6-*dinitrodi*cyclo*hexylamine*, m. p. 96—97° [*hydrochloride*, m. p. 163°; *nitrosoamine*, m. p. 145—150° (decomp.)], and (2) with alcoholic hydrazine hydrate to give a *hydrazo*-compound, $(C_6H_{10}O_2N)_2N_2H_2$, m. p. 138—140°.

Ethyl nitrate reacts with *cyclo*hexanone in presence of potassium ethoxide to give the *potassium* salt of 2-nitro*cyclo*hexanone, acidification of the aqueous solution of which may or may not lead to a crystalline specimen of 2-*nitro*cyclo*hexanone*, m. p. 37°, a substance behaving similarly to *aci*-phenylnitromethane. This substance forms a *bromo*-derivative when treated with bromine in methyl alcohol, gives a *semicarbazone*, m. p. 184° (decomp.), and is converted by a benzenediazonium solution into a *product*, $C_{12}H_{15}O_4N_3$ (?), decomp. 118°. An oxime or a phenylhydrazone could not be obtained from 2-nitro*cyclo*hexanone, but with phenylhydrazine the bisphenylhydrazone of *cyclo*hexane-1 : 2-dione, m. p. 150°, was obtained.

The above condensation using ethyl nitrate always gives rise to some of the *potassium* salt of 2 : 6-*dinitro*cyclo*hexanone*, this being obtained best by using twice the proportions of ethyl nitrate and potassium. When it is carefully treated with dilute acid the *potassium hydrogen* salt is obtained, whilst excess of acid affords 2 : 6-*dinitro*cyclo*hexanone* itself, m. p. 110·5°.

*cyclo*Pentanone so readily condenses with ethyl nitrate in presence of potassium ethoxide that the potassium salt of the mononitroketone cannot be obtained pure. The *potassium* salt of 2 : 5-dinitro*cyclo*pentanone explodes and melts at 241—245°, and is convertible into the *potassium hydrogen* salt and finally into 2 : 5-*dinitro*cyclo*pentanone*, which, after first being crystalline, turns into a liquid.

E. E. TURNER.

Benzylation and phenylation of 2-methyl*cyclo*hexanone. R. CORNUBERT and H. LE BIHAN (Compt. rend., 1928, **186**, 1126—1128; cf. this vol., 416).—When 2-methyl*cyclo*hexanone is treated with sodamide and benzyl halides under conditions calculated to produce monobenzylation, there are produced benzyl-2-methyl*cyclo*hexanone, b. p. 167—169°/17 mm. (chief product), 2 : 6-dibenzyl-2-methyl*cyclo*hexanone, m. p. 105° (also formed by hydrogenation of the benzylidene derivative of 2-benzyl-2-methyl*cyclo*hexanone), and an *isomeride* of the last-named compound, b. p. 230—232°/15 mm. The mixture of benzyl-2-methyl*cyclo*hexanones affords 6-*benzylidene-2-benzyl-2-methyl*cyclo*hexanone*, m. p. 80—81° (hydrogen chloride additive *compound*, m. p. 124°), and the pyrone-like compound, m. p. 191°, already prepared from 6-benzyl-2-methyl*cyclo*hexanone (Cornubert and Borrel, A., 1926, 953). From the latter results it is calculated that the benzyl-2-methyl*cyclo*-

hexanones contain 9% and 10—11% of the 2 : 6-isomeride when prepared by the use of benzyl bromide and chloride respectively. G. A. C. GOUGH.

[Preparation of] benzophenone. C. S. MARVEL and W. N. SPERRY (Org. Syntheses, 1928, **8**, 26—29).

[Preparation of] benzylacetophenone [phenyl β-phenylethyl ketone]. R. ADAMS, J. W. KERN, and R. L. SHRINER (Org. Syntheses, 1928, **8**, 36—37).—Phenyl styryl ketone is catalytically reduced with hydrogen in presence of platinum oxide.

A. A. ELDRIDGE.

[Preparation of] anthrone. K. H. MEYER (Org. Syntheses, 1928, **8**, 8—9).

[Preparation of] nitroanthrone. K. H. MEYER (Org. Syntheses, 1928, **8**, 78—79).

Carbon rings. X. Monocyclic diketones containing sixteen, eighteen, and thirty carbon atoms in the ring. L. RUZICKA, W. BRUGGER, C. F. SEIDEL, and H. SCHINZ (Helv. Chim. Acta, 1928, **11**, 496—512).—The action of heat on thorium azelate gives, in addition to *cyclo*octanone (A., 1926, 615), about 1% of cyclo*hexadecane*-1 : 9-*dione* (I), b. p. 180°/2 mm., m. p. 83—84° (*dioxime*, m. p. 185—186°), and a very small amount of a *diketone*, $C_{23}H_{44}O_2$, m. p. 75—76° (*semicarbazone*, m. p. 128—130°). Reduction of (I) by Clemmensen's method gives a mixture of cyclo*hexadecane*, m. p. 61°, and *cyclo*hexadecanone. When (I) is treated with benzaldehyde in presence of sodium ethoxide, the resulting product heated with potassium hydrogen sulphate at 200—210°, and this product ozonised, there is obtained after esterification with methyl alcohol *dimethyl η-ketotetradecane-αζ-dicarboxylate*, m. p. 45° (free *acid*, m. p. 109—110°; cf. A., 1927, 1189). When ethyl hydrogen azelate is heated with iron powder at 280—290° and the resulting product heated wth 20% hydrochloric acid, neutral and acidic substances are formed. Esterification of the acid fraction with methyl alcohol gives *dimethyl θ-ketopentadecane-αο-dicarboxylate*, m. p. 57—59°. When the *thorium* salt of the *acid*, m. p. 115—116°, is heated (I) is obtained.

During the preparation of *cyclo*nonanone from thorium sebacate a small amount of cyclo*octadecane*-1 : 10-*dione*, m. p. 96—97° (*dioxime*, m. p. 166—168°; *semicarbazone*, decomp. above 230°), is obtained, which is reduced by Clemmensen's method to cyclo*octadecane*, m. p. 72°, and *cyclo*octadecanone.

As by-products in the preparation of *cyclo*pentadecanone there are formed *ditetradecyl ketone*, b. p. 225—230°/2 mm., m. p. 65—66°, d_4^{70} 0·8100 (*oxime*, m. p. 41—42°; iso*oxime*, m. p. 84°), and cyclo*triacontane*-1 : 16-*dione*, m. p. 74—75° (*semicarbazone*, m. p. 218—219°; *dioxime*, m. p. 130—131°). Oxidation of *benzylidene*cyclo*triacontane*-1 : 16-*dione* with ozone gives 14-*keto-octacosane*-1 : 28-*dicarboxylic acid*, m. p. 101—103°, reduced to octacosane-1 : 28-dicarboxylic acid, m. p. 110° (cf. Fairweather, A., 1926, 668). Reduction of the diketone gives cyclo*triacontane*, m. p. 53—54°, and cyclo*triacontanone* (*semicarbazone*, m. p. 149—150°).

Benzaldehyde and *cyclo*pentadecanone react in presence of sodium methoxide, and elimination of water from the product by heating with potassium hydrogen sulphate at 200° gives *benzylidene*cyclo*pentadecanone*, b. p. 190°/1 mm., which when ozonised yields tridecane-αν-dicarboxylic acid.

H. BURTON.

Ring strain and radical formation. G. WITTIG and M. LEO (Ber., 1928, **61**, [*B*], 854—862).—The hypothesis is advanced that the strain within a suitable carbon ring assisted by sufficient loading of two carbon atoms must enhance the tendency towards rupture of the ring with resultant production of a "diradical" with two tervalent carbon atoms. Working from the reverse direction, it is shown that ring strain tends to enhance the tendency towards dissociation.

pp'-*Dibenzoyldiphenylmethane*, m. p. 147·5—148·5°, is prepared from benzoyl chloride, diphenylmethane, and aluminium chloride in the absence of solvent or from *pp'*-diaminodiphenylmethane by conversion by Sandmeyer's method into the corresponding nitrile and treatment of the latter with magnesium phenyl bromide. It is transformed by the Grignard reagent into pp'-*di(hydroxydiphenylmethyl)diphenylmethane*, $CH_2(C_6H_4{\cdot}CPh_2{\cdot}OH)_2$, which could not be caused to crystallise, but when acted on by hydrogen chloride gives pp'-*di(chlorodiphenylmethyl)diphenylmethane*, m. p. 157—160°. When shaken in benzene or ether solution with copper powder in the absence of light, the dichloro-compound yields intensely coloured solutions, decolorised by air with production of the *peroxide*, $C_{39}H_{30}O_2$. The free *radical*, $C_{39}H_{30}$, isolated by addition of light petroleum to its solution in benzene, absorbs oxygen with unusual avidity. In benzene solution it appears mainly unimolecular.

pp'-*Dibenzoyl-αβ-diphenylethane*, m. p. 174·5—176°, prepared similarly to the methane derivative, yields pp'-*di(hydroxydiphenylmethyl)-αβ-diphenylethane*, m. p. 176—178° after softening, and pp'-*di(chlorodiphenylmethyl)-αβ-diphenylethane*, m. p. 184—186° (decomp.). The latter substance affords the corresponding *radical*, $C_{40}H_{32}$, which is largely unimolecular when dissolved in benzene; it yields a *peroxide*, $C_{40}H_{32}O_2$. The diradical is also produced by the action of sodium triphenylmethyl on *pp'*-di(chlorodiphenylmethyl)-αβ-diphenylethane.

pp'-Dibenzoyldibenzyl is transformed by magnesium methyl iodide into pp'-*di-(α'-hydroxy-α-phenyl)-αβ-diphenylethane*, m. p. 113—114·5°, which passes in boiling glacial acetic acid into pp'-*di-(α'-phenylethenyl)-αβ-diphenylethane*, m. p. 117—119°. The glycol is converted by the protracted action of cold, methyl-alcoholic hydrogen chloride into the corresponding *dimethyl ether*, m. p. 144—148°, transformed by sodium–potassium alloy in presence of dioxan in an atmosphere of nitrogen into the *dipotassium* compound. The latter compound is immediately decolorised by tetramethylethylene bromide in dioxan with production of the *compound* $(C_{30}H_{28})_x$, m. p. (indef.) 110—115°, instead of the desired diradical; it is transformed by alcohol into pp'-*di-(α'-phenylethyl)-αβ-diphenylethane*, m. p. 97—98°.

H. WREN.

Compounds with tervalent carbon. S. GOLDSCHMIDT [with A. SADLER, E. GELBER, H. SCHUSSLER, and A. VOGT] (Ber., 1928, **61**, [*B*], 829—838).—In the hope of preparing ββ-dibenzoyl-ααα-triphenylethane,

triphenylmethyl chloride has been condensed with dibenzoylmethane in the presence of sodamide, whereby the main products are uncrystallisable materials, triphenylmethylamine, and triphenylmethyl peroxide, with small amounts of a compound, $C_{34}H_{26}O_2$, m. p. 165—166°; if, however, condensation of the reactants in concentrated benzene solution in complete absence of air and moisture is effected by metallic potassium, the substance is formed in 30% yield accompanied by much smeary matter and greater or less quantities of triphenylmethane. Since oxidation of the substance by chromic acid in glacial acetic acid solution affords benzoic and *p*-benzoylbenzoic acids, it is regarded as *ω′ω′-dibenzoyl-ωω-diphenyl-*p*-xylene*, $CHPh_2\cdot C_6H_4\cdot CHBz_2$. This conception is supported by the observation that it is transformed by the energetic action of bromine into *ω′ω′-dibenzoyl-ωω-diphenyl-*p*-xylylene bromide*, $CBrPh_2\cdot C_6H_4\cdot CBrBz_2$, m. p. 171—173°, oxidised by chromic acid to benzoic and *p*-benzoylbenzoic acids. Treatment of the dibromide with boiling methyl alcohol yields the *bromocarbinol*, $C_{34}H_{25}O_3Br$, m. p. 181°, and ultimately causes almost quantitative replacement of bromine. Treatment of ω′ω′-dibenzoyl-ωω-diphenyl-*p*-xylylene bromide with copper or silver causes loss of only one bromine atom, with the production of the *radical*, $C_{34}H_{24}O_2Br$. The substance yields dark brownish-red solutions, which are shown by determinations of mol. wt. and conformity to Beer's law to be free from the dimeride. It has not been caused to crystallise. It reacts only very slowly with oxygen, but not with nitric oxide, triphenylmethyl, diphenylnitrogen, or diphenyltrinitrophenylhydrazyl. It is sensitive towards nitrogen peroxide, with which it does not give a crystalline derivative, halogens, and halogen acids; it is reconverted by bromine into the dibromide. In its properties it is related to the ketomethyls rather than to triphenylmethyl, and hence is formulated, $CBrPh\cdot C_6H_4\cdot CBz_2$. The action of zinc dust in the presence of boiling benzene on ω′ω′-dibenzoyl-ωω-diphenyl-*p*-xylylene bromide causes loss of both atoms of bromine with production of ω′ω′-dibenzoyl-ωω-diphenyl-*p*-xylene and (?) the *peroxide carbinol*, $OH\cdot C_{34}H_{24}\cdot O\cdot O\cdot C_{34}H_{24}\cdot OH$, m. p. 195—196°.

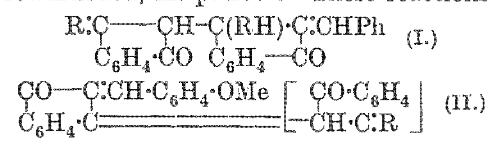
H. Wren.

[Preparation of] dibenzoylmethane (phenyl α-hydroxystyryl ketone). C. F. H. Allen (Org. Syntheses, 1928, 8, 60—62).

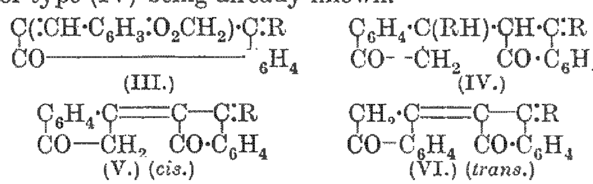
***C*-Methylation of 1 : 3-diketones and methyl-*p*-methoxydibenzoylmethane [γ-phenyl-α-*p*-methoxyphenyl-β-methylpropane-αγ-dione].** C. Weygand [with H. Forkel and C. Bischoff] (Ber., 1928, **61**, [*B*], 687—690).—Methylation of αγ-diketones and γ-ketonic esters may frequently be effected in acetone its homologues which, when warm, usually dissolve the alkali enolates freely. Thus, methylbenzoylacetone is obtained in 88% yield from methyl iodide and the sodium derivative of benzoylacetone in acetone. Methyldibenzoylmethane and tribenzoylmethane are analogously prepared. Methylation of *p*-methoxydibenzoylmethane could not be effected through the sodio-compound; the corresponding *potassio*-derivative is transformed by methyl iodide in boiling acetone into *γ-phenyl-α-*p*-methoxyphenyl-β-methylpropane-αγ-dione*, b. p. 249°/12 mm., m. p. 71·5—72°, which does not give a coloration with ferric chloride. The corresponding enolic *variety*, m. p. 80° (*copper* salt, m. p. 178°), reverting when crystallised to the diketone, m. p. 72°, is described. With phenylhydrazine, the diketone yields the two isomeric N-3(5)-*diphenyl*-5(3)-*p*-*anisyl-4-methylpyrazoles*, thus apparently placing its structure beyond doubt. The compound differs in an unexplained manner from the "α-anisoylpropiophenone" obtained by Bradley and Robinson (A., 1926, 1145) from *p*-methoxypropiophenone and ethyl benzoate in presence of sodamide.

H. Wren.

Truxenequinone. Genetic relation between indanedione, di-indone, and truxenequinone. II. V. Ionescu (Bull. Soc. chim., 1928, [iv], 43, 447—453).—Further investigations have shown that the additive reactions of di-indone with carbindogenides, like the substitution reactions in presence of piperidine (cf. A., 1927, 669, 880), are determined by the nature of the aryl group. Thus di-indone and benzaldehyde in pyridine afford *benzylideneindandionylideneindanedionedi-indone* (I; R: = $C_6H_4<^{CO}_{CO}>C:$), yellow, m. p. 255—256°, whilst anisaldehyde yields *anisylideneindandionylidenebis-di-indone* (II), yellow, m. p. 242°, and piperonal the true bisindone indigenoid, *piperonylidenedi-indone* (III), brownish-red, m. p. 267°. These reactions are



in accordance with those which theory predicts from the genetic relations already established (*loc. cit.*) between indanedione and di-indene derivatives. The mechanism previously suggested to explain the formation of truxenequinone from di-indone admits of the intermediate stages (IV) and (V) or (VI), derivatives of type (IV) being already known.

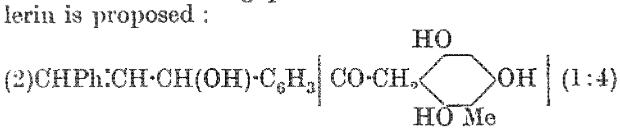


A *trans*-derivative of type (VI), trans-*anhydrotris-indanedione*, m. p. 332—335°, has now been isolated in about 20% yield, by the action of indandione in benzene solution on di-indene in xylene in presence of piperidine, thus confirming the views previously advanced.

R. Brightman.

Constitution of rottlerin from Indian Kamala. S. Dutt and D. P. Gaswami (J. Indian Chem. Soc., 1928, 5, 21—24; cf. A., 1925, i, 1296).—Nitration of hepta-acetylrottlerin with nitric acid (*d* 1·52) at the ordinary temperature yields *hexanitrohepta-acetylrottlerin*, decomposing or exploding when heated (hexanitrorottlerin, exploding violently at about 200°, described), which, when oxidised with potassium permanganate in neutral solution, affords 2 : 4-dinitrobenzoic, 3 : 6-dinitrophthalic, and 2 : 5-dinitro-

terephthalic acids. Nitration of rottlerin hexamethyl ether under similar conditions leads to the formation of hexanitrorottlerin hexamethyl ether, decomp. on heating, which yields the same oxidation products. Hepta-acetylrottlerin, on bromination in acetic acid solution at 170°, affords *hexabromohepta-acetylrottlerin*, decomp above 300° (*hexabromorottlerin*, unmelted on heating, described), which may be similarly oxidised to 2 : 4-dibromobenzoic, phthalic, and terephthalic acids. The following probable constitution of rottlerin is proposed :



The substituting nitro-groups enter the *o*- and *p*-positions in the styryl side-chain, the 3 : 6-positions in the central nucleus, and the unoccupied positions in the phenolic nuclei. G. A. C. GOUGH.

Salicylic acid primeveroside. M. BRIDEL and P. PICARD (Bull. Soc. Chim. biol., 1928, **10**, 381—385).—See this vol., 424.

Condensation of ketocholanic acids. I. Condensation with furfuraldehyde. K. KAZIRO (J. Biochem. Japan, 1927, **7**, 283—291).

CHEMICAL ABSTRACTS.

Gossypol. III. Oxidation of gossypol. E. P. CLARK (J. Biol. Chem., 1928, **77**, 81—87).—Gossypol, when oxidised with cold alkaline potassium permanganate, yielded formic, acetic, and *iso*butyric acids; the yield of the last-named, approximately one molecular proportion, is taken to indicate the presence of the *iso*butyl group in the side-chain of gossypol.

C. R. HARINGTON.

Conjugated unsaturated compounds. V. Constitution of carotin and bixin. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1928, **11**, 427—431).—The resemblance of the colour reactions of carotin to those given by the unsaturated hydrocarbons described by the authors (this vol., 281) is noted. A summary of the facts relative to the structure of bixin is given. H. BURTON.

Plant-colouring matters. IV. Colouring matter from saffron. II. P. KARRER and H. SALOMON (Helv. Chim. Acta, 1928, **11**, 513—525).—Details are given for the extraction from saffron of α-*crocin*, $C_{24}H_{28}O_5,2C_{12}H_{20}O_{10},2H_2O$, m. p. 186° (decomp.), which on acid hydrolysis gives dextrose. α-Crocetin (see A., 1927, 571) is a dibasic acid, $C_{22}H_{26}O(CO_2H)_2$, whilst β-crocetin is its monomethyl ester. γ-Crocetin is the dimethyl ester and is formed from both α- and β-crocetin by methylation with diazomethane. Conversely, the β- and γ-crocetins are converted into α-crocetin by hydrolysis with alcoholic potassium hydroxide. Catalytic reduction of γ-crocetin gives a *dimethyl* ester, $C_{22}H_{42}O(CO_2Me)_2$, b. p. 198—200°/1 mm., whilst oxidation with ozone gives glyoxal as the only recognisable product. It is concluded that α-crocetin is an aliphatic dicarboxylic acid with eight conjugated double linkings, and not a dihydric phenol (*loc. cit.*). H. BURTON.

Saponins and related substances. XX. Ursolic acid. II. Action of acetic anhydride on ursolic acid. A. W. VAN DER HAAR (Rec. trav. chim., 1928, **47**, 585—590).—When ursolic acid is treated with acetic anhydride there is formed a *compound*, m. p. 200—201°, α_D^{15} +62·5° in chloroform (cf. A., 1924, i, 643), consisting of 1 mol. of *diacetylursolic anhydride*, m. p. 320—322°, and 1 mol. of acetic anhydride (cf. this vol. 68). *Monoacetylursolic acid*, m. p. 279—280°, is obtained by the action of alcohol on the above compound. H. BURTON.

Formation of 3-*p*-menthone and 3-*p*-menthol from Δ³-*p*-menthene. A. KOTZ and G. BUSCH (J. pr. Chem., 1928, [ii], **119**, 1—42).—Treatment of 8-*p*-menthanol with potassium hydrogen sulphate at 200° gives Δ^3-*p*-menthene, which when heated with trichloroacetic acid yields 4-*p*-menthanol. Consecutive treatment of Δ^3-*p*-menthene with perbenzoic acid at −18°, sodium ethoxide at −10°, and sulphuric acid at −7° affords p-*menthene oxide* (91%), b. p. 70—75°/15 mm., d^{14} 0·8989, α_D^{15} +45° 40′, 1·44809, reduced catalytically by Willstatter's method to *p*-menthane. Hot methyl-, propyl-, butyl-, and amyl-alcoholic hydrochloric acid convert this oxide into 3-*p*-menthone, whilst the action of hypochlorous acid is to form an impure *menthenechlorohydrin* (*chloromenthol*). It was not possible to esterify chloromenthol, and oxidation experiments did not yield a ketone, thus indicating a tertiary hydroxyl group, *i.e.*, one in position 4. Reduction of chloromenthol with hydrogen in presence of palladium-black and dilute alcohol gives some 3-*p*-menthol (*hydrogen phthalate*, m. p. 98—100°). Most of the reduction experiments described give halogen-free products, although, in a medium of acetic acid and sodium acetate, a chlorine-containing fraction of b. p. 72—93°/11 mm. was obtained which when treated with moist silver oxide yielded a product, b. p. 200°, with a strong menthol odour (neomenthol ?). When chloromenthol is boiled for 3 hrs., hydrogen chloride and *p*-menthene oxide are produced, whilst heating with methyl and propyl alcohols and 3-*p*-menthol under pressure at 120—200° affords 3-*p*-menthone (40—85%). Reduction of chloromenthol with zinc dust and acetic acid gives 3-*p*-menthone, and the action of acetyl chloride and pyridine is to form *chloromenthene* (89%), b. p. 92—98°/13 mm., d^{13} 0·9726. Δ^3-*p*-Menthene with phosphorus pentachloride yields a small amount of chloromenthene, which when treated with an excess of silver oxide or 50% potassium hydroxide solution furnishes 3-*p*-menthone.

Reduction of 2-chloro*cyclo*hexanol with sodium and ethyl alcohol gives 2-ethoxy*cyclo*hexanol (87%), b. p. 82—90°/15 mm., whilst similar treatment of chloromenthol affords *p*-menthene oxide (74%).

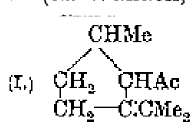
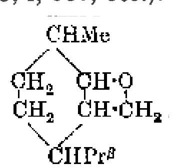
H. BURTON.

Action of menthol on phosphorus chlorides and oxychloride. T. MILOBENDZKI and (MME.) H. KOLITOVSKA (Bull. Soc. Amis Sci. Poznan, 1926, **2**, 14—17).—In presence of pyridine, menthol and phosphorus trichloride give a quantitative yield of menthyl phosphite, $P(OC_{10}H_{19})_3$, m. p. 44—45°, [α] −30°, which when heated at 240° in a vacuum affords menthene (80%), or when treated with dry hydrogen chloride affords menthyl chloride and 13% of the acid ester, $P(OH)(OC_{10}H_{19})_2$. Sodium menthoxide

and phosphorus oxychloride yield quantitatively menthyl phosphate, m. p. 86°, [α] −100°, which when heated in a vacuum quantitatively affords menthene, or with dry hydrogen chloride affords the compound $PO(OH)(OC_{10}H_{19})_2$ and menthyl chloride. Menthol and phosphorus oxychloride yield menthyl phosphate (70%), menthyl chloride (7%), and the acid phosphate. Menthol or sodium menthoxide and phosphorus pentachloride give a quantitative yield of menthyl chloride and phosphorus oxychloride; the latter then reacts as above. The reaction between menthol and phenyl dichlorophosphate was also examined.

CHEMICAL ABSTRACTS.

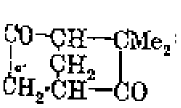
Catalytic reduction of unsaturated hydroaromatic compounds. H. RUPE and K. SCHAFER (Helv. Chim. Acta, 1928, **11**, 463—477).—Benzylmenthone, b. p. 195°/13 mm., d_4^{20} 0·9915, 1·51834, 1·53604, n_D^{20} 1·52279, $[\alpha]_D$ +12·37°, is obtained in 90% yield by reducing benzylidenepulegone with hydrogen in presence of 82% alcohol and nickel. Similar reduction of potassium pulegenate at 80°/10 atm. affords dihydropulegenic acid, b. p. 138°/11 mm., d_4^{20} 0·9642, $[\alpha]_D$ −0·36°. Pulegenyl chloride and zinc dimethyl react in benzene solution yielding *pulegyl methyl ketone* (I), b. p. 98°/13·5 mm., d_4^{20} 0·9126, $[\alpha]_D$ +40·48° (*semicarbazone*, m. p. 144°; *oxime*, b. p. 130°/10·5 mm.). *Pulegyl ethyl ketone*, b. p. 107—112°/10 mm. (*semicarbazone*, m. p. 136°), and *dihydropulegyl methyl ketone*, b. p. 86°/10 mm., d_4^{20} 0·8862, $[\alpha]_D$ −3·56° (*semicarbazone*, m. p. 174°), are described (cf. Wallach, A., 1903, i, 567, etc.).

(I.)   (II.)

Catalytic reduction of hydroxymethylenetetrahydrocarvone yields the *oxide* (II), b. p. 109°/11 mm., d_4^{20} 0·9232, $[\alpha]_D^{20}$ +31·72°, formed by elimination of water from the corresponding glycol, *methylenetetrahydrocarvone* (III), b. p. 102°/11 mm., d_4^{20} 0·9152, $[\alpha]_D$ −5·81° (*semicarbazone*, m. p. 177°), *tetrahydrocarvylcarbinol* (IV), b. p. 142°/11 mm., d_4^{20} 0·9947, $[\alpha]_D^{20}$ −40·16° (*benzoate*, m. p. 105°), and a small amount of s-*di(ketotetrahydrocarvyl)ethane*, b. p. 219—220°/11 mm. When (IV) is heated with 75% sulphuric acid, dehydration into (III) takes place. Oxidation of (III) with chromic and acetic acids gives an aldehyde isolated as its *semicarbazone*, $C_{12}H_{17}O_2N_3$, m. p. 182°.

H. BURTON.

Oxidation products of camphane, fenchane, and camphenilane derivatives with chromic acid. J. BREDT and P. PINTEN [with H. GERMAR, T. LIESER, and H. DE GREIFF] [J. pr. Chem., 1928, [ii], **119**, 81—107).—Oxidation of *i*-camphenilone in acetic acid solution with chromic acid yields after 4—5 weeks, dl-p-*ketocamphenilone* (I), b.p. 118°/13 mm., m. p. 56° [*monosemicarbazone*, m. p. 201—202° (decomp.)], in about 10% yield. The oxidation conditions have been determined in some detail. Optically active *p*-ketocamphenilone, $[\alpha]_D$ −90·03° in methyl alcohol, has m. p. 74°.



Bromination of (I) yields *bromoketocamphenilone* (Br=H in α′ in I), m. p. 84·5°, having $[\alpha]_D$ −353·64° in methyl alcohol when prepared from the optically active diketone. Heating this bromo-compound with sodium hydrogen carbonate solution causes elimination of hydrogen bromide and the formation of *ketocamphenilolenic acid*, m. p. 156° (*semicarbazone*, decomp. 225°), together with two *by-products* having m. p. 232—235° and 251°, respectively.

Bromination of *p*-ketofenchone (A., 1924, i, 408) gives *bromoketofenchone*, m. p. 132°, $[\alpha]_D^{25}$ +324·05° in methyl alcohol, which eliminates hydrogen bromide, yielding *ketofencholenic acid*, m. p. 126—127° (*oxime*, decomp. 160°; *semicarbazone*, decomp. 212—216°). When this acid is treated with bromine, a *dibromide*, m. p. 136—137°, is formed which readily loses hydrogen bromide, yielding *bromoketofencholenic acid*, m. p. 152—153°, whilst oxidation with 1% potassium permanganate gives dimethylmalonic acid together with a γ- or δ-*lactonic acid*, $C_{10}H_{14}O_6$, m. p. 175—176°, derived from the acid,
$CO_2H{\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CMe(OH){\cdot}CO_2H$.

Bromination of diketocamphane (*loc. cit.*) furnishes a *bromodiketocamphane* (either *bromoketocamphor* or epi*bromoketocamphor*), m. p. 144·5—145° (*dibromo-compounds*, m. p. 128—129° and above 190°), which yields either *ketocampholenic* or epi*ketocampholenic acid*, m. p. 124·5° (*semicarbazone*, decomp. 216—218°).

Oxidation of *dl*-bornyl acetate affords dl-p-*ketobornyl acetate*, b. p. 136—137°/9·5 mm., m. p. 73—75° (*semicarbazone*, decomp. 238°), which is hydrolysed by aqueous potassium hydroxide to dl-*ketoborneol*, m. p. 236°. Oxidation of this with chromic acid affords dl-*diketocamphane*, m. p. 210° (corr.). Bromination of *p*-ketobornyl acetate and *p*-ketobornyl chloride (A., 1927, 156) gives *bromoketobornyl acetate*, m. p. 100—101°, and *bromoketobornyl chloride*, m. p. 184°, respectively.

H. BURTON.

Structure of additive compounds of bornylene and halogen acids. O. ACHMATOWICZ (Rocz. Chem., 1928, **8**, 55—70).—Hydrogen chloride adds on to bornylene dissolved in a number of solvents at 0° to yield a *hydrochloride*, m. p. 149—149·5°, $[\alpha]_D$ +15·43°, of a new isomeric hydrocarbon (*hydrobromide*, m. p. 124—125°, $[\alpha]_D$ +6·52°; *hydriodide*, m. p. 22—25°, $[\alpha]_D$ +55·18°). On heating in a sealed tube with water at 100° for 12·5 hrs., 75% of the chlorine is removed; in this respect the new hydrochloride occupies an intermediate position between bornyl and *iso*bornyl hydrochlorides. The residue is identified as cyclene. Alcoholic silver nitrate removes chlorine, bromine, or iodine almost quantitatively from the corresponding hydrohalides. Bornylene hydrobromide on reduction with zinc dust yields bornylane, the ring structure of which must therefore be possessed by the hydrobromide. An additional product of reduction is *endo*borneol (A., 1927, 250); the bromine atom must therefore occupy the α-position. Magnesium forms a Grignard compound with the hydrobromide or hydriodide, which on hydrolysis yields a mixture of bornylane, borneol, a space isomeride of hydrodicamphene, and a number of unsaturated hydrocarbons. The latter on oxidation yields *i*-camphoric acid, which can have originated only from bornylene. Bornylene

hydrochloride or hydrobromide yields *endo*borneol on treatment with silver acetate. Bornylene hydrochloride when heated with aniline yields mainly cyclene, together with traces of unsaturated compounds, indicating the bridged ring structure of the hydrohalide. Thus the above group of additive compounds are *endo*borneol derivatives, as distinct from the borneol series, which are bornylene derivatives.

R. TRUSZKOWSKI.

Chemical individuality of humulene. A. C. CHAPMAN (J.C.S., 1928, 785—789).—Careful fractionation of the crude sesquiterpene obtained from clove oil shows that it consists substantially of caryophyllene with a rotation of about $[\alpha]_D$ $-8°$, together with a small proportion (5—10%) of humulene. No evidence of the existence of the so-called inactive α-caryophyllene (Deussen, A., 1911, i, 549) could be obtained. Whereas caryophyllene forms a crystalline dihydrochloride and a solid alcohol, no corresponding solid derivative can be obtained from humulene. Further comparison of derivatives of the two substances leads to the conclusion that humulene is a definite chemical individual.

M. CLARK.

Production of mercaptans of the furfuryl series. INTERNAT. NAHRUNGS- U. GENUSSMITTEL A.-G.—See B., 1928, 327.

Cyanidin. I. Comparative investigation of cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. T. MALKIN and M. NIERENSTEIN (Ber., 1928, **61**, [*B*], 791—799).—Whereas cyanidin chloride is oxidised by hydrogen peroxide to a yellow, crystalline substance which, contrary to Willstätter and Everest (A., 1913, i, 1371), is not a flavone, 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride does not yield this substance (cf. Pratt and Robinson, A., 1925, i, 422), so that the supposed identity of the chlorides cannot be maintained. Further comparison of cyanidin chloride from cornflowers and rose leaves with 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride discloses marked qualitative similarity, but almost complete quantitative differences, particularly with regard to colour reactions. The Röntgen spectra of the natural and synthetic chlorides and the absorption spectra of the compounds and the corresponding colour bases exhibit sufficient individuality to exclude the hypothesis of identity. The possible presence of impurity in the natural cyanidin chloride is discounted by the identical behaviour of the compound from the two different sources. Difficulties possibly arising in the demethylation of the intermediate substances of the synthesis of 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride do not appear to arise, since the product is free from methoxyl when tested by Zeisel's method, and is completely identical with a substance prepared as follows. Protocatechuic acid is converted by cold acetic anhydride and anhydrous potassium acetate into diacetylprotocatechuic acid, m. p. 162°, and thence by phosphorus pentachloride in carbon tetrachloride into the corresponding *chloride*, m. p. 55°. The latter compound with diazomethane in ether affords ω-*chloro*-3 : 4-*diacetoxyacetophenone*, m. p. 94°, which is treated successively with potassium acetate in boiling glacial acetic acid and 2 : 4 : 6-triacetoxybenzaldehyde; the product thus formed is converted by boiling hydrochloric acid into 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride identical with the compound of Pratt and Robinson (*loc. cit.*). The differences between the natural and synthetic products cannot be ascribed to molecular relationships, since they have the same mol. wt. in alcohol and their dispersion in ethyl alcohol is unimolecular. Cyanidin chloride must therefore be regarded as an isomeride of the flavylium chloride to which a constitution cannot at present be ascribed. Freudenberg's reduction (A., 1925, i, 1165) of cyanidin chloride to epicatechin does not appear reconcilable with his conversion of 3 : 5 : 7-pentamethoxyflavylium chloride into pentamethylepicatechin.

H. WREN.

Colour variations of cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride as related to acidity and alkalinity. C. M. FEAR and M. NIERENSTEIN (Biochem. J., 1928, **22**, 615—616).—The instantaneous production of a pure blue colour on addition of sodium carbonate takes place in the case of natural cyanidin chloride at p_H 8·04, whereas with synthetic pentahydroxyflavylium chloride this happens at p_H 11·57.

S. S. ZILVA.

Constitution of irigenin and iridin. I. W. BAKER (J.C.S., 1928, 1022—1033).—The extraction of the glucoside iridin, which occurs to the extent of 1% in Florentine orris root, is described. Hydrolysis of iridin with dilute sulphuric acid yields irigenin (I), m. p. 185° (dimorphous), shown by investigation of its reactions to possess the constitution 5 : 7 : 3′-trihydroxy-6 : 4′ : 5′-trimethoxy*iso*flavone (cf. A., 1894, i, 47; 1925, i, 1299). Benzoylation of (I) yields 7 : 3′-dibenzoylirigenin, m. p. 155—160° (lit. 123—126°), whilst acetylation gives 5 : 7 : 3′-triacetylirigenin, m. p. 127—128° (lit. 122°), readily converted by partial hydrolysis into 7 : 3′-diacetylirigenin. The two last-named compounds are erroneously described in the literature as di- and mono-acetylirigenin, respectively. Methylation of (I) with methyl sulphate yields *irigenin trimethyl ether* (II), m. p. 163°, decomposed by alkali into 3 : 4 : 5-trimethoxyphenylacetic acid and antiarol (3 : 4 : 5-trimethoxyphenol). Demethylation of (I) yields *irigenol*, 5 : 6 : 7 : 3′ : 4′ : 5′-hexahydroxy*iso*flavone ($+H_2O$), m. p. 331° (decomp.) (*hexa-acetyl* derivative, m. p. 237—238°; *oxonium sulphate*).

Methylation of (I) with 3 mols. of methyl iodide and alkali in a sealed tube gives *irigenin* 7 : 3′-*dimethyl ether* (III), m. p. 166—167° (*acetyl* derivative, m. p. 191°), decomposed by aqueous alkali at 100° in hydrogen to 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol. Further methylation of (III) with methyl sulphate gives (II). Long-continued methylation of (I) with an excess of methyl iodide and alkali gives a *compound*, m. p. 154·5°. Methylation of iridin in methyl alcohol with an excess of diazomethane gives a resinous, methylated glucoside, yielding on hydrolysis *irigenin* 5 : 3′-*dimethyl ether*, m. p. 218°. The last-named compound gives the same products on decomposition with alkali as its isomeride (III), and is converted by further methylation into (II). The dextrose nucleus in iridin is therefore present in the 7-position. The

dyeing properties of irigenin, iridin, and irigenol are described. M. CLARK.

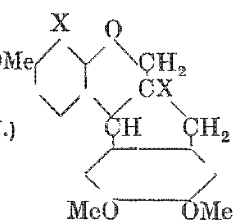
Stability of the double linking in dixanthylene. O. MAGIDSON and W. DAMASKINA (Trans. Sci. chem.-pharm. Inst., 1926, [**16**], 51—52; Chem. Zentr., 1928, i, 59).—Treatment of dixanthylene with phosphorus pentachloride yields a dichloro-derivative, $O:(C_6H_4)_2:CCl_2$, which, however, cannot be isolated, xanthone being obtained. The compound, $O:(C_6H_4)_2:CH\cdot CCl:(C_6H_4)_2:O$, m. p. 189—190°, is also obtained. Xanthone is also produced when dixanthylene is heated in a tube at 200° with a saturated solution of hydrogen chloride in acetic acid.

A. A. ELDRIDGE.

[Behaviour of dixanthylene when heated.] F. ARNDT and L. LORENZ (Ber., 1928, **61**, [*B*], 869; cf. A., 1925, i, 57).—A reply to Schönberg and Schütz (this vol., 526). H. WREN.

Brazilin and hæmatoxylin. VII. Syntheses of trimethylbrazilone and tetramethylhæmatoxylone. P. PFEIFFER, O. ANGERN, E. HAACK, and J. WILLEMS (Ber., 1928, **61**, [*B*], 839—843; cf. this vol., 426).—Trimethylanhydrobrazilin (cf. A., 1927, 1198) suspended in glacial acetic acid is reduced by hydrogen in presence of spongy platinum to *trimethyldeoxybrazilin* (I; X=H), m. p. 107—109° after softening at 106°, which is oxidised by chromic acid in glacial acetic acid to trimethylbrazilone, m. p. 167° (decomp.) after softening at 165°, identical with the product obtained by degradation of brazilin and yielding acetyltrimethylanhydrobrazilone, m. p. 185° after softening at 175—176°, identical with that derived from "analytical" trimethylbrazilone. Similarly, tetramethylanhydrohæmatoxylin (cf. this vol., 426) is reduced to *tetramethyldeoxyhæmatoxylin* (I; X=OMe), m. p. 151° after softening at 147°, oxidised to tetramethylhæmatoxylone, identical with the product derived from tetramethylhæmatoxylin. Synthetic evidence in favour of the constitutions assigned on analytical grounds to brazilin and hæmatoxylin by Perkin and co-workers is thus advanced, the only uncertainty being with regard to the position of the alcoholic hydroxyl group, which, in all probability, occupies the position marked X. H. WREN.

(I.)



Derivatives of 1 : 3-dithiolan and of 1 : 3-dithian. J. C. A. CHIVERS and S. SMILES (J.C.S., 1928, 697—702; cf. A., 1926, 947).—Introduction of the alkylthiol grouping into substances such as malonic acid and deoxybenzoin may be effected by interaction of these compounds with alkyl disulphoxides (alkyl thiolsulphonates) in presence of potassium acetate. Benzyl disulphoxide reacts with deoxybenzoin yielding the benzylmercaptol of benzil, isolated, after oxidation with hydrogen peroxide, as the *dioxide*, m. p. 167°. With ethyl malonate it yields, after hydrolysis with hydrochloric acid, benzylthiolacetic acid. Ethane α^{β}-di-*p*-toluenethiolsulphonate yields with deoxybenzoin 2-benzoyl-2-phenyl-1 : 3-dithiolan, and with ethyl malonate it gives after hydrolysis 1 : 3-*dithiolan-2-carboxylic acid*, m. p. 90° (*dibromide*; *di-iodide*), together with a little ethylenedithiolacetic acid. *Propane* $\alpha\gamma$-*di*-p-*toluenethiolsulphonate*, m. p. 65—67° (from $\alpha\gamma$-dibromopropane and potassium *p*-tolylthiolsulphonate), yields with deoxybenzoin 2-*benzoyl*-2-*phenyl*-1 : 3-*dithian*, m. p. 99—100°. With ethyl malonate it gives after hydrolysis 1 : 3-*dithian*-2-*carboxylic acid*, m. p. 115—116° (*di-iodide*). No ring closure can be induced with *pentane* $\alpha\varepsilon$-*di*-p-*toluenethiolsulphonate* (from $\alpha\varepsilon$-dibromopentane and potassium *p*-tolylthiolsulphonate) and ethyl malonate, only *pentane*-$\alpha\varepsilon$-*dithiolacetic acid*, m. p. 91—92°, being isolated from the reaction mixture. M. CLARK.

Manufacture of substituted guanidines. CHEM. FABR. VORM. SCHERING.—See B., 1928, 327.

β-Vinylpiperidine. R. MERCHANT and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 1197—1201).—3-Piperidylcarbinol (cf. this vol., 427) [*chloroplatinate*, m. p. 174° (decomp.) (also $+H_2O$); *chloroaurate*, m. p. 153—154° (decomp.); 1-*benzoyl* derivative, m. p. 80—81°, b. p. 153°/0·01—0·02 mm., n_D^{25} 1·5690], and 48% hydrobromic acid give crude 3-*bromomethylpiperidine hydrobromide*, which is converted by benzoylation and boiling with aqueous-alcoholic sodium cyanide into nearly pure 1-*benzoyl*-3-*cyanomethylpiperidine*, b. p. 165—175°/0·1 mm., d_4^{20} 1·1056, n_D^{20} 1·5602. When hydrolysed and esterified this yields *ethyl* 3-*piperidylacetate*, b. p. 101—103°/6 mm., n_D^{25} 1·4643, d_4^{25} 1·0131 (*chloroplatinate*, m. p. 181°), which is reduced by sodium and absolute alcohol to β-3-*piperidylethyl alcohol*, b. p. 121—123°/6 mm., n_D^{25} 1·4888, d_4^{25} 1·0106. 3-*Vinylpiperidine*, b. p. 152—155°, n_D^{25} 1·4731, d_4^{25} 0·9274 [*chloroplatinate*, m. p. 223—224° (decomp. from 220°)], is prepared in small yield by dehydrating this alcohol by means of phosphoric oxide at 180—190°. 3-*Methylenepiperidine*, b. p. 138°, d_4^{20} 0·9342, n_D^{20} 1·4807 (*hydrochloride*), is obtained similarly from 3-piperidylcarbinol.

H. E. F. NOTTON.

Manufacture of isatins of the naphthalene series. I. G. FARBENIND.—See B., 1928, 327.

Carbazine syntheses. V. Derivatives of C-dimethylcarbazine. VI. Derivatives of C-diethylcarbazine. H. GOLDSTEIN and W. KOPP (Helv. Chim. Acta, 1928, **11**, 478—486, 486—489).—V. Magnesium methyl iodide reacts with methyl 4′-aminodiphenylamine-2-carboxylate, yielding 3-*amino*-5 : 5-*dimethyldihydroacridine* (*acetyl* derivative, chars at 150° after previous darkening), which is oxidised by ferric chloride to 5 : 5-*dimethyldihydroacridine*-3-*imine* (*perchlorate*, decomp. gradually at the ordinary temperature). Similarly, methyl 4 : 4′-diaminodiphenylamine-2-carboxylate gives 3 : 7-*diamino*-5 : 5-*dimethyldihydroacridine* (*diacetyl* derivative, m. p. 208° after softening), oxidised to 7-*amino*-5 : 5-*dimethyldihydroacridine*-3-*imine* (*perchlorate* $+H_2O$, green). Methyl 4-amino-4′-dimethylaminodiphenylamine-2-carboxylate furnishes 3-*amino*-7-*dimethylamino*-5 : 5-*dimethyldihydroacridine* (*acetyl* derivative, decomp. 180°), oxidised to 7-*dimethylamino*-5 : 5-*dimethyldihydroacridine*-3-*imine* (I) (*hydrochloride*; *perchlorate*; *diperchlorate*). When a solution of a salt of (I) is treated with alkali, partial precipitation of the

base occurs and the alkaline liquor is coloured bluish-violet. It is suggested that this phenomenon is due to the formation of an iminium hydroxide. When an aqueous-alcoholic solution of (I) is boiled with sodium carbonate solution there is produced 7-*amino*-5 : 5-*dimethyl*-3-*carbazone*, violet (*acetyl* derivative, red, m. p. 235°), also formed by oxidation of the reaction product from magnesium methyl iodide and methyl 4-amino-4′-hydroxydiphenylamine-2-carboxylate. If (I) is boiled with sodium hydroxide solution, 7-*hydroxy*-5 : 5-*dimethyl*-3-*carbazone*, decomp. 200°, is produced.

VI. 3-*Amino*- (*acetyl* derivative, m. p. 145°), 3 : 7-*di-amino*- (*diacetyl* derivative, m. p. 241° after softening), and 3-*amino*-7-*dimethylamino*-5 : 5-*diethyldihydro-acridines* [*acetyl* derivative, m. p. 191° (decomp.)] have been prepared from magnesium ethyl iodide and the requisite substituted diphenylamine-2-carboxylic esters. Oxidation of these with ferric chloride gives 5 : 5-*diethyl*-, 7-*amino*-5 : 5-*diethyl*- (*perchlorate* $+H_2O$), and 7-*dimethylamino*-5 : 5-*diethyl-dihydroacridine*-3-*imines* (*perchlorate*), respectively. H. BURTON.

Molecular symmetry of acetonylpyrrole. S. B. HENDRICKS (J. Amer. Chem. Soc., 1928, **50**, 1205—1208).—Mol. wt. determinations on acetonyl-pyrrole (cf. Dennstedt and Zimmermann, A., 1887, 1052) by the method of differential vapour pressures are in agreement with the doubled formula, $C_{28}H_{36}N_4$. Laue and X-ray spectrum photographs on single crystals (cf. Fock, Z. Krist., 1888, **14**, 541) indicate that the unit cell contains four such molecules and has the dimensions $a=b=10{\cdot}09$ Å., $c=23{\cdot}85$ Å. The space grouping is C_4^3 or C_4^4, the molecules being in the general positions and thus not necessarily having an element of symmetry. H. E. F. NOTTON.

Reduction potentials of organic compounds. II. Pyridine. M. SHIKATA and I. TACHI (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 53).—The reduction of pyridine proceeds reversibly; two waves of reduction were observed in acid and neutral solutions, the first being the reduction of pyridine ions, and the second that of undissociated molecules.

CHEMICAL ABSTRACTS.

Influence of a third substance on the rate of reaction of organic halogen derivatives with amines. B. V. TRONOV and A. T. HERSCHKEVITSCH (J. Russ. Phys. Chem. Soc., 1928, **60**, 171—180).—The effect on the rate of reaction of the addition of so-called inert solvents in concentrations similar to those of the reacting substances was investigated. The rates of reaction of pyridine with benzyl chloride, benzyl bromide, and trichloronitromethane were determined alone and in the presence of hydrocarbons, alcohols, ethers, aldehydes, ketones, esters, nitro-compounds, nitriles, amines, inert halogen derivatives, and carbon disulphide, at 18° and relative molecular concentrations of about 3 : 2. Substances which dissolved the pyridine salt accelerated the reaction, whilst those which did not retarded it, some by as much as 10 times. The former were also the more active chemically and had a tendency to form loose complexes with the reacting substances.

Experiments were also performed to investigate whether the mechanism of reactions of the halogen compounds was ionic or not. M. ZVEGINTZOV.

Condensation of crotonaldehyde with ammonia in presence of alumina. A. E. TSCHITSCHIBABIN and M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1927, **59**, 1125—1128).—See A., 1927, 1086.

Manufacture of 2-chloropyridine. DEUTS. GOLD- UND SILBER-SCHEIDEANSTALT.—See B., 1928, 348.

Manufacture of derivatives of 2-aminopyridine. CHEM. FABR. VORM. SCHERING.—See B., 1928, 389.

Production of new pyridine derivatives [pyridylhydrazones etc.]. DEUTS. GOLD- UND SILBER-SCHEIDEANSTALT.—See B., 1928, 389.

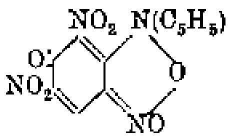
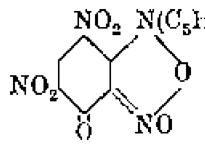
Nitroamines of the pyridine series. 3-Nitro-aminopyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 338—345).—See this vol., 185.

Quaternary pyridine bases. O. MAGIDSON and G. MENSCHIKOV (Trans. Sci. Chem.-Pharm. Inst., 1926, [**16**], 7—20).—See A., 1926, 844.

Friedel and Crafts' reaction in the pyridine series. C. M. JEPHCOTT (J. Amer. Chem. Soc., 1928, **50**, 1189—1192).—Additive compounds from pyridine or quinoline and alkyl or acyl halides do not condense with phthalic anhydride in presence of aluminium chloride. Using benzene and aluminium chloride (cf. Just, A., 1898, i, 42; Halla, A., 1911, i, 1021), quinolinic anhydride and naphthalene give a mixture of quinolinic acid, 3-α-*naphthoylpicolinic acid*, m. p. 155° (*silver* salt; *hydrochloride*, m. p. 179—180°; *methyl* ester, m. p. 100—101°), and 3-β-*naphthoyl-picolinic acid*, m. p. 145° (*hydrochloride*, m. p. 172—173°; *methyl* ester, m. p. 80—82°; *hydrate*, m. p. 109°), which gives β-naphthoic acid when fused with alkali and is reduced by zinc in ammoniacal solution to -*naphthylpyridophthalide*, m. p. 127°. Similarly, acenaphthene gives 3-(4′-*acenaphthoyl*)*picolinic acid*, m. p. 168—169° (*hydrochloride*, m. p. 175°; *methyl* ester, m. p. 113—114°; *hydrate*, m. p. 121°), and diphenyl a mixture of 3-benzoylpicolinic acid (from the benzene) and 3-p-*phenylbenzoylpicolinic acid*, m. p. 170—171°. Phenylpyridophthalide and aluminium chloride yield with benzene 3-*diphenyl-methylpicolinic acid*, m. p. 153° (*methyl* ester, m. p. 109°), which is decarboxylated at 170° to 3-*pyridyl-diphenylmethane*, m. p. 78—79°, and with toluene, 3-*phenyl*-p-*tolylmethylpicolinic acid*, m. p. 161°. 3-*p*-Toluoylpicolinic acid is reduced to p-*tolylpyrido-phthalide*, m. p. 144°. The methyl hydrogen quinolin-ate of m. p. 123° must be the 2-carboxylic ester, since its acid chloride condenses with toluene to 3-*p*-toluoyl-picolinic acid. The isomeric ester-acid of m. p. 108 must be a mixture, since it combines with benzene in the same way, forming 3-benzoylpicolinic acid as well as 2-benzoylnicotinic acid, m. p. 285° (*methyl* ester, m. p. 87°) (cf. Kirpal, A., 1910, i, 504), which is reduced to the *lactone*, m. p. 128°, of 3-carboxy-2-pyridyl-phenylcarbinol. Attempts to prepare diphenyl-pyridophthalide are described. 2 : 3-*Dibenzoylpyrid-ine*, m. p. 186—187°, and 2-*toluoyl*-3-*benzoylpyridine*, m. p. 190—193°, are prepared from 3-benzoyl-picolinyl chloride. H. E. F. NOTTON.

Reciprocal exchange of aromatically combined hydroxyl and halogen. III. W. BORSCHE and E.

FESKE (Ber., 1928, **61**, [*B*], 690—702; cf. A., 1918, i, 11; 1927, 239).—Styphnic acid, prepared by the successive sulphonation and nitration of resorcinol under defined conditions, is unexpectedly converted by *p*-toluenesulphonyl chloride in presence of pyridine into 3-*hydroxy*-2 : 4 : 6-*trinitrophenylpyridinium betaine* (I or II), m. p. about 330° (decomp.) after

(I.)   (II.)

darkening at 270°. It dissolves readily in fuming hydrochloric acid but is precipitated unchanged when the solution is diluted. Hydrogen chloride in glacial acetic acid at 145° converts it into a *substance* (?) $(NO_2)_3C_6H(OH)\cdot N\colon CH\cdot[CH\colon CH]_2Cl$, m. p. 158—159°, transformed by warm pyridine into the betaine. With diethylamine in methyl-alcoholic solution the betaine affords a *compound* from which 3-amino-2 : 4 : 6-trinitrophenol, m. p. 178°, is obtained by the action of hydrochloric acid. Piperidine and the betaine yield the two, interconvertible forms of the *compound*, $C_5H_{10}{>}NH,OH\cdot C_6H(NO_2)_3\cdot N\colon CH\cdot[CH\colon CH]\cdot_2N{<}C_5H_{10}$ (α-variety, needles, m. p. 124—125°; β-form, leaflets, m. p. 127—128°), the isomerism of which is not explained. Dilute sulphuric acid transforms either variety into an unidentified *substance*, m. p. 139°, from which 3-amino-2 : 4 : 6-trinitrophenol is readily derived by the further action of mineral acid. When the betaine is warmed with aniline, 3-hydroxy-2 : 4 : 6-trinitrodiphenylamine, m. p. 158—159°, is produced, presumably through the glutacondialdehyde derivative. Under similar conditions, *p*-toluidine yields 3-*hydroxy*-2 : 4 : 6-*trinitrophenyl*-p-*tolylamine*, m. p. 176—177° [*p*-toluidine *compound*, m. p. 191—193° (decomp.)], also derived from the diethylaniline compound of *p*-toluenesulphonylstyphnic acid and *p*-toluidine. 3-*Chloro*-2 : 4 : 6-*trinitrodiphenylamine*, m. p. 141—142°, is obtained from the hydroxydiphenylamine, *p*-toluenesulphonyl chloride, and diethylaniline or by the action of hot 2*N*-hydrochloric acid on *trinitrodiphenylaminepyridinium*-p-*toluenesulphonate*, m. p. 206—208°. Aminopicric acid, diethylaniline, and *p*-toluenesulphonyl chloride afford 3-*chloro*-2 : 4 : 6-*trinitroaniline*, m. p. 185—186°.

2 : 4-Dinitroresorcinol, m. p. 147—148° (the preparation from dinitrosoresorcinol is described in detail), is converted by *p*-toluenesulphonyl chloride in diethylaniline into the corresponding p-*toluenesulphonate*, m. p. 126—127°, whereas in the presence of pyridine it gives a mixture of 3-*hydroxy*-2 : ?-*dinitrophenylpyridinium* p-*toluenesulphonate*, m. p. 134°, and 3-*hydroxy*-2 : ?-*dinitrophenylpyridiniumbetaine*, decomp. about 325° after blackening at 300°. The betaine is converted by hydrogen chloride in glacial acetic acid into 3-*chloro*-2 : ?-*dinitrophenol*, m. p. 112—114°, by piperidine into the glutacondialdehyde *derivative*, $C_{21}H_{28}O_7N_6$ (labile α-form, m. p. 144—146°; stable β-variety, m. p. 171—172°), by aniline into dinitro-*m*-aminophenol, m. p. 220—222°, and phenylpyridinium chloride (additive compound with mercuric chloride, m. p. 145°), and by *p*-anisidine into p-*anisylpyridinium chloride*, m. p. 127—129°. The *p*-toluenesulphonyl derivative of 2 : 4-dinitroresorcinol (see above) is converted by boiling aniline into 2 : ?-*dinitrodi-3-hydroxyphenylamine*, m. p. 124—125°, which is converted by *p*-toluenesulphonyl chloride into 2 : ?-*dinitro-3-anilinophenylpyridinium* p-*toluenesulphonate*, $NHPh\colon C_6H_2(NO_2)_2\cdot N(C_5H_5)\cdot O\cdot SO_2\cdot C_7H_7$, m. p. 216—218°, and 2 : ?-*dinitro-3-anilinophenyl* p-*toluenesulphonate*, m. p. 151°, in presence of pyridine and diethylaniline, respectively.

4 : 6-Dinitroresorcinol and *p*-toluenesulphonyl chloride in pyridine afford 4 : 6-dinitro-3-hydroxyphenylpyridiniumbetaine, decomp. 320°, obtained by Reitzenstein and Rothschild (A., 1906, i, 454) from 1 : 3-dichloro-4 : 6-dinitrobenzene and hot pyridine (cf. Zincke and Weisspfenning, A., 1910, i, 585); it is converted by the successive action of piperidine or aniline and hydrochloric acid into 3-amino-4 : 6-dinitrophenol. 4 : 6-*Dinitro*-3-*hydroxyphenyl* p-*toluenesulphonate*, m. p. 135° (*diethylaniline* salt, m. p. 109—110°), is obtained from the reactants in diethylaniline. 4 : 6-Dinitroresorcinol is converted by *p*-toluenesulphonyl chloride in absence of diethylaniline into a mixture of 5 : 5′-*dichloro*-2 : 4 : 2′ : 4′-*tetranitrodiphenyl ether*, m. p. 232—234°, and 1 : 3-dichloro-4 : 6-dinitrobenzene.

H. WREN.

Quinoline derivatives. VIII. Derivatives of 4-hydroxy-2-phenylquinoline. IX. 4-Thiol-2-phenylquinoline and 2-phenylquinoline-4-sulphonic acid. H. JOHN [with E. WÜNSCHE]. **X. 4-(2-Phenylquinolyl)aminobenzoic acids.** H. JOHN (J. pr. Chem., 1928, [ii], **119**, 43—48, 49—55, 56—60).—VIII. The following derivatives of 2-phenylquinoline are described: 4-*acetoxy*-, m. p. 70°; 4-*benzoyloxy*-, m. p. 90—91°; 4-*ethoxy*-, m. p. 100—102°; 4-*phenoxy*-, m. p. 252°; 4-m-*tolyloxy*-, m. p. 241—243°; 4-p-*nitrophenoxy*-, m. p. 88—90°; 4-p-*aminophenoxy*-, m. p. 81°; 4-o-*methoxyphenoxy*-, m. p. 246°, and 4-m-*methyl*-o-iso*propylphenoxy*-, m. p. 252°. Numerous salts of the above have been prepared but not characterised.

IX. 4-Chloro-2-phenylquinoline reacts with potassium hydrosulphide at 150—160° to give 4-*thiol*-2-*phenylquinoline*, m. p. 175—176° (*picrate*, m. p. 204°), which when exposed to air for some time passes into *di*-(2-*phenyl*-4-*quinolyl*) *disulphide*, m. p. 175—176° (*picrate*, m. p. 197°). 4-*Methylthiol*-, m. p. 64° (*picrate*, m. p. 225°), 4-*ethylthiol*-, m. p. 84·5° (*picrate*, m. p. 192°), 4-iso*amylthiol*-, m. p. 170—171°, and 4-*allylthiol*-, m. p. 169°, -2-*phenylquinolines* are described. *Di*-(2-*phenyl*-4-*quinolyl*) *sulphide*, obtained from 4-thiol-2-phenylquinoline and 4-chloro-2-phenylquinoline in presence of alcoholic potassium hydroxide, has m. p. 95°. Numerous salts of the above compounds are described.

4-Chloro-2-phenylquinoline reacts with sodium hydrogen sulphite yielding 2-*phenylquinoline*-4-*sulphonic acid*, m. p. above 290° (22 *salts* described).

X. 4-Chloro-2-phenylquinoline and anthranilic acid react in boiling amyl alcohol to form o-(2′-*phenyl*-4′-*quinolylamino*)*benzoic acid*, m. p. 232—236° (decomp.) (23 *salts* described), which when treated with hot concentrated sulphuric acid gives small amounts of alkali-soluble and -insoluble products, both

having m. p. above 305°. m-(2'-*Phenyl-4'-quinolylamino*)*benzoic acid*, m. p. 273° (*ethyl* ester, m. p. 174°; 23 *salts* described), and p-(2'-*phenyl-4'-quinolylamino*)-*benzoic acid*, m. p. 305° (*ethyl* ester, m. p. 92°; 23 *salts* described), are prepared similarly. H. BURTON.

Condensation of acetaldehyde and paracetaldehyde with aniline in presence of alumina. A. E. TSCHITSCHIBABIN and M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1927, **59**, 1129—1134).—See A., 1927, 1086.

Doebner reaction [preparation of a benzeneazoquinoline]. A. CREMONINI (Gazzetta, 1928, **58**, 127—130).—Benzylideneaminoazobenzene when heated with pyruvic acid in alcohol gives a product from which is obtainable, in 3% yield, 6-*benzeneazo-2-phenylcinchoninic acid*, m. p. 248° (decomp.) (soluble *hydrochloride*, $2C_{22}H_{15}O_2N_3,2HCl,3H_2O$, m. p. 210°). The main product is a yellow, alkali-insoluble *substance*, $C_{34}H_{26}ON_6$, derived by the elimination of water from 2 mols. of aminoazobenzene, 1 mol. of benzaldehyde, and 1 mol. of pyruvic acid. By a similar condensation of 4-α-naphthaleneazo-α-naphthylamine, 6-α-*naphthaleneazo-2-phenyl-α-naphthaquinoline-4-carboxylic acid*, m. p. 238°, is obtained in 0·75% yield, whilst 1-benzeneazo-β-naphthylamine yields a *phenylstyrylnaphthatriazole*(?), $C_{25}H_{19}N_3$, m. p. 197°.
E. W. WIGNALL.

Manufacture of new polyamino-[quinoline] compounds. I. G. FARBENIND.—See B., 1928, 347.

Acridines. IV. Preparation of hydroxyacridines and 5-substituted acridine derivatives. H. JENSEN and F. RETHWISCH (J. Amer. Chem. Soc., 1928, **50**, 1144—1150).—The new acridine synthesis (A., 1927, 575) has been extended by using halogenated phenol ethers and by substituting *o*-aminophenyl ketones for *o*-aminobenzaldehyde. In this way are prepared: 3-*ethoxyacridine*, m. p. 99° (*picrate*, m. p. above 250°; *hydrochloride*, decomp. 200°), hydrolysed by hydriodic acid to 3-*hydroxyacridine*, m. p. above 250°; 1-*methoxyacridine*, m. p. 130—131° (*picrate*, decomp. 250°), hydrolysed to 1-hydroxyacridine (Matsumura, A., 1927, 467), the constitution of which is thus confirmed; 5-*methylacridine*, m. p. 114° (*picrate*, m. p. 213—214°); 5-phenyl-3-methylacridine; 1-nitro-5-phenylacridine, m. p. 189—190° (cf. Mayer and Freund, A., 1922, i, 865); 3-nitro-5-phenylacridine; 3-*methylacridine picrate*, m. p. 226°, and 3-*ethoxy-5-phenylacridine*, m. p. 105—107°. 2-Chloro-5-nitroacetophenone, unlike *o*-chloroacetophenone, readily forms with aniline, 4-*nitro-2-acetyldiphenylamine*, m. p. 125°, which, like 4-*nitro-2'-acetyldiphenylamine*, m. p. 152°, from *o*-aminobenzaldehyde and *p*-bromonitrobenzene, is converted by sulphuric and acetic acids into 3-*nitro-5-methylacridine*, m. p. above 300°. 3 : 5-*Dimethylacridine* (*picrate*, m. p. 225°, darkening at 215°), prepared by the authors' method or from acet-*p*-toluidide, has m. p. 90°, the substance obtained in the latter way by Bonna (A., 1887, 927) being probably 2 : 5-dimethylacridine. Acridine-5-carboxylic acid (A., 1926, 526) is not esterified by sulphuric acid or hydrogen chloride in ethyl alcohol; the *ethyl* ester, m. p. 78° (*picrate*, m. p. 226°; *hydrochloride*, m. p. above 250°), and *methyl* ester, m. p. 126·5—127·5° (*picrate*, m. p. 229—230°; *hydrochloride*, m. p. above 250°), are prepared from the acid chloride. H. E. F. NOTTON.

Syntheses in the indole series. III. Theory of anhydronium base formation and constitution of methosulphates. Fluorescence of 5 : 6-benz-4-carboline and its derivatives. W. O. KERMACK and R. H. SLATER (J.C.S., 1928, 789—797).—5 : 6-*Benz-4-carboline methosulphate* (+0·5MeOH, m. p. 235°), prepared from the carefully-dried base and methyl sulphate in dry benzene, yields, on treatment with alkalis, 4-*methyl-5 : 6-benz-4-ψ-carboline*, m. p. 205°. The constitution of this anhydro-base is established by the fact that it yields with methyl sulphate 1 : 4-*dimethyl-5 : 6-benz-4-carbolinium methyl sulphate*, m. p. 300°, identical with the salt prepared directly from 1-methyl-5 : 6-benz-4-carboline and methyl sulphate. 3 : 4-*Dimethyl-5 : 6-benz-4-ψ-carboline*, m. p. 225°, from 3-*methyl-5 : 6-benz-4-carboline methosulphate*, m. p. 270°, and alkali, yields in a similar manner 1 : 3 : 4-*trimethyl-5 : 6-benz-4-carbolinium methyl sulphate*, m. p. 292° (also prepared directly from 1 : 3-dimethyl-5 : 6-benz-4-carboline). 1-*Methyl-5 : 6-benz-4-carboline*, m. p. 142°, 3-*ethyl-5 : 6-benz-4-carboline methosulphate*, m. p. 250°, and 1 : 3-*dimethyl-5 : 6-benz-4-carbolinium methyl sulphate*, m. p. 296°, are described. The fluorescence of a number of carboline derivatives is examined and the influence of substituents in various positions in the ring is noted.
M. CLARK.

Intermolecular condensation of acetylmethylanthranilic acid by means of phosphorus pentachloride and formation of a complex *iso*cyanine dye. I. M. HEILBRON, S. L. HOLT, and F. N. KITCHEN (J.C.S., 1928, 934—941; cf. A., 1923, i, 245).—Phosphorus pentachloride (½ mol.) reacts on heating with acetylmethylanthranilic acid (1 mol.) in presence of acetyl chloride, giving the *acid chloride* (I) of 3-o-*carboxyphenylmethylcarbamyl-1 : 2-dimethyl-4-quinolone* (II). The free acid (II) has m. p. 247° ($+1H_2O$, m. p. 130—131°) (*methyl* ester, m. p. 244°; *anilide*, m. p. 115°). The *ethyl* ester (III), m. p. 245° ($+1H_2O$, m. p. 124°), is hydrolysed by boiling concentrated hydrochloric acid, giving 1 : 2-dimethyl-4-quinolone and methylanthranilic acid. The acid chloride (I) reacts with concentrated ammonia, giving 4 : 4'-*diketo-1 : 1' : 2'-trimethyl-1' : 4'-dihydro-2(3')-quinolylquinazoline*, m. p. 260°, and with excess of aniline, giving 4-*anilino-3-o-anilinophenylmethylcarbamyl-1-methyl-2-methylene-1 : 2-dihydroquinoline*, m. p. about 165°. When acetylmethylanthranilic acid (1 mol.) is heated with phosphorus pentachloride (1·5 mols.), an acid chloride results, which is decomposed by ethyl alcohol, giving 4-*chloro-3-o-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride* (IV), m. p. 209° (decomp.) [*methoperchlorate*, m. p. 224—225° (decomp.); *methiodide*, decomp. 215°; *methopicrate*, decomp. 168—169°], hydrolysed by boiling concentrated hydrochloric acid with formation of 4-hydroxy-2-methylquinoline methochloride. 4-*Chloro-3-o-carbomethoxyphenylmethylcarbamyl-2-methylquinoline methochloride*, m. p. 189—190°, yields a corresponding *methiodide*, m. p. 214° (decomp.). The ethyl ester (IV) reacts with aniline in acetic acid solution, giving 4-*anilino-3-o-carbethoxyphenylmethylcarbamyl-1-methyl-*

2-*methylene*-1 : 2-*dihydroquinoline*, m. p. 191—192°, and with piperidine, giving the corresponding 4-*piperidinomethylene base*, m. p. 260°. When an alcoholic solution of the ester (IV) is heated with dilute ammonia and the resultant reddish-purple solution is treated with concentrated potassium iodide solution, 4′-*chloro*-3 : 3′-*di*-(o-*carbethoxyphenylmethylcarbamyl*)-1 : 2 : 1′-*trimethyl*ψ*cyanine iodide*, m. p. 203° (decomp.) (*perchlorate*; *picrate*), is obtained. The following are also described: 5-*bromomethylacetylanthranilic acid*, m. p. 204°; 6-*bromo*-3-p-*bromo*-o-*carbethoxyphenylmethylcarbamyl*-1 : 2-*dimethyl*-4-*quinolone*, m. p. 212° (+H_2O, m. p. 123°); 4-*chloro*-6-*bromo*-3-p-*bromo*-o-*carbethoxyphenylmethylcarbamyl*-2-*methylquinoline methochloride*, m. p. 194°.

M. CLARK.

Manufacture of barbituric acid soporifics. I. G. FARBENIND.—See B., 1928, 389.

Pyrrole derivatives. II. W. KÜSTER and G. KOPPENHOFER (Z. physiol. Chem., 1928, **172**, 126—137; cf. A., 1922, i, 857).—Condensation of 4-carbethoxy-3 : 5-dimethylpyrrole-2-aldehyde with 2 : 5-diketopiperazine yields 2 : 2-*bis*-(4′-*carbethoxy*-3′ : 5′-*dimethylpyrrylmethylene*)-2 : 5-*diketopiperazine*, m. p. 268—269°, red, which in alcoholic solution gives two sharp absorption bands, one about 525 μμ and a broader band with centre about 475 μμ, and on reduction affords 2 : 2-*bis*-(4′-*carbethoxy*-3′ : 5′-*dimethylpyrrylmethyl*)-2 : 5-*diketopiperazine*, colourless, m. p. 122°; on heating with 20% barium hydroxide the latter gives β-4-*carbethoxy*-3 : 5-*dimethyl*-2-*pyrrylalanine*, decomp. about 180—186°. An alternative method for the synthesis of these substituted pyrrylamino-acids is given. 4-Carbethoxy-3 : 5-dimethylpyrrole-2-aldehyde when heated with rhodanine and sodium acetate in acetic acid solution yields 4-*carbethoxy*-3 : 5-*dimethyl*-2-*pyrrylmethylenerhodanine*, m. p. 253—255°, which gives a *phenylhydrazone*, m. p. 272—275° (decomp.), and yields on heating with 20% barium hydroxide or 15% sodium hydroxide solution β-4-*carbethoxy*-3 : 5-*dimethylpyrryl*-α-*thiopyruvic acid*, decomp. 196°. With hydroxylamine this acid gives hydrogen sulphide and an α-*oxime*, m. p. 218°, which on reduction gives the β-4-carbethoxy-3 : 5-dimethylpyrrylalanine described above. β-4-Carbethoxy-3 : 5-dimethylpyrryl-α-thiopyruvic acid on heating at 140° with chloroacetic acid yields β-4-*carbethoxy*-3 : 5-*dimethylpyrrylpyruvic acid*, m. p. 192°. Condensation of aminoacetal with ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate yields β-*amino*-αα-*bis*-3-*carbethoxy*-(1-*phenyl*-2 : 5-*dimethyl*-4-*pyrryl*)*ethane*, m. p. 246° (sinters at 242°). The ethyl pyrrolecarboxylate, when heated in alcoholic solution with dilute hydrochloric acid and formaldehyde, yields *bis*-(4-*carbethoxy*-1-*phenyl*-2 : 5-*dimethyl*-3-*pyrryl*)*methane*, m. p. 102°.

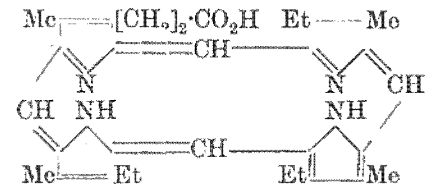
A. WORMALL.

Action of cyanogen bromide on tertiary iminazoles. W. LANGENBECK (J. pr. Chem., 1928, [ii], **119**, 77—80).—When 1 : 4-dimethylglyoxaline is treated with ethereal cyanogen bromide there is produced 2-*bromo*-1 : 4-*dimethylglyoxaline*, b. p. 89—90°/3 mm., m. p. 51—52° [*hydrochloride*, m. p. 240° (decomp.)], nitrated to 2-bromo-5-nitro-1 : 4-dimethylglyoxaline (Pyman and Timmis, J.C.S., 1923, **123**, 494). 2-*Bromopilocarpine hydrochloride*, m. p. 240°, $[\alpha]^{18}_{63}$ +81·9° in water, and 2-*bromoisopilocarpine hydrochloride*, m. p. 201°, are prepared similarly. The pharmacological effects of 2-bromopilocarpine are given.

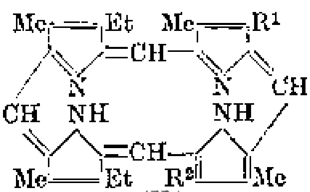
H. BURTON.

Dicyanotriazole. J. A. FIALKOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 715—725).—See A., 1927, 1205.

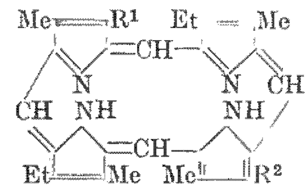
Porphyrin syntheses. XIV. Synthesis of porphinmonocarboxylic acids and some of their complex salts. H. FISCHER, H. GROSSELFINGER, and G. STANGLER (Annalen, 1928, **461**, 221—244).—Alkali degradation of chlorophyll is known to give phyllo- and pyrro-porphyrin, *i.e.*, two of the eight (sixteen, assuming tautomerides) possible monocarboxylic acids of ætioporphyrin. The present authors now describe the synthesis of five of these acids (or their esters). Particular attention is paid to the porphyrin (III) (R^1=Et, R^2=·$[CH_2]_2$·CO_2H), obtained by condensing (2 : 4-dimethyl-3-carboxyethylpyrrolenyl)-(2′ : 4′-dimethyl-3′-ethylpyrryl)methene (cf. Fischer and Schubert, A., 1924, i, 544) with



(I.)



(II.)



(III.)

bis-(2-bromo-3-methyl-4-ethylpyrryl)methene, using glacial acetic acid and hydrogen bromide at 165—170°. Some ætioporphyrin is formed in this condensation, owing to decomposition of the unsymmetrical methene (the bis-methene gives no porphyrin under the conditions of this condensation, whilst the unsymmetrical methene gives a basic and an acidic porphyrin). Pyridine as a condensing agent leads to the formation of basic porphyrins. By previous introduction of a bromine atom into each of the 2-methyl groups in the unsymmetrical methene (cf. this vol., 76), followed by heating the product with the bis-methene in presence of succinic acid, or, better still, with hydrobromic acid in addition, the desired porphyrin (III, as above) was obtained in good yield (35%), unaccompanied by ætioporphyrin. The crude porphyrin was purified through the *methyl* ester, m. p. 216°, which was converted (1) by ferrous acetate, sodium chloride, and acetic acid into the corresponding *iron* salt (a *hæmin*), $C_{34}H_{40}O_2N_4ClFe$ (also +1AcOH), (2) by magnesium methyl iodide into the corresponding *phyllin*, $C_{34}H_{40}O_2N_4Mg$ (compared spectrographically with phyllophyllin), (3) by copper acetate and acetic acid into the *copper* salt, $C_{34}H_{40}O_2N_4Cu$, and (4) by concentrated potassium hydroxide in presence of a little pyridine into the free *acid* (III, as above) (well-defined *hydrochloride*; *copper* salt, m. p. 280°). The

properties of the acid are compared in detail with those of phyllo- and pyrro-porphyrin.

Condensation by the succinic acid method of (4-methyl-2-bromomethyl-3-ethylpyrryl)(4′-methyl-2′-bromomethyl-3′-ω-carboxyethylpyrrolenyl)methene hydrobromide with bis-(2-bromo-4-methyl-3-ethylpyrryl)methene hydrobromide gave the *methyl* ester of (I), m. p. 263° (*iron* salt, $C_{34}H_{38}O_2N_4ClFe$).

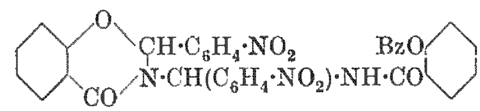
(2 : 4-*Dimethyl-3-ethylpyrryl*)(2′ : 3′-*dimethyl-4′-ω-carbomethoxyethylpyrrolenyl*)*methene hydrobromide*, m. p. 180°, was obtained from methyl hæmopyrrolecarboxylate and cryptopyrrolealdehyde in presence of hydrogen bromide and methyl alcohol, and on bromination afforded (4-*methyl-2-bromomethyl-3-ethylpyrryl*)-(3′-*methyl-2′-bromomethyl-4′-ω-carbomethoxyethylpyrrolenyl*)*methene hydrobromide*, decomp. 225°. The latter, when condensed by the succinic acid method with bis-(2-bromo-4-methyl-3-ethylpyrryl)methene hydrobromide, gave the *methyl* ester, m. p. 207—208°, of (II) (R^1=·$[CH_2]_2$·CO_2H, R^2=Et), also obtained, but with m. p. 220° (*iron* salt, m. p. 263°, and *phyllin*, m. p. 200°, of the methyl ester), by the succinic acid method from bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)-methene hydrobromide and (4-*methyl-2-bromomethyl-3-ω-carboxyethylpyrryl*)(3′-*methyl-2′-bromomethyl-4′-ethylpyrrolenyl*)*methene hydrobromide*, obtained by bromination of (2 : 4-*dimethyl-3-ω-carboxyethylpyrryl*)-(2′ : 3′-*dimethyl-4′-ethylpyrrolenyl*)*methene hydrobromide*, decomp. 176°, which in turn resulted from the condensation in methyl-alcoholic hydrobromic acid of cryptopyrrolecarboxylic acid with hæmopyrrolealdehyde.

Condensation of (4-methyl-2-bromomethyl-3-ω-carboxyethylpyrryl)(3′-methyl-2′-bromomethyl-4′-ethylpyrrolenyl)methene hydrobromide with bis-(2-bromo-4-methyl-3-ethyl-5-pyrryl)methene hydrobromide gave the *methyl* ester of (II) (R^1=Et, R^2=·$[CH_2]_2$·CO_2H); this methyl ester, m. p. 238°, depresses the m. p. of the phyllo- and pyrro-porphyrin esters, m. p. 234° and 241°, respectively, and gives an *iron* salt, m. p. 258°.

Methyl hæmopyrrolecarboxylate, condensed with hæmopyrrolealdehyde in methyl-alcoholic hydrobromic acid, affords (2 : 3-*dimethyl-4-ω-carboxyethylpyrryl*)(2′ : 3′-*dimethyl-4′-ethylpyrrolenyl*)*methene hydrobromide*, m. p. 185°, giving on bromination (3-*methyl-2-bromomethyl-4-ω-carboxyethylpyrryl*)(3′-*methyl-2′-bromomethyl-4′-ethylpyrrolenyl*)*methene hydrobromide*. The latter undergoes (succinic acid) condensation with bis-(2-bromo-4-methyl-3-ethylpyrryl)methene hydrobromide to give, ultimately, the *methyl* ester of (III) (R^1=·$[CH_2]_2$·CO_2H, R^2=Et) (*iron* salt of ester, m. p. 254°).

The properties of the various products are compared with those of various derivatives of phyllo- and pyrro-porphyrin. E. E. Turner.

Condensation products from acid amides and aldehydes. Constitution of the transformation products of the benzometoxazones. E. Glazer and S. Frisch (Arch. Pharm., 1928, **266**, 103—116).—The investigation of nitro-compounds (Glaser and others, A., 1923, i, 694; 1924, i, 797; 1926, 608) has been extended as follows. By simply being melted together at about 100°, *m*-nitrobenzaldehyde and salicylamide yield m-*nitrophenylbenzometoxazone*, $C_{14}H_{10}O_4N_2$ (cf. Titherley, J.C.S., 1907, **91**, 1419). The condensation is also smoothly carried out in alcoholic solution in presence of a little hydrochloric acid. The product has m. p. 220° (N-*acetyl* derivative, m. p. 116°; N-*benzoyl* derivative, m. p. 173°). When it is treated with a cold solution of potassium hydroxide and acetone, it dissolves and is reprecipitated by acidifying as an amorphous form (m. p. 115—135°) of the "phenolic modification," which is more conveniently obtained, in a crystalline form (m. p. 175°), by use of other solvents, *e.g.*, pyridine. This product solidifies again above its m. p., being re-converted into the true metoxazone, m. p. 220°. Titherley's hypothesis that *syn-* and *anti*-forms of the phenolic form exist is shown to be unfounded: the "phenolic" form is not a true tautomeric modification; it is strictly a dimeride of the formula :



This is very easily dissociated, so that the mol. wt. (in phenol) is intermediate between that of the true metoxazone and that corresponding with the formula given, and is dependent on how long the substance has been heated in phenol solution. The O-*acetate*, $C_{30}H_{22}O_9N_4$, m. p. 187—188° (decomp.), and the O-*benzoate*, $C_{35}H_{24}O_9N_4$, m. p. 161° (decomp.), show similar behaviour in mol. wt. determinations. When attempts are made to methylate the true metoxazone it is converted into the phenolic dimeride. It resists oxidation with chromic anhydride in acetic acid but is disrupted by the action of bromine in glacial acetic acid, yielding dibromosalicylamide.

m-Nitrobenzaldehyde and benzamide condense together in alcoholic solution on addition of a little hydrochloric acid, yielding m-*nitrobenzylidenedibenzamide*, m. p. 224°. The following analogues were obtained in a similar way: o-*nitrobenzylidenedibenzamide*, m. p. 217—218°; m-*nitrobenzylidenediacetamide*, m. p. 236—237°; o-*nitrobenzylidenediacetamide*, m. p. 231—232°. From ethylurethane there were prepared m-*nitrobenzylidenediurethane*, NO_2·C_6H_4·$CH(NH·CO_2Et)_2$, m. p. 192—193°, and o-*nitrobenzylidenediurethane*, m. p. 179°.

W. A. Silvester.

***iso*Oxazole ψ-bases and salts.** E. P. Kohler and A. H. Blatt (J. Amer. Chem. Soc., 1928, **50**, 1217—1226).—The additive product of 3 : 4 : 5-triphenyl*iso*oxazole and methyl sulphate is converted by ferric chloride and hydrochloric acid into 3 : 4 : 5-*triphenyl-2-methyl*isooxazolinium *ferrichloride*, m. p. 162° (corresponding *picrate*, m. p. 174°). The yellow *bromide* (I) (decomposed at a low temperature into triphenyl*iso*oxazole and methyl bromide) of this base is formed, together with phenyl αβ-diphenylstyryl ketone, when 2-methyl-3 : 4-diphenyl*iso*oxazolone (this vol., 430) is treated with magnesium phenyl bromide and the product decomposed with hydrobromic acid. It gives a *perbromide*, m. p. 152°, which is debrominated by acetone to a colourless *bromide* (II). The somewhat ill-defined products (I) and (II), which may represent salts of isomeric oxonium and

ammonium ions, are converted by alkali into an oily ψ-base, $\begin{matrix}\text{CPh.CPh} & \text{O}\\ | & |\\ \text{CPh(OH)}\cdot & \text{NMe}\end{matrix}$. The alkaline degradation of less highly substituted *iso*oxazolinium salts (cf. Claisen, A., 1909, i, 185; Mumm and Münchmeyer, A., 1911, i, 79) may be explained by the intermediate formation of similar products. With picric acid the ψ-base forms the above picrate and with sodium methoxide a *methyl ether*, m. p. 135°. In ethereal solution it passes irreversibly with loss of water into a *substance*, m. p. 140—141°, tentatively regarded as CPhBz:CPh·N:CH_2. This gives, by addition to the double linking, a *picrate*, m. p. 184°, and a methyl alcohol additive *product*, m. p. 104°, which are isomeric with the picrate and methyl ether obtained from the ψ-base. It decomposes when kept, liberating formaldehyde, is hydrolysed by acids to dibenzoylphenylmethane, and ozonised to equivalent quantities of benzil and benzoic acid. With magnesium phenyl bromide it forms *benzyltriphenylvinylamine*, m. p. 134°, which is hydrolysed to dibenzoylphenylmethane and benzylamine. H. E. F. NOTTON.

Formation of thiazole derivatives from thiocyano-amines. H. P. KAUFMANN (Arch. Pharm., 1928, **266**, 197—218).—The general method of Kaufmann and Oehring (A., 1926, 392) for the introduction of the thiocyano-group into aromatic amines has been applied to compounds in which the *ortho*-position to the amino-group is unsubstituted. *o*-Thiocyanoamines result, which readily change into the corresponding thiazoles. Ethyl *p*-aminobenzoate, sodium thiocyanate, and bromine react in acetic acid solution, giving *ethyl* 4-*amino*-3-*thiocyanobenzoate*, m. p. 97—98°, which affords *bis*-(2-*amino*-5-*carbethoxyphenyl*) *disulphide*, m. p. 153°, when treated with alcoholic sodium hydroxide solution. The thiocyanogen compound changes quantitatively on keeping an acetic acid solution into *ethyl* 1-*aminobenzthiazole*-5-*carboxylate*, m. p. 241°. The following compounds are obtained in a similar manner: 5-*chloro*-1-*aminobenzthiazole*, m.p. 198°; 5-*chloro*-2-*amino*-3 *methylbenzthiazole*, m. p. 206°. *p*-Toluidine furnishes 3 : 5-*dithiocyano*-p-*toluidine*, m. p. 123°; 1-*amino*-5-*methylbenzthiazole*, m. p. 136°, and 1-*amino*-3-*thiocyano*-5-*methylbenzthiazole*, m. p. 225°; both of these aminobenzthiazoles may be diazotised and coupled with R-salt, giving brown to reddish-brown dyes. 2-*Amino*-α-*naphthathiazole*, m. p. 261°, is obtained from 1-thiocyano-β-naphthylamine, whilst *p*-thiocyanoaniline affords 2 : 4-*dithiocyanoaniline*, m. p. 107—108°, and 1-*amino*-5-*thiocyanobenzthiazole*, m. p. 198°. Other compounds described are 2-*amino*-5-*thiocyano*-p-*xylene*, m. p. 65°, *bis*-(4-*amino*-2 : 5-*dimethylbenzene*) *disulphide*, m. p. 192°, 1-*amino*-5-*thiocyano*-3 : 6-*dimethylbenzthiazole*, m. p. 231°, and 2-*amino*-8-*thiocyano*-α-*naphthathiazole*, m. p. 272°. The abovementioned thiazole derivatives are unchanged by sodium hydroxide or lead tartrate solutions. S. COFFEY.

Chloroaurates of nucleic bases. F. A. HOPPE-SEYLER and W. SCHMIDT (Z. physiol. Chem., 1928, **175**, 304—309).—Like adenine, guanine and hypoxanthine yield crystalline gold salts, the formation of which, unless accurate analytical data are obtained, does not serve as a means of differentiating adenine from the other nucleic bases. When hypoxanthine in warm dilute hydrochloric acid solution is treated with an excess of chloroauric acid, a *chloroaurate* (I), $C_5H_4ON_4$,HCl,$AuCl_3$, m. p. 240—242° (decomp.), is obtained. Addition of the chloroauric acid to a hot concentrated solution in hydrochloric acid yields a second *chloroaurate*, $C_5H_4ON_4$,2HCl,$AuCl_3$, m. p. 259—262° (decomp.), which is converted into (I) by crystallisation from dilute hydrochloric acid. Similarly, from guanine in hot concentrated hydrochloric acid solution is obtained the *chloroaurate*, $C_5H_5ON_5$,2HCl,$AuCl_3$, m. p. 235—240° (decomp.), which is unchanged by crystallisation (cf. the almost identical composition of the adenine salt $C_5H_5N_5$,2HCl,$AuCl_3$,H_2O). The normal salt could not be obtained pure, owing, apparently, to its extreme solubility and instability. Xanthine similarly yields a very unstable salt which could not be obtained pure. J. W. BAKER.

[**Synthesis of evodiamine.**] T. ASAHINA and T. OHTA (Ber., 1928, **61**, [*B*], 869; cf. this vol., 432).—*N*-Methylisatoic anhydride has been described previously by Houben (A., 1909, i, 921). H. WREN.

Manufacture of soluble salts of ergotoxine. WELLCOME FOUNDATION ETC.—See B., 1928, 348.

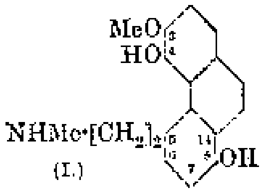
Spontaneous resolution of externally compensated mixtures. L. ANDERSON and D. W. HILL (J.C.S., 1928, 993—997).—Fractional crystallisation of atropine sulphate from absolute alcohol gives a product which may contain up to 75% excess of *l*-hyoscyamine sulphate. The partial resolution is not brought about in aqueous alcohol or in methyl alcohol–ethyl acetate mixtures. The phenomenon is ascribed to inoculation of the solution by dust particles from the laboratory atmosphere. M. CLARK.

Harmine from a South American liane. O. WOLFES and K. RUMPF (Arch. Pharm., 1928, **266**, 188—189).—This paper confirms and amplifies the independent work of Elger (this vol., 311). The harmine isolated was identified by its properties, composition, and by conversion into harmol, m. p. 322°. The plant from which it was isolated appears to belong to the *Malpighiaceæ*. Villalba's results (A., 1925, i, 828) are not confirmed. W. A. SILVESTER.

Constitution of thebenine. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1928, 921—934).—14-Hydroxycodeine is unaffected by boiling hydrochloric acid (*d* 1·07, the strength used in preparation of thebenine). Prolonged heating with acetic anhydride yields no triacetylthebenine, but gives a mixture of two *bases*, one crystalline, m. p. 304°, and the other amorphous. In consideration of these facts, Schopf's theory of the formation of thebenine from codeinone (A., 1927, 472) appears to be improbable.

The positions of the methoxyl and hydroxyl groups of thebenine (I) have been determined by Pschorr (A., 1910, i, 423), but the evidence for placing the side-chain in position 5 is inconclusive. Conclusive evidence is now brought forward. 3 : 4 : 8-Trimethoxy-5-vinylphenanthrene (II), obtained by the

complete alkylation and exhaustive methylation of thebenine, is converted by permanganate into 3 : 4 : 8-trimethoxyphenanthrene-5-carboxylic acid (III), m. p. 236—237° (*lit.* 224—226°), and 5-aldehydo-3 : 4 : 8-trimethoxyphenanthrene (IV), m. p. 151° [*semicarbazone*, m. p. 243—246° (decomp.)], termed by Pschorr "oxymethebenol." The *methyl* ester, m. p. 149—151°, of the acid (III) readily yields the corresponding *hydrazide*, m. p. 177°, converted by the action of nitrous acid into the *azide*, which decomposes at 65° on slow heating (it explodes at 80° if suddenly heated) giving the *lactone* (V), m. p. 246—247°, of 4-*hydroxy*-3 : 8-*dimethoxyphenanthrene-5-carboxylic acid*.



(I.)

The aldehyde (IV) yields an *oxime* ($+\frac{1}{2}C_6H_6$), softening at 140—142°, m. p. 153° (*sodium* salt), which gives, on dehydration by boiling with acetic anhydride and sodium acetate, 3 : 4 : 8-*trimethoxy*-5-*cyanophenanthrene* (VI), m. p. 145—146°, and 3 : 8-*dimethoxythebenidine*, m. p. 229—230°. The nitrile (VI) is converted, either by boiling with a mixture of hydrochloric and acetic acids or by hydrolysis of the corresponding imino-ester hydrochloride, into the lactone (V). Demethylation of the last-named compound gives the *lactone* of 3 : 4 : 8-*trihydroxyphenanthrene-5-carboxylic acid*, decomp. from 305°. The preparation of 3 : 4 : 5 : 8-tetramethoxyphenanthrene for comparison with a synthetic product of known constitution thus proves to be impracticable. Catalytic reduction of (II), however, gives 3 : 4 : 8-*trimethoxy-5-ethylphenanthrene*, m. p. 112—113°, identical with a specimen prepared from 2-nitroveratraldehyde and 6-methoxy-3-ethylphenylacetic acid. The side-chain is therefore in position 5 and thebenine has the constitution (I). *p*-Ethylanisole is converted by Adams and Levine's method (cf. A., 1924, i, 860) into 6-*methoxy*-3-*ethylbenzaldehyde*, b. p. 261—262° (*semicarbazone*, m. p. 226—227°), which reacts with hippuric acid, sodium acetate, and acetic anhydride, giving 5-*keto-2-phenyl*-4-(6'-*methoxy*-3'-*ethylbenzylidene*)-4 : 5-*dihydro-oxazole*, m. p. 159°. This azlactone is converted by long boiling with sodium hydroxide solution into 6-*methoxy-3-ethylphenylpyruvic acid* (VII), m. p. 185°, which reacts with *o*-phenylenediamine, giving 3-*hydroxy*-2-(6'-*methoxy*-3'-*ethylbenzyl*)*quinoxaline*, m. p. 184—185°. The *sodium* salt ($+\frac{1}{2}H_2O$), m. p. 184°, of the acid (VII) is oxidised by hydrogen peroxide, giving, on acidification, 6-*methoxy*-3-*ethylphenylacetic acid*, m. p. 68—69° (*sodium* salt), which condenses with 2-nitroveratraldehyde at 100° in presence of acetic anhydride, giving a mixture of trans-α-(6'-*methoxy*-3'-*ethylphenyl*)-2-*nitro*-3 : 4-*dimethoxycinnamic acid* (VIII), m. p. 193—194° (*ammonium* salt), and trans-2-*nitro*-3 : 4-*dimethoxycinnamic acid*, m. p. 229°. Reduction of (VIII) gives trans-α-(6'-*methoxy*-3'-*ethylphenyl*)-2-*amino*-3 : 4-*dimethoxycinnamic acid*, m. p. 151—152°, and an aqueous methyl-alcoholic solution of the diazonium sulphate of this acid yields, on boiling or on addition of copper powder, 3 : 4 : 8-*trimethoxy*-5-*ethylphenanthrene*-9-*carboxylic acid*, m. p. 207°. Elimination of the carboxyl group then gives 3 : 4 : 8-trimethoxy-5-ethylphenanthrene, identical with that prepared from (II). The following are described: dimethylmethebenine methosulphate, m. p. 283—285° (lit. 268—270°); 2-*amino*-3 : 4-*dimethoxycinnamic acid*, m. p. 173—178° (decomp.) [*hydrochloride*; *acetyl* derivative, m. p. 253° (decomp.)]; 7 : 8-*dimethoxycarbostyril*, m. p. 166—168°; the *lactone*, m. p. 165°, of 8-*hydroxy*-3 : 4-*dimethoxy*-5-*ethylphenanthrene*-9-*carboxylic acid* (?), m. p. 155—157°.

M. Clark.

Purification of brucine. F. Saunders (J. Amer. Chem. Soc., 1928, 50, 1231).—Pure brucine is conveniently obtained by slow crystallisation from a solution of the hydrochloride in 20% alcohol rendered alkaline with ammonia. H. E. F. Notton.

Organic compounds of arsenic. XI. Action of thionyl chloride on primary and secondary arsinic acids. W. Steinkopf and S. Schmidt (Ber., 1928, 61, [*B*], 675—678).—Phenylarsinic acid reacts vigorously with thionyl chloride, giving about half the expected quantity of phenyldichloroarsine, $AsPhO(OH)_2 + 2SOCl_2 = AsPhCl_2 + SO_2Cl_2 + SO_2 + H_2O$; chlorobenzene and arsenic trichloride are simultaneously produced, $AsPhO(OH)_2 + 2SOCl_2 = PhCl + AsCl_3 + 2SO_2 + H_2O$. With 1-anthraquinonylarsinic acid only the second type of change is realised, the product being 1-chloroanthraquinone. 1-*Anthraquinonyldichloroarsine*, m. p. 237°, is prepared by reduction of the acid in the usual manner. Diphenylarsinic acid and thionyl chloride afford diphenylarsenic trichloride, m. p. 191°. *Dichloroarsinoacetic acid*, $CO_2H{\cdot}CH_2{\cdot}AsCl_2$, m. p. 123—125°, is obtained by simultaneous reduction and chlorination from phosphorus trichloride and arsinoacetic acid. The corresponding *methyl* ester, b. p. 78°/5 mm., is described (cf. Gibson and Johnson, this vol., 311).

H. Wren.

Organic compounds of arsenic. XII. Action of acid chlorides on diphenylarsine. W. Steinkopf, I. Schubart, and S. Schmidt (Ber., 1928, 61, [*B*], 678—682; cf. Job and Reich, A., 1923, i, 873).—Diphenylarsine reacts vigorously with acetyl chloride in an atmosphere of carbon dioxide, giving *diphenylacetylarsine*, b. p. 167—168°, decomposed by oxygen in presence of water into diphenylarsinic and acetic acids. Under similar conditions, chloro- and bromoacetyl chloride yield, respectively, diphenylchloroarsine and diphenylbromoarsine. Carbonyl chloride, probably by elimination of carbon monoxide from the intermediate compound, $AsPh_2{\cdot}COCl$, affords diphenylchloroarsine, which also results when phosphorus trichloride is used. Benzoyl chloride and diphenylarsine evolve hydrogen chloride and give diphenylarsinic acid. Diphenylarsine and benzenesulphonyl chloride afford diphenylchloroarsine, diphenyl sulphide, and a compound, m. p. 106—108° to a turbid liquid, which becomes clear at 109°; since the compound is obtained more simply and in better yield from diphenylarsinic acid and benzenesulphonyl chloride, it is regarded as the mixed *anhydride*, $AsPh_2O{\cdot}O{\cdot}SO_2Ph$. Phenyldichloroarsine and chlorosulphonic acid afford benzenesulphonyl chloride, whereas diphenylchloroarsine with the same reagent yields benzenesulphonyl chloride and the compounds $AsPh_2O(OH),HCl$ and $2AsPh_2O(OH),HCl$. Fluoro-

sulphonic acid and diphenylchloroarsine yield benzenesulphonyl fluoride and the *sulphate*, $2AsPh_2O(OH),H_2SO_4$, m. p. 117°, more conveniently prepared from diphenylarsinic acid and 50% sulphuric acid. The following esters are incidentally described: *di*iso*amyl phenylarsinite*, b. p. 173—176°/11 mm.; iso*amyl diphenylarsinite*, b. p. 188—189°/11 mm.; iso*amyl diphenylthioarsenite*, b. p. 215—220°/11 mm.; *allyl diphenylarsinite*, b. p. 280·5—281·5°/11 mm.

H. Wren.

Synthesis of 4-amino-3-hydroxyphenylarsinic acid. I. E. Balaban (J.C.S., 1928, 809—813).—The mixture of 4 nitro- and 6-nitro-chloroacetanilides obtained (cf. Mayes and Turner, this vol., 513) by nitration of *m*-chloroacetanilide yields, on hydrolysis with 25% sulphuric acid, the corresponding chloronitroanilines, readily separable by means of their difference in basicity. 3-Chloro-4-nitroaniline undergoes the Bart–Schmidt reaction, giving a 45% yield of 3-*chloro*-4-*nitrophenylarsinic acid*, decomp. 200° (*barium*, *calcium*, and *magnesium* salts). This acid is converted on boiling with 25% aqueous sodium hydroxide into 4-*nitro*-3-*hydroxyphenylarsinic acid* (*magnesium* and *barium* salts), reduced by dextrose to 4-amino-3-hydroxyphenylarsinic acid (I) [acetyl derivative (II) (*magnesium* and *sodium* salts)]. The following were also prepared: 2-nitro-4-acetamido-3-hydroxyphenylarsinic acid (*calcium, magnesium*, and *barium* salts); 2-nitro-4-amino-3-hydroxyphenylarsinic acid (*monohydrate*; *magnesium* salt); 2-*amino*-4-*acetamido*-3-*hydroxyphenylarsinic acid* (*diazo-oxide*; *calcium* and *magnesium* salts), and 2 : 4-*diacetamido*-3-*hydroxyphenylarsinic acid.* When 3-*chloro*-6-*nitrophenylarsinic acid*, m. p. 250° (*magnesium* salt), prepared from 3-chloro-6-nitroaniline, is treated with alkali it undergoes dearsenication, giving *p*-nitrophenol. Reduction of the acid with ferrous sulphate gives 3-chloro-6-aminophenylarsinic acid [*calcium* and *barium* salts; *acetyl* derivative (III) (*magnesium* salt)], which is converted, on heating with chloroacetamide on the water-bath, into 6-*glycineamide*-3-*chlorophenylarsinic acid* (IV), m. p. 195° (decomp.) (*magnesium* and *calcium* salts). The following are described: 4-*amino*-4′-*acetamido*-3 : 3′-*dihydroxyarsenobenzene*, 3 : 4′-*diamino*-4 : 3′-*dihydroxyarsenobenzene*, 4 : 4′-*diacetamido*-3 : -*dihydroxyarsenobenzene*, and 3 : 4′-*diacetamido*-4 : 3′-*dihydroxyarsenobenzene*. The trypanocidal action on infected mice of these compounds, of 4 : 4′-diamino-3 : 3′-dihydroxyarsenobenzene, and of compounds (I), (II), (III), and (IV) is described.

M. Clark.

Triphenylstibine sulphide. O. Magidson [with B. Susskind] (Trans. sci. chem.-pharm. inst., Moscow, 1923, 6, 21—28; Chem. Zentr., 1927, ii, 2542).—Good yields of triphenylstibine sulphide are obtained by a modification of Michaelis and Reese's method, the time of reaction being shortened, and half the usual quantity of sodium employed.

A. A. Eldridge.

Organic selenium compounds; derivatives of aromatic seleno-ethers. D. G. Foster and S. F. Brown (J. Amer. Chem. Soc., 1928, 50, 1182—1188).—Fuming nitric acid does not nitrate the ethers of selenophenol but converts them into selenoxide nitrates which are ionogenic in aqueous solution. The selenoxides, liberated by sodium carbonate, yield, with concentrated hydrochloric acid, dialkylselenodichlorides. These are also formed from the dialkyl selenides, (*a*) by oxidising them with aqueous permanganate and saturating the solution with hydrogen chloride, (*b*) by treatment with chlorine in ether. The following are described: *phenylmethylselenoxide nitrate*, m. p. 97°; *phenylmethylselenodichloride*, m. p. 122° (decomp.); *phenyl ethyl selenide*, b. p. 214—216° (*dichloride*, m. p. 64—65°); oily *phenylethylselenoxide nitrate*; *phenyl* iso*amyl selenide*, b. p. 105°/3 mm. (*dichloride*, m. p. 80°); oily *phenyl*iso*amylselenoxide nitrate*, which is converted by sodium carbonate followed by hydrochloric acid into benzeneseleninic acid; *diphenylselenoxide nitrate*, m. p. 97°, and diphenylselenodichloride, m. p. 142° (decomp.) (cf. Krafft and Vorster, A., 1894, i, 88).

H. E. F. Notton.

Position occupied by acetatomercuric (Hg·OAc) groups in anilines having in the nucleus a halogen group or a hydrocarbon residue. II. L. Vecchiotti (Gazzetta, 1928, 58, 181—190; cf. A., 1927, 1098).—The action of mercuric acetate on *m*-bromoaniline in alcohol yields 4-*acetatomercur bromoaniline*, m. p. 181° (*acetyl* derivative, m. p. 215°); the corresponding *hydroxymercuri*-compound has m. p. 170°, the *bromidomercuri*-compound, m. p. 215°, and *mercury di*-o-*bromo*-p-*aminophenyl*, m. p. 185°. The constitution of the acetato-compound is determined by treating it with bromine in acetic acid, when 3 : 4-*dibromoacetanilide*, m. p. 158°, hydrolysed to 3 : 4-dibromoaniline, is obtained. With excess of mercuric acetate in aqueous solution, 2 : 4 : 6-*triacetatomercuri*-3-*bromoaniline*, m. p. 229° (*acetyl* derivative, m. p. 240°, decomp.), is obtained, which with bromine in acetic acid yields 2 : 3 : 4 : 6-*tetrabromoacetanilide*, m. p. 128°, hydrolysed to 2 : 3 : 4 : 6-tetrabromoaniline.

E. W. Wignall.

Mercuration of naphthalene derivatives. J. Kryński (Rocz. Chem., 1928, 8, 71—87).—The following compounds in which mercury is substituted in the nucleus were prepared by the action of a salt of mercury on the appropriate naphthalene derivative: 2 : 4-*diacetomercuri*-α-*naphthol*, $C_{10}H_5(Hg{\cdot}OAc)_2{\cdot}OH$, m. p. 140°, readily changing into 2-*mercuri*-4-*acetomercuri*-1 : 2-*naphthaquinone*, 1-*acetomercuri*-β-*naphthol*, m. p. 168—170°, yielding on hydrolysis 1-*mercuri*-1 : 2-*naphthaquinone*, *acetomercuric* 4-*nitro*-α-*naphtholate*, 2-*acetomercuri*-4-*nitro*-α-*naphthol*, m. p. 142°, yielding on iodination 2-*iodo*-4-*nitro*-α-*naphthol*, m. p. 115° (decomp.), 4-*acetomercuri*-2-*nitro*-α-*naphthol*, m. p. 185° (decomp.), 1-*acetomercuri*-2-*ethoxynaphthalene*, m. p. 103—104°, 1-*acetomercuri*-2-*bromonaphthalene*, m. p. 128—130°, N-*mercuri*-α-*naphthylamine*, $C_{10}H_7{\cdot}N{:}Hg$, m. p. 203° (decomp.), 1 : 1′-*diacetomercuri*-2 : 2′-*dinaphthylamine*, m. p. 198°, and the corresponding 1 : 1′-*di*-*iodo*-derivative, m. p. 165—166° (decomp.). Mercuration of naphthols, nitronaphthols, naphthyl ethers, and amines proceeds more readily than that of chloronaphthalenes. The mercury always occupies the *ortho*- and *para*-positions, never the *meta*-position; in this way mercury behaves as a halogen. The tenacity with which mercury is retained by the nucleus depends on other

substituents already present; thus the nitro-group produces a stabilising influence as compared with the hydroxy-group. R. TRUSZKOWSKI.

Salt formation of chromium pentaphenyl hydroxide, $CrPh_5{\cdot}OH$. F. HEIN [with O. SCHWARTZKOPFF, K. HOYER, H. KLAR, W. EISSNER, and W. CLAUSS] (Ber., 1928, **61** [*B*], 730—753).—The production of salts from chromium pentaphenyl hydroxide has been examined with numerous acids and phenols, whereby in part chromium pentaphenyl and in part chromium tetraphenyl salts are obtained. The strength of the acid has some influence on the production of the penta- or tetra-phenyl salts, but is certainly not the sole decisive factor. The fate of the phenyl group, if eliminated, has not been ascertained. *Chromium pentaphenyl hydrogen carbonate*, $CrPh_5HCO_3,3H_2O$, m. p. 120° (also *di-* and *mono-hydrate*), is prepared by saturating a methyl-alcoholic solution of the base with carbon dioxide. With acetic acid in water or chloroform the hydroxide affords *chromium pentaphenyl acetate tetrahydrate*, m. p. 118° (also *dihydrate*); an *acid acetate*, $CrPh_5{\cdot}OAc,AcOH$, m. p. 108—110°, and a basic *salt*, m. p. 51—53° after softening at 45°, are also described. Monochloroacetic acid yields a *chromium pentaphenyl* salt (trihydrate, m. p. 103°, and anhydrous), whereas dibromomalonic acid smoothly yields *chromium tetraphenyl hydrogen dibromomalonate*, m. p. 88·5°. *Chromium tetraphenyl hydrogen oxanilate*, m. p. 141°, *acid* r-*α-chlorophenylacetate*, m. p. 118°, and *acid α-bromocinnamate*, m. p. 127°, are described. Equivalent amounts of the pentaphenyl hydroxide and benzoic acid in chloroform afford *chromium tetraphenyl benzoate trihydrate*, m. p. 99°, whilst with excess of acid the corresponding *acid benzoate dihydrate*, m. p. 84°, is obtained. Anthranilic acid, on the other hand, affords *chromium pentaphenyl acid anthranilate*, m. p. 141—142°. From *p*- and *m*-aminobenzoic acid the *salts* $3NH_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CrPh_4,2NH_2{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 141°, and $2NH_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CrPh_4,NH_2{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 130°, are derived. *N*-Phenylanthranilic acid differs from the parent acid in giving the *chromium tetraphenyl* salt, $2NHPh{\cdot}C_6H_4{\cdot}CO_2{\cdot}CrPh_4,NHPh{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 105°. *Chromium tetraphenyl* o-*chlorobenzoate*, m. p. 107° after blackening at 104°, the m-*bromobenzoate*, $2C_6H_4Br{\cdot}CO_2{\cdot}CrPh_4,C_6H_4Br{\cdot}CO_2H$, m. p. 97°, *chromium tetraphenyl* m-*nitrobenzoate*, m. p. 90°, and the corresponding *acid* 3 : 5-*dinitrobenzoate*, blackening above 149°, are described. *Chromium tetraphenyl acid* 5-*nitrosalicylate* has m. p. 132°. *Chromium pentaphenyl sulphate tetrahydrate* (also anhydrous, m. p. 130°, and $+3COMe_2$, m. p. 143—144°) is prepared from the reactants in alcoholic solution. On the other hand, sulphonic acids give *chromium tetraphenyl* salts of which the 1 : 2 : 3 : 4-*tetrahydronaphthalene-2-sulphonate*, m. p. 131° (decomp.), and the *azobenzene*-p-*sulphonate monohydrate*, m. p. 167° (decomp.), are described. *Chromium tetraphenyl sulphanilate*, m. p. 90°, and the *compound* $CrPh_4Cl,0{\cdot}5CHCl_3$, m. p. 118°, are described incidentally.

Phenol in absolute alcoholic solution gives the *compound* $CrPh_5{\cdot}OPh,PhOH$, m. p. 127°, whereas in aqueous alcohol abnormal salt formation occurs with production of the *substance* $CrPh_4{\cdot}OPh,PhOH$, m. p. 145°, identical with the product of the action of an excess of phenol on chromium tetraphenyl hydroxide. *m*-Chlorophenol and chromium pentaphenyl hydroxide in absolute alcohol afford the *compound* $C_6H_4Cl{\cdot}O{\cdot}CrPh_5,C_6H_4Cl{\cdot}OH$, m. p. 112·5—113°, which when crystallised from a mixture of alcohol and acetone or submitted to protracted washing with ether gives the *tetraphenyl* derivative, $C_6H_4Cl{\cdot}O{\cdot}CrPh_4,C_6H_4Cl{\cdot}OH$, m. p. 129·5—131°, thus illustrating the influence of the solvent on the course of the change. *p*-Cyanophenol and *m*-nitrophenol give the *chromium pentaphenyl* salts, $2CN{\cdot}C_6H_4{\cdot}O{\cdot}CrPh_5,CN{\cdot}C_6H_4{\cdot}OH$, m. p. 123·5°, and $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CrPh_5,NO_2{\cdot}C_6H_4{\cdot}OH$, m. p. 86°, whereas all the other phenols investigated afford chromium tetraphenyl derivatives. From *o*- and *p*-nitrophenol the *compounds* $NO_2{\cdot}C_6H_4{\cdot}OCrPh_4$, m. p. 130°, and $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CrPh_4,NO_2{\cdot}C_6H_4{\cdot}OH$, m. p. 134°, are obtained, whereas *p*-bromophenol affords the salt $C_6H_4Br{\cdot}O{\cdot}CrPh_4,C_6H_4Br{\cdot}OH$, m. p. 121°. Pyrocatechol, resorcinol, and quinol afford sparingly soluble, well-crystallised *salts*, $OH{\cdot}C_6H_4{\cdot}O{\cdot}CrPh_4,C_6H_4(OH)_2$, m. p. 153·5°, 180—181°, and 206° (decomp.) after softening, respectively. 3-Nitropyrocatechol and 2-nitroquinol give *compounds*, $OH{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CrPh_4$, m. p. 157° and decomp. 175°, whereas 2-nitroresorcinol yields the *substance* $NO_2{\cdot}C_6H_3(O{\cdot}CrPh_2)_2,2NO_2{\cdot}C_6H_3(OH)_2$, m. p. 162·5° (decomp.). *Chromium tetraphenyl* o-*nitro*-p-*tolyloxide* has m. p. 135°. 2 : 6-Dinitrophenol affords the normal *salt*, m. p. 160° (violent explosion), whereas dibromoquinol yields the *compound* $C_6H_2Br_2(O{\cdot}CrPh_4)_2,C_6H_2Br_2(OH)_2$, m. p. 184—185°. 2 : 4 : 6-Tribromophenol and picrolonic acid give the *substances* $C_6H_2Br_3{\cdot}O{\cdot}CrPh_4$, m. p. 153°, and $C_{34}H_{27}O_5N_4Cr$, m. p. 176°.

The chloroform layer obtained during the preparation of chromium pentaphenyl hydroxide is repeatedly shaken with water, dried over potassium carbonate, and evaporated over paraffin in a vacuum. The residue is treated with ether and extracted with alcohol. After removal of ionic halogen by silver hydroxide, stable alcoholic solutions remain which are used in the preparation of the following salts: *dibromogallates*, $(OH)_3C_6Br{\cdot}CO_2{\cdot}CrPh_5$ and $(OH)_3C_6Br{\cdot}CO_2{\cdot}CrPh_4$, and the *compound* $[(CNS)_4Cr(NH_3)_2]CrPh_5,Et_2O$. H. WREN.

Synthesis of dipeptide anhydrides containing arginine. M. BERGMANN and H. KOSTER (Z. physiol. Chem., 1928, **173**, 259—267; cf. A., 1927, 755).—d-*Phenylalanyl*-d-*arginine anhydride* has been prepared from the salicylaldehyde compound of *d*-phenylalanyl-*d*-arginine and also by the action of methyl-alcoholic ammonia on the ester hydrochloride of the dipeptide, as the *hydrochloride*, m. p. 261—262°, *sulphate*, m. p. 270°, and *picrate*, m. p. 246°. *d*-Phenylalanyl-*d*-arginine anhydride is readily hydrolysed by alkalis and in aqueous solution it undergoes "autohydrolysis" due to the alkalinity of its guanidine group; the hydrolysis can be prevented by the addition of 1 mol. of hydrochloric acid. Free arginine has a similar hydrolytic action on aqueous solutions of glycine anhydride. The possible influence of the

arginine present in proteins containing diketopiperazine structures on the hydrolysis of these proteins in aqueous solution is discussed. Inactive *phenylalanylarginine anhydride* has been prepared as the *hydrochloride*, m. p. 242°. A. WORMALL.

Preparation of *l*-histidine from protein. J. KAPFHAMMER and H. SPORER (Z. physiol. Chem., 1928, **173**, 245—249).—The "Reineckate" method (cf. this vol., 527, 542) has been utilised for the preparation of *l*-histidine, which forms a relatively insoluble "Reineckate," the solubility of this compound being between those of the similar compounds of *l*-proline and *l*-hydroxyproline. The protein (hæmoglobin etc.) is hydrolysed by acid, the arginine precipitated as flavianate, and the filtrate treated with "Reinecke" acid, whereby the "Reinecke" compounds of *l*-histidine, *l*-proline, and *l*-hydroxyproline are precipitated. To remove the "Reinecke" acid the precipitate is treated with copper sulphate and sulphur dioxide in methyl-alcoholic solution, the filtered solution is freed from copper, sulphuric acid, and chromium, and after concentration in a vacuum, *l*-histidine is precipitated as the insoluble picrolonate, leaving *l*-hydroxyproline and *l*-proline in solution; the proline is then separated as the double salt with cadmium chloride. 12·2 g. of histidine hydrochloride, 5·9 g. of the proline–cadmium chloride compound (corresponding with 2·17 g. of proline), and 4·0 g. of hydroxyproline have been obtained from 250 g. of hydrolysed hæmoglobin. The properties of *histidine "Reineckate,"* $C_6H_9N_3O_2,2C_4H_7N_6S_4Cr,4H_2O$, decomp. 220°, are given. A. WORMALL.

Behaviour of polypeptides and their derivatives towards alkalis and acids. V. Polypeptides built up from glycine. E. ABDERHALDEN and S. SUZUKI (Z. physiol. Chem., 1928, **173**, 250—258).—Tetraglycylglycine, pentaglycylglycine, and heptaglycylglycine are hydrolysed by *N*-hydrochloric acid at 16° and more quickly at 37°, but the hydrolysis by *N*-sodium hydroxide is more marked, a result similar to that obtained previously with glycylglycine, diglycylglycine, and triglycylglycine (this vol., 81). Measurements of the rate of hydrolysis by 0·5*N*- and *N*-sodium hydroxide of these polypeptides and their benzoyl and β-naphthalenesulphonyl derivatives show that the velocity of the hydrolysis increases with the length of the chain or with the introduction of the benzoyl group; the benzoyl group has a greater accelerating effect than the addition of one glycine molecule to the chain, whilst the β-naphthalenesulphonyl group has an inhibitory effect. Tetraglycylglycine is hydrolysed at 37° in concentrations of alkali as low as p_H 9·16 and to a slight extent at p_H 8. The preparation of the benzoyl and β-naphthalenesulphonyl derivatives of triglycylglycine, tetraglycylglycine, and pentaglycylglycine is described. A. WORMALL.

Tetrapeptide from gliadin. R. NAKASHIMA (J. Biochem. Japan, 1927, **7**, 441—446).—A tetrapeptide composed of tyrosine (1 mol.) and glutamic acid (3 mols.) was completely hydrolysed by erepsin, but not by trypsin. CHEMICAL ABSTRACTS.

Porphyrins. XIV. Addition of halogen to hæmin. W. KUSTER and H. BOSCH. **XV. Porphyrin formation from monoethylated hæmins.** W. KÜSTER and R. FLEISCHMANN (Z. physiol. Chem., 1928, **172**, 72—97, 98—125; cf. A., 1927, 980).—XIV. The action of aniline on acetic acid-hæmin differs from that of pyridine, and the solution of the hæmin in pyridine gives a hæmochromogen spectrum, whilst the aniline solution gives a hæmatin spectrum. Addition of bromine to de(hydrochloride)hæmin results in the elimination of hydrogen bromide and the formation of *dibromohæmin bromide*, $C_{34}H_{30}O_4N_4Br_3Fe$; this product by the action of hydrogen bromide and acetic acid and subsequent treatment with methyl alcohol yields the same dimethyl ether of dibromohæmatoporphyrin (no definite m. p.) as that produced from dibromodimethylhæmin bromide. Acetic acid-hæmin consists of a double molecule which is dissociated by pyridine into radical molecules and the iron tends to go to the ferrous state, as shown by the hæmochromogen spectrum, whilst there is wandering of the pyridinium structure ($C_5H_5NCl{\cdot}Fe<$) formed from pyridine and the chloroferri-group to the radical position. The different action of aniline is explained as the decomposition of the double molecule with the addition of a hydrogen atom to each portion; in addition, aniline has a reducing action, the aniline being thereby oxidised to dianiloquinoneanil. Aniline subsequently attaches itself to the chloroferri-group and to the lactone group; if the aniline solution is treated with dilute acetic acid, formation of the carboxyl and free hydroxyvinyl groups occurs. The relationship between these differences in the action of aniline and pyridine and the lactone structure of hæmin is discussed.

XV. Experiments made to determine the constitution of the prosthetic group of hæmoglobin indicate that isomerides of acetic acid-hæmin, monomethylated and dimethylated hæmins exist. Three preparations of monoethylhæmin chloride obtained by different methods have been examined and compared. The first, prepared from the blood of a horse inoculated with glanders, is soluble in chloroform, is not methylated by diazomethane, and is insoluble in 5% sodium hydroxide at the ordinary temperatures, although on digestion with this alkali 71% of the chlorine is removed. In chloroform solution 2 atoms of chlorine can be added (without substitution), and this dichloroethylhæmin chloride, on decomposition with hydrogen bromide and acetic acid and treatment with methyl alcohol, yields a *dimethyl ether* of *chlorohæmatoporphyrin*, $C_{36}H_{39}O_6N_4Cl$ (complex *zinc* salt), which on treatment with diazomethane takes up two methyl groups. It is concluded that addition of chlorine to the vinyl group of the hæmin occurs and that the second side-chain retains its lactone structure until the treatment with hydrogen bromide. A second ethylhæmin chloride, prepared from the same blood by a modified method, is soluble in chloroform, soluble in cold sodium hydroxide, and insoluble in sodium hydrogen carbonate, whilst 64% of the chlorine is removed by treatment with the latter; on long treatment with diazomethane one methyl group is added. The porphyrin derivative prepared from it is a mixture of the dimethyl ether of chlorohæmatoporphyrin and the dimethyl ether of chlorobromomesoporphyrin, $C_{36}H_{40}O_6N_4ClBr$, these being separ-

ated as the zinc salts. A betaine structure is suggested for this second ethylhæmin chloride. From the same blood a third ethylhæmin chloride can be obtained by making the sulphuric acid–ethyl alcohol extract of the blood alkaline with alcoholic potassium hydroxide, extracting the precipitate with acidified alcohol, and precipitating from the boiling extract with hydrochloric acid. Of the crude product 75% is soluble in chloroform and this portion is soluble in sodium hydroxide, insoluble in sodium hydrogen carbonate (in which it loses 65% of its chlorine), and is slowly monomethylated by diazomethane; addition of chlorine occurs without substitution to give a crystalline dichloroethylhæmin chloride. The porphyrin preparation obtained by the method used before is the same mixture as is obtained from the second hæmin derivative, with, however, more of the dimethyl ether of chlorobromomesoporphyrin. By the action of hydrogen bromide and acetic acid on a preparation obtained by decomposition of coagulated blood-corpuscles with methyl alcohol at 180°, a mixture of a porphyrin and proline is obtained. No combination of proline and hæmochromogen occurs in an atmosphere of carbon monoxide. A. WORMALL.

Natural porphyrins. XXII. Hæmin obtained from yeast. H. FISCHER and F. SCHWERDTEL (Z. physiol. Chem., 1928, **175**, 248—260).—The presence of hæmin, identical with that obtained from animal origin, has been demonstrated in a vegetable organism by its isolation, using special experimental precautions, from yeast. The yeast is first plasmolysed for 48 hrs. with salt solution and then extracted with a mixture of pyridine and ether until 80% of the hæmin present has been removed. The filtered solution, which exhibits an intense hæmochromogen spectrum, is extracted with water. Removal of the pyridine from the aqueous layer by extraction with ether causes the precipitation of a flocculent material. The first fraction of the precipitate is yellowish-brown and gives a negative Teichmann reaction, but the main fraction is brownish-violet and gives an intense hæmochromogen spectrum and a typical positive Teichmann reaction. This precipitate is heated with acetic acid and salt and, after 24 hrs., the separated solid is filtered and extracted with a pyridine–chloroform mixture. After repetition of this process of purification a crystalline specimen of hæmin, identical in physical and chemical properties with animal hæmin, is obtained. It is considered probable that some of the hæmin exists in the yeast in the free state, whilst a portion is combined with albumins and is liberated by the yeast enzymes during the (necessary) prolonged period of plasmolysis. In some cases a by-product is obtained which, from spectroscopic evidence, appears to be a tin salt of protoporphyrin. The proportion of coproporphyrin and protoporphyrin formed in the autolysis of yeast depends on the hydrogen-ion concentration. When alkali is used much coproporphyrin and no protoporphyrin is obtained, whilst with acids very little of the former and much of the latter is produced, the proportion of hæmin being the same in each case. J. W. BAKER.

Blood pigments. IV. W. KUSTER and K. KIMMICH (Z. physiol. Chem., 1928, **172**, 199—224).—It has been shown (Chem. Zelle Gewebe, 1926, **13**, 66) that hæmoglobin contains a sterol as an integral constituent, the quantity of free sterol isolated together with steryl esters in the preparation of hæmin being greater from blood-corpuscles than from total blood of the same animal.

Purified, crystalline oxyhæmoglobin, freed from uncombined sterol by ether extraction at 15°, undergoes alteration when extracted for 24 hrs. with boiling, dry ether, being no longer completely soluble in water but containing, with unchanged oxyhæmoglobin, soluble methæmoglobin and insoluble cathæmoglobin; sterol is liberated during this process, and also during the subsequent separation of the methæmoglobin by coagulation at 55°, and of the oxyhæmoglobin at 70°. The crude sterol in each case contains an oxidised sterol, m. p. 240—241°. The structural relationship between hæmoglobin and methæmoglobin is discussed in the light of these facts.

The preparation of oxy- and met-hæmoglobins, the fission of crystallised hæmoglobin by diazomethane in chloroform, and by hydrochloric acid, and the fission of crystallised oxyhæmoglobin by ether and by water in a closed vessel, are detailed.

C. HOLLINS.

Blood. V. Isomeric non-alkylated hæmins. W. KÜSTER [with A. JOB and M. GREISS] (Z. physiol. Chem., 1928, **172**, 138—158).—Chlorohæmin has been prepared from ox-blood, horse-blood, and cow's blood by various methods. Older animals give a larger yield than young animals, possibly due to the presence in the former of more readily decomposable hæmoglobin. Acetone-chlorohæmin crystallises in two forms at least—needles and Teichmann's crystals—and from the differences in the properties of the various preparations obtained it is suggested that at least four modifications of the isomeric substances of formula $(C_{34}H_{29}O_4N_4FeCl)_2$ exist. This would be possible on the assumption of a betaine structure (cf. A., 1926, 315) or a lactone structure, whilst if hæmin exists as a double molecule (which is highly probable) the number of possible isomerides is even larger. The results of experiments with diazomethane indicate that besides methylation other changes usually occur which render the methylated hæmins non-crystallisable. Aniline has an action similar to that of pyridine on the chloroferri- and the lactone groups, but no dissociation of the double molecule occurs with the former solvent. The significance of the differences in the action of these two bases and the possible structures of the chlorohæmins are discussed. A. WORMALL.

Fluorohæmin. W. KÜSTER and O. NEUNHÖFFER (Z. physiol. Chem., 1928, **172**, 179—181).—Monoethyl(chloro)hæmin, prepared by the glacial acetic acid method, is suspended in acetone and boiled with excess of aqueous silver fluoride. After removal of silver chloride by filtration, *monoethylfluorohæmin*, $(C_{34}H_{29}O_4N_4FFe)_2$, is obtained from the acetone solution as a black, indistinctly crystalline power, showing an absorption band at 605—630µ.

C. HOLLINS.

Bromoporphyrin I and tetramethylhæmatoporphyrin iron salt. II. H. FISCHER and G.

HUMMEL (Z. physiol. Chem., 1928, **175**, 75—96; cf. A., 1927, 886).—Bromination of tetramethylhæmatoporphyrin iron salt in chloroform gives a crystalline product identical with the complex iron salt of the ester of bromoporphyrin I, which yields bromoporphyrin I on removal of iron by sulphuric acid, hydrobromic–acetic acid, or hydriodic–acetic acid, and on oxidation bromocitraconimide, m. p. 178°. The identity of the bromoporphyrin I is confirmed by preparation of the methyl ester, m. p. 277°, and its copper salt, m. p. 283° (sometimes 272°), and iron salt, m. p. 295°; oxidation of the ester gives hæmatic acid, m. p. 114°. The bromine in bromoporphyrin I is not removed by 5% potassium hydroxide at 140°, potassium methoxide at 180°, or hydrobromic–acetic acid at 180°. Bromoporphyrin I results when tetramethylhæmatoporphyrin is brominated in acetic acid.

By the action of methyl-alcoholic hydrogen chloride on hæmin, or hæmin crystallised from acetic anhydride, there are formed tetramethylhæmatoporphyrin and its iron salt, methyl alcohol being added at the side-chain double linking. Tetramethylhæmatoporphyrin iron salt is converted by hydrobromic–acetic acid at 180° into mesoporphyrin methyl ester, m. p. 204°. Protoporphyrin reacts with methyl-alcoholic hydrogen chloride more slowly than hæmin. Oxidation of protoporphyrin with permanganate yields a new *porphyrin*. C. HOLLINS.

Crystallisation of casein. S. S. PEROV (Trans. Volgoda Dairy Inst., 1925, Bull. **50**. 1—15).—Casein from milk (100 c.c.) and acetic acid (10%, 5 c.c.) is collected, washed with water, alcohol, and ether, and then precipitated from alkaline solution (1 g. and 8·2 c.c. of 0·1*N*-sodium hydroxide) with acetic acid (2 c.c. of 10% acid for 1 g. of soluble sodium salt), washed with alcohol, then with ether, and dried at 45°. Of this substance (equivalent weight 1220), 0·081 g. is dissolved in 0·68 c.c. of 0·1*N*-sodium hydroxide and diluted to 500 c.c., and 500 c.c. of *N*/7500 hydrochloric acid are added, with stirring. Several drops of toluene are added, and the solution is left in the dark for 9—10 days. Monoclinic and triclinic crystals are obtained. CHEMICAL ABSTRACTS.

Products of oxidation of keratin by permanganate. II. T. LISSIZIN (Z. physiol. Chem., 1928, **173**, 309—311).—Acid hydrolysis of a product formed by the oxidation of keratin (human hair) by potassium permanganate yields *dl*-cysteic acid. A. WORMALL.

Proteins. IV. Hypobromite reaction with amino-acid derivatives. P. BRIGL, R. HELD, and K. HARTUNG (Z. physiol. Chem., 1928, **173**, 129—154).—The ability of the following amino-acid derivatives to react with hypobromite has been tested: δ-benzamidovaleric acid, *dl*-ornithuric acid, δ-benzoylornithine, barium carbamylacetate, glycylglycinecarboxylic acid, barium carbamate of glycylglycine, carbonylbisglycylglycine, *N*-carbamyl-leucine, 5-*n*-butylhydantoin, creatine, creatinine, arginine, dibenzoylarginine, and ε-guanido-*n*-hexoic acid. The results are given in tabular form, particular attention being paid to the rapid uptake, during some 10—15 min., of hypobromite. Acylation of the amino-group, even with carbonic acid, prevents the uptake of hypobromite, exceptions to this rule being substituted carbamides, such as carbonylbisglycylglycine and leucineuraminic acid. . The guanido-group reacts with hypobromite unless acylated. The results are discussed in regard to the modes of linking of amino-acids in the protein molecule. H. D. KAY.

Basic proteins and their development. A. KOSSEL and E. G. SCHENCK (Z. physiol. Chem., 1928, **173**, 278—308).—Protamines may be classified as mono-, di-, and tri-protamines according to the nature of the hexone bases present; cyprinin which contains arginine and lysine is a diprotamine, as is percin which contains arginine and histidine. Most of the known histones contain all three hexone bases. It is suggested that a third group of basic proteins should be added, "basic peptones," which, like the protamines, are to be classified as mono-, di-, and tri-peptones according to the hexone bases present. These basic peptones contain no sulphur or phosphorus, but contain hexone bases which account for 25—65% of the total nitrogen; they differ from the protamines and histones in giving no precipitate with ammoniacal protein solution, potassium ferrocyanide, or sulphosalicylic acid. They are digested to some extent by pepsin, yielding basic peptones with a different composition from that of the original product. Carp sperm contains a protamine (cyprinin), basic di- and tri-peptones, and in one preparation a cyprohistone, all of which have been examined and analysed; on digestion with pepsin, the histone yields products intermediate between histones and basic peptones, whilst the basic dipeptones yield products (basic peptones) which are less rich in bases. Similar investigations have been carried out with herring sperm, and several clupeins, basic clupeodipeptones, and a small amount of clupeotripeptone separated. Barbel sperm, but not salmon or sturgeon sperm, yields basic peptones. Trout sperm contains a monoprotamine ("truttin") which may be identical with salmin. The sperm of the carp at different stages in ripening of the testes has been examined to determine the relationship between the different groups of basic proteins. From February to May there is a marked decrease in the basic peptones, with a decrease in the hexone base content of these proteins. The relationship between the basic proteins of carp sperm and the history of the development of these proteins are discussed. A. WORMALL.

Scleroproteins. R. O. HERZOG (Helv. Chim. Acta, 1928, **11**, 529—533).—A lecture delivered to the Swiss Chemical Society. H. BURTON.

Physico-chemical analysis of changes in proteins by heat. Reversibility of albumin denaturation. M. SPIEGEL-ADOLF (Naturwiss., 1927, **15**, 799—803; Chem. Zentr., 1927, ii, 2316).—Heat-treatment of globulin affects the terminal amino- and carboxyl groups; the peptide linkings are modified to a small extent only. The effect of heating on the solubility in alkali and reprecipitation on neutralisation of globulin, serum-albumin, and ovalbumin is discussed. Ring-closure is more probable than hydrolysis. A. A. ELDRIDGE.

Determination of the equivalent weight of proteins. A. E. STEARN (J. Gen. Physiol., 1928, **11**, 377—389).—Results are given of experiments indicating that the same amount of 0·1*N*-acid is equivalent to 1 g. of gelatin whether the gelatin is titrated with acid or the acid with gelatin. In the case of gelatin and sodium hydroxide, a slightly higher equivalent weight for gelatin is obtained when titrating base with protein than when protein is added to base. From this it is concluded that in the case of gelatin, the reactions are due to chemical neutralisation, and any adsorption of acid or alkali is negligible.

E. A. LUNT.

Determination of diamino-nitrogen in the products of hydrolysis of proteins. J. C. KERNOT and J. KNAGGS (Biochem. J., 1928, **22**, 528—534).—The percentage of nitrogen precipitated by phosphotungstic acid from the products of hydrolysis of a protein depends on the concentration of nitrogen in the solution, the conditions of precipitation, such as temperature, the concentration of the acid used for the hydrolysis of the protein, and the period of contact of the protein with the cold acid before hydrolysis.

S. S. ZILVA.

Variation of the Carius method for sulphur determination. V. C. ROGERS and G. DOUGHERTY (J. Amer. Chem. Soc., 1928, **50**, 1231—1232).—The amount by which the rate of oxidation of sulphonal by nitric acid (*d* 1·60) is accelerated by the addition of equivalent amounts of bromine, barium bromide, barium nitrate, barium chloride, and sodium chloride increases in the order given. Accordingly, the use with difficultly oxidisable substances of 0·3—0·4 g. of sodium or potassium chloride and 3 c.c. of nitric acid is recommended.

H. E. F. NOTTON.

Micro-phosphorus determination. A. ELEK (J. Amer. Chem. Soc., 1928, **50**, 1213—1214).—A rapid and accurate modification of Lieb's method (cf. A., 1924, ii, 781). The substance (3—6 mg.) is oxidised to phosphate by fusion with potassium hydroxide and nitrate in a platinum crucible. Results are given for some nucleic acid derivatives.

H. E. F. NOTTON.

Unification of bromination methods of analysis as applied to phenols and aromatic amines. A. R. DAY and W. T. TAGGART (Ind. Eng. Chem., 1928, **20**, 545—547).—Koppeschaar's bromination method for the determination of phenols and aromatic amines, in which an excess of bromine is used and the excess determined by addition of potassium iodide and titration with sodium thiosulphate, is, when applicable, more satisfactory then direct titration with potassium bromate. A general procedure for the excess method is described and good results were obtained with phenol, *o*-, *m*-, and *p*-nitrophenols, 2 : 4-dinitrophenol, *p*-chlorophenol, salicylic acid, *m*-hydroxybenzoic acid, methyl salicylate, acetylsalicylic acid, phenyl salicylate, *m*- and *o*-cresols, resorcinol, β-naphthol, thymol, aniline, *p*-chloroaniline, *o*- and *m*-nitroanilines, acetanilide, sulphanilic acid, metanilic acid, anthranilic acid, *m*-aminobenzoic acid, and *o*-, *m*-, and *p*-toluidines.

E. H. SHARPLES.

Determination of tannic acid. S. KRISHNA and N. RAM (Ber., 1928, **61**, [*B*], 771—781).—Tannic acid may be determined by adding to its aqueous solution an excess of titanium chloride, removal of the precipitated *titanium tannate*, $TiO(C_{14}H_{10}O_9)$, in an atmosphere of carbon dioxide, and titration of the excess of titanium chloride by ferric alum; precipitation is incomplete at 22°, but becomes quantitative at 40—50°. Gallic, salicylic, mandelic, and other hydroxy-acids yield precipitates with titanium chloride, but these can be retained in solution without affecting the precipitated titanium tannate if hydrochloric acid within certain limits of concentration is added. On the assumption that the mol. wts. of the technical tannins are all approximately equal, the method can be applied to the determination of tannins in extracts of *Acacia Arabica* and myrobalans if similar precautions with regard to the concentration of hydrochloric acid are taken. Comparison with the hide powder method shows that the latter indicates only 90% of the tannic acid present and is seriously affected by the simultaneous presence of gallic acid.

H. WREN.

Determination of phenylalanine by an oxidative method. G. KOLLMANN (Biochem. Z., 1928, **194**, 1—14).—A method is described for the determination of phenylalanine by oxidation to benzoic acid with potassium dichromate in acid solution. Using pure phenylalanine or adding it to the protein hydrolysate, the method gave a mean determination of 95·2%. The phenylalanine contents of the following proteins are: caseinogen, 3·10%; fibrin, 2·11%; edestin, 3·47%; hæmoglobin, 3·57%; zein, 6·57%, legumin, 5·10%; gelatin, 0·24%. The nitrogen is almost entirely liberated as ammonia. By oxidation of caseinogen, about 17% of the carbon is left in the form of volatile acids, chiefly *iso*valeric acid, 7% as succinic acid, 32% as carbon dioxide; oxalic and other acids are also present. For complete oxidation, however, the amount of dichromate used only corresponds with about one third of that necessary to oxidise it completely to carbon dioxide, ammonia, and water.

P. W. CLUTTERBUCK.

Alkalimetric determination of amino-acids and peptides by the method of Willstatter and Waldschmidt-Leitz. E. TAKAMIYA (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 66—67).—Temperature and dilution are without influence. Alcoholic solutions of amino-acids do not react as acids towards either rosolic acid or *p*-nitrophenol. Acids and alkalis depress the titration values, the depression being the greater the lower is the concentration of alcohol. Manganese and magnesium salts must be absent.

CHEMICAL ABSTRACTS.

Identification of organo-magnesium halides by crystalline derivatives prepared from α-naphthylcarbimide. H. GILMAN and M. FURRY (J. Amer. Chem. Soc., 1928, **50**, 1214—1216).—Small quantities of Grignard reagents and similar organometallic derivatives may be rapidly identified by means of α-naphthylcarbimide. The resulting acyl-α-naphthylamines are usually easily separated from *s*-di-α-naphthylcarbamide. In this way *hexahydrobenzoyl*-, m. p. 188° (uncorr.); *phenylacetyl*-, m. p. 166°; *cinnamoyl*-, m. p. 217°; p-*toluoyl*-, m. p. 173°,

and *α-naphthoyl-*, m. p. 236°, *-α-naphthylamines* have been prepared. H. E. F. NOTTON.

Volumetric determination of carbamide by oxidation of xanthylcarbamide. H. CORDEBARD (Bull. Soc. Chim. biol., 1928, **10**, 461—471).—When xanthhydrol is added to a boiling aqueous solution of sulphuric acid and potassium dichromate, it is partly converted into xanthane, which volatilises and escapes oxidation. By preliminary treatment at the ordinary temperature with the oxidising agent only xanthone is obtained, and this, on boiling the solution, is quantitatively oxidised to carbon dioxide and water. These facts are applied to the determination of small amounts of carbamide, which, when isolated in the form of the dixanthyl derivative by precipitation with an excess of xanthhydrol and acetic acid, may be titrated with a standard solution of potassium dichromate and sulphuric acid. Three mols. of dixanthylcarbamide require 58 mols. of potassium dichromate for complete oxidation.

G. A. C. GOUGH.

Detection of hydroxylamine. J. BLOM.—See this vol., 674.

Biochemistry.

Concentration of carbon dioxide in successive portions of an expired breath. R. S. AITKEN and A. E. CLARK-KENNEDY (J. Physiol., Proc. Physiol. Soc., 1927, **64**, xvii—xviii).—An S-shaped curve is obtained. A. A. ELDRIDGE.

Identification of blood in the insoluble state. F. PISANI (Arch. Farm. sperim., 1928, **44**, 260—264).—The blood spot is dissolved in potassium hydroxide solution, when globin and hæmatin are produced. The alkaline solution is shaken with saturated ammonium sulphate solution and pyridine; this precipitates the protein and the hæmatin and the latter dissolves in the pyridine, which is shaken with saturated ammonium sulphate solution. A few drops of the clear pyridine solution are evaporated at 70—80° on a microscope slide and the residue is treated with acetic acid and sodium chloride; the hæmin crystals appear as long, thin, reddish-brown prisms. The remainder of the pyridine solution is examined spectroscopically, the spectrum exhibiting a very pronounced line just beyond the *D* line and being extinguished towards the blue. Addition of a few drops of ammonium sulphide to the pyridine solution of the alkaline hæmatin converts this into hæmochromogen, which shows two absorption lines, one between *D* and *E* in the yellow and the other between *E* and *F*. T. H. POPE.

Occurrence of ergosterol in ox blood. W. KÜSTER and O. HÖRTH (Ber., 1928, **61**, [*B*], 809—811).—Ergosterol, identified crystallographically and by Salkowski's reaction, has been isolated from the alcohol–sulphuric acid extract of ox blood obtained by treatment of the whole blood by Morner's method.

H. WREN.

Displacement of the isoelectric point of erythrocytes depending on their age. A. H. ANDRES (Zhur. exp. Biol. Med., 1927, **6**, 285—299).—The isoelectric point of erythrocytes from white rats, determined in a buffered 8% sucrose solution, is at p_H 4·4—4·8. CHEMICAL ABSTRACTS.

Preparation and properties of erythrocyte-stromata. F. HAUROWITZ and J. SLÁDEK (Z. physiol. Chem., 1928, **173**, 268—277).—Erythrocytes free from plasma, leucocytes, and platelets have been obtained by the following method. Fresh horse blood is mixed with an equal volume of citrate solution (0·75% sodium citrate and 0·9% sodium chloride), kept, and the erythrocyte layer filtered through cotton wool. The filtrate is treated with citrate solution, centrifuged, and the deposit filtered, and the process repeated four times. The suspension of erythrocytes is washed repeatedly with 0·9—1·2% sodium chloride, water and toluene are added, and the mixture is shaken and kept in an ice-chest for 48 hrs. After complete hæmolysis the solution is centrifuged and yields three layers, a bottom layer of hæmoglobin solution, a colourless middle layer of stromata, and the toluene layer. The stromata have been analysed and figures are given for the total lipins (part soluble in toluene, part in ether, and part soluble in hot alcohol but insoluble in ether), phosphatide, cholesterol (which accounts for the whole of the unsaponifiable matter), and fatty acids. The distribution of phosphatide, unsaponifiable matter, and fatty acids varies considerably with different preparations. The proteins of the stromata, from which nucleoprotein and globulin are almost entirely absent, have been examined quantitatively and the nitrogen distribution has been determined. The stroma-protein powder still contains some hæmoglobin and an analysis has been made of the nitrogen distribution of that part which is digested by pepsin (hæmoglobin ?) and that undigested. The latter (true stroma-protein) is not digested by pepsin or trypsin, is almost free from phosphorus, and contains small quantities only of sulphur; it is thus not of the keratin type.

A. WORMALL.

Formation of crystals within the red blood-corpuscle. H. W. KRANZ (Z. Biol., 1928, **87**, 258—268).—When viewed through the polarising microscope red blood-corpuscles fixed by dichromate according to a method fully described show a spherulitic appearance indicating the presence of crystals within them. The conditions of formation and properties of these crystals are described.

W. O. KERMACK.

Preparation of oxyhæmoglobin crystals from ox blood. W. MARSHALL (J. Physiol., Proc. Physiol. Soc., 1927, **64**, xxv—xxvi).—The corpuscular mass is washed three times with 1% sodium chloride solution, shaken with tap-water, and the mixture shaken with ether. The bottom clear solution is separated after 12 hrs., and 0·5 vol. of a mixture of 96% alcohol (70 parts) and ether-saturated water (30 parts) is added with agitation. After 30 min. the mixture is

barium chloride (at high concentrations a slight peptising action is observed) and peptised by saponin and bile salts. The latter also peptise cholesterol. The inhibitory action of egg-protein and blood-serum on the hæmolysis of the red blood-corpuscles of sheep is due to antagonistic action of the peptising and sensitising agents. Sodium glycocholate is a much more powerful hæmolytic agent than sodium taurocholate. G. A. C. GOUGH.

Antigenic character of albumins modified by heat and their specific differentiation by precipitant sera. E. NICOLAS and K. KATRANDJIEV (Compt. rend., 1928, **186**, 1068—1070).—The properties of the antisera obtained by the inoculation of rabbits with ox sera which have been coagulated at 80°, 100°, 110°, and 120° have been studied. The heat-coagulated proteins of the serum are antigens, this property being maintained even after heating at 120°. The antiserum obtained precipitates the antigen which has not been heated, and the alteration produced in the proteins by heat, treatment with sodium hydroxide, or even formaldehyde has no effect on their specificity of action. The antisera obtained will also precipitate the heated antigens and will react with an aqueous or 0·4% sodium chloride extract of the meat-muscle and blood-proteins. It is possible to prepare suitable solutions of the latter which after neutralisation and dilution react with the antisera obtained from rabbits which have been treated with the coagulated sera, but give only very feeble reactions with those obtained when a serum which has not been heated has been used. By these methods the specific differentiation of cooked meats can be achieved. J. W. BAKER.

Acetone method applied to study of distribution of antibodies on agglutinating sera during immunisation. M. PIETTRE and A. CHRÉTIEN (Compt. rend., 1928, **186**, 1240—1242).—The distribution of agglutinants between the three protein fractions obtained by acetone treatment of anti-paratyphoid-*B* serum, from a horse injected subcutaneously with washed bacilli, is demonstrated. The agglutinating action of the above serum, and also that of the protein constituents brought to the same concentration as in the serum, was compared under the same conditions. The serum-globulin was employed in faintly alkaline solution and the "myxoprotein" in physiological saline. The serum-globulin is the most active during the first phases and the serum-albumin later. The amount of total extract and particularly that of the serum-albumin increases with agglutinating power, a fact which was noted also during immunisation against rattlesnake venom. J. D. FULTON.

Specificity of muscle- and serum-proteins of animals. I. T. TADOKORO, M. ABE, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1927, **19**, 107—115).—Differences in the isoelectric point, specific rotatory power, and amino-acid content of myosin, myogen, and serum-globulin of the ox, horse, cock, and man are recorded.

CHEMICAL ABSTRACTS.

Egg-yolk oil. K. SUZUKI (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 54—55).—The oil (from white leghorns and Chinese hens) contained, as saturated fatty acids, *iso*palmitic and palmitic acids (2 : 1), and as unsaturated fatty acids, oleic with some linoleic acid. That from the former variety contained stearic acid, and from the latter a little arachidonic acid.

CHEMICAL ABSTRACTS.

Charcot–Leyden–Bottcher–Neumann crystals. A. NEUMANN (Z. physiol. Chem., 1928, **173**, 69—71).—A note, with reference to the publication of Wrede, Bolt, and Buch (A., 1927, 478) on the same subject. J. STEWART.

Oil from the abdomen of the queen ant. J. B. DA ROCHA (Bol. Soc. Chim. Sao Paulo, 1928, **1**, 27—30).—The abdomina of queens of the leaf-cutting ant *Atta sexdens* yielded 29% of oil by expression. The oil had the following properties: yellowish-red colour, rancid odour, setting point 8°, m. p. 13·5—15°, d^{15} 0·9753, n^{40} 1·456, butyrorefractometric index 46·0 at 40°, Reichert-Meissl value 1·43, total acid (as oleic acid) 48·5%, soluble acid (as butyric acid) 9·5%, iodine value (Hübl) 84, saponification value 187, soluble in 5 parts of boiling alcohol, in 50 parts at 25°, miscible with chloroform and ether, and, with slight deposit on keeping, with light petroleum, carbon disulphide, and benzene; ash (chiefly potassium sulphate and carbonate) 0·263%. A trace of lecithin was present. Extraction of the residue by carbon disulphide yielded 13·2% of its weight of solid, which, re-extracted and evaporated, gave a product of m. p. 46°, d^{25} 0·9196, total acid (as oleic acid) 91·9%. Subsequent extraction by alcohol removed 11·7% of reddish oil. R. K. CALLOW.

Chemistry of the placenta; presence of choline. H. SIEVERS (Z. Biol., 1928, **87**, 319—326).—From an aqueous placental extract spermine, neosine, and choline have been isolated. The presence of choline accounts for certain of the physiological properties of the extract. W. O. KERMACK.

Presence of a lactacidogen-like substance in glands. II. F. KRAUSE (Z. physiol. Chem., 1928, **173**, 235—244; cf. A., 1927, 901).—Stimulation of the salivary gland (parotid) of the dog by pilocarpine produces no increase in phosphoric acid, but the concentration of lactic acid (corrected for the increase in volume) increases slightly, the maximum increase being 20%. Muscle, liver, or pancreas pulp liberates phosphoric acid from the neutralised Schenck filtrate prepared from the resting gland (pancreas or liver). The precursor of this phosphoric acid is not nucleic acid, which was suggested as the source of the phosphoric acid liberated on incubation of pulped glands (*loc. cit.*), but is considered to be an organic phosphoric acid. No hexosemonophosphoric acid could be isolated, however, from ox pancreas or salivary glands by the method of Embden and Zimmermann (A., 1925, i, 729). A. WORMALL.

Identity of "kanirin" with trimethylamine oxide. F. A. HOPPE-SEYLER (Z. physiol. Chem., 1928, **175**, 300—303).—By a comparison of the physical constants and analytical data of the base, its hydrochloride, platinate, and picrate, "kanirin," isolated from the Japanese giant crab by Suzuki, Inouye, and Bharatkar (J. Coll. Agric. Tokyo, 1913,

5, 9), is shown to be identical with trimethylamine oxide. J. W. BAKER.

Isolation of various natural phosphoric acid compounds and their homogeneity. K. LOHMANN (Biochem. Z., 1928, **194**, 306—327).—Methods for the preparation of phosphagen and lactacidogen and for the determination of inorganic-, phosphagen-, and total phosphate are described. Investigation of the kinetics of the hydrolysis of the various phosphoric esters by acid shows that Embden's and Robison's esters, which are 30% hydrolysed in 3—4 hrs., cannot be identical with Neuberg's ester, which is 75% hydrolysed. It is suggested therefore that Neuberg's ester consists chiefly of a readily hydrolysable ketose ester together with a smaller amount of a difficultly hydrolysable aldose component, the latter predominating in the other two esters. The course of reaction of creatine phosphate in acid solution is, however, that of a unimolecular reaction. P. W. CLUTTERBUCK.

Occurrence of labile phosphorus in various kinds of muscles. L. IRVING and P. H. WELLS (J. Biol. Chem., 1928, **77**, 97—113).—The presence of labile phosphorus of the nature of phosphagen (cf. Eggleton and Eggleton, A., 1927, 271, 990) was demonstrated in the striated muscles of all vertebrates except fishes; it could not be detected in any muscle of invertebrates nor in plain muscle and heart muscle of vertebrates; its distribution seems, therefore, to run parallel with that of creatine.

C. R. HARINGTON.

Extractives of muscle. XXVII. Determination of carnosine. L. BROUDE (Z. physiol. Chem., 1928, **173**, 1—16).—By the action at the ordinary temperature, in an atmosphere of carbon dioxide, of an aqueous solution of sodium nitrite in presence of acetic acid, the β-alanine residue of carnosine is converted quantitatively into β-hydroxypropionic acid. Excess of nitrous acid is destroyed by treatment with aluminium in an alkaline solution, and after 22 hrs. the diluted solution is acidified with sulphuric acid and distilled (avoiding the use of rubber stoppers). Acrylic acid is determined in the distillate by its absorption of bromine. The method failed to determine more than 86·3% of the carnosine present, but is specific for this substance. J. STEWART.

New base from ox muscle, and its constitution. W. LINNEWEH (Z. physiol. Chem., 1928, **175**, 91—96). —The lysine fraction of the bases precipitated by phosphotungstic acid from Liebig's meat extract which has been freed from substances precipitable by tannic acid contains *crotonbetaine* [methylbetaine of γ-dimethylaminocrotonic acid], $NMe_3·CH_2·CH\!:\!CH·CO_2$, which is isolated as *chloroaurate*, m. p. 215—217° (corr.). The *chloride* is converted into the *ethyl ester chloroplatinate*, m. p. 223—225° (decomp.), and is hydrogenated to γ-butyrobetaine. The easy reduction indicates the presence of an α- rather than a β-double linking. C. HOLLINS.

Determination of amino-acid-nitrogen in animal tissues. J. M. LUCK (J. Biol. Chem., 1928, **77**, 1—12).—The fresh tissue is frozen in liquid air, powdered, and a sample weighed; the sample is extracted with boiling dilute acetic acid, and the extract cleared by successive treatment with trichloroacetic acid and kieselguhr; ammonia is removed by boiling after addition of sodium hydroxide and the amino-nitrogen is then determined by the method of Van Slyke. C. R. HARINGTON.

Determination of mineral matter in various parts of a cell by micro-incineration. A. POLICARD (Compt. rend., 1928, **186**, 1066—1067).—By use of 48 hr. cultures of the cells of the spleen of the white rat in very dilute plasma, and improvement in the optical conditions of examination, it is possible to apply the author's method of micro-incineration (A., 1924, i, 119) to animal cells. It is thus found that the nucleus contains an appreciable amount of mineral matter (probably calcium and magnesium), whilst only a small amount is present in the surrounding cytoplasm. J. W. BAKER.

Phosphatides of milk. G. BISCHOFF (Z. physiol. Chem., 1928, **173**, 227—232).—Repeated extraction of 10 kg. of dried milk with boiling ethyl alcohol yields a phosphatide mixture containing 15 g. of crude lecithin and 7 g. of crude kephalin; these constituents have been separated and purified. Butter yields a much smaller amount of phosphatide under these conditions, and the conclusion is reached that in the preparation of butter most of the phosphatide remains in the butter-milk. The phosphatide of milk is associated, therefore, with the water-soluble fraction rather than with the fat. A. WORMALL.

Relationship of blood-sugar content to milk production in cows. K. SCHWARZ and E. MEZLER-ANDELBERG (Biochem. Z., 1928, **194**, 362—375).—The blood-sugar values of a large number of milking cows varied in 5% of the animals between 40 and 50, in 20% between 50 and 60, in 45% between 60 and 70, in 20% between 70 and 80, and in 10% was above 80 mg. per 100 g. of blood, being usually lower than in non-milking animals (82 mg. per 100 g. of blood). A direct relationship between the amount of milk and the blood-sugar content was not found nor was any sudden fall in blood-sugar after calving detected.

P. W. CLUTTERBUCK.

Nephelometric determination of peptones in sodium chloride solutions (1 in 1000). H. SURMONT and R. PROVINO (Bull. Soc. Chim. biol., 1928, **10**, 406—412; cf. A., 1927, 376).—The nephelometric determination of peptones in aqueous media (0·1—0·3%; 0·5 c.c.) is best made by the use of 30% aqueous trichloroacetic acid (9·5 c.c.), which gives the maximum and most permanent precipitates at that concentration, or 3% sulphosalicylic acid at the ordinary temperature. At 80°, the nephelometric values fall rapidly with time. Since these values, even under the standard conditions, are not strictly proportional to the peptone concentration, it is essential to construct a calibration curve.

G. A. C. GOUGH.

Nephelometric determination of protein derivatives in gastric fluids. H. SURMONT and R. PROVINO (Bull. Soc. Chim. biol., 1928, **10**, 413—414). —In gastric fluid containing ovalbumin, albuminoses, and peptones, the material derived from proteins may be determined by the trichloroacetic acid method (preceding abstract). The peptone content may be

found by the same method after preliminary removal of the first two components by coagulation with acetic acid. G. A. C. GOUGH.

Buffering power of gastric fluids. M. POLONOVSKI and J. SWYNGEDAUW (Bull. Soc. Chim. biol., 1928, **10**, 443—449).—The buffering power of gastric fluid is determined by the hydrogen electrode method and is expressed as the quantity of sodium hydroxide necessary to change the p_H by a fixed amount. Although great variations, due to pathological conditions and time of digestion, are observed, in general there is maximum buffering power at p_H 3·5 with a lower maximum at p_H 8. G. A. C. GOUGH.

Ursodeoxycholic acid in the bile of bears, and its physiological action. M. SHODA (J. Biochem. Japan, 1927, **7**, 505—517).—Ursodeoxycholic acid has m. p. 198—200°, $[\alpha]^{130}$ +44·5°. It stimulates the action of lipase and hæmolyses red blood cells at a concentration of 1 in 320. CHEMICAL ABSTRACTS.

Reducing substances in urine. R. D. LEAS (J. Lab. Clin. Med., 1926, **12**, 15—19).—Administration of sodium salicylate, "cinchophen," or "tolysin" is followed by the appearance of lævorotatory reducing (but non-fermentable) substances in the urine. CHEMICAL ABSTRACTS.

Detection of urochromogen in urine. E. SCHUMTERMANN (Beitr. Klin. Tuberkul., 1927, **65**, 773—776; Chem. Zentr., 1928, i, 99).—Concentrated sulphuric acid (1 c.c.) containing a little sodium perborate is added (cold) to 2 c.c. of the urine; the mixture is again cooled and extracted with ether (3 c.c.). Normally the ether becomes light yellow; in the presence of urochromogen it acquires an intense lemon-yellow colour. A. A. ELDRIDGE.

Colorimetric determination of small quantities of bismuth in urine. B. GLASSMANN (Z. physiol. Chem., 1927, **172**, 300—309).—If potassium iodide is added to a solution containing very small quantities of bismuth and a little free acid, a yellow colour is produced (Tresh, Z. anal. Chem., 1883, **22**, 432). On the basis of this reaction, which is not affected by the presence of mercury or silver, a method is given in detail for the determination of bismuth in urine, in amounts of from 0·5 mg. to 0·005 mg. per 50 c.c. H. D. KAY.

Phosphate content of renal capsular fluid in *Necturus*. F. O. SCHMITT and H. L. WHITE (Amer. J. Physiol., 1928, **84**, 401—406).—In fourteen samples out of fifteen tested the "inorganic phosphate" concentration varied between 1·3 and 2·0 mg. of phosphorus per 100 c.c. The corresponding plasma values were 5·4—8·9 mg. % and the urine 1·0—8·3 mg. %. It would appear that only one third to one fourth of the plasma "inorganic phosphate" was diffusible through the glomerular membrane. R. K. CANNAN.

Determination of stercobilin. A. BAREGGI (Folia Clin. Chim. Micro., 1926, **1**, 194—197).—According to Pietra and Bozzolo (Policlinico, Med. Sect., 1924, No. 3), stercobilinogen may be determined by mixing 1 g. of the fæces with 50 c.c. of 95% alcohol, treating with an oxidising agent (5—6 drops of nitrous–nitric acid and 11—12 drops of Obermeyer's reagent) to complete the transformation of stercobilinogen into stercobilin, and heating the liquid to b. p. for 30 min. Of the clear decanted extract 1 c.c. is employed for the determination by the fluorescence method using Nencki's reagent. The author considers that this method does not give accurate results and that it may be vitiated by the presence of bilirubin. Use of the spectroscopic method is recommended, the liquid being continuously diluted with alcohol until the characteristic absorption band of stercobilin disappears, and it is considered advisable to take 5 g. instead of 1 g. of the sample. The Riva–Zoia method, in which chloroform is used for extracting the fæces, gives results about one half of those furnished by the Pietra and Bozzolo method, but serves well for ordinary clinical purposes. T. H. POPE.

Reaction of tissue. II. Hydrogen-ion concentration in the tissue during experimental acidosis and alkalosis. J. OGAWA (Proc. Imp. Acad. Tokyo, 1928, **4**, 82—83).—When acidosis is produced in an animal, whether by nephrectomy or by the injection of acids, the intracellular p_H decreases and it increases when alkalosis is produced by the administration of sufficient alkali. Injection of insulin increases the intracellular p_H. W. O. KERMACK.

Hæmocidal properties of blood-serum with reference to pernicious anæmia. O. H. HORRALL and T. E. BUCHMAN (Arch. Int. Med., 1928, **41**, 482—498).—Hæmolytic substances are present in the serum of patients suffering from certain forms of anæmia. A test for clinical use based on this finding is described. W. O. KERMACK.

Fate of secretin in pancreatic diabetes. T. NAKAGAWA and M. HARADA (J. Biophys., 1927, **2**, xxxviii—xxxix).—The amount of secretin in the intestine of depancreatised dogs was not subnormal. CHEMICAL ABSTRACTS.

Comparative study of the physical characters and chemical components of blood and of serous discharges. A. ORSI and L. VILLA (Folia Clin. Chim. Micro., 1926, **1**, 190—193).—The density of inflammatory discharges approaches that of the plasma. The refraction and viscosity increase with exudates and, after a discharge, change in a manner depending on the rapidity with which the discharge re-forms; in the plasma these characters increase after a discharge and in the case of transudates diminish in both the liquid and the plasma. In general, the electrical conductivity varies inversely with the protein concentration, systematic variations in relation to certain salts (chlorides) being apparent. The p_H value varies greatly with liquids of either similar or different character, and the alkaline reserve in general follows the p_H value. The ratio between the amounts of chloride in the plasma and the corresponding liquid remains constant, and the proportions of total non-protein nitrogen and of carbamide vary within very narrow limits. Dextrose is always found, being usually in less amount in the liquids. Cholesterol is present in minimum amounts in the transudates, but the exudates contain it in determinable quantity, even when that present in the plasma is normal.

Bilirubin is constantly present in the liquids in smaller proportion than in the plasma. T. H. POPE.

Iodine problem and exophthalmic goitre prophylaxis from the point of view of agricultural chemistry. K. SCHARRER (Münch. med. Woch., 1927, **74**, 1788—1790; Chem. Zentr., 1928, i, 218—219).—Administration of sodium iodide in the fodder of goats and cows considerably increases the iodine content of the milk and blood, and larger quantities increase the yield of milk. The milk obtained after moderate administration of iodine is readily tolerated by infants. Application of fertilisers containing iodine considerably increases the iodine in plants. A. A. ELDRIDGE.

Basal metabolism in diseases of the thyroid and the effect of certain therapeutic measures. T. KAMEI (Folia endocrinol. japon., 1927, **3**, 211—265). CHEMICAL ABSTRACTS.

Pathological significance of the variations of the free and latent acid in gastric fluids. H. SURMONT and J. SWYNGEDAUW (Bull. Soc. Chim. biol., 1928, **10**, 450—455).—The p_H and the latent, free, and total acid of a large variety of pathological gastric juices are given. At the higher values there is little latent acidity, since protein ionisation and pepsin action are inhibited. In cases of permeability of the pyloric orifice the latent acidity almost disappears after 1 hr. of digestion, whilst in cases of stenosis the latent acidity persists since some of the partly hydrolysed protein remains in the stomach. G. A. C. GOUGH.

Inflammation. V. Acetone compounds in the blood of inflamed tissue. F. BRICKER (Arch. exp. Path. Pharm., 1928, **129**, 285—287).—The venous blood from a rabbit's ear injured by immersion in hot water or hot oil contains more acetone than does the venous blood from the uninjured ear. This observation confirms the view that inflamed tissues often fail to effect complete oxidation.

W. O. KERMACK.

Inflammation. D. ALPERN and L. TUTKEVICH (Zhur. exp. Biol. Med., 1927, **6**, 177—186).—A study of the blood-potassium/calcium ratio in inflammation.

CHEMICAL ABSTRACTS.

Cause of the delay in the Van den Bergh reaction in icteric serum. N. SOFUE (Proc. Imp. Acad. Tokyo, 1928, **4**, 27—29).—Stromata of hæmolysed blood-corpuscles cause a delay in the Van den Bergh reaction whether these stromata are previously injected into the animal from which serum is obtained or whether they are added *in vitro* to the serum. The stromata react with bilirubin *in vitro*, oxidising the latter and producing colours analogous to those obtained in Gmelin's test. The biphasic and delayed reactions appear to depend on this phenomenon. W. O. KERMACK.

Parathyroidectomised dogs. Blood-mineral changes in tetany. C. I. REED, R. W. LACKEY, and J. I. PAYTE (Amer. J. Physiol., 1928, **84**, 176—188).—Tetany almost always appeared in the operated animals when the ratio of calcium to phosphorus in the plasma fell to or below unity. The severity of the symptoms, however, was not related to the value of this ratio or to the absolute concentrations of either element.

R. K. CANNAN.

Serum-calcium in pulmonary tuberculosis and on intravenous injection of calcium. W. BROCKBANK (Quart. J. Med., 1927, **20**, 431—448).—In pulmonary tuberculosis the serum-calcium varied from 8·6 to 12·0 mg. per 100 c.c., being decreased in the acute stage and gradually increased after healing, but the value is not a trustworthy criterion of activity. Intravenous, but not oral, administration of calcium raised the value above normal.

CHEMICAL ABSTRACTS.

Causes of malignant tumours. V. Cysteine content of normal and tumour tissues. R. BIERICH and K. KALLE (Z. physiol. Chem., 1928, **175**, 292—299).—Cysteine, as determined colorimetrically by the Sullivan reaction, is found to be absent from absolutely fresh tissues, with the exception of the kidney, of rats, rabbits, and pigs, but prolonged contact with air alters the tissue and a positive result is then obtained, except in the case of the suprarenal gland, in which case the reaction is probably hindered by the presence of adrenaline. The behaviour, in this respect, of malignant human tumours is similar to the normal animal tissue. Yeast gives a negative reaction for cysteine. Suprarenal extract contains, in addition to glutathione, a substance which absorbs iodine in acid solution. J. W. BAKER.

Preparation of colloidal lead. S. W. PENNYCUICK and A. E. SCOTT (Austral. J. Exp. Biol., 1928, **5**, 95—99).—Details are given for the preparation of solutions of colloidal lead by sparking in presence of gelatin solution, and data are given relating to their stability. When used in cancer therapy, very pure samples, prepared in presence of nitrogen, proved less effective than those obtained by the ordinary method; the presence of hydroxide is therefore considered to be essential. E. A. LUNT.

Chlorides and nitrogenous substances in the duodenal fluid in uræmia. C. AUGUSTE (Bull. Soc. Chim. biol., 1928, **10**, 386—396).—The duodenal fluid of uræmics as compared with that of normal subjects contains larger amounts of water and of chloride, the concentration of which is greater than that of the urine. In both the normal and the pathological states more nitrogen is liberated from the urine by sodium hypobromite than from the duodenal fluid; the latter values, which represent only about 40—70% of the total nitrogen, are smaller than the corresponding blood values, which represent almost the entire nitrogen content. G. A. C. GOUGH.

Changes in blood during fasting and subsequent refeeding. II. S. MORGULIS (Amer. J. Physiol., 1928, **84**, 350—362).—The electrolyte concentrations of the plasma of dogs were maintained remarkably constant during inanition. Striking changes occurred only in advanced starvation. There was a diminution in chlorides accompanied by a rise in hydrogen carbonate. Normal relations rapidly reappeared on renewed feeding. There was a fall in the calcium concentration during fasting which may be due to a change in the globulin–albumin ratio.

R. K. CANNAN.

Growth on synthetic diet containing small amounts of sodium. J. L. St. John (J. Biol. Chem., 1928, **77**, 27—32).—Normal growth in rats could not be obtained on diets containing 0·3% or less of sodium. C. R. Harington.

Calcification *in vitro*. III. Inorganic factors determining calcification. D. H. Shelling, B. Kramer, and E. R. Orent (J. Biol. Chem., 1928, **77**, 157—170).—Calcification of rachitic cartilage incubated in blood-serum is favoured by a p_H similar to that of normal blood-serum, and is inhibited by increase in the ionic strength of the serum produced by excess of either sodium or potassium chloride; the inhibiting effect of such increase in ionic strength is more marked the lower the concentration of calcium and phosphorus. Calcification is also inhibited by magnesium, but this effect can be neutralised by addition of phosphate. C. R. Harington.

Phosphorus metabolism. A. Charit and A. Livschitz (Arch. Sci. biol. [Moscow], 1927, **27**, 89—99; Chem. Zentr., 1927, ii, 2688).—The phosphorus metabolism of dogs is discussed. The blood-serum contains $3·1—7·2\times10^{-5}$ g./c.c. of inorganic phosphorus, and $2·6—3·5\times10^{-4}$ g./c.c. of total phosphorus. A. A. Eldridge.

Behaviour of ethyl diethylacetoacetate in the organism. E. Pace (Arch. Farm. sperim., 1928, **44**, 265—272).—In a dose of 0·007 g., ethyl diethylacetoacetate exerts a depressing effect on the central nervous system of a frog weighing 20 g., the general action being similar to, but more intense than, that of ethyl acetoacetate (A., 1927, 1218). When administered to the rabbit, the diethylacetoacetate is not decomposed, but is excreted in combination with glycuronic acid. T. H. Pope.

β-Oxidation of δ-aminovaleric acid. W. Keil (Z. physiol. Chem., 1927, **172**, 310—313).—After subcutaneous administration, to a dog, of 40 g. of sodium δ-aminovalerate, 1·5 g. of the chloroaurate of methyl β-ammoethyl ketone has been isolated from the urine, and identified by analysis. At least a part, therefore, of the δ-aminovaleric acid suffers β-oxidation in the animal body. H. D. Kay.

Action of ions on the metabolism of sugars. O. Kauffmann-Cosla (Bull. Soc. Chim. biol., 1928, **10**, 397—405; cf. A., 1926, 1063).—The urine of normal dogs, to which increasing doses of dextrose are administered without exceeding the limit above which the sugar is only partly oxidised, shows increasingly large calcium values, whilst the fæcal calcium remains almost constant. It is suggested that there is some relation between cellular oxidation and calcium metabolism. The calcium content of the urine falls slightly when the dextrose is not completely assimilated. G. A. C. Gough.

Carbohydrate metabolism and ammonia formation in the blood. A. Gigon (Schweiz. med. Woch., 1927, **57**, 294—296; Chem. Zentr., 1928, i, 84).—A distinct relation exists between dextrose and ammonia in blood. Ingestion of urea causes an increase in the blood-ammonia, with a parallel hyperglycæmia; injection of dextrose reduces the ammonia value. A. A. Eldridge.

Ammonia content of and ammonia formation in muscle and its relationship to function and changes of condition. V. Course of traumatic formation of lactic acid and ammonia and their dependence on inhibiting factors. S. Chrzaszczewski and W. Mozolowski (Biochem. Z., 1928, **194**, 233—243).—When a muscle is macerated with sand and water, the lactic acid formed in 2 min. is ten times the resting value and the course of formation is similar to that of ammonia. The traumatic formation of lactic acid and of ammonia is inhibited by borate solution of p_H 9·3. By means of sodium fluoride solution (1%) the traumatic formation of lactic acid is entirely abolished whereas the formation of ammonia is only somewhat inhibited, the two processes being thereby separable. No direct relationship exists between the formation of ammonia and lactic acid in muscle (A., 1927, 694; this vol., 198). P. W. Clutterbuck.

Transformation of creatine into creatinine by the male and female human organism. W. C. Rose, R. H. Ellis, and O. C. Heming (J. Biol. Chem., 1928, **77**, 171—184).—After long continued feeding of creatine to human subjects larger amounts were excreted unchanged in the female than in the male, but, of the remainder, the same proportion (about one third) was excreted as creatinine in both sexes; the results suggest the existence of two metabolic processes concerned with creatine, one leading to creatinine and the second to some other end product; a lower efficiency of the latter process may account for creatinuria in women. C. R. Harington.

Excretion of creatinine and the height of energy loss in man. L. Garot (Arch. int. physiol., 1927, **29**, 326—341).—During the first 15 yrs. of life the creatine : creatinine excretion ratio, at first unity, changes, the latter gradually replacing an equivalent amount of the former. The creatinine excretion per kg. diminishes with increasing age and size, and corresponds with, but is not proportional to, the change in production of heat. Chemical Abstracts.

Specific dynamic action and nitrogen elimination following intravenous administration of various amino-acids. C. M. Wilhelmj and J. L. Bollman (J. Biol. Chem., 1928, **77**, 127—149).—Intravenous injections of glycine, alanine, and phenylalanine cause immediate increases in heat production accompanied by rise in the respiratory quotient; the specific dynamic effects of these amino-acids, expressed as calories of extra heat produced per millimol. of amino-acid, are in the ratio 1·3 : 1 : 2. Following administration of a racemic amino-acid, more than 50% of the nitrogen may be excreted as carbamide, indicating a small utilisation of the non-biological isomeride. C. R. Harington.

Metabolism of amino-acids. J. M. Luck (J. Biol. Chem., 1928, 77, 13—26).—After oral administration of various amino-acids to rats the ammonia content of the liver and muscles remained unchanged; the amino-acid nitrogen of the liver was increased to a variable extent; that of the muscles showed an increase only after administration of glycine, which also produced the largest rise in the amino-nitrogen

of the liver; the rise in the latter does not, apparently, depend on the concentration of amino-nitrogen attained in the blood. C. R. Harington.

l-Hydroxyproline and l-proline as sugar formers. Metabolic investigations with dogs dosed with phloridzin. J. Kapfhammer and C. Bischoff (Z. physiol. Chem., 1928, **172**, 251—254; cf. Dakin, A., 1913, i, 225).—The amount of extra sugar excreted in the urine of phloridzinised dogs after injection of *l*-hydroxyproline corresponds closely with the utilisation of three carbon atoms for sugar formation. Pure *l*-proline gives about the same quantity of extra sugar as the proline (66% *dl*, 34% *l*) used by Dakin. C. Hollins.

Synthesis of hippuric acid in the animal organism. VII. Rate of elimination of hippuric acid after ingestion of sodium benzoate, benzyl alcohol, and benzyl succinate. S. L. Diack and H. B. Lewis (J. Biol. Chem., 1928, **77**, 89—95).—The urinary excretion of hippuric acid after oral administration of benzyl alcohol to rabbits is almost as rapid as that resulting from ingestion of sodium benzoate; recovery of benzyl succinate as hippuric acid in the urine amounted to 61% in 24 hrs. and that of sodium benzyl succinate to 45%, although the excretion of hippuric acid in the first hour after ingestion was more rapid in the latter case.

C. R. Harington.

Regulation of the metabolism of the liver by the nervous system. I. P. Astanin, I. Kriwsky, and W. Rubel. **II. Influence of the vegetative nervous system on the carbamide and sugar formation in the liver.** P. Astanin and W. Rubel (Biochem. Z., 1928, **194**, 254—261; 262—272).—I. When the surviving liver is perfused with difibrinated blood, the carbamide content of the blood is always increased, whilst by addition of ammonium carbonate the carbamide content is considerably but not proportionately increased, the acid–base equilibrium is scarcely affected, and the amounts of sugar and residual nitrogen are increased.

II. The carbamide content of blood perfusing a surviving liver is increased by stimulating the vagus but not affected by stimulating the sympathetic, whilst the sugar content is increased by stimulating the sympathetic but is not affected or slightly decreased by stimulating the vagus.

P. W. Clutterbuck.

Physiological study of glutathione by liver perfusion. R. Fabre and H. Simonnet (J. Pharm. Chim., 1928, [viii], **7**, 447—449).—See this vol., 196.

Metabolism of the bile acids. C. H. Greene, M. Aldrich, and L. G. Rowntree (J. Physiol., Proc. Physiol. Soc., 1927, **64**, vii—viii).—By adaptation of Pettenkofer's reaction, glycocholic acid (0·1—0·5 mg.) is determined with an error of 5%. Intravenous injection of whole bile or bile salt markedly increases the blood bile acid, but the acids rapidly leave the blood; oral administration leads to an increase of the amount in the blood of the portal, but not of the jugular, vein. A. A. Eldridge.

Site of formation of bilirubin. K. Taniguchi (Arch. exp. Path. Pharm., 1928, **130**, 37—48).—Although extra-hepatic formation of bilirubin does occur, the liver is the chief site of its formation. After administration of tolylenediamine or phenylhydrazine to a dog, icterus occurs only when the liver is present. W. O. Kermack.

Sense of taste in bees. II. K. von Frisch (Naturwiss., 1928, **16**, 307—315; cf. *ibid.*, 1927, **15**, 321—327).—Fasting bees can differentiate between $M/4$ and $M/8$ solutions of sucrose, but $M/16$ solutions are neglected. A threshold concentration for the recognition of sweetness is indicated. Without fasting, however, $M/8$ and $M/12$ solutions receive little attention, whilst $M/2$ (17%) solutions are invariably attractive. Bees will absorb solutions containing two sweet constituents when the concentrations are below the limiting values, provided the additive concentration is sufficiently high. Tasteless substances exert no such additive effect. The following compounds are sweet both to men and bees: dextrose, lævulose, α-methylglucoside, sucrose, trehalose, maltose, melibiose, whereas bees neglect galactose, mannose, sorbose, mannitol, dulcitol, sorbitol, arabinose, xylose, rhamnose, erythritol, cellobiose, and raffinose. No simple relationship between chemical constitution and sweetness emerges either from the work on the bee or on the human sense of taste.

R. A. Morton.

Calcium and ultra-violet irradiation. Effect on serum-calcium. Effect on calcium utilisation on a calcium-poor diet. L. T. Fairhall (Amer. J. Physiol., 1928, **84**, 378—385).—On a normal diet irradiated rats had a somewhat higher concentration of calcium in the serum than did normal rats of the same age. Irradiation increased calcification in rats both on a normal and on a calcium-poor diet; nevertheless, on the latter diet irradiated rats, although their growth appeared normal, contained only about 50% of the calcium of normal rats on a normal diet. R. K. Cannan.

Influence of nucleic acids of various origin on the growth and longevity of the white mouse. T. B. Robertson (Austral. J. Exp. Biol., 1928, **5**, 47—67).—The effect of nucleic acid of various origins on the growth and longevity of mice has been investigated. Thymus nuclei in daily doses corresponding with 0·5 g. of fresh tissue, and yeast-nucleic acid, daily dose 25 mg., have no effect on the growth curve; the former, however, results in a 12·6% increase in life-duration for the male and a 17% increase for the female; the latter results in a 16% increase for the male. Mice receiving a daily dose of 15 mg. of spleen-nucleic acid exhibit an increase of growth over the controls between the 18th and 72nd weeks of age but show no increase in life-duration.

E. A. Lunt.

Effect of mental fatigue on the excretion of organic phosphorus in the urine. L. E. Taranowitsch (Biochem. Z., 1928, **194**, 461—465).—The organic phosphorus of the urine is not directly dependent on the phosphorus content of the food absorbed, but both the organic phosphorus and the ratio of organic to total phosphorus increase in all cases of fatigue by continuous mental work.

P. W. Clutterbuck.

Constitution and [physiological] action. Aromatic fluorine compounds. F. LEHMANN (Arch. exp. Path. Pharm., 1928, **130**, 250—255).—The action of the following compounds has been determined on frogs: toluene, ω-trifluorotoluene, ω-trichlorotoluene, ω-chloro-ω-difluorotoluene, ω-trifluoro-*m*-nitrotoluene, sodium ω-trifluoro-*m*-toluate, ω-trifluoro-*m*-toluidine hydrochloride, *m*-toluidine hydrochloride, and aniline hydrochloride. The toxicity of toluene is increased by the introduction of chlorine and still more by the introduction of fluorine into the side-chain, whilst the toxicity of ω-trifluorotoluene is further increased by the presence of an amino-group or to a smaller extent of a nitro- or carboxyl group in the *meta*-position.

W. O. KERMACK.

Effect of drugs on the protein content of the cerebrospinal fluid of rabbits. L. F. HEWITT and H. FLOREY (J. Physiol., Proc. Physiol. Soc., 1927, **64**, xxvii—xxviii).—The protein content of the cerebrospinal fluid of rabbits is not increased by administration of hexamethylenetetramine, histamine, or pilocarpine; *p*-phenylenediamine causes a 25% increase, an increase negligible in comparison with that caused in man by tubercular meningitis.

A. A. ELDRIDGE.

Metabolic action of "synthalin" with special reference to the analysis of the organs. A. BOEDEKER and P. JUNKERSDORF (Arch. exp. Path. Pharm., 1928, **129**, 354—366).—After administration of synthalin the blood-sugar usually rises and then shows a fairly marked fall. Glycogen tends to disappear from the liver and peptone appears in the urine, and it is suggested that synthalin may possess a toxic action. W. O. KERMACK.

Guanidine derivatives which lower the blood-sugar. T. KUMAGAI, S. KAWAI, and Y. SHIKINAMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 23—26).—A large number of guanidine derivatives have been prepared and their blood-sugar lowering actions determined when administered to rabbits by mouth or subcutaneously. The action is exerted particularly by the polymethylenediguanidines. The following compounds have been prepared by the condensation of the corresponding polymethylenediamines with ψ-thiocarbamide in presence of hydriodic acid: agmatine sulphate, m. p. 228°, tetramethylenediguanidine sulphate (not easily obtained pure), pentamethylenediguanidine sulphate, decomp. 330°, and hexamethylenediguanidine hydrochloride, m. p. 175—176·5°. W. O. KERMACK.

Chemical constitution and physiological action. K. KINDLER (Arch. Pharm., 1928, **266**, 19—33).—A lecture. W. A. SILVESTER.

Excretion of barbituric acid derivatives in the urine of the dog. M. REINERT (Arch. exp. Path. Pharm., 1928, **130**, 49—60).—When diethylbarbituric acid, phenylethylbarbituric acid, or *iso*propylallylbarbituric acid is administered to dogs 70% of the first is excreted in the urine during 7—8 days and about 25—30% destroyed in the organism, 20% of the second is excreted during about 9—10 days and 80% is destroyed, whilst 20% of the third is excreted within 2 days and 80% is destroyed. W. O. KERMACK.

Influence of convulsions on the gases and the reaction of blood: mechanism of action of strychnine. S. DIETRICH and H. EBSTER (Arch. exp. Path. Pharm., 1928, **129**, 339—353).—The difference in their powers to combine with carbon dioxide between oxygenated and reduced rabbit's blood is of the same order as that between oxygenated and reduced human blood. A formula is given for the calculation of the carbon dioxide content of the plasma from that of the whole blood and the hæmoglobin content. The mechanism of the circulatory and respiratory changes in strychnine poisoning are discussed. W. O. KERMACK.

Uptake, fixation, and decomposition of digitalis compounds and their action on the heart. H. FISCHER (Arch. exp. Path. Pharm., 1928, **130**, 111—193).—A pharmacological investigation has been made of the mode of action of digitoxin and bigitaligenin and of the methods by which their activity *in vivo* is neutralised, whether by elimination from the organism, by fixation in the tissues, or by chemical decomposition. W. O. KERMACK.

Photodynamic action of hæmatoporphyrin. E. N. RASK and W. H. HOWELL (Amer. J. Physiol., 1928, **84**, 363—377).—The photodynamic action of hæmatoporphyrin is limited to those tissues directly exposed to light. From observations on frogs, mice, guinea-pigs, rabbits, and dogs sensitised with hæmatoporphyrin and on the isolated turtle's heart, it is suggested that the hæmatoporphyrin combines slowly with some constituent or constituents of the tissues. The resultant effects are attributed to the effect of light on these compounds. R. K. CANNAN.

Antiseptic action of water-soluble dyes. C. SCHWEIZER (Mitt. Geb. Lebensm. Hyg., 1928, **19**, 1—43).—Chiefly a discussion of the mechanism of the toxic action of dyes on cells and micro-organisms. Many basic triphenylmethane dyes and, to a smaller extent, the basic azo-dyes of the chrysoidine class, possess a powerful action on yeast-cells. Dyes of the acid-pyrone and eosin classes have only an inhibitive action. G. A. C. GOUGH.

Distribution of arsenic in the tissues after serial administration of neoarsphenamine. F. P. UNDERHILL and A. DIMICK (Amer. J. Physiol., 1928, **84**, 56—60).—The greatest quantity of arsenic was found in the kidney, the amounts found in other tissues being in the descending order spleen, liver, adrenals, heart, muscle, reproductive organs, and brain. The amounts found did not, in general, bear any simple relation to the amount administered or to the number of injections. This distribution of arsenic is in striking contrast to that found in arsenious oxide poisoning. R. K. CANNAN.

Concentration of enzyme solutions. B. N. SASTRI (J. Indian Inst. Sci., 1928, **11A**, 14—15).—Enzyme solutions may be concentrated by freezing, the solution being stirred continuously to favour the formation of small ice crystals. F. E. DAY.

Micro-method for the determination of enzyme activity. B. N. SASTRI and M. SREENIVASAYA (J. Indian Inst. Sci., 1928, **11A**, 31—39).—The method is an adaptation of Barger's micro-method

for mol. wt. determination. Alternate drops of substrate+active enzyme and substrate+inactivated (boiled) enzyme are introduced into a narrow glass tube and the resulting short liquid columns measured microscopically. As the vapour pressure changes with the alteration of molecular concentration due to action of the enzyme in the former solution, the volume of the drops adjusts itself sufficiently rapidly to give a time-value graph agreeing in form with that determined by chemical methods. Examples are given for taka-diastase and invertase, and sources of error and possible improvements are discussed.

F. E. DAY.

Extraction of amygdalin and emulsin from bitter almond cake. M. BRIDEL and M. DESMAREST (Bull. Soc. Chim. biol., 1928, **10**, 373—380).—A more detailed account of previous work (this vol., 201).

G. A. C. GOUGH.

Hydrolysis of lichenin and cellulose by the enzymes of barley malt. H. PRINGSHEIM and K. BAUR (Z. physiol. Chem., 1928, **173**, 188—210).—The hydrolysis of lichenin and cellulose, by the same enzymes yielding dextrose as the final product, occurs in three stages, the decomposition of the micelle of the polysaccharide into its structural molecules (glucose anhydrides), synthesis to cellobiose, and hydrolysis of cellobiose to dextrose. To prepare licheninase an extract of green malt is fermented by yeast to remove reducing sugars, or these may be removed by dialysis. Adsorption of the enzyme on kaolin in acid solution and elution with a phosphate buffer of p_H 6·8 yields a solution with enzymic activity 1·7 times that of the malt extract, whilst adsorption on β-alumina (Willstatter) at p_H 3 and elution in a secondary phosphate solution produces an increase of 2·3 times in the activity of the enzyme solution. The kinetics of the hydrolysis of ordinary and purified lichenin by the enzyme preparations have been studied and it has been found that the results vary with different preparations and mainly with the purity and age of the lichenin. With a pure heated lichenin the hydrolysis follows the unimolecular law up to 60% hydrolysis, the reaction velocity being approximately equal to the amount of enzyme used; similar results are obtained for the cellobiase activity of the malt extracts. The extent of hydrolysis of cellulose by the enzyme solution depends on the degree of dispersion of the cellulose; of the cellulose solutions used, cellulose dispersed by heating in a saturated calcium thiocyanate solution is most readily hydrolysed.

A. WORMALL.

Purification of the lactic acid-forming enzyme of muscle. O. MEYERHOF and K. MEYER (J. Physiol., Proc. Physiol. Soc., 1927, **64**, xvi).—The extract from frog or rabbit muscle, at p_H 5 with an acetate buffer, precipitates protein and enzyme; the latter is redissolved on elution with phosphate solution at p_H 8. The process is repeated, and the activity of the preparation may be increased by adsorption on aluminium hydroxide. The co-enzyme and phosphoric esters are removed during the process.

A. A. ELDRIDGE.

Mutase. H. VON EULER and E. BRUNIUS (Z. physiol. Chem., 1928, **175**, 52—67).—The dismutation of acetaldehyde (oxido-reduction into alcohol and acetic acid) by aldehyde-mutase shows no parallelism with the decolorisation of methylene-blue by redoxase even in presence of excess of co-zymase and donators. The experiments afford no evidence for or against the identity of aldehyde-mutase with redoxase.

C. HOLLINS.

Effect of temperature on catalase reaction. VI. Heat-inactivation of catalase at different p_H. S. MORGULIS and M. BEBER (J. Biol. Chem., 1928, **77**, 115—126).—Catalase is most stable towards heat at p_H 6·0; at more acid or alkaline reactions heat-inactivation is slow below 50°, but rapidly increases above this temperature; at 65° inactivation is instantaneous whatever be the reaction. The experiments lead to the supposition that the isoelectric point of catalase is at p_H 6·0, which involves modification of the previous view (A., 1926, 976) that the enzyme acts as a weak acid.

C. R. HARINGTON.

Glycerophosphate fission by means of kidney phosphatase and its activation. H. ERDTMAN (Z. physiol. Chem., 1928, **172**, 182—198).—Dialysis of a phosphatase preparation, obtained by extraction of pig's kidney with water and toluene and precipitation with alcohol, considerably reduces its activity. The activator thus removed appears to be an organic substance with high stability towards heat, alkalis, and acids. It is present in urine and in Liebig's meat extract, and is obtained from the latter in purified form as a colourless, amorphous mass, soluble in water and methyl alcohol, by precipitation with baryta and treatment with lead acetate.

C. HOLLINS.

Liver esterase, its purification and stability. H. KRAUT and H. RUBENBAUER (Z. physiol. Chem., 1928, **173**, 103—117).—Pig's liver is dried with acetone and ether and the dried powder extracted with 40 times the volume of 0·025*N*-ammonia. The extract is dialysed against running water for 3 days, with slight loss of enzyme. The contents of the dialyser are filtered, and certain impurities, together with some 30% of the esterase, are adsorbed from the acidified (0·01*N*-acetic acid) solution first with kaolin, and then with aluminium hydroxide. The remaining purified solution is evaporated in a vacuum to one quarter of its bulk, keeping the reaction of the fluid neutral throughout with ammonia. There is a 15—20% loss of activity during this operation. After filtering through kieselguhr, a small quantity of aluminium hydroxide is added. Further impurities together with some enzyme are removed thereby. The solution is then rendered acid (0·01*N*-acetic acid) and kaolin added. This now adsorbs 80% of the remaining enzyme. After elution with 0·25*N*-ammonia, the enzyme solution is again rendered acid and adsorbed on aluminium hydroxide, from which it is again eluted by ammonia to give an enzyme preparation which may possess 650 times the activity of the dried liver per g. of dry weight. The enzyme gives now no Millon's reaction.

In strong contrast to the esterase of the original dried tissue, which even after months retains the greater part of its activity, the purified enzyme is very unstable, losing 50% of its activity in a single

day, and becoming completely inactivated in eight weeks. H. D. KAY.

Configurational specificity of esterases in various stages of purification. R. WILLSTÄTTER, E. BAMANN, and J. WALDSCHMIDT-GRASER (Z. physiol. Chem., 1928, **173**, 155—168).—Esterases derived from the pancreas, stomach, and liver of the pig have been investigated, using ethyl *r*-mandelate and *r*-phenylchloroacetate as substrates. In no case has it been found possible, by purification, to alter the original optical selective power of the enzyme for one or other of the two optical isomerides in the substrate. Configurational specificity is thus most probably an attribute of the enzyme itself, and not of associated impurities. For an equivalent total amount of hydrolysis the specific rotation of the product increases with increasing purity of gastric esterase. The esterases of corresponding organs in different animal species are not necessarily the same. Thus the gastric esterase of the dog gives the dextrorotatory acid first when acting on ethyl *r*-phenylchloroacetate, but that from the pig gives first the *l*-isomeride. Using a number of different racemic esters, the stereochemical identity of two or more esterases may be tested. H. D. KAY.

Asparaginase. W. F. GEDDES and A. HUNTER (J. Biol. Chem., 1928, **77**, 197—229).—Asparaginase has been prepared from yeast and from calf liver. From the former source the enzyme is best extracted by water or 50% glycerol from the dried and powdered material, at p_H 7·0. Treatment of the aqueous solution with alcohol or acetone causes inactivation of the enzyme; the latter is adsorbed by ferric hydroxide and by kieselguhr, but cannot be satisfactorily recovered from the adsorbate. It is also precipitated at 4·5. The enzyme is most conveniently concentrated by precipitation with safranine; the activity of preparations so obtained is greatest at p_H 7·9—8·1, and is limited to the hydrolysis of the amide-nitrogen of asparagine and of glutamine. The course of the enzymic hydrolysis is not that of a unimolecular reaction but is expressed by an equation of the same form as that given by Michaelis and Menten (A., 1913, i, 540) for the action of invertase on sucrose. C. R. HARINGTON.

Plant proteases. R. WILLSTÄTTER. X. Mode of action of yeast polypeptidase. W. GRASSMANN and H. DYCKERHOFF (Z. physiol. Chem., 1928, **175**, 18—37).—By fractional adsorption of yeast proteases on alumina a dipeptidase and a polypeptidase may be completely separated. The latter is unable to attack dipeptides, but breaks down tri- and tetrapeptides. *dl*-Leucylglycylglycine is hydrolysed by yeast polypeptidase almost quantitatively into *dl*-leucine and glycylglycine; glycylglycyl-*l*-leucine similarly gives glycine and glycyl-*l*-leucine with no trace of leucine. From *dl*-leucyldiglycylglycine the polypeptidase liberates *dl*-leucine and diglycylglycine, and from triglycylglycine glycine and diglycylglycine. In the presence of leucine the tripeptide, diglycylglycine, is protected from attack. In each case the amino-acid linked through its carboxyl group is removed. Benzoylglycylglycine, benzoyldiglycylglycine, and β-naphthalenesulphonylglycyl-*l*-tyrosine are unattacked by yeast polypeptidase. C. HOLLINS.

Plant proteases. II. R. WILLSTÄTTER and co-workers. **Specificity of yeast peptidases.** W. GRASSMANN and H. DYCKERHOFF (Ber., 1928, **61**, [*B*], 656—670).—Observations are recorded on the action of yeast dipeptidase, polypeptidase, and protease on a number of peptides. In all the cases examined, the dipeptides behave exclusively as substrates of dipeptidase, whereas the higher peptides without exception are hydrolysed by polypeptidase. The presence of a free carboxyl group in the position characteristic for normal dipeptides appears essential for susceptibility of the substrate to yeast dipeptidase. Amides of dipeptides, including the tripeptides and higher polypeptides, decarboxylated peptides, and dipeptides such as glycyl-β-aminobutyric acid, in which the carboxy-group has an unusual position with respect to the peptide linking, are without exception resistant to homogeneous yeast dipeptidase (which thus differs from intestinal erepsin), whereas the dipeptide esters cannot be investigated owing to their instability under optimal conditions of activity of dipeptidase. The attack of yeast polypeptidase appears to occur by reason of the presence of a free amino-group in the substrate. Hydrolysis of tri- and tetra-peptides by the enzyme invariably and exclusively occurs in such a manner that the peptide linking at the amino-end of the peptide chain is ruptured. In conformation it is noted that benzoyldiglycylglycine is not hydrolysed by polypeptidase. The presence of a free carboxyl group appears unnecessary for susceptibility to yeast polypeptidase; hydrolysis of tripeptide esters takes place initially at the peptide linking and only towards the end of the change does the ester hydrolysis assume considerable proportions. Unexpectedly, esters of dipeptides are hydrolysed by yeast polypeptidase as rapidly as similarly constituted tripeptides and reaction occurs mainly (almost exclusively at its commencement) at the peptide linking. This is also true for the amides of dipeptides. Esterification, amidation, and lengthening of the peptide chain at the carboxyl group transform a dipeptide from a substrate for dipeptidase into one for polypeptidase. The proximity of a free carboxyl group to the peptide linking hinders the attack of polypeptidase. H. WREN.

Specificity of peptidases. II. Comparison of the peptide–sugar condensation with the mode of action of erepsin. E. WALDSCHMIDT-LEITZ and G. RAUCHALLES (Ber., 1928, **61**, [*B*], 645—656).—The condensation of dextrose with peptides, which shows many points of similarity with the action between aldehydic sugars and simple amino-acids (stoicheiometric course of the change, dependence on concentration of the components), differs remarkably from the latter reaction in its relationship to the hydrogen-ion concentration. This corresponds, at any rate approximately, with the difference in electrochemical character between peptides and amino-acids, since glycylglycine or leucylglycine condenses most readily with dextrose at p_H 8·0 and only to an inappreciable extent at 9 0, whereas the

action between the sugar and glycine or alanine becomes appreciable only in a more alkaline medium. The p_H curve for the hydrolysis of glycylglycine by intestinal erepsin coincides within the limits of experimental error with that of the rate of condensation of glycylglycine with dextrose. It appears therefore justifiable to assume that the peptide reacts with similar groups in each case and that the union of peptide and erepsin is similar to that of peptide and aldose and hence is due to a free aldehydic group of the enzyme. In confirmation, it is observed that corresponding with the indifference of acylated peptides towards erepsin their condensation products with dextrose are not decomposed by the enzyme. No diminution of susceptibility is observed in the case of lævulose, which does not condense with peptides. Further support of the view that the power of erepsin to unite with the substrate depends on a free aldehydic group is found in the comparison of the condensibility of simple amino-acids with their restrictive capacities towards the action of erepsin; the condensibility of glycine and alanine and their restrictive action towards enzymic hydrolysis of peptides increases with increasing alkalinity of the solution. It appears that the hydrogen ions in the preceding case affect the rate of union of enzyme and substrate and not its rate of decomposition and that the velocity of erepsin action is conditioned by the rate of formation of the enzyme–substrate compound. The mechanism of the action of erepsin therefore differs fundamentally from the enzymic hydrolysis of sucrose. H. WREN.

Specificity of animal proteases. XIII. Specificity and mode of action of erepsin, trypsin, and trypsin kinase. E. WALDSCHMIDT-LEITZ and W. KLEIN (Ber., 1928, **61**, [*B*], 640—645; cf. this vol., 550).—The behaviour of intestinal erepsin and trypsin kinase towards β-naphthalenesulphonylglycyltyrosine, glycylglycinecarboxylic acid, carbethoxyglycyl-leucine, carbethoxypentaglycine, acetylglycylglycine, acetylphenylalanylalanine, benzoyl-di-, -tri-, -tetra-, and -penta-glycine, phthalyldiglycine, glycylleucineamide, tetraglycineamide, and carbethoxytetraglycineamide has been investigated. Introduction of acyl groups into dipeptides renders the latter incapable of hydrolysis by erepsin and hydrolysable by trypsin, apparently without dependence on the nature of the amino-acid residue in the peptide. Conversion of the carboxyl group of peptides into the carboxylamido-group, like esterification, does not affect the behaviour towards erepsin, whereas simultaneous acylation again causes immunity to the hydrolysing action of the ferment. Hydrolysis of carbethoxyglycyl-leucine and acetylphenylalanylalanine by trypsin is not accelerated by activation of the latter with enterokinase, whereas this is notably the case with β-napththalenesulphonylglycyltyrosine. H. WREN.

Inactivation of trypsin by Röntgen rays of different hardness. K. ROTHSTEIN (Amer. J. Roentgenol. Rad. Therapy, 1927, **18**, 528—536).—The effect on buffered trypsin solutions, p_H 5·42, is an exponential function of the ionisation dose, and is independent of the wave-length between 0·18 and 1. CHEMICAL ABSTRACTS.

Invertase. I. Preparation and purification of the enzyme. B. N. SASTRI and R. V. NORRIS (J. Indian Inst. Sci., 1928, **11***A*, 1—13).—Washed brewer's yeast (10 lb.) was allowed to autolyse with twice its weight of water at the ordinary temperature in presence of toluene. The filtered autolysate is stable if kept under toluene. After concentrating by freezing out about half the water, 5 litres of the liquid were treated with 500 g. of purified kaolin, which selectively adsorbs impurities. To each 640 c.c. of the cleared liquid, 400 g. of ammonium sulphate were added, the whole was shaken for 30 min., and kept at 0° for 30 hrs. The precipitate was centrifuged, washed twice with saturated ammonium sulphate solution, and extracted with successive small quantities of water, totalling about 560 c.c. This solution was dialysed in collodion bags in distilled water for 3 days at 0°, the solution diluted to 1 litre, and the enzyme was adsorbed on alumina cream equivalent to 1 g. of Al_2O_3. The alumina after two washings with distilled water was shaken with 180 c.c. of 1% disodium phosphate solution in 1% aqueous glycerol for 30 min., the liquid filtered through kieselguhr, and again dialysed for 72 hrs. Three preparations yielded products giving Willstatter's "time values" of 0·91, 0·80, and 1·10 min., respectively. F. E. DAY.

Cell-free fermentation. A. LEBEDEV (Z. physiol. Chem., 1928, **173**, 89—102).—Partly polemical. The claim of Kostytschev, Medvedev, and Sysojeva (A., 1927, 902) that cell-free fermentation does not exist is criticised. Different samples of the same dried yeast yield on maceration extracts of approximately the same fermentative power, whether few or many cells pass through the filter-paper. The fermentative power of such extracts depends to a large extent on the conditions under which the yeast is dried, and is usually less in extracts made from dried yeast which contains a relatively large number of living cells. The evidence against Kostytschev's view is overwhelming. H. D. KAY.

Comparison of the fermentability of the zymohexoses. Glycogen and starch. J. LEIBOVITZ (Z. physiol. Chem., 1928, **173**, 84—88).—The fermentation of the polysaccharides is much slower and less complete than that of dextrose and sucrose. It is unlikely, either in fermentation by yeast or in glycolysis by muscle, that a direct degradation of the polysaccharides occurs. J. STEWART.

Alcoholic fermentation. XIV. Fermentation of polyhydric alcohols by yeast. S. KOSTYTSCHEV and V. FAERMANN (Z. physiol. Chem., 1928, **173**, 72—79).—Mannitol and glycerol are disrupted to carbon dioxide and alcohol by yeast only when abundant oxygen is available. This indicates that yeast is able to activate the hydrogen of a hydroxyl group. J. STEWART.

Alleged co-enzyme for oxidoreductase of yeast. A. LEBEDEV (Z. physiol. Chem., 1927, **172**, 255—276).—Neither the reducing enzyme of yeast, prepared by the author's method (A., 1926, 1061), nor the reducing enzyme of milk, prepared by the method of Sbarski and Michlin (A., 1926, 977), is dependent for its activity on the presence of a

co-enzyme. What has hitherto been regarded as a co-enzyme is, in fact, a mixture of oxidisable materials which can be separated from boiled yeast extract by precipitation with alcohol. On dialysis the enzyme loses part of its activity which cannot be restored by addition of boiled yeast extract. After long-continued dialysis the activity of the oxido-reductase solution may slightly increase, possibly owing to the removal of inhibitory substances. Yeast oxidoreductase is probably protein in nature, or associated with a protein carrier. H. D. Kay.

Co-zymase requirement of yeast in the fermentation of hexosemonophosphate and hexosediphosphate. A. Gottschalk (Z. physiol. Chem., 1928, **173**, 184—187).—The fermentation of hexosemonophosphate (Robison) by dried bottom yeast requires larger amounts of co-zymase than does the fermentation of hexosediphosphate (Harden and Young), but not as much as an equivalent amount of dextrose. It is concluded therefore that this hexosemonophosphate is not an intermediate product formed from the hexosediphosphate, and it is suggested that from the latter a labile hexosemonophosphate (fructosemonophosphate ?) is first formed. A. Wormall.

Production of a yeast-growth stimulant by heating media under pressure. E. I. Fulmer and B. Huesselmann (Iowa State Coll. J. Sci., 1927, **1**, 411—417).—Sterilisation of media *C* and *D* (cf. A., 1921, i, 292) produces a stimulant for the growth of *Saccharomyces cerevisiæ*; the stimulation is not due to change of p_H. Chemical Abstracts.

Intracellular hydrogen-ion concentration. I. Method. II. *Entamœba histolytica* and *E. coli*. J. Ogawa (Proc. Imp. Acad. Tokyo, 1928, **4**, 76—78, 79—81).—I. The intracellular hydrogen-ion concentration is determined by a slight modification of Schmidtmann's method (injection of indicator into the cell) and the results are compared with those obtained by Graff's method. The intracellular p_H of animal tissues decreases fairly rapidly after they have been removed from the body.

II. The p_H of the protoplasm of *E. histolytica* and of *E. coli* usually lies between 6·0 and 7·0. W. O. Kermack.

Detection of hydroxylamine. J. Blom (Biochem. Z., 1928, **194**, 385—391).—Hydroxylamine (down to 0·0001 g. litre) may be detected colorimetrically by means of *p*-bromonitrosobenzene and α-naphthol. P. W. Clutterbuck.

Formation of hydroxylamine by the reduction of nitrates by micro-organisms. J. Blom (Biochem. Z., 1928, **194**, 392—409).—The formation of hydroxylamine in culture media is detected by the author's method (see preceding abstract) and in presence also of acetone, the amount of acetoxime is greatly increased. The mechanism of the reaction is discussed. P. W. Clutterbuck.

Quantitative metabolism of paratyphoid-*B* bacillus, *B. coli*, and *B. pyocyaneus*. F. Friedlein (Biochem. Z., 1928, **194**, 273—291).—The smallest amounts of a number of substances necessary to produce luxuriant growth of the three bacteria in 24 hrs. on a lactic acid–ammonia medium are determined and the quantities of these substances required for an optimal synthetic nutritive medium are tabulated. Potassium, sodium, and chlorine are unnecessary to maintain life when omitted singly from media containing the other two, whilst magnesium and sulphur, although unnecessary, stimulate growth. Carbon, nitrogen, and phosphorus are necessary for life. Sodium lactate is as good a source of carbon and energy as dextrose or succinate. Ammonium chloride is as good a source of nitrogen as the sodium salt of asparagine. P. W. Clutterbuck.

Physical chemistry of d'Herelle's phenomenon. K. von Angerer (Zentr. Bakt. Par., 1927, I, **104**, 261—262; Chem. Zentr., 1927, ii, 2685).—The association of the bacteriophage and bacteria accords with the adsorption laws. The exponent $1/n$ of the adsorption isothermal is 0·75—0·80. Only at a certain large concentration of the bacteria in the course of growth is the lysin, at first free, combined. A. A. Eldridge.

Behaviour of d'Herelle's lytic principle (bacteriophage) towards collodion membranes and in distilled water. L. Villa (Folia clin. chim. microscop., 1926, **1**, 52—57; Chem. Zentr., 1927, ii, 2685).—The lytic principle behaves like a colloid with large micelles. It does not pass a collodion filter. In distilled water the active bacteriophage can be isolated, and is apparently visible with an ultramicroscope. A. A. Eldridge.

Antigenic properties of the distillates of certain bacterial cultures. Z. Jermoljewa (Z. Immunitatsforsch. exp. Ther., 1927, **53**, 101—111; Chem. Zentr., 1927, ii, 2684).—Cultures of cholera and other vibrios were distilled with magnesium oxide, and the ability of the distillate to produce bacteriolytic and complement-binding antibodies in the serum was investigated. Diphtheria toxin was similarly studied. A. A. Eldridge.

Antigenic properties of anatoxin. M. Isabolinski and V. Gitovitch (Zhur. exp. Biol. Med., 1927, **4**, 844—849).—The combining power of anatoxin is of greater importance in determining its immunising effect than its precipitability. Addition of neutralised formaldehyde to the toxin diminishes the antigenic activity of the anatoxin. Chemical Abstracts.

Physico-chemical nature of diphtheria toxin and anatoxin. V. Kulikov and N. Smirnov (Zhur. exp. Biol. Med., 1927, **4**, 833—841).—Diphtheria toxin shows a wide precipitation zone with increasing acidity, and a narrow zone of maximum toxicity of the precipitate. Factors influencing the toxicity are discussed. It is possible to prevent the heat inactivation of the toxin by means of substances which interfere with the coagulation and adsorption on the protein particles. Chemical Abstracts.

Non-colloidal cryptotoxic substances. H. Vincent (Compt. rend., 1928, **186**, 1175—1177).—The addition of sodium salts of mono- or di-carboxylic acids of the benzene series, non-colloidal in character, even in small quantities, to lethal doses of tetanus toxin renders the latter inactive, especially after 2

or 3 days' contact at 39°. Sodium salicylate is especially active in this respect. An amount of toxin corresponding with 200—400 lethal doses may be injected into a guinea-pig after addition of sodium salicylate, and the injections repeated with larger doses so that the animal becomes accustomed to the poison. The effect of adding varying amounts of the salt to the toxin is described. Successive doses render the blood of a rabbit antitoxic. Sodium salicylate likewise destroys the lethal powers of malignant œdema toxin injected into the blood-stream of a rabbit. Sodium benzoate, hippurate, butyrate, pyruvate, and mucate possess the properties of sodium salicylate to a lesser degree. J. D. FULTON.

Prolonged storage of bacteriological nutrient media. W. PLAHL (Z. Unters. Lebensm., 1927, **54**, 371—373).—In order to prevent the drying of the medium during prolonged storage, the test-tube containing it is inserted plug first into a larger test-tube, 5 cm. longer. A plug 1 cm. thick is inserted into the larger test-tube against the end of the inner tube, then a suitable disc of writing paper, followed by another plug of cotton wool similar to the first. During sterilisation the outer tube has its mouth downwards. When the medium has cooled, the mouth of the outer tube is turned upwards, and the outer plug is soaked through to the paper disc with a gelatin–salicylic acid solution (containing 1% of salicylic acid). The inner surface of the glass, in contact with the plug, is thoroughly moistened with the solution. A cork, previously dipped in the same solution, is inserted in the mouth of the test-tube. For long storage periods, the projecting part of the cork, and the adjacent glass, may be coated with paraffin. The same process may be applied in the incubation of inoculated tubes under constant moisture conditions. A simple device allows the application of the method to tubes containing a liquid medium. W. J. BOYD.

Destruction of chloroform by animal putrefaction. G. SENSI and D. SIRI (Annali Chim. Appl., 1928, **18**, 78—86).—By means of Lallemand and Duroy's method it is shown that chloroform does not prevent animal putrefaction. Chloroform was gradually destroyed as a result of the putrefaction of flesh and was not detectable after the lapse of 52 days. T. H. POPE.

Absorption and disinfection. I. G. LOCKEMANN and H. PICHER (Z. Hyg. Infect.-Krankh., 1927, **108**, 125—145; Chem. Zentr., 1928, i, 223).—A comparative study of the absorption of silver and mercury salts on textile fibres and their disinfecting power. A. A. ELDRIDGE.

Toxic effect of some metals and alloys on bacteria. G. TAMMANN and W. RIENÄCKER (Z. anorg. Chem., 1928, **170**, 288—300).—The poisonous action of various metals when immersed in nutrient media inoculated with *B. coli communis*, *B. brassicæ*, *B. gossypii*, *Sarcina agilis*, or *Penicillium glaucum* has been investigated by observing the size of the organism-free areas round the metals after incubation. The action of some salts has also been examined. Of the metals used, mercury, copper, nickel, cobalt, and antimony have the greatest effect, zinc and cadmium are less toxic, and aluminium, chromium, manganese, iron, bismuth, gold, and platinum have little or no action. Silver ions first begin to exert a poisonous effect at concentrations of 1×10^{-5}—1×10^{-8}, but even over this range the action is extremely variable, and the sensitivity of the organisms also varies from time to time. Copper salts, on the other hand, display a fairly sharp limit of toxicity at about 5×10^{-3} g.-atom/litre. Observations have also been made with alloys of copper or silver with varying amounts of gold, the results indicating that the present method is not suited for the investigation of the small amounts of metals given off by alloys. The size of the sterile areas round the metals is, in fact, too much influenced by purely secondary factors. R. CUTHILL.

Photo-biological action of light. J. RISLER, A. PHILIBERT, and J. COURTIER (Compt. rend., 1928, **186**, 1152—1154).—No bacteriophage is obtained by the addition of the filtrate of a culture of organisms, previously killed by the action of light in the presence of fluorescent dyes, to a similar living culture. *B. tuberculosis* is partly destroyed by the light of the neon lamp in the presence of many dyes (especially those of the pinacyanol class). The great bactericidal action of the light produced by the electrical volatilisation of aluminium wire is described. G. A. C. GOUGH.

Analysis of an insulin preparation containing 40 units per mg. A. BOIVIN and R. GUILLEMET (Bull. Soc. Chim. biol., 1928, **10**, 415—421).—The activity of insulin from ox pancreas could not be raised above 20 units per mg. by the picrate method (A., 1923, i, 967) owing probably to the continuous contamination by extraneous proteins. By repeated precipitation at p_H 5 with hydrochloric acid and sodium acetate, a non-crystalline sample (40 units of activity; maximum) was obtained which gave the following values: C, 51·8; H, 5·8; O, 25·4; N, 14·0; S, 2·96; ash, 0% (microanalysis). G. A. C. GOUGH.

Acetylation of insulin. K. FREUDENBERG and W. DIRSCHERL (Naturwiss., 1927, **15**, 832; Chem. Zentr., 1928, i, 211). A. A. ELDRIDGE.

Insulin. II. Acetylation of insulin. K. FREUDENBERG and W. DIRSCHERL (Z. physiol. Chem., 1928, **175**, 1—17).—When insulin, precipitated from methyl alcohol by benzene, is treated with pyridine and acetic anhydride at 0° for 3 hrs., it yields an *acetyl* derivative (3—4% Ac) which is almost inactive. By the action of 0·03*N*-alkali at 1—3° for 24 hrs. (conditions under which insulin is unattacked) acetylinsulin is converted into a "regenerated" substance (0·8% Ac) three to five times as weak as insulin, which, however, loses only 20% of its activity by a second acetylation and hydrolysis. If insulin is assumed to be a single individual, acetylation in the first place probably attacks hydroxyl, amino-, and imino-groups, and only acetoxy-groups are hydrolysed by the dilute alkali; the *N*-acetyl present constitutes less than 1% of the acetylinsulin. The "regenerated" substance is much more stable to alkali than is insulin. C. HOLLINS.

Action of insulin on the utilisation of carbohydrate by the starving animal. B. FÖRSTNER (Biochem. Z., 1928, **194**, 422—440).—Injection of

insulin into starving, curarised, artificially respiring dogs is accompanied by a moderate increase in oxygen utilisation, but change of respiratory quotient, indicating increased utilisation of carbohydrate, does not occur. P. W. CLUTTERBUCK.

Effect of insulin on amino-acid content of blood. J. M. LUCK, G. MORRISON, and L. F. WILBUR (J. Biol. Chem., 1928, **77**, 151—156).—Administration of insulin lowers the amino-acid nitrogen of the blood, the molecular decrease of the amino-acids being almost as great as that of the sugar; the decrease in the amino-acids appears not to be a secondary effect of the hypoglycæmia.

C. R. HARINGTON.

Distribution of lipins in normal and abnormal liver tissue. II. Effect of insulin on lipins of rabbit liver. E. R. THEIS (J. Biol. Chem., 1928, **77**, 75—80).—Prolonged administration of insulin to rabbits causes a decrease in the total lipins of the liver; the livers of animals killed shortly after injection of insulin show a relatively greater decrease in the phospholipin fraction. C. R. HARINGTON.

Action of pepsin and trypsin-kinase on insulin. A. HARTENECK and W. SCHULER (Z. physiol. Chem., 1927, **172**, 289—299).—Both pepsin and trypsin (the latter purified by adsorption on alumina, and activated by enterokinase) inactivate insulin when the mixtures are allowed to digest at suitable hydrogen-ion concentrations. The enzymic inactivation of insulin is irreversible. Its rate depends on the amount of enzyme used. An increase in amino-nitrogen (formol titration) indicates that the insulin (or the accompanying protein) suffers hydrolysis.

H. D. KAY.

Recovery of a pancreatic secretory excitant by vivi-dialysis of the circulating blood. H. NECHELES and R. K. S. LIM (J. Physiol., Proc. Physiol. Soc., 1927, **64**, xxviii—xxix).—The presence of a pancreatic excitant in the circulating blood is proved, and preliminary experiments on its separation by vivi-dialysis have been performed.

A. A. ELDRIDGE.

Influence of thyroid alone and of thyroid administered together with nucleic acids on the growth and longevity of the white mouse. T. B. ROBERTSON (Austral. J. Exp. Biol., 1928, **5**, 69—88).—The daily administration of 1·5 mg. of desiccated thyroid tissue to white mice accelerates early growth and diminishes the life-duration period by 17%. The combined effect of the administration of thyroid and either thymus- or spleen-nucleic acid appears to be approximately additive. E. A. LUNT.

"Antithyroidin (moebius)." A. GURBER and O. GESSNER (Arch. exp. Path. Pharm., 1928, **129**, 370—379).—The active principle of "Antithyroidin-moebius" is insoluble in alcohol and ether, stable when illuminated or heated to 56°, non-dialysable, and is precipitated practically entirely with the euglobulin fraction of the protein, from which it cannot be separated. Further, normal sheep serum contains a substance inhibiting the metamorphosis of tadpoles, but it is less active than "Antithyroidin-moebius." Phenol 1 : 20,000 to 1 : 40,000 accelerates the metamorphosis of tadpoles under the influence of thyroid. W. O. KERMACK.

Insects as test animals in vitamin research. I. Vitamin requirements of the flour beetle, *Tribolium confusum*, Duval. M. D. SWEETMAN and L. S. PALMER (J. Biol. Chem., 1928, **77**, 33—52).—The above insect could be reared on a diet lacking fat and fat-soluble vitamins and vitamin-*C*; vitamin-*B* was, however, necessary to growth, and was present in considerable amount in the bodies of the larvæ.

C. R. HARINGTON.

Hydrogenation of sterol-free unsaponifiable matter of cod-liver oil. I. Z. NAKAMIYA and K. KAWAKAMI (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 62—66).—Hydrogenation of biosterin (vitamin-*A*) yielded nonacosane, batyl alcohol, octadecyl alcohol, palmitic ester, myricyl alcohol, and an unidentified saturated alcohol. CHEMICAL ABSTRACTS.

Mode of action of vitamin-*B*. H. BIERRY and M. KOLLMANN (Compt. rend., 1928, **186**, 1062—1064).—When the external secretion of the pancreas is suppressed the islet tissue hypertrophies. A similar phenomenon is observed in pigeons suffering from beriberi, but ingestion of small quantities of vitamin-*B* in such cases maintains the normal balance of the functions of the pancreas. Similarly a condition of hyperglycæmia is developed in pigeons which have been deprived of the vitamin, but is removed by subsequent injection of the vitamin. It is concluded that vitamin-*B* exerts a stimulating action on the glands both of internal and external secretion.

J. W. BAKER.

Differentiation between vitamins-B_1 and -B_2. H. M. EVANS and G. O. BURR (J. Biol. Chem., 1928, **77**, 231—240).—The concentrate tikitiki prepared from an alcoholic extract of rice polishings (Wells, B., 1922, 77A) contains almost exclusively vitamin-B_1; it is also found that commercial maize-starch and commercial caseinogen both contain appreciable amounts of vitamin-B_2. C. R. HARINGTON.

Avitaminosis. Behaviour of some blood ferments in avitaminosis. Antitryptic action of serum in experimental avitaminosis. F. GENTILE (Arch. fisiol., 1927, **25**, 21—32, 33—42; Chem. Zentr., 1928, i, 87).—In pigeons (with experimental beriberi diet) and guinea-pigs (with diet free from vitamin-*C*) the glycolytic power of the blood is decreased; in hunger the blood glycolysis is greatly increased. The catalase value for guinea-pigs (on a scorbutic diet) sinks at first, and then gradually rises to and above the normal. With pigeons fed with polished rice there is a considerable rise in the antitryptic ferment content, with a fall on the appearance of symptoms. With guinea-pigs there is an increase of tryptic ferment on a scorbutic diet, and a diminution in hunger. A. A. ELDRIDGE.

Avitaminosis and autoclave-sterilised food. G. GUERRINI (Biochim. terap. sperim., 1927, **14**, 22—35; Chem. Zentr., 1928, i, 87).—Sterilisation of food in an autoclave effects changes, additional to the destruction of vitamins, which cause disease in pigeons. A. A. ELDRIDGE.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1928.

General, Physical, and Inorganic Chemistry.

Primary dark space of a Geissler discharge. K. B. EMELEUS and (MISS) N. M. CARMICHAEL (Phil. Mag., 1928, [vii], **5**, 1039—1048).—Some of the properties of the primary dark space on the cold cathode of a Geissler discharge can be accounted for by an application of the equations developed by Langmuir for the positive ion sheaths present on exploring cathodes. There are, however, discrepancies which indicate that the cathode receives fast electrons from adjacent parts of the discharge which could subsequently produce a secondary electronic emission from the metal. A. E. MITCHELL.

Emission of particles from hot platinum in air at atmospheric pressure. W. D. FLOWER (Phil. Mag., 1928, [vii], **5**, 1084—1094).—The Wilson cloud method has been employed for the ultramicroscopic examination of the large ions and nuclei emitted from a hot platinum wire in air at normal pressure. After removing the source of the nuclei it was found that the number visible increased to a maximum and then diminished, a result which is explained on the theory that at emission the nuclei are too small to be seen and subsequently coagulate. The coagulation of the nuclei has been observed and the rate of coagulation is expressed by the equation $dn/dt=-kn^2$, where n is the number of particles present and k is a constant$=0{\cdot}15\times10^{-8}$ cm.^{3}/sec. This value is in fair agreement with the value $0{\cdot}13\times10^{-8}$ cm.^{3}/sec., obtained by Kennedy for large ions and nuclei from a Bunsen flame. A. E. MITCHELL.

Fine structure of the spectrum lines of thallium in the ultra-violet. W. MOHAMMAD and S. B. L. MATHUR (Phil. Mag., 1928, [vii], **5**, 1111—1114).—Of the twenty-one lines of thallium reported by Exner and Haschek between 6550·15 and 2580·25 Å., only eleven have sufficient intensity to be photographed by the aid of a quartz Lummer–Gehrcke plate. The fine structure of these lines has been examined and the positions of the satellites are given. A. E. MITCHELL.

Distribution of electrons among atomic levels. E. C. STONER (Proc. Leeds Phil. Soc., 1928, **1**, 226—231).—Theoretical. It is shown that electrons may be divided into n, k groups, but a subdivision into n, k, j grouplets is not justifiable. For an n, k group for which the maximum number of electrons is z [$z=2(2k-1)$] the X-ray sub-level scheme is appropriate when the group contains 1 or $z-1$ electrons. For other numbers of electrons, the level scheme is completely different, corresponding with other multiplicities. W. E. DOWNEY.

Spectrum of ionised sodium. K. MAJUMDAR (Indian J. Physics, 1928, **2**, 345—354).—The spectral lines of sodium have been classified by the application of the irregular doublet law. An approximate value of 47 volts is deduced for the ionisation potential of sodium. M. S. BURR.

Extension of the irregular doublet law to complex spectra. M. SAHA and P. K. KICHLU (Indian J. Physics, 1928, **2**, 319—342).—The data for Millikan and Bowen's irregular doublet law have been collected and tabulated, and the law has been shown to hold good in the case of complex spectra. On the basis of this law the ionisation potential of carbon should be approximately 11 volts. This has been confirmed experimentally (Fowler, Nature, 1928, **121**, 304). Predictions have also been made with regard to spectral lines which are still unknown, belonging to other elements. M. S. BURR.

Regularities in the spectra of sexavalent elements. D. S. JOG (Indian J. Physics, 1928, **2**, 343—344).—The structure of spectra may be elucidated by comparing the spectra of successive elements which, by electric discharge, have been reduced to the same electronic configuration, *e.g.*, O, F^+, and Na^{++}. Several lines have been identified as belonging to these elements by the help of the extension of the irregular doublet law discussed by Saha and Kichlu (cf. preceding abstract). M. S. BURR.

Scattering of electrons by crystals. H. BETHE (Naturwiss., 1927, **15**, 786—788; Chem. Zentr., 1928, i, 154).

Excitation function of spectral lines. W. HANLE (Naturwiss., 1927, **15**, 832—833; Chem. Zentr., 1928, i, 158).—The excitation function (excitation probability in relation to the acceleration voltage of the bombarding electrons) of the mercury line 2537 Å. has been observed in the neighbourhood of the excitation potential. A. A. ELDRIDGE.

New type of discharge in neon tubes. J. W. RYDE, L. JACOB, and B. S. GOSSLING (Nature, 1928, **121**, 794).

Rydberg term tables. F. PASCHEN (J. Opt. Soc. Amer., 1928, **16**, 231—243).—Values of $Z^2N/(m+a)^2$ are tabulated for $Z=1$, 2, 3, and 4, Z being the number of the spectrum, N Rydberg's constant, m the order number of the term, and a the Rydberg correction. C. W. GIBBY.

New regularities in the band spectrum of helium. G. H. DIEKE, T. TAKAMINE, and T. SUGA (Nature, 1928, **121**, 793—794).—More than 20 new

bands, and parts of other bands, have been found; most of the new bands have the $2p$ state as final state. Besides bands in which terms of a new type are involved, there were found new bands originating from the combination of Curtis' terms with the vibrational quantum number 1 and 2.

A. A. ELDRIDGE.

K-Electron ionisation by direct impact of cathode rays. D. L. WEBSTER (Proc. Nat. Acad. Sci., 1928, **14**, 339—344).—The assumptions underlying the theory of indirect K-ionisation used in previous work (this vol., 691) and here, are first tested by finding the ratio of the indirect $K\alpha$-line rays of silver to its continuous spectrum rays of the same wave-length. This should be independent of all questions of resolving power, sensitivity function, etc. The results obtained are of the right order, although not strictly accurate. The probability of direct K-ionisation by a cathode ray in silver is found to be 0·9 times the probability of an equivalent quantum emission in the continuous spectrum; the ratio is practically constant with change of voltage, and therefore must hold, not only for ordinary thick targets, but for infinitely thin targets also. The absolute probability of direct K-ionisation is also estimated with large limits of error, and found to agree with Thomas' theory. It seems probable that the process of direct ionisation is not usually an internal photo-electric effect, but rather a process of repulsion between electrons obeying laws much like the inverse square law.

A. J. MEE.

Analysis of spectra arising from quadruply-ionised tin, Sn V. R. C. GIBBS and H. E. WHITE (Proc. Nat. Acad. Sci., 1928, **14**, 345—348).—Most of the strong lines in the spectrum of Sn V have been identified. A table showing the intensities, wave-lengths, and frequencies of the identified lines is given, and the spectrum is analysed.

A. J. MEE.

Structure of some spectra with regard to recent theoretical considerations. T. L. DE BRUIN (Arch. Néerland., 1928, [iii], **A**, **11**, 70—153).—A comprehensive paper giving the results of researches which confirm the spectroscopic displacement law of Sommerfeld and Kossel. The arc and spark spectra of several elements were photographed, using the method of discharge without electrodes. The spectrum of potassium was examined and the existence of two characteristic spectra shown. One is yellowish-green and the other is bluish-violet. The former is due to the neutral atom, K I, the latter to the singly-ionised atom, K II, and is comparatively simple. The spectrum of K II was analysed and compared with that of neutral neon, Ne I, and neutral argon, A I. It shows some analogy to both these spectra, as it should do if the Bohr theory is correct. The structure of the spectrum is discussed in relationship to the configuration of the atom. It is also shown that the 3_3 structure is more stable than the 4_2, which is not so for the rare gases. The Zeeman effect in the case of the K II lines was examined partly for ordering the spectrum, and partly in an attempt to verify the theory of Landé and Heisenberg, but the diffuse way in which the lines split made measurements impossible. The spectra of doubly-ionised potassium, K III, and triply-ionised potassium, K IV, were difficult to study, but should be equivalent to those of non-ionised fluorine, F I, and chlorine, Cl I, and singly-ionised fluorine, F II, and chlorine, Cl II, respectively. The spectrum of fluorine was obtained by passing a discharge without electrodes through silicon tetrafluoride. The theoretical scheme for terms of F I is drawn up, and the terms found are experimentally identified. The ionisation potential of fluorine calculated from the fundamental term is found to be 16·7 volts. The spectrum of singly-ionised fluorine F II was investigated and compared with the analogous spectra of non-ionised oxygen, O I, and non-ionised sulphur, S I; the structure is shown to be similar. The spectrum of singly-ionised neon, Ne II, was analysed and shown to be analogous to that of non-ionised fluorine, whilst that of doubly-ionised neon, Ne III, is similar to that of singly-ionised fluorine. The structure of the terms of the spectra examined conforms to the new theory of Heisenberg and Hund on complex spectra. The spectra of selenium, arsenic, and indium were investigated by the same method with a view to relate them with the theory of Hund.

A. J. MEE.

Spectrum of ionised neon. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 2—13).—180 Lines of the spectrum of ionised neon (Ne II) have been classified in a term scheme and the deepest quadruplet terms identified. The Ne II spectrum has a structure analogous to that of the F I spectrum. This is in agreement with the theory according to which the spectra of the ionised rare gases should have the same structure as the F I spectrum (cf. A., 1927, 82). In Ne II the terms have approximately double the value of the analogous terms of F I.

M. S. BURR.

Intensity measurements in the secondary spectrum of hydrogen. L. S. ORNSTEIN, W. KAPUSCINSKI, and (MISS) J. G. EYMERS (Proc. Roy. Soc., 1928, **A**, **119**, 83—91).—The figures given by McLennan for the intensities in the secondary spectrum of hydrogen (A., 1927, 1004) are only densities, and it is shown that, since the relations between density and intensity are not simple, McLennan's values could not be used for theoretical investigations of the secondary spectrum. The intensities of about 230 lines over the region 4500—4900 Å. have now been measured by the Utrecht method. In this region, the value of the sensitivity of the photographic plate depends strongly on the wave-length, and allowance was made for this. The method used for the analysis of closely adjacent lines is described in detail. The intensity values are compared with McLennan's densities; for moderate intensities the ratio of the results is almost constant, but no proportionality is shown for higher intensities.

L. L. BIRCUMSHAW.

Relation between mean stopping power and mean range of β-rays. E. J. WILLIAMS (Proc. Camb. Phil. Soc., 1928, **24**, 315—319).—The true rate of loss of energy or "stopping power" of β-rays is the quantity dT/dx, where dT is the mean energy lost by rays of energy T in travelling a distance dx

along their paths. The cloud method enables only the total ranges of β-particles to be observed, and in deducing the stopping power from the mean range R, dT/dR is not exactly the same as dT/dx, owing to straggling. The relation between these two quantities is calculated so that the cloud method may be rigorously interpreted. For rays of 10,000 volts traversing light elements the correction is about 7%, whilst for α-rays it is negligible. C. J. SMITHELLS.

Absolute intensity measurements on the sodium flame. Duration of the excited state. L. S. ORNSTEIN and E. F. M. VAN DER HELD (Ann. Physik, 1928, [iv], **85**, 953—960).—The absolute intensity of the green mercury line from a quartz lamp was first measured and then photographic comparisons were made of the sodium flame and the yellow light from a Nitra lamp, and the green line with the green light from the Nitra lamp. For the sodium flame, 250 quanta per sec. per atom are emitted at 1970° Abs. The Einstein equation leads to the value 5×10^{-8} sec. for the period of excitation as against the values 1·6 and $3{\cdot}8\times10^{-8}$ sec. due to Minkowski (A., 1926, 650) and Kerschbaum (A., 1926, 652), respectively. R. A. MORTON.

Methods of estimating the intensities of spectral lines. W. H. J. CHILDS (Proc. Physical Soc., 1928, **40**, 132—148).—A critical discussion of several methods of spectral photometry applied to the special case of the band spectrum of helium is given. The preferred method is to photograph the line spectrum in the usual way and then calibrate the plate by illuminating the slit with a tungsten-filament lamp in such a way that on development a number of continuous spectra of progressively increasing density are obtained. From these images the relation between the intensity of light and density of image, and between plate sensitivity and wave-length, may be ascertained. Density measurements are obtained by means of a selenium cell microphotometer. C. J. SMITHELLS.

Structure of the second order spectrum of sulphur. J. GILLES (Compt. rend., 1928, **186**, 1354—1355).—The values of the combinations of the multiplets amp^4S and^4P of the S II spectrum, are deduced from those previously published (cf. this vol., 565). J. GRANT.

Certain multiplets in the spectra of Cd III and In IV. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], **31**, 776—781).—With the aid of the transitions from ^3PDF, $^1PDF(4d^95p)$ to ^3D, $^1D(4d^95s)$ already determined for Pd I and Ag II, the corresponding lines in the spectra of Cd III and In IV have been identified and tabulated; the transitions from $^3D_1$, $^3P_1$, and $^1P_1(4d^95p)$ to $^1S_0(4d^{10})$, the lowest level, have also been identified for Ag II, Cd III, and In IV. The validity of the irregular doublet law is confirmed. A. A. ELDRIDGE.

Application of the X-ray laws to optical spectra of higher rank, and the classification of Ga IV and Ge V. J. E. MACK, O. LAPORTE, and R. J. LANG (Physical Rev., 1928, [ii], **31**, 748—772).—The $(3d^94s)$ and $(3d^94p)$ levels of Ga IV and Ge V, and a tentative $(3d^{10})$ level for Ga IV have been found, and the levels formerly classified as $^3D_1$, $^1P_1(3d^94p)$ of Zn III have been interchanged. Evidence is adduced to show that of the ^3D, $^1D(d^9s)$ the $^3D_2$ level approaches the limit $^2D_3(d^9)$, contrary to Hund's theory. Distinctions between X-ray and optical spectra in application of the X-ray laws are considered, as also is the shape of the σ_1 (first order screening number) curve for isoelectronic spectra. The irregular doublet law is not always valid. A. A. ELDRIDGE.

Arc spectrum of germanium. C. W. GARTLEIN (Physical Rev., 1928, [ii], **31**, 782—792).—The wave-lengths (±0·03 Å.) of germanium arc lines above 1870 Å. are tabulated; the relative energy levels have been determined and transitions corresponding with 73 lines identified. The first resonance potential is 4·65 volts and the ionisation potential determined by the limit $^2P_1$ is 7·85 volts. Similarities in the arc spectra of silicon, germanium, tin, and lead are considered. A. A. ELDRIDGE.

Lowest terms in the spark spectrum of nickel and copper (Ni II and Cu II). R. J. LANG (Physical Rev., 1928, [ii], **31**, 773—775).—In the spark spectrum of nickel the lowest terms $^2D_{2\,3}(d^9)$ lie 6884 and 8391 cm.$^{-1}$ below $a^4F'_8$; in that of copper $^1S_0(d^{10})$ lies 21925 cm.$^{-1}$ below a^3D_3. A. A. ELDRIDGE.

Arc and spark spectra of titanium. I. Spark spectrum, Ti II. II. Arc spectrum, Ti I. H. N. RUSSELL (Astrophys. J., 1927, **66**, 283—328, 347—438).—I. All but the weakest lines have been classified; 33 doublet and 17 quadruplet terms have been identified. Three series of two members each indicate an ionisation potential of 13·6 volts. Hund's theory of the relation of spectral lines to electronic configurations in the atom is confirmed. A comparison of the spectra of Ti II and Sc I shows that Moseley's law is closely satisfied.

II. The arc spectrum is complicated; 43 singlet, 65 triplet, and 34 quintuplet terms have been identified. There are no intercombinations between singlets and quintuplets. Hund's theory is again confirmed. Seventeen series, converging to seven different limits, all terms of Ti II, have been identified; the ionisation potential is 6·81 volts. The spectra of Ti I and V II are similar in structure; comparison indicates that the ionisation potential of V II is approximately 14·1 volts. A. A. ELDRIDGE.

Zeeman effect and spectral terms in the arc spectrum of platinum. A. C. HAUSSMANN (Astrophys. J., 1927, **66**. 333—346).—The Zeeman effect of 173 arc lines of platinum was investigated in the region 5500—2500 Å.; 33 of the lines could be identified from their patterns. Twelve low levels have been identified; the ground term is $^3D_3$, d^9s. There are 45 intermediate and 15 high levels. Practically all the strong lines in the arc spectrum are attributed to combinations between these levels.

A. A. ELDRIDGE.

Wave-lengths of carbon, oxygen, and nitrogen in the extreme ultra-violet with a concave grating at grazing incidence. J. B. HOAG (Astrophys. J., 1927, **66**, 225—232).—With a vacuum spectrograph of special design, wave-lengths from 1658 to 558 Å. for spark discharge through mag-

nesium and carbon electrodes were obtained; by passing gases through the electrodes, gaseous and metallic spectra are simultaneously obtained.

A. A. ELDRIDGE.

Secondary standards of wave-length; interferometer measurements of iron and neon lines. H. D. BABCOCK (Astrophys. J., 1927, 66, 256—282).—Standard wave-lengths are recorded for 286 iron lines, λ 3407—6677 Å., and for 11 neon lines, λ 5852—6506 Å., measured in terms of the primary standard, 6438·4696 Å., of cadmium. The neon wave-lengths agree precisely with the values adopted as secondary standards, but the iron wave-lengths are systematically smaller than the adopted values. The differences are discussed.

A. A. ELDRIDGE.

Absorption spectrum of mercury at high pressure admixed with nitrogen. H. R. MOORE (Science, 1927, 66, 543—544).—The bands already observed (Mohler and Moore, A., 1927, 917) have been extended towards the red to 3087 Å. at 215—305°, and towards the violet to 2666 Å. at 425—530°, by the addition of nitrogen. Forty-two such bands were observed. The band at 2528 Å. was always obtained with mixtures of mercury and nitrogen, and appears to be definitely conditioned by the presence of nitrogen. Resonance broadening increases with the pressure of the nitrogen. The extension of the bands may be ascribed to the increase in concentration of Hg_2 molecules resulting from the combined effect of the nitrogen and the radiation used as a source, or they may represent the vibrational spectra of HgN_2 molecules, unstable or quasi-stable, formed between nitrogen molecules and excited mercury atoms.

A. A. ELDRIDGE.

Band spectrum of mercury excited by a high-frequency discharge. J. G. WINANS (Nature, 1928, 121, 863—864).—The spectrum of the discharge showed the mercury arc lines and the mercury bands with maxima at 4850, 3300, 2540, and 2345 Å.; distilling vapour is necessary for the excitation of the bands 4850, 3300, and 2345 in a high-frequency discharge. The band at 4850 Å. is destroyed by local heating. The initial excited state for the band 4850 Å. differs from that of the band at 3300 Å. and from those of the bands at 2345 and 2540 Å., but the final states of the bands at 2345 and 2540 Å. are the same.

A. A. ELDRIDGE.

Spectra of doubly- and trebly-ionised titanium. (Ti III and Ti IV). H. N. RUSSELL and R. J. LANG (Astrophys. J., 1927, 66, 13—42).—Thirty-one new lines of Ti IV and 90 lines (mostly new) of Ti III have been identified between 5492 and 423 Å.; all the former and all but four of the latter have been classified. Twelve terms are tabulated for Ti IV; the $3D$ term is the lowest, and the ionisation potential is 43·06 volts. Nineteen terms were identified for Ti III; the estimated ionisation potential is 27·6±1·0 volts. The spectrum of Sc III is briefly discussed.

CHEMICAL ABSTRACTS.

Photography of the infra-red solar spectrum. H. D. BABCOCK (Nature, 1928, 121, 830—831).—About 12 lines between 10000 and 10750 Å. have been observed on prismatic plates, one at 10049·8 Å. being specially conspicuous; it is evidently the fourth member of the Paschen series of hydrogen. On grating plates a number of lines were also observed.

A. A. ELDRIDGE.

Application of the irregular doublet law to complex spectra. K. MAJUMDAR and G. R. TOSHNIWAL (Nature, 1928, 121, 828—829).—Saha and Kichlu's application of the irregular doublet law to complex spectra (this vol., 209) is confirmed in the groups Ne, Na^+, Mg^{++} and A, K^+, Ca^{++}. The view that the spectrum of the solar corona is composed of the lines of Ca^{++} is not supported. The ionisation potential of Ca^{++} is about 52 volts.

A. A. ELDRIDGE.

Related lines in the spectra of the elements of the iron group. H. N. RUSSELL (Astrophys. J., 1927, 66, 184—216).—The arc and spark spectra of potassium, calcium, scandium, titanium, vanadium, chromium, iron, cobalt, nickel, copper, and zinc have been classified sufficiently to illustrate the similarity of spectral groups resulting from similar electron transitions. Homologous terms and homologous lines as n varies from 1 to 12 are tabulated.

CHEMICAL ABSTRACTS.

Spectrum of ionised sodium. O. LAPORTE (Nature, 1928, 121, 941).—By using one of the differences between pairs of lines in the Na II spectrum (Newman, this vol., 210), it is possible to arrange numerous strong lines as combinations of four s terms with ten p terms corresponding with the transition $3s^1\,{}^3P—3p^1\,{}^2\,(S,P,D)$.

A. A. ELDRIDGE.

Optical characterisation of spark emission spectra. G. I. POKROWSKI (Z. Physik, 1928, 48, 586—593).—By assuming that the energy consumed in a spark is proportional to the square of the root mean square value of the current flowing through the arc, the total intensity I of n spectral lines is shown to be related to the current i and to the absorptive power, k, of the metal vapour through which the spark takes places by the expression $I=ai^2+b(1-e^{-kci^2})$, where a, b, and c are constants. It is also shown that for a given value of i, I is linearly related to the width of the spark gap. Data relating to lines 5000, 5200, 5890 Å. in the spark between copper and electrodes are shown to be in agreement with the above expression.

R. W. LUNT.

Active nitrogen. P. K. KICHLU and D. P. ACHARYA (Nature, 1928, 121, 982—983).—The spectrum of active nitrogen includes a band system from 7500 to 8900 Å., doubtless originating from the N_2 molecule, and presumably analogous to A, B, α bands of oxygen. The results of McLennan, Ruedy, and Anderson (this vol., 456) are criticised.

A. A. ELDRIDGE.

New photo-electric phenomenon with thin sheets of alkali metals. R. SUHRMANN (Naturwiss., 1928, 16, 336).—When thin sheets of alkali metals are illuminated with the mercury 240 μμ line, the light intensity–voltage characteristic reaches a sharp saturation value at a few volts. At the red limit (313 μμ), however, it rises steadily with increasing potential. The same phenomenon is found but to a less degree with thicker sheets.

J. W. SMITH.

Predicted ionisation potential of radon. S. C. BISWAS (Phil. Mag., 1928, [vii], 5, 1094—1098).—It

is shown that the ionisation potential of an atom is given by the expression $I_{(volts)}=3 \cdot 83kn/r^2$, where k and n are respectively the azimuthal and radial quantum numbers of the external electron and r^2 is the mean square radius of the nk orbit. Since for elements of the same group of the periodic classification k is constant, it follows that the ionisation potentials of these elements will be proportional inversely to the square of the radius and directly to the radial quantum number. From crystal structure and other measurements it is shown that the atomic radius of radon should be 1·81±0·03 Å., whence taking the quantum numbers in question as 6 and 2 the ionisation potential should be 14·0±0·5 volts, a result in general accordance with the known values for krypton and xenon, but in disagreement with the predictions of Turner (A., 1924, ii, 797) and others.

A. E. MITCHELL.

Cause of loss of thermionic activity of thoriated tungsten filaments under certain voltage conditions. (MISS) A. C. DAVIES and (MISS) R. N. MOSS (Phil. Mag., 1928, [vii], 5, 989—1010).—It is found that loss of thermionic activity is due to the bombardment of the filament by positive ions which originate in their turn from the electron bombardment of the grid and plate. W. E. DOWNEY.

Electron theory of metals. A. SOMMERFELD (Naturwiss., 1927, **15**, 825—832; 1928, **16**, 374—381).—The old electron theory of metals is discredited, but it can be rehabilitated without the adoption of new physical assumptions. The statistical treatment of the assumptions of Drude and Lorentz must be replaced by a new treatment based on the wave-mechanics. The present work is concerned mainly with the development of a wave-mechanical theory of conductivity in metals, and the variations with changes in temperature and pressure. Starting from the Pauli principle and the Fermi–Dirac statistics, it is shown that the mean velocity of an electron-gas is independent of temperature; wave-lengths in terms of de Broglie's ideas are then calculated, and after considering the Richardson and Volta effects, it is possible to develop the theory of metallic conduction so as to obtain satisfactory agreement between the observed and calculated data. A final section is devoted to the direction-dependence of conductivity and the thermal forces in unicrystalline material.

R. A. MORTON.

Electron emission in intense electric fields. R. H. FOWLER and L. NORDHEIM (Proc. Roy. Soc., 1928, A, **119**, 173—181).—The phenomenon of electron emission in intense fields can be accounted for in a satisfactory quantitative way by Sommerfeld's revived electron theory of metals (see preceding abstract). Nordheim's results (this vol., 452) are extended to include the effect of an external field, using the same methods and the same underlying picture of the metal. The formula $I=CF^2e^{-a/F}$ is established, independent of the temperature at low temperatures, in agreement with experiment. No theoretical justification is found for the general formula for the current, valid over wide ranges of temperature and field strength, suggested by Millikan and Lauritsen (Proc. Nat. Acad. Sci., 1928, **14**, 45). Exception is taken to the assertion of these authors that the conduction electrons, unlike the thermions, do not share in the thermal energy of agitation of the atoms. It is found that Sommerfeld's picture of a metal yields the formula both for strong fields and for thermionic emission, a single set of free conduction electrons distributed according to the Fermi–Dirac statistics sufficing for both purposes.

L. L. BIRCUMSHAW.

Liberation of electrons from a metal surface by positive ions. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 14—23).—In order to get more information as to the part played by positive ions in a gas discharge, two methods have been devised for determining experimentally the number of positive ions required to liberate one electron from a metal surface. In neon, the number of electrons liberated by one positive ion at zero velocity from a copper or iron surface, is of the order of 0·05. In argon α_0 is smaller than in neon, but at a magnesium surface it is larger than at a copper surface. Measurements have also been carried out with hydrogen to compare the method with that employed by Baerwald (Ann. Physik, 1921, [iv], **65**, 167), but, for a potential of 1000 volts, the value of α was only 10% of that found by Baerwald.

M. S. BURR.

Hydrogen activated by the electric discharge. A. DE HEMPTINNE (Bull. Acad. roy. Belg., 1928, [v], **14**, 8—17).—See this vol., 139.

Photo-electric threshold and heat of dissociation of the potassium molecule. R. W. DITCHBURN (Proc. Camb. Phil. Soc., 1928, **24**, 320—327).—Absorption curves and photo-ionisation experiments agree and give for the molecular photo-electric threshold value of potassium 2555±20 Å. The energy of dissociation of the potassium molecule is $0 \cdot 50_5 \pm 0 \cdot 01$ volt, and the heat of dissociation 11400 g.-cal. Between 200° and 500° the fraction associated varies from 10^{-4} to 10^{-2}.

C. J. SMITHELLS.

High-frequency electric discharge at low pressures. J. TAYLOR and W. TAYLOR (Proc. Camb. Phil. Soc., 1928, **24**, 259—267).—Experiments have been carried out under widely varied conditions on discharges through gases, under the influence of high-frequency oscillations (order 10^7 cycles per sec.), using tubes of the electrodeless type. The influence of the wall material is shown by the fact that on pumping down tubes not previously baked out, the order in which the discharges were first obtained on increasing the voltage was: soft glass, pyrex, and quartz. Even at the highest degree of exhaustion and with the mercury vapour (from the pumps) frozen out, faintly luminous discharges could be obtained. With a high frequency of alternation there will be no separation of charges, and the nett effect will be a periodic movement of the electrons through an atmosphere of positive ions, the observed luminosity arising from recombinations proceeding between oppositely charged particles. The discharge passes more easily in wide tubes than in narrow ones, with a dark space between the glow and the wall. The luminosity can be conducted along the tube by

moving an earthed conductor such as the hand along the outer walls. By lining the inside of a tube with metal gauze connected to a voltage supply, it is shown that the luminosity is destroyed by a unipotential wall. Injection of slow electrons into the glow has little effect. A new type of spherical glow has been obtained in bulbs, and discharges of this kind are regarded as uniform high-temperature enclosures of electrons and positive ions maintained artificially. R. A. MORTON.

Electrodeless discharge through gases. J. J. THOMSON (Proc. Physical Soc., 1928, **40**, 79—89).—An electrodeless discharge is produced by placing outside a glass tube containing gas at a low pressure a solenoid connected to the outsides of two Leyden jars, the insides of which are connected to the terminals of an induction coil. Rapidly alternating currents pass through the solenoid, and the electromagnetic induction starts currents in the exhausted vessel which flow in rings co-axial with the solenoid. The theory of the discharge is discussed. There is a critical gas pressure, depending on the frequency, at which the discharge passes most easily. With heavy currents the magnetic force is greatest near the walls of the bulb and produces a condition resembling the Heaviside layer. The discharge is assisted by the action of light, which is attributed to the absorption of energy by the gas molecules rendering them more easily ionised. The effect of impurities in the bulb is investigated. Free electrons become attached to electronegative elements like phosphorus and sulphur and ionisation is reduced. Metals also hinder the discharge by combining with gas molecules which are in a more active state than normal. The normal oxides of magnesium, calcium, and zinc combine with oxygen under the influence of the discharge to form higher oxides. C. J. SMITHELLS.

Excitation of the *D*-lines by the green sodium band. E. L. KINSEY (Nature, 1928, **121**, 904—905).—In accord with the views of Wood and Kinsey (this vol., 687), the green sodium band excites the *D*-lines in pure sodium vapour, but only in a narrow temperature range; the atomic lines appear somewhat below 400°, are maximal at 410°, and disappear above 450°. At 410° the molecules are probably only 55% dissociated. A. A. ELDRIDGE.

Space-distribution of the photo-electrons ejected by *X*-rays. E. C. WATSON (Physical Rev., 1928, [ii], **31**, 728—741).—Rutherford's theory of nuclear scattering, together with the assumption that all the electrons start from the parent atom in the same direction, accord with the observed distribution of the photo-electrons ejected by *X*-rays.
A. A. ELDRIDGE.

Photo-electric effect and thermionic emission. P. W. BRIDGMAN (Physical Rev., 1928, [ii], **31**, 862—866).—A correction and extension of previous work (this vol., 213). A. A. ELDRIDGE.

Voltage-intensity relations in the mercury spectrum. W. D. CROZIER (Physical Rev., 1928, [ii], **31**, 800—811).—Voltage-intensity curves were obtained for 20 mercury lines, when excited by electron impact. There is no significant change in the number of atoms in a given energy state as the ionisation potential is passed. The probability of different transitions down from a given energy state may not be independent of the way in which this state is excited. A. A. ELDRIDGE.

Series and ionisation potentials of the elements of the iron group. H. N. RUSSELL (Astrophys. J., 1927, **66**, 233—255).—Series, usually of two members only, have been identified in the arc spectra of potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and in the spark spectra of calcium, scandium, titanium, manganese, nickel, copper, and zinc; approximate series limits are determined and tabulated. Four important modes of ionisation of the neutral atom and three for the second ionisation are indicated. The following principal and second ionisation potentials are recorded: potassium 4·32, —; calcium 6·09, 11·82; scandium 6·57, 12·80; titanium 6·80, 13·60; vanadium 6·76, 14·7; chromium 6·74, 16·6; manganese 7·40, 15·70; iron 7·83, 16·5; cobalt 7·81, 17·2; nickel 7·64, 18·2; copper 7·69, 20·34; zinc 9·36, 17·89. New high terms, arising from configurations involving a 5*s* electron, have been identified in the spectra of vanadium, manganese, cobalt, and ionised manganese.
A. A. ELDRIDGE.

Astrophysical estimates of ionisation potentials of iron, yttrium, and lanthanum. A. V. DOUGLAS (Nature, 1928, **121**, 906).—Ionisation potentials are estimated, from astrophysical data, to have the following values: iron, 6·6 (by comparison with scandium and titanium), 5·5 (by comparison with strontium and barium); yttrium, 6·6; lanthanum, 4·9 volts. A. A. ELDRIDGE.

Ionisation by metastable atoms. F. M. PENNING (Naturwiss., 1927, **15**, 818; Chem. Zentr., 1928, i, 155).—The condition for the reduction of the sparking potential of an inert gas for large values of *pd* (pressure × separation of electrodes) on admixture of another gas is $V_{met} > V_{i'}$ (V_{met}=excitation potential of the metastable form of the inert gas; $V_{i'}$=ionisation potential of the admixed gas). The explanation is based on the scheme: metastable atom+foreign atom=normal atom+foreign ion. Measurements were made on neon with admixed mercury, krypton, argon, hydrogen, and nitrogen, and on argon with admixed iodine, mercury, xenon, and krypton. A. A. ELDRIDGE.

Current density of the normal cathode fall. W. DE GROOT (Naturwiss., 1927, **15**, 818; Chem. Zentr., 1928, i, 155).—The current density was smaller in a mixture of neon (containing 30% of helium) and argon (0·1—2%) than in the separate gases; two types of discharge were observed.
A. A. ELDRIDGE.

Loss of charge of positive rays and the influence of neighbouring metallic walls. E. RUCHARDT (Z. Physik, 1928, **48**, 594—599).—Polemical. A reply to Koenigsberger (A., 1927, 806). J. W. SMITH.

Mobilities of the positive ions formed by alpha-rays in air, hydrogen, and helium. J. S. ROGERS (Phil. Mag., 1928, [vii], **5**, 881—903).—From the

experimentally observed decrease in the mobility of ions during their life it is concluded that an ion, in a very short time after its formation, has developed into a cluster. The mobility changes in definite steps. If the changes in mobility were due to the gradual addition of neutral molecules, a gradual change in the mobility with the life of the ion would be expected. This step change in mobility is unexplained.

W. E. DOWNEY.

Measurement of displacements of negative carriers in flames. E. MARX and P. KAPPLER (Physikal. Z., 1928, **29**, 261—269).—A flame is charged with solutions of alkali metal salts and the variation of the "displacement" K_2, where $K_o'=\beta K_2$ (β being the charge-number and K_2 the mobility) with the concentration c determined. K_2 varies as $(1/c)^{\frac{1}{2}}+$constant, and the magnitude $K_o' \times$ (at. wt.)$^{\frac{1}{2}}$ is the same for rubidium, potassium, and sodium at a given normality; lithium is anomalous.

R. A. MORTON.

Reflexion of electrons by a crystal of nickel. C. J. DAVISSON and L. H. GERMER (Proc. Nat. Acad. Sci., 1928, **14**, 317—322).—In continuation of previous work (A., 1927, 492), an electron beam was directed against a {111} face of a nickel crystal at various angles of incidence, and the intensity of scattering in the incidence plane measured as a function of bombarding potential and direction. Whenever the speed of the incident electrons is comprised within any of certain ranges, changing in location as the angle of incidence is varied, a sharply-defined beam of scattered electrons issues from the crystal in the direction of regular reflexion. In each of these ranges there is an optimum speed where the intensity of the reflected beam is a maximum. The phenomenon is the analogue of the regular selective reflexion of X-rays, but the Bragg formula does not hold, although there is a simple correlation between the observed positions of the maxima and the positions calculated by the Bragg formula. A. J. MEE.

Luminous beads of metal particles sputtered by disruptive discharge in magnetic field. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 106—108).—Photographs are given showing the peculiar beaded tracks of metal particles sputtered in a magnetic field. Various explanations of the phenomena are offered, the most probable cause being the alternate formation and loss of an oxide film on the surface of the particle. C. J. SMITHELLS.

Relation between colour and magnetism of ions. B. MALYSCHEV (Ann. Physik, 1928, [iv], **85**, 794).—In connexion with the work of Joos (A., 1927, 94) it is suggested that the investigation of the magnetic susceptibilities of the carbonyls of paramagnetic metals in the gaseous, liquid, and solid states should prove interesting. R. A. MORTON.

Radiations emitted at the impact of hydrogen canal rays on metals. C. GERTHSEN (Ann. Physik, 1928, [iv], **85**, 881—912).—The possibility of exciting characteristic radiations by means of the impact of canal rays on metals has been investigated (cf. A., 1926, 655). Optical reflexion from a concave mirror makes possible the detection of weak rays emitted from the points of impact, but it has not proved possible to decide whether the rays are characteristic radiations from the atoms of the surface, or whether they correspond with the excitation of the Lyman series. The effects observed by Thomson (A., 1926, 988) are ascribed to reflected canal rays. An experiment designed to separate the wave-radiation effect from the reflected positive-ray effect showed that some of the canal rays are scattered with almost unchanged velocities. These reflected rays increase in velocity as the velocity of the primary rays increases. The scattering from different materials follows the laws for the scattering of α-particles at atomic nuclei, namely, proportionality with the number of atoms per c.c., and with the square of the atomic number. R. A. MORTON.

Positive-ray analysis of water vapour ionised by impact of slow electrons. H. A. BARTON and J. H. BARTLETT, jun. (Physical Rev., 1928, [ii], **31**, 822—826).—By the use of an electromagnetic method the ions H_2O^+ and OH^+ were detected, the former being the more abundant, with small quantities of a third ion, probably H_3O^+; no negative ions were observed, and scarcely any H^+ and H_2^+ ions. The ionisation potential corresponding with H_2O^+ was $13\pm1{\cdot}5$ volts, and that of OH^+ was not distinguishably different. The H_2O^+ ion is probably the primary ion. A. A. ELDRIDGE.

Detection and determination of ions in a gaseous discharge by optical methods. W. DE GROOT and L. BLOK (Physica, 1927, **7**, 315—320).—Light from a carbon arc passes through an arc formed in neon between a tungsten cathode and a nickel anode with a barium core; the light from the carbon arc is cut off in phase with an alternating current superimposed on the direct current for the barium arc, so that the absorption effects can be observed during those periods when the barium arc is extinguished. The barium lines 4934 and 4554 were observed in absorption. A positive-column discharge tube with argon and mercury vapour showed the mercury line 2847 Å. at 20° and −12°, but not at 120°. The absorption is dependent on the effective number of absorbing atoms and the thickness of the absorbing layer. For barium, the number of ions per c.c. at 3 amp. arc current is 10^{12}.

CHEMICAL ABSTRACTS.

Ionisation in positive-ion sheaths. P. M. MORSE and W. UYTERHOEVEN (Physical Rev., 1928, [ii], **31**, 827—832).—The positive-ion current to a plane auxiliary collector placed in a neon discharge is double that anticipated; the increase is probably caused by the ionisation of the metastable atoms within the sheath by radiation from the discharge. A similar increase is to be expected in helium and argon. A. A. ELDRIDGE.

Active nitrogen. J. KAPLAN and G. CARIO (Nature, 1928, **121**, 906—907).—The long life and behaviour in the presence of catalysts of active nitrogen indicates that it is atomic, and that metastable molecules are formed under the influence of the recombination of atoms to molecules. This process is considered to be accompanied by the formation of metastable atoms. This view is shown to be in accord with experimental data. A. A. ELDRIDGE.

Active nitrogen. B. Lewis (Nature, 1928, **121**, 864—865).—Polemical and explanatory (cf. Willey, this vol., 341). A. A. Eldridge.

Active nitrogen. B. Lewis (Nature, 1928, **121**, 938—939).—On introduction of pure oxygen (1%) into glowless nitrogen immediately after discontinuing the electrodeless discharge, no glow was produced; further, subsequent subjection of the mixture to the discharge caused little or no glow. The observation accords with those of Herzberg (this vol., 457) and of Bonhoeffer and Kaminsky (A., 1927, 801). Intense nitrogen after-glows have been obtained in mixtures containing up to 57% of oxygen in the electrodeless discharge at or below 0·2 mm. pressure. At higher pressures the type of afterglow changes, until at about 1 mm. and up to 2 mm. (in air) only the continuous after-glow spectrum of oxygen is observed. A. A. Eldridge.

Nitrogen after-glow. S. P. McCallum and W. E. Perry (Nature, 1928, **121**, 942).—A nitrogen after-glow appears when a discharge is passed through a mixture of air and argon at low pressures; the relative proportions of the mixture may be varied over a fairly wide range. Mixtures of neon and helium are ineffective. A. A. Eldridge.

Action of "active nitrogen" on iodine vapour. L. H. Eason and R. W. Armour (Proc. Roy. Soc. Edin., 1928, **48**, 1—9).—The spectrum of iodine excited by active nitrogen was investigated and, in addition to the iodine line at 206 $\mu\mu$, a line at 185 $\mu\mu$ was found. In order to dissociate the iodine and raise the atom to the level of electronic energy required to emit this line, a total of 189,000 g.-cal., or 8·4 volts, is necessary. There must therefore be some form of nitrogen present capable of supplying the energy. The high energy level can be accounted for on the view that the glow is produced by the combination of atoms of nitrogen. An experiment was conducted to find what pressure of iodine vapour was required to increase the velocity of "reaction" between the iodine and the nitrogen so that simple decay could be neglected. It is concluded from the fact that the pressure of iodine required to produce practically nothing but iodine glow is of the order of 1/15th part of the active nitrogen present, and that the glow is practically instantaneous, that chemical action is very unlikely, and that the iodine receives energy and radiates it over and over again. The view is confirmed by the fact that even with pressures of iodine 1/1250th part of the partial pressure of active nitrogen, there is still a decided photographic effect due to the iodine. By attempting to measure the duration of the glow by means of a kinematographic camera it was found that when the pressures of iodine vapour and of active nitrogen were of the same order the glow did not last for more than 0·01 sec. A. J. Mee.

Chemical at. wt. determination and true at. wt. G. Kirsch (Naturwiss., 1928, **16**, 334—335).—A discussion of the discrepancy between the chemically determined at. wt. of radium-*G* and that deduced from the disintegration series and of the difficulty of reconciling these with the at. wts. of lead found by Aston. J. W. Smith.

At. wt. of actinium-lead, the last member of the actinium series. F. Lotze (Z. anorg. Chem., 1928, **170**, 213—221).—The published at. wt. determinations with lead of purely radioactive origin, and therefore consisting of radium-*G*, thorium-*D*, and actinium-*D*, have been examined. Calculating the amounts of thorium-*D* and radium-*G* from the proportions of thorium and uranium, respectively, in the original minerals, the mean value of 207 is obtained for the at. wt. of actinium-*D*. R. Cuthill.

Separation of isotopes of potassium. G. von Hevesy and M. Logstrup (Z. anorg. Chem., 1928, **171**, 1—13).—By subjecting potassium to the process of ideal distillation (cf. A., 1922, ii, 149), a residue was obtained having at. wt. 39·109, corresponding with an increase of 4·8% in the proportion of the isotope K^{41}. As the radioactivity increased at the same time by 4·2%, it is concluded that this isotope is probably responsible for the radioactivity of potassium. R. Cuthill.

Determination of isotopes by spectral lines. E. K. Plyler (J. Elisha Mitchell Sci. Soc., 1927, **43**, 24).—The band spectra of sulphates of isotopes are multiple. Nickel, potassium, and magnesium contain, respectively, 2, 2, and 3 isotopes. Chemical Abstracts.

Purification of radon. L. Wertenstein (Phil. Mag., 1928, [vii], **5**, 1017—1027).—An all-glass apparatus in which radon preparations of high purity may be made is described. Purification is effected by the usual reagents, copper oxide, copper, potassium hydroxide, and phosphoric anhydride, and condensing the gas by liquid air. Pressures are measured by means of a calibrated Knudsen gauge. Evacuation is effected by a mercury diffusion pump, and in order to avoid contamination with hydrocarbons from tap grease a mercury seal is employed to isolate the apparatus from the pump. Considerable difficulty was encountered in removing the last traces of carbon dioxide. It is concluded that carbon dioxide is the only gas left as an impurity. In general quantities of radon of the order of 50—100 millicuries can be concentrated by this method so that they contain only 20—50% of carbon dioxide. A. E. Mitchell.

Ranges of the α-particles of uranium I and II. G. C. Laurence (Phil. Mag., 1928, [vii], **5**, 1027—1038).—A more detailed account, based on a greater number of observations, of previous work (this vol., 4) is given. The ranges of the α-particles from uranium I and uranium II were found to be respectively 2·73 and 3·28 cm., at 150° and 760 mm. These results are in close agreement with the preliminary determinations and the probable error is less than 1%. The decay constant of uranium II calculated from the above figure is $1 \cdot 7 \times 10^{-12}$ sec.$^{-1}$, equivalent to a half-life period of 13,000 years. A. E. Mitchell.

Formation of a gaseous helide of radium active deposit. D. M. Morrison (Proc. Camb. Phil. Soc., 1928, **24**, 268—275).—On the assumption that the helium atom can exist in hydrogen-like form, in which one electron is relatively far from the nucleus, the formation of compounds corresponding with hydrides may be expected. Helium was passed over

radium active deposit in a high-frequency discharge tube and the formation of a gaseous compound detected by counting scintillations in a bulb containing a zinc sulphide screen. The effect is attributed to the formation of a radioactive helide, and not to radium emanation or impurities in the gas.

C. J. SMITHELLS.

Passage of electrons through hydrogen at low pressures. H. JONES and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1928, **1**, 239—241).—Electrons from a tungsten filament were passed through 2 cm. of hydrogen at 0·01—0·02 mm. After passing through the gas, the electrons were accelerated and a magnetic spectrum was formed. Electrons suffering inelastic collision produce radiation corresponding with a loss of 12·2 and 9·1 volts. The interpretation of these results is discussed. W. E. DOWNEY.

Passage of electrons through slits. R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1928, **1**, 242—245).—Using the technique previously described (cf. preceding abstract) and an oxide-coated filament, lines were obtained at 3·9, 9·6, 11·4, 19·8, 22·6, 26·4, 32·3, 38·7, and 45·0 volts loss. When pure platinum was used as emitter, the spectrum was much simpler, giving lines only at 4·0 and 7·5 volts loss. Various possible causes of these " lines " are discussed.

W. E. DOWNEY.

Scission of hydrogen molecules by electronic collision, and chemical detection of the atoms produced. K. E. DORSCH and H. KALLMANN (Naturwiss., 1927, **15**, 788—789; Chem. Zentr., 1928, i, 154—155).—The formation of atoms by electronic collision in hydrogen takes place directly, and (above the ionisation potential) indirectly, thus: $H_2^+ + H_2 = H_3^+ + H$. The atoms are detected by the reduction of lead chloride to lead. A. A. ELDRIDGE.

Saha theory and the conductivity of flames containing alkali metal vapours. H. A. WILSON (Proc. Roy. Soc., 1928, A, **119**, 1—11).—Theoretical. The expression for the equilibrium constant of the reaction $M = M^+ + e$ (where M is an atom of an alkali metal and e an electron) in terms of quantities which can be measured is independent of the fraction f of the salt reduced to metal in the flame and of the fraction q of the negative ions which are free electrons in the flame. The calculation of the equilibrium constants by Noyes and the author (A., 1923, i, 112) is therefore unaffected, even if the fractions f and q are not equal to unity as assumed. There are strong reasons for believing that in flames at about 2000° Abs. the fractions f and q are constants independent of the concentration of the solution sprayed into the flame, and it is probable that at this temperature f and q are both nearly equal to unity. The relative conductivities of the alkali metals in flames at about 2000° Abs., as found by different observers, are tabulated, and are found to be in rough agreement with Saha's theory of the ionisation of metallic vapours at high temperatures. Zachmann's values for the relative conductivities of sodium and lithium are probably erroneous. L. L. BIRCUMSHAW.

Activation of hydrogen by electric discharge. G. A. ELLIOTT (Nature, 1928, **121**, 985).—A brief discussion. A. A. ELDRIDGE.

Particles of high velocity in the chromosphere. R. W. GURNEY (Month. Not. Roy. Astron. Soc., 1928, **88**, 377—379).—A discussion of the kinetics of the rapidly moving particles in the chromosphere.

J. W. SMITH.

The Debye-Huckel theory and stellar atmospheres. J. A. GAUNT (Month. Not. Roy. Astron. Soc., 1928, **88**, 369—377).—Mathematical. Whilst showing some indications in favour of the Debye-Hückel theory, the reasoning developed is claimed to indicate that statistical mechanics provides no firm basis for the use of Boltzmann's theorem on an atomic scale. A summary is also given of an abortive attempt to distinguish between bound and free electrons in the manner suggested by Eddington.

J. W SMITH.

Statistical interpretation of quantum mechanics. A. E. RUARK (Proc. Nat. Acad. Sci., 1928, **14**, 328—330).—An experiment is suggested to decide between the views of Born and of Darwin on the meaning to be attached to the probability functions occurring in wave mechanics. A. J. MEE.

Theory of Hartree's atomic fields. J. A. GAUNT (Proc. Camb. Phil. Soc., 1928, **24**, 328—342).—Mathematical. The expressions for the total energy of the atom are theoretically more sound than those for the separate X-ray terms, although of less practical value. Hartree's wave-functions (this vol., 216) are shown to be good approximations. R. A. MORTON.

Rotation of the nitrogen nucleus. R. DE L. KRONIG (Naturwiss., 1928, **16**, 335).—A discussion of the kinetics of the nitrogen atom. J. W. SMITH.

Statistical deduction of the properties of the elements. E. FERMI (Atti R. Accad. Lincei, 1928, [vi], **7**, 342—346).—From a statistical analysis of the electrons surrounding the nucleus considered as a completely degenerated gas, the general characteristics and some of the anomalies of the periodic classification of the elements can be predicted.

R. W. LUNT.

Rutherford satellite theory. G. SENTILE (Atti R. Accad. Lincei, 1928, [vi], **7**, 346—349).—Arguments are advanced to show that nuclear systems discussed in Rutherford's theory are unstable and that the theory is therefore invalidated.

R. W. LUNT.

Atomic constants and the properties of matter. M. BORN (Z. physikal. Chem. Unterr., 1927, **40**, 241—252; Chem. Zentr., 1928, i, 285).—A discussion. A. A. ELDRIDGE.

Ultra-violet absorption spectrum of cod-liver oil. J. W. WOODROW (Phil. Mag., 1928, [vii], **5**, 944).—Using a photo-electric spectrophotometer, three ultra-violet bands have been found in cod-liver oil. The maxima of these bands occur at 2700, 2800, and 2900 Å. These bands coincide with those of ergosterol as determined by Heilbron and others (A., 1927, 381; this vol., 92). W. E. DOWNEY.

New radiation. C. V. RAMAN (Indian J. Physics, 1928, **2**, 387—398).—A new type of fluorescence has been observed which appears to be universal, since about eighty different liquids which were examined all showed the effect. It differs from ordinary fluor-

escence, being of an entirely different order of intensity and requiring a very powerful incident beam of light to make it visible. It is also polarised almost to the same extent as ordinary scattered light, whereas ordinary fluorescence is usually unpolarised. The new radiation, in fact, appears to occupy a position between scattering and fluorescence. Spectroscopic examination shows that each line in the incident spectrum gives rise to at least two lines in the scattered spectrum, one in the original or unmodified position, and a second in a position of longer wave-length, thus showing a striking analogy with the Compton effect in the *X*-ray region. There is a marked similarity between the spectra obtained with different liquids. When the wave-length 4358 Å. only was used, most liquids showed, in the spectrum of the scattered light, a bright line in the neighbourhood of 5000 Å., the position of which was practically the same for chemically similar liquids such as pentane, hexane, and octane. There was, however, a recognisable difference in the position of the modified line when other liquids, such as benzene or water, were used. In many liquids the scattered spectrum shows, in addition to sharp lines, a continuous spectrum which is less markedly polarised than the former. The origin of the radiation is discussed, and whether it is an exclusively molecular effect or is related in any way to thermodynamics. The effect has also been observed with gases and vapours and with solids such as crystal ice and optical glass. Some experiments with carbon dioxide vapour, and with mixtures of carbon disulphide and methyl alcohol, indicate that the modified scattered radiations from the different molecules are not incoherent with one another. M. S. Burr.

Near infra-red absorption bands of some hydrocarbons. J. Barnes and W. H. Fulweiler (J. Amer. Chem. Soc., 1928, **50**, 1033—1035).—The two strongest absorption bands of pentane, decane, and tetradecane exhibit doublets, the frequency difference at 0·92 μ being 7×10^{12} sec.$^{-1}$ and that at 0·75 μ, 8×10^{12} sec.$^{-1}$ Weak single bands at 0·81 μ and 0·97 μ were also observed. The 0·874 band of benzene and the 0·877 μ band of toluene are also doublets with a frequency difference of 3×10^{12} sec.$^{-1}$ S. K. Tweedy.

Beats produced when rotating and vibrating anisotropic molecules diffuse visible or ultraviolet light. J. Cabannes (Compt. rend., 1928, **186**, 1201—1202).—The new radiations discovered by Raman (this vol., 101, 348) may be considered as optical beats due to the variation of the amplitude of vibration of an optically anisotropic molecule owing to its rotation, or to the harmonic vibration of one of its atoms. This involves a displacement towards the violet of the rays of the diffusion spectrum produced from the fluid by means of monochromatic light (cf. Rocard, this vol., 571). J. Grant.

"Phosphorescing" liquid. S. Vavilov and V. Levschin (Naturwiss., 1927, **15**, 899—900; Chem. Zentr., 1928, i, 161).—The luminosity of a solution of uranyl sulphate in sulphuric acid continues for 10^{-5} to 10^{-4} sec. after illumination, and fades approximately exponentially. Rise of temperature, addition of water, or increase of concentration shortens the duration of luminosity. A. A. Eldridge.

Sulphide phosphors. I. Schaper (Ann. Physik, 1928, [iv], **85**, 913—952).—The methods of the Lenard school have been applied to antimony phosphors and to magnesium sulphide phosphors. Calcium sulphide–antimony phosphors show three principal emission bands; the emission is green at the ordinary temperature with a maximum at 530 μμ (α) in some phosphors and 510 μμ (δ) in others. A lavender-blue emission in the region 420—510 μμ, with a maximum at 450 (β), occurs on heating. With some phosphors an orange emission γ occurs at 580—650 μμ, maximum 600 μμ, at the temperature of liquid air. Comparison of bismuth and antimony phosphors indicates close resemblances; *e.g.*, the γ band is shown well at −180° in both cases and the maxima are at 595 and 600 μμ, respectively. The β bands are both obtained between 200° and 400°, but the maxima are at 522 μμ for bismuth and at 465 μμ for antimony. The α and δ bands occur best at 20°, and the wave-lengths are 470, 450, 443 for bismuth and 530, 510 for antimony. Similar temperature effects are shown with strontium sulphide–antimony phosphors; the maxima are as follows, bismuth data being in brackets: α 555 [520]. δ 535 [420], β 480 [535], γ 620 [630] μμ.

The phosphorescence in magnesium sulphide has been investigated for the following metals, the figures in brackets indicating the wave-lengths in μμ of the principal bands: bismuth [443], antimony [531], manganese [665], copper [535], silver [460], lead [530]. The samarium, praseodymium, and neodymium phosphors have also been studied. Comparison shows that the wave-lengths of the maxima of corresponding bands with a heavy metal phosphor increase as a rule in the order magnesium, calcium, and strontium sulphides as the basis of the phosphor. The dielectric constant of a phosphor depends to a marked extent on the temperature at which the preparation is carried out.

A number of contributions to the analysis of the different phosphorescence processes have also been made. R. A. Morton.

Oscillation quantum of the mercury molecule. H. Kuhn (Naturwiss., 1928, **16**, 352—353).—Rayleigh (A., 1927, 1122) has recorded a series of symmetrical emission bands for mercury in the region 2350—2290 Å., merging into a continuous spectrum stopping at 2270 Å. Superposed on the band structure is a much finer structure with a small initial spacing of about 20 cm.$^{-1}$ It is suggested that the small spacing corresponds with the oscillation quantum of the normal molecule, whilst the larger period represents the oscillation quantum of the excited molecule.

R. A. Morton.

Swan band spectrum of carbon. W. E. Pretty (Proc. Physical Soc., 1928, **40**, 71—78).—The Swan band spectrum was obtained in carbon monoxide and in the carbon spark in the absence of hydrogen. A discussion of the results of experiment and theory leads to the conclusion that the emitter of the Swan band system is the molecule of carbon C_2. This conclusion has been reached independently by Shea (this vol., 104). C. J. Smithells.

Extinction coefficient of mixtures of ferric chloride and organic acids in the ultra-violet as experimental evidence in favour of the formation of unstable intermediate compounds. II. J. C. Ghosh and B. N. Mitra (J. Indian Chem. Soc., 1928, **5**, 191—202).—The rise in the extinction coefficient when ferric chloride is mixed with various organic acids, which it oxidises in the presence of light, has been determined in the way previously described for uranyl salts (this vol., 14). The results may be explained by supposing that there is an equilibrium in solution between ferric chloride and acid as reactants and an intermediate complex formed by the loose combination of one molecule of each of the reactants, and by assuming a definite value of the molecular extinction coefficient, for each wavelength, for the intermediate complex so formed. The following acids have been studied : formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, citric, and mandelic. The value of K, the dissociation constant of the intermediate complex, is approximately double that of the corresponding uranyl salt complex (*loc. cit.*). The values of the molecular extinction coefficients of the intermediate compounds are also correspondingly greater. Certain regularities were observed between the values of K and the constitution of the acids; *e.g.*, K diminishes with each addition of CH_2 and increases as the hydrogen atom of a methyl group is replaced by carboxyl, or when it is replaced by a hydroxyl group.

M. S. Burr.

Fluorescence spectrum of sodium vapour in the vicinity of the *D* lines. R. W. Wood and E. L. Kinsey (Physical Rev., 1928, [ii], **31**, 793—799).—Radiation of wave-length 5100—5250 Å. excites the D lines in sodium vapour mixed with hydrogen, air, or nitrogen at 2—3 mm. Apparently excitation of the molecule first occurs, followed by collisions of the second kind with atoms or by dissociation into a normal and an excited atom. The conditions governing the appearance of a fluorescence band group previously studied (Wood and Galt, Astrophys. J., 1911, **33**, 72) were investigated.

A. A. Eldridge.

Quenching of mercury resonance radiation by foreign gases. M. W. Zemansky (Physical Rev., 1928, [ii], **31**, 812—821).—A relation between the quenching and the number of impacts of the second kind per sec. per c.c. is obtained for all foreign gases on the basis of Milne's theory of the diffusion of imprisoned resonance radiation, it being assumed that the number of impacts of the second kind per sec. per c.c. is proportional to the number of excited mercury atoms per c.c. The reaction velocity near the incident face of the absorption cell is proportional to the 0·6 power of the pressure, a result which suggests that the dissociation of the foreign gas is catalysed by adsorbed metastable mercury atoms.

A. A. Eldridge.

Luminescence excited by *X*-rays in colloidal alkaline-earth salts. C. H. Boissevain and W. F. Drea (Physical Rev., 1928, [ii], **31**, 851—857).—Gelatinous calcium, strontium, or barium fluoride precipitated in presence of excess of metal ions, but not of fluoride ions, is luminescent in X-rays, particularly after the precipitate has been heated to redness. By washing with dilute alkali solution the positively-charged colloids are converted into negative colloids and cease to exhibit luminescence. When precipitated in presence of excess of tungstate ions, calcium or barium tungstate (negative colloid) exhibits similar luminescence. The presence of impurities diminishes the luminescence. It is suggested that the luminescence is due to a thin layer of metallic oxide formed from the double layer of ions which is adsorbed on the surface of the colloidal particles.

A. A. Eldridge.

Infra-red reflexion spectra of sodium chlorate and sodium bromate. G. Laski (Z. Krist., 1927, **65**, 607—614; Chem. Zentr., 1928, i, 8).—The characteristic frequency is 25 μ for sodium chlorate and 23 μ for sodium bromate; both substances exhibit absorption between 40 and 120 μ, with a maximum at 83 μ and 82 μ, respectively. A triangular configuration is postulated for the chlorate and bromate radicals.

A. A. Eldridge.

Observed relative intensities of Stark components of H_α. J. S. Foster and (Miss) M. L. Chalk (Nature, 1928, **121**, 830—831).—The discrepancy between Schrodinger's calculated and Stark's observed intensities for the parallel components of H_α is apparently due merely to experimental error.

A. A. Eldridge.

Infra-red emission of carbon dioxide. C. R. Bailey and K. H. Lih (Nature, 1928, **121**, 941).—Analysis of the emission spectrum of burning carbon monoxide shows that most of the carbon dioxide bands have shifted towards the longer wave-lengths, and so become exact multiples of a frequency, $\nu=16\times10^{11}$, in the far infra-red.

A. A. Eldridge.

Pure rotation spectrum of ammonia. R. M. Badger (Nature, 1928, **121**, 942).—The absorption spectrum of gaseous ammonia between 55 and 130 μ is unexpectedly simple; six lines approximately equally spaced in the frequency scale are represented by the equation $1/\lambda_m=19{\cdot}957m-0{\cdot}00508m.^3$ The molecule is relatively elastic and stretches considerably in higher rotational states.

A. A. Eldridge.

Absorption spectra of silver bromide and silver chloride films. J. Eggert and R. Schmidt (Z. Physik, 1928, **48**, 541—544).—The absorption spectra of thin sheets of microcrystalline silver bromide and silver chloride have been investigated photographically. The converging frequencies in the long-wave region were found to be 480 for silver bromide and 400 $\mu\mu$ for silver chloride. The amount of silver liberated from the bromide under the action of the light (10^{-5} to 10^{-3} per mille) caused no perceptible change in the absorption spectrum.

J. W. Smith.

Molecular spectrum of sulphur. B. Rosen (Z. Physik, 1928, **48**, 545—555).—In continuation of work previously recorded (A., 1927, 608) the absorption and emission bands of the S_2 molecule in the blue-violet and ultra-violet regions have been examined. These were in agreement with the formula previously deduced.

J. W. Smith.

Homopolarity of the hydrogen halides. V. KONDRATJEW (Z. Physik, 1928, **48**, 583—585).—The probability that hydrogen iodide, on absorption of light of a suitable wave-length, yields a hydrogen atom and an excited iodine atom (cf. Franck and Kuhn, A., 1927, 711) is held to indicate that hydrogen iodide is a homopolar molecule. In the cases of hydrogen chloride and hydrogen bromide, the dissociation energies calculated from the infra-red vibration spectra according to the method of Franck and Kuhn are shown to be in good agreement with the values obtained from thermochemical data. Hence it is concluded that the molecules of all the hydrogen halides are homopolar in character. J. W. SMITH.

Limit of photoelectric sensitivity of ammonium amalgams in the long wave-length region. SANDER and NITSCHE (Z. Elektrochem., 1928, **34**, 244—246).—The photoelectric sensitivity limit of ammonium amalgam lies at a lower wave-length than those of potassium and sodium, the order being ammonium, sodium, potassium. H. F. GILLBE.

Dielectric constant of benzil. L. SAINT-ANTOINE (Compt. rend., 1928, **186**, 1429—1431).—For solutions of benzil in benzene, ε increases almost proportionally with the concentration, but decreases with a rise in temperature. For molten benzil (m. p. 94°) it varies from 13·04 at 95° to 12·12 at 120°. It was measured with an accuracy of 3—4% from the change in wave-length produced when a cylindrical air-condenser was immersed in the liquid concerned, the resonance between a resonator and an oscillator being determined from the wave-lengths of the oscillations of the latter when its frequency was varied (cf. De Mallemann, A., 1927, 1130). J. GRANT.

Change of the dielectric constant of liquid helium with temperature. Provisional measurements. M. WOLFKE and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 81—89).—A compensation method for determining the dielectric constant of liquid helium is described. Two series of provisional measurements have been made between 1·80° and 4·21° Abs. and, in each case, a discontinuity was observed, which may be related to the discontinuities noted in other physical properties between these temperatures. The possibility of experimental error is not, however, excluded. M. S. BURR.

Disappearance and reversal of the Kerr effect. C. V. RAMAN and S. C. SIRKAR (Nature, 1928, **121**, 794).—Observations on the Kerr effect with octyl alcohol confirm Raman and Krishnan's theory of electric birefringence in liquids (cf. A., 1927, 397). A. A. ELDRIDGE.

Spectrochemical observations on azo-compounds. K. VON AUWERS and P. HEIMKE (Ber., 1928, **61**, 1030—1036).—Observations on methyl and ethyl azo*iso*butyrate give the value D=3·179 for the unconjugated –N:N– group, which is in good agreement with the datum D=3·266 deduced by Lochte, Noyes, and Bailey (A., 1922, i, 329) from experiments on azo*iso*propane. Observations on purely aromatic azo-compounds are hampered by the difficulty of obtaining homogeneous products by reduction of nitro-compounds in alkaline solution since these usually contain varying amounts of azoxy-substances; homogeneous azo-derivatives are obtained by treating pure hydrazo-compounds with the necessary amount of bromine. The colour of the substances usually inhibits measurement except with the H_α and sometimes the yellow He line. In cases where the high m. p. of the compound necessitates the use of a solvent, quinoline is found very serviceable. The specific exaltations for azobenzene and its homologues are grouped closely round the mean value +3·05. This high value is due to the structure of the substances, since the value of EE_D^{20} for the analogously constituted *m*-methylstilbene is +3·1; the twice-broken, treble conjugations C:CR·C:C·CR:C and C:CR·N:N·CR:C are therefore spectroscopically equivalent. Entry of a hydroxyl or an alkoxyl group into the azobenzene molecule invariably increases these exaltations, but the action of the groups is unequally strong and depends on their position. The following data, amongst others, are recorded for the homogeneous substances: methyl azo*iso*butyrate, $d_4^{17·3}$ 1·0365, $n_\alpha^{17·3}$ 1·43335; ethyl azo*iso*butyrate, $d_4^{18·9}$ 0·9932, $n_\alpha^{18·9}$ 1·42831; phenylazoethane, $d_4^{21·9}$ 0·9628, 1·53133; azobenzene, $d_4^{78·1}$ 1·0362, $n^{78·1}$ 1·62662; *m*-methylazobenzene, $d_4^{17·0}$ 1·0658, $n^{17·0}$ 1·64822; *oo'*-dimethylazobenzene, $d_4^{65·3}$ 1·0215, $n_\alpha^{65·3}$ 1·61804; *mm'*-dimethylazobenzene, $d_4^{66·2}$ 1·0123, $n^{66·2}$ 1·61519; *o*-methoxyazobenzene, d_4^{100} 1·0728, n_α^{100} 1·62652; *p*-ethoxyazobenzene, $d_4^{99·6}$ 1·0400, $n_\alpha^{·6}$ 1·62355; benzeneazothymol, $d_4^{100·2}$ 1·0328, $n^{100·2}$ 1·63169; benzeneazothymol ethyl ether, d_4^{100} 0·9791, n_α^{100} 1·59345; *n*-propyl *p*-hydroxybenzoate, $d_4^{102·1}$ 1·0630, $n^{102·1}$ 1·50503; *n*-propyl anisate, d_4^{100} 1·0054, n^{100} 1·47977. Measurements are also recorded for certain of the compounds dissolved in quinoline, absolute alcohol, or propyl butyrate. The *ethyl ether* of *benzeneazothymol*, m. p. 85°, has not been described previously. H. WREN.

Spectrochemistry and constitution of azoxy-compounds. K. VON AUWERS and P. HEIMKE (Ber., 1928, **61**, [*B*], 1037—1041).—Homogeneous azoxy-compounds are most readily prepared by oxidising azo-compounds with hydrogen peroxide. The following data, amongst others, are recorded for the homogeneous substances: azoxybenzene, d_4^{26} 1·1590, n_α^{26} 1·65103; *oo'*-azoxytoluene, $d_4^{99·9}$ 1·0548, $n_\alpha^{·9}$ 1·57686; *mm'*-azoxytoluene, $d_4^{21·6}$ 1·1136, $n_\alpha^{21·6}$ 1·63345; α-*p*-bromoazoxybenzene, $d_4^{99·9}$ 1·4068, $n_\alpha^{99·9}$ 1·64967; β-*p*-bromoazoxybenzene, d_4^{100} 1·4138, n_α^{100} 1·64497; α-*p*-ethoxyazobenzene, $d_4^{99·7}$ 1·1082, $^{·7}$ 1·62363; β-*p*-ethoxyazobenzene, $d_4^{100·1}$ 1·1068, $n_\alpha^{100·1}$ 1·61348; *p*-ethoxyhydrazobenzene, $d_4^{100·5}$ 1·0556, $n_\alpha^{100·5}$ 1·57491; *p*-phenetidine, $d_4^{15·9}$ 1·0652, $n^{15·9}$ 1·55715. Observations for certain compounds in quinoline are also given. The data strongly support the constitution assigned to azoxy-compounds by Angeli. The behaviour of *oo'*-azoxytoluene is, however, exceptional and may possibly indicate the presence of a three-membered ring. H. WREN.

Valency and refraction equivalents. K. VON AUWERS (Ber., 1928, **61**, [*B*], 1041—1049; cf. Strecker and Spitaler, A., 1926, 1082).—Any change in the spectroscopic constants of a substance cannot

be attributed solely to a single component of the molecule, but is due to the sum of the actions exercised by two atoms combined with one another. From this point of view the molecular refractions of a series of azo- and azoxy-compounds are compared, thus leading to the conclusion that the atomic refraction of quinquevalent nitrogen is lower than that of tervalent nitrogen, since the entering oxygen atom never increases the molecular refraction of the compound to the extent expected from doubly-bound oxygen. On the other hand, great exaltation of the molecular refraction is observed when an oxygen atom is added to a benzylideneamine or an oxime *O*-ether; the increase is in all cases greater than the atomic refraction of carbonyl oxygen, particularly so with mixed aliphatic aromatic substances. Spectroscopic data support the constitutions and CPh·N:O for dimethylfurazan and benzonitrile oxide, respectively. Diminution in the atomic refraction of carbon with increasing valency is shown by comparison of ethyl carbonate and carbon monoxide diethylacetal (cf. Scheibler, A., 1926, 711). Less striking results are obtained by comparison of carbylamines and carbimides, thus supporting the view that the terminal carbon atom of the former is not pronouncedly bi- or quadri-valent and that therefore the effect of the entering oxygen atom is only partly balanced by the change in character of the carbon atom. With carbylamines and thiocarbimides the increase in molecular refraction corresponds approximately with the refraction equivalent for S″; conclusions with regard to dispersion cannot be reached.

The following data, amongst others, are recorded: *o*-chlorobenzylideneaniline, $d_4^{14\cdot6}$ 1·1857, 1·65689; benzonitrile, $d_4^{11\cdot6}$ 1·0109, $n_{He}^{11\cdot6}$ 1·53258; methylcarbimide, $d_4^{14\cdot9}$ 0·9744, $n_{He}^{14\cdot9}$ 1·37400; ethylcarbimide, $d_4^{14\cdot7}$ 0·9065, $n_{He}^{14\cdot7}$ 1·38262; phenylcarbimide, $d_4^{11\cdot6}$ 1·1010, 1·54032; phenylthiocarbimide, $d_4^{20\cdot3}$ 1·1303, 1·64974; benzonitrile oxide, $d_4^{12\cdot2}$ 1·2190, $n_{He}^{12\cdot2}$ 1·59687. H. WREN.

Magnetism and the structure of some simple and complex molecules. D. M. BOSE (Phil. Mag., 1928, [vii], 5, 1048—1067).—The author's modification (A., 1927, 805) of Hund's theory of paramagnetism has been employed for the calculation of the magnetic moments of molecules containing elements of the first transition group. Up to manganese the agreement between calculated and observed values is good, but the simple salts of the ferromagnetic elements give values considerably in excess of those predicted, the deviation being apparently associated with the addition of the sixth, seventh, and eighth electrons to the M_3 shell of the central atom. In certain fourfold co-ordination compounds the predicted magnetic moments are in close agreement with observed values, and it is concluded that in these compounds the valency shell of eight electrons contributed by the four atomic groups forms an octet shell outside the core of the central atom. In sixfold co-ordination compounds it is concluded that if there are vacancies in the M_3 shell of the central atom for four electrons, then four of the twelve shared electrons occupy this shell, whilst the remaining eight form an octet shell round the core, and if the M_3 shell cannot accommodate all four electrons these move in orbits outside the octet shell. It is shown that the co-ordination linkings contributed by the atomic groups usually found in co-ordination compounds can be accounted for satisfactorily on the new theory. A. E. MITCHELL.

Electronic theory of valency. V. Molecular structure of strong and weak electrolytes: (*a*) Complete ionisation. T. M. LOWRY (Phil. Mag., 1928, [vii], 5, 1072—1080).—From the electronic theory of valency previously developed (A., 1923, ii, 480, 848; A., 1925, ii, 15) it follows that compounds in which neutralisation of the ionic charges is prevented by the laws of valency generally behave as strong electrolytes in solution, whilst if a salt is dissolved in a medium of low dielectric constant the resulting solution will have a low conductivity and abnormal variations of conductivity with dilution are to be expected. It is suggested that the high conductivity of some fused salts is a result of the formation of multi-charged ionic aggregates, whilst the low conductivity of others is attributed to the breaking down of the crystal lattice into neutral doublets on fusion. On the theory of complete ionisation the term hydrolysis can have no significance unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt with formation of a covalent compound. A. E. MITCHELL.

Electric moment and space-orientation of atoms in some *para*-derivatives of benzene. J. W. WILLIAMS (Physikal. Z., 1928, 29, 271—272).—The assumption that *para*-substituents lie in the plane of the benzene ring leads to the view that with equal substituents the symmetrical molecule should exhibit no electric moment. This expectation is fulfilled in the cases of *p*-xylene, *p*-dichlorobenzene, and *p*-dinitrobenzene, since the values for the electric moment are less than $0{\cdot}3\times10^{-18}$ (e.s.u.). For quinol diethyl ether and quinol diacetate the values are, however, 1·7 and $2{\cdot}2\times10^{-18}$, respectively. This result indicates that the substituents need not necessarily lie in the plane of the benzene ring; either the OR-groups may be bent away from the plane or the oxygen atoms may remain in the plane with the ethyl groups out of alinement. R. A. MORTON.

Dipole moment of symmetrical compounds, and *cis–trans*-isomerism at "single" linkings. A. WEISSBERGER (Physikal. Z., 1928, 29, 272—273).—The demonstration (A., 1927, 9) that compounds of the type $C(OR)_4$ exhibit a dipolar character and that the valencies of the carbon atom may be regarded as directed towards the corners of a tetragonal pyramid opens up the possibility of a new type of enantiomorphism. The existence of a considerable electric moment in certain compounds of the type $C_6H_4a_2$ (cf. preceding abstract) likewise makes possible a type of *cis–trans*-isomerism not involving double linkings. It is suggested that the yellow and colourless benzil derivatives studied by Schonberg and his co-workers (1922, *et seq.*) and hitherto regarded as αβ-diketones and isomeric peroxides may be enantiomorphs of this kind. R. A. MORTON.

The shared-electron chemical linking. L. PAULING (Proc. Nat. Acad. Sci., 1928, **14**, 359—362).—London's theory of the formation of valency linkings is equivalent in simple cases to G. N. Lewis' theory of the shared electron pair. A number of new results have been obtained in extending London's simple theory, taking into account quantitative spectral and thermochemical data. A sensitive test to determine whether a compound is polar or non-polar is put forward, and it is concluded that hydrogen fluoride is polar, whilst the chloride, bromide, and iodide are probably non-polar. If quantisation can be changed, as it can in the case of some elements in the first row of the periodic system where the interchange energy resulting from the formation of shared-electron linkings is large enough to bring it about, very stable shared-electron linkings are possible. Hence the stable shared-electron linkings of saturated carbon compounds, and the relatively stable double linkings of carbon. The tetrahedral arrangement of the four linkings of quadrivalent carbon can be shown to be the stable one as a result of the resonance phenomenon. A. J. MEE.

Electrostatic explanation of complex formation. A. E. VAN ARKEL and J. H. DE BOER (Rec. trav. chim., 1928, **47**, 593—605; cf. A., 1927, 189).—After a discussion of the application of Kossel's theory of the chemical linking as a purely electrostatic phenomenon (Ann. Physik, 1916, [iv], **49**, 229) made by numerous authors, the problem of complex formation is considered. Strong polarisation of the outer ions of a complex ion may be due to a small radius of the central atom which causes it, or also to a polarisation of this central atom itself. In the latter case the electrical field of ions which surround the central atom induces a dipole in the central atom which acts on the outer ions of the complex ion, thus strengthening the linking. A dipole can arise in the central atom only if the polarisability of this central atom is so great that an unsymmetrical arrangement of the outer ions results, as is the case with H_2O,NH_3,NH_4^+. The complexes formed by ammonia fall into two principal groups, (1) to which compounds obtainable only as solids belong, *e.g.*, $[Na(NH_3)_6]I$, which loses ammonia completely on dissolution in water, and (2) the compounds in which, in aqueous solution, the ammonia is present in the cation, *e.g.*, $[Co(NH_3)_6]Cl_3$. In group (1) the hydrates are more stable than the ammonia complexes, whilst in group (2) the relation is reversed. Since the electric dipole of the ammonia molecule is smaller than that of the water molecule and furthermore the radius is somewhat larger, the stronger union of water molecules is to be expected. The behaviour of compounds of group (2) may be explained by a deformation of the whole ammonia molecule. An increase in the dipole already present would result, so that as the deformability of the ammonia molecule is greater than that of the water molecule the increase in the dipole in the case of ammonia is greater than in that of water. In the case of non-polarisable central ions there is a definite distance between the central ion and water or ammonia molecule at which the energies of formation are equal. If in a given instance the distance is smaller than the critical value then the ammonia complex is the stable compound and, if greater, the hydrate. An approximate calculation of this critical distance is made. H. INGLESON.

Electron theory of valency based on an extension of the Bohr–Stoner electron distribution in atoms. O. STUHLMAN, jun. (J. Elisha Mitchell Sci. Soc., 1927, **43**, 19).—Stoner's modification of the Bohr electron distribution in atoms is extended and co-ordinated with ionisation and critical potential data. Anion valency is attributed to the action of the completed doublet levels, and cation valency to the action of the external levels acting in conjunction with the incompleted paired levels. CHEMICAL ABSTRACTS.

Hypothesis of valency deflexion. C. K. INGOLD and J. F. THORPE (J.C.S., 1928, 1318—1321).—A reply to the criticism of the Thorpe–Ingold hypothesis of valency deflexion made by Hückel (Fortschr. Chem., 1927, **19**, [4]). H. INGLESON.

Complex compounds. F. EPHRAIM (Helv. Chim. Acta, 1928, **11**, 431—436).—In order to account for the formation of complex compounds, an electrostatic field valency is postulated in addition to the ordinary electro- and co-valent linkings. The theory is developed on the basis of the octet model of the atom and is applied to the case of the constitution and isomerism of the metal ammines. F. J. WILKINS.

Law of molecular forces. A. W. PORTER (Trans. Faraday Soc., 1928, **24**, 108—111).—Theoretical. Difficulties in calculating intermolecular forces are discussed. L. F. GILBERT.

Molecular numbers. P. VINASSA (Gazzetta, 1928, **57**, 178—180).—It is held from an extended survey of compounds that the law of molecular numbers is valid for most chemical compounds naturally occurring and otherwise; the known exceptions to the law are tabulated. R. W. LUNT.

Spontaneous division of drops of microscopic dimensions. N. VON RASCHEVSKY (Z. Physik, 1928, **48**, 513—529).—A former theory (cf. this vol., 474) is extended to cases where diffusion processes and chemical changes occur in a drop, the rate of growth of which is very small. The conditions under which such a drop can split are deduced. The stability of polyphase drops is also discussed. J. W. SMITH.

Scattering of electrons by crystals. H. BETHE (Naturwiss., 1928, **16**, 333—334).—It is shown that the true analogues of the reflected electron beams observed by Davisson and Germer (A., 1927, 492) are the *X*-ray beams of next shorter wave-length, and not those of longer wave-length as suggested by them. J. W. SMITH.

Positions of *X*-ray spectra as formed by a diffraction grating. A. W. PORTER (Phil. Mag., 1928, [vii], **5**, 1067—1071).—It is pointed out that for accurate *X*-ray spectral measurements with diffraction gratings it is insufficient to apply the usual methods of ordinary spectroscopy applicable to Fraunhofer spectra, but that a factor, correcting for the lack of parallelism of the *X*-ray beam, must be applied to

wave-lengths determined in the ordinary way. For conditions of nearly grazing incidence this factor is shown to be $(1+3X^2/20l_0^2)$, where X is the length of the grating and l_0 is the shortest distance between the source and the grating. A. E. MITCHELL.

Apparent irregularities in experiments with heterogeneous *X*-ray beams, with special reference to the *J*-phenomenon. R. T. DUNBAR (Phil. Mag., 1928, [vii], 5, 962—989).—Two experimental methods designed to observe the *J*-discontinuities in the absorption of scattered heterogeneous *X*-radiation failed to show any such discontinuities. It is thereby shown that the irregularities observed by Barkla are probably due to the assumption that a heterogeneous beam should give nearly the same results as a homogeneous beam, the latter having an absorption coefficient equal to the half-value absorption coefficient of the former. W. E. DOWNEY.

Diffraction of *X*-rays by means of line gratings. Spectrography of the intermediate region. J. THIBAUD (Physikal. Z., 1928, 29, 241—261).—A full account is given of researches which have already been briefly reported (A., 1925, ii, 176; 1926, 333, 651; 1927, 286, 803). It is shown that tangential gratings with 200 lines per mm. permit the investigation of *X*-rays in air, and ultra-violet rays down to 140 Å. in a vacuum. A new type of vacuum spectrograph is described and data on the spark spectrum of copper are given. The gap between *X*-rays and the extreme ultra-violet has been bridged by the use of an improved vacuum spectrograph with a tangent grating ruled with 1180 lines per mm. Wave-lengths in the region 17·7—65·0 Å. together with their origins are given for various elements. The continuous spectrum and the *K*-absorption limit have been studied for carbon, nitrogen, and oxygen.

For wave-lengths near 17 Å. the line grating and the crystal lattice methods are in good accord, whilst at about 70 Å. a definite discrepancy arises, due, it is shown, to refraction of the rays by the material (fatty acid) composing the lattice. Oil-sensitised (non-Schumannised) plates record rays between 600 and 100 Å.

The lines of advance in this field are indicated.

R. A. MORTON.

Relation between chemical constitution and *X*-ray diffraction in liquids. I. Mono- and di-substituted benzene derivatives. P. KRISHNAMURTI (Indian J. Physics, 1928, 2, 355—364; cf. Sogani, A., 1927, 924, 1129).—A number of *o*-, *m*-, and *p*-disubstituted benzene derivatives have been subjected to *X*-ray examination. The diffraction haloes for the *o*- and *m*-compounds have two distinct rings. In the *o*-compounds the outer ring increases in brightness as the sizes of the substituents are increased. In the corresponding *m*-compounds, however, the rings are smaller, but the outer ring increases in brightness relatively to the inner more than in the case of the *o*-compounds. Only one broad ring is obtained for *p*-compounds, and this diffuses outwards. Substitution in the first carbon group of the side-chain produces no interference effects tending to the formation of two rings. Benzene derivatives with a single long side-chain show a similarity to the corresponding aliphatic derivatives. Ethyl benzoate is similar to acetic acid, since both of them show a faint inner ring. M. S. BURR.

***X*-Ray diffraction in carbon tetrachloride (liquid).** C. M. SOGANI (Indian J. Physics, 1928, 2, 377—386).—The diffraction photographs of liquid carbon tetrachloride obtained with the Cu K_α rays have been studied. The pattern shows an inner ring which is sharper than for any other organic liquid hitherto examined and is explained by the nearly spherical form of the molecule. Separated from the inner ring by a clear space is a diffuse outer ring. There is, however, a fair amount of scattering at small angles which is to be ascribed to the compressibility of the liquid. The Bragg spacing, 5·3 Å., for the inner ring agrees well with the value of $(m/d)^{1/3}$, namely, 5·43 Å., where m is the mass of a molecule and d the density. The spacing for the outer halo is 2·9 Å. The presence of the second ring is discussed in relation to a similar phenomenon in the case of mercury and argon which are monatomic, and it is suggested that the second ring, which, in general, is considered to be due to a pronounced asymmetry of the molecule, is in this case merely a second order effect. A possible alternative explanation is that it may be due to the shape of the molecular *F*-curve. There is an analogy between the *X*-ray diffraction in liquids with spherical molecules and the diffraction of visible light by homogeneous chromatic emulsions. M. S. BURR.

Direct and indirect characteristic *X*-rays: their ratio as a function of cathode-ray energy. D. L. WEBSTER (Proc. Nat. Acad. Sci., 1928, 14, 330—339).—The work of a previous paper (A., 1927, 803) on the ratio of direct rays to total indirect *X*-rays produced from any ordinary *X*-ray target is extended. The apparatus was reconstructed to obtain greater accuracy and the same method was used as in the previous work. The calculation was carried out in practically the same way as before, except that the assumption that all the primary continuous spectrum *X*-rays originate in the surface is replaced by the assumption that they originate at a depth equal to the average depth as measured by the absorption limit method. The value of the ratio of direct rays to total incident rays for silver is found to be almost constant, the data giving 1·83 at 35 kilovolts, and 1·96 at 80 kilovolts. The probable error is high, amounting to 10—20%. The variation of the ratio is not sufficient to vitiate current comparisons of observed line intensities with theories.

A. J. MEE.

***X*-Ray examination of saturated dicarboxylic acids and amides of the fatty acid series.** E. HENDERSON (Proc. Roy. Soc. Edin., 1928, 48, 20—27).—In continuation of former work (A., 1927, 612) several additional normal saturated dicarboxylic acids have been investigated by means of *X*-rays, the results being in agreement with the earlier work. In order to study the effect on crystal structure of expanding the molecule without altering the distance between the carboxyl groups, the mono- and di-alkylmalonic acids were investigated. The d_1 spacing increases by 1·0—1·3 Å. per CH_2 group added, and it

is concluded that this d_1 spacing is a measure of the length of the molecule, and that there is only one molecule between successive reflecting planes. The fact that in long-chain compounds having a "chemically active" terminal group, *e.g.*, carboxyl, successive reflexion planes are separated by the length of two molecules oriented in opposite directions can be explained by assuming that the two molecules are held together by forces due to free partial valencies of the terminal group. In the case of the malonic acids the two carboxyl groups mutually saturate each other so that there is insufficient residual affinity to attract another molecule. This theory was tested by examining the fatty acid amides by means of X-rays, when it was found that successive reflexion planes were separated by the length of two molecules placed end to end and oppositely oriented. In the case of dialkylmalonic acids the angle between the alkyl groups diminishes as the series is ascended. The theory of Muller and Shearer regarding the nature of the chain structure of long-chain compounds is discussed, and it is shown that whilst this theory assumes that the tetrahedral angle of the carbon atom will be maintained throughout the chain, this cannot be so. The molecule will probably be spiral in form.

A. J. Mee.

Excitation of soft X-rays. II. O. W. Richardson and F. C. Chalklin (Proc. Roy. Soc., 1928, A, **119**, 60—83; cf. *ibid.*, 1926, A, **110**, 247).—The gap left between 130 and 200 volts in the investigation on iron is now filled up, and the range is extended from 600 to 720 volts. The apparatus has been improved and is capable of greater sensitiveness. Three discontinuities are observed between 600 and 720 volts, and eight between 130 and 200 volts. All the known observations of critical potentials of iron obtained by various observers are tabulated, and very satisfactory agreement is found between the different values. Rollefson's claim to have found a number of critical voltages of iron in the low-voltage region which follow a Rydberg series (cf. A., 1924, ii, 216) is discussed, and the existing data are critically examined. Thomas' values for iron, cobalt, nickel, and copper (cf. A., 1925, ii, 336; 1926, 1186) are used to determine A and b in the equation $V(n)-A-b/n^2$. The experimental evidence for the reality of the series is strong in the case of iron, cobalt, and nickel, but much less decisive in the case of copper. In a discussion of the theoretical interpretation of such a classsification the difficulty raised by the high value of the constant b is emphasised. This is 2420 volts for iron and 2357 volts for cobalt and nickel, and corresponds with an attracting centre with about 13 times the electronic charge. This fact, and a large number of otherwise unco-ordinated facts, might be explained by assuming that in the case of iron, cobalt, and nickel, at any rate, it is possible for an electron to function as a series electron in relation to the structure bounded by the completed L shell without being profoundly affected by the surrounding electrons. In order to test whether the discontinuities under investigation are instrumental or are real properties of the materials, the emission from a carbon target as successive layers of tungsten are gradually deposited on it has been examined. The various deposited inflexions are not equally interdependent, but can be classified in groups such that the members of each group appear and disappear, or strengthen and weaken, together independently of the other groups. Four groups of critical voltages were obtained, one group being due to tungsten, whilst the majority of the inflexions found must be attributed to contamination (possibly nickel). As a result of the present investigations, some of the critical potentials given in the former paper (*loc. cit.*), are reconsidered. In the case of carbon, the weak inflexion at 265·0 volts is probably due to tungsten, and the strong inflexion at 81·2 volts is due to an impurity which may be nickel.

L. L. Bircumshaw.

Intensity of reflected X-rays and the distribution of electrons in crystals. G. E. M. Jauncey and W. D. Claus (Physical Rev., 1928, [ii], **31**, 717—727).—A reply to Havighurst's criticisms (this vol., 224). By trial a reasonable Bohr model of the chlorine ion has been found which gives modified F values at all angles in good agreement with the experimental values. The Fourier analysis method of unravelling atomic structure is still considered invalid.

A. A. Eldridge.

K-Absorption edges of potassium and chlorine in various compounds. J. M. Nuttall (Physical Rev., 1928, [ii], **31**, 742—747).—Experiments were performed with sylvine, orthoclase, lepidomelane, and phlogopite. The fine structure of the potassium edge extended from 3429 to 3365X, or over a range of about 67 volts, and that of chlorine from 4383 to 4341X, or about 27 volts. The view that the ejected electrons stop in an outer orbit appears inadequate to explain the complicated structure of the edges.

A. A. Eldridge.

Physical purity and powder rontgenograms. N. H. Kolkmeijer (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 151—154).—X-Ray powder spectrograms have been made of mixtures of the white and grey modifications of tin, in order to determine the extent to which the physical purity of a substance, or freedom from its enantiomorph, may be tested. The composition of the mixtures was previously determined by density measurements. The results show that, with a normal exposure, an admixture of as much as 10% of a second modification might be unnoticed. The bearing of this result on Levi's conclusion (A., 1924, ii, 860), that yellow and red mercuric oxide are crystallographically identical, is discussed.

M. S. Burr.

Scattering by free gratings and the statistical significance of the distribution of grating spectra on the interference of plane waves. A. Wintner (Z. Physik, 1928, **48**, 495—512).—Mathematical.

J. W. Smith.

X-Ray investigation of the structures of the oxides of iron. H. Groebler (Z. Physik, 1928, **48**, 567—570).—Ferric oxide was reduced to different stages by carbon monoxide at 800° and the X-ray spectra of the products were examined. It was shown that ferrosoferric oxide can contain only 5% of ferrous oxide in solid solution. Above this percentage the ferrous oxide forms a second solid phase. With 39% of ferrosoferric oxide present the magnetite

structure breaks down and until pure ferrous oxide is reached the crystal structure of the latter persists. The solubility of iron in ferrous oxide is only very slight. J. W. SMITH.

Is crystal reflexion of *X*-rays entirely a classical phenomenon? G. E. M. JAUNCEY and W. D. CLAUS (Nature, 1928, **121**, 983).

Influence of relative ionic sizes on the properties of ionic compounds. L. PAULING (J. Amer. Chem. Soc., 1928, **50**, 1036—1045).—Some of the results of a theory which expresses the interionic forces in a crystal in terms of the radii of the ions are considered. Many crystal properties depend both on the "radius sum," *i.e.*, the distance between neighbouring ions, and also on the "radius ratio," *i.e.*, on the relative sizes of the cation and the anion. The latter quantity accounts for many irregularities in the properties (*e.g.*, m. p., b. p.) of the alkali halides formerly attributed to deformation phenomena, and is of significance in all crystal properties depending on the crystal energy. S. K. TWEEDY.

Production and absorption of the *K*-rays of aluminium. F. HOLWECK (Compt. rend., 1928, **186**, 1203—1205).—The absorption coefficients of rays produced from a water-cooled aluminium anode with an incandescent cathode in a highly evacuated metallic tube provided with an aluminium window are 550 and 7400 (approximately) for wave-lengths slightly greater and less than the *K*-discontinuity, respectively. This gives a value of about 13 for the ratio *J*, which is in agreement with that found (14) from the values obtained for the absorption in air at voltages above the critical potential using an aluminium filter 15 μ thick, and from the absorption coefficient of the soft rays of oxygen and nitrogen. J. GRANT.

Rontgenographic examination and eutropic relations of alkaline-earth fluorides. F. THILO (Z. Krist., 1927, **65**, 720—722; Chem. Zentr., 1928, i, 150).—The following values for calcium, strontium, and barium fluorides, respectively, are recorded: a (Å.) 5·45, 5·81, 6·20; $d_{\text{calc.}}$ 3·18, 4·24, 4·83; n 1·434, 1·438, 1·475; solubility (mg. in 1 litre of water at 18°) 16, 117, 1630. A. A. ELDRIDGE.

Structure of quartz. B. GOSSNER (Zentr. Min. Geol. Palaont., 1927, *A*, 329—338; Chem. Zentr., 1928, i, 152—153).—The unit cell, containing three molecules, of quartz has a 4·89, c 5·46 Å. The most probable atomic co-ordinates of β-quartz are: Si $(\frac{1}{2}, 0, 0)$, $(\bar{\frac{1}{2}}, \bar{\frac{1}{2}}, \frac{1}{3})$, $(0, \frac{1}{2}, \frac{2}{3})$; O $(v\ v, \frac{5}{6})$, $(2v, v, \frac{1}{6})$, $(v, 2v, {}^{1})$, $(2v, v, \frac{1}{6})$, $(v, v, \frac{5}{6})$, $(v, 2v, \frac{1}{2})$, where $v=0·197$. Conversion into α-quartz is accompanied by a slight variation of these co-ordinates.

A. A. ELDRIDGE.

Lattice constants of skapolite and apophyllite. B. GOSSNER (Zentr. Min. Geol. Palaont., 1927, *A*, 338—342; Chem. Zentr., 1928, i, 153).—Skapolite (mixed crystals of various plagioclases) and apophyllite (the unit cell of which contains 2 mols. of $8CaSiO_3[K_2H_2SiO_4,7H_4SiO_4],4H_2O$) have, respectively, a 17·26, 12·71 Å., c 7·65, 15·86 A.; d 2 65, 2·36; space-group C_{4h}^{5} or C_{4h}^{6}, D_{4}^{1} to D_{4h}^{16}.

A. A. ELDRIDGE.

Broadening of Debye lines with cold-worked metals. U. DEHLINGER (Z. Krist., 1927, **65**, 615—631; Chem. Zentr., 1928, i, 157).—With cold-worked silver, copper, tantalum, and α-brass the $K\alpha$ doublet is not resolved, whereas with cold-worked aluminium and zinc it is sharp. Hence periodic strain and distortion may be a cause of broadening of Debye–Scherrer lines. A. A. ELDRIDGE.

Charged spheres, the photo-electric effect, and the fluorescence spectra of *X*-rays. L. DECOMBE (Compt. rend., 1928, **186**, 1291—1293).—The production of the characteristic and continuous *X*-ray spectra is explained on the assumption that all monochromatic *X*-radiation of given frequency is due to the beats arising from the pulsatory frequencies of two cathodic electrons considered as small pulsating spheres, one of which is brought to rest by impact, whilst the other has a restricted speed less than that of impact. The explanation is also applied to the photo-electric effect of *X*-rays, to resonance, and to the Compton effect. J. GRANT.

Hemihedry of zinc blende and *X*-ray reflexion. S. NISHIKAWA and K. MATUKAWA (Proc. Imp. Acad. Tokyo, 1928, **4**, 96—97).—Friedel's law that hemihedrism due to lack of a centre of symmetry cannot be revealed by the *X*-ray diffraction method was tested in the case of zinc blende. Tungsten *L* radiation, the spectral lines of which cover the range including the *K* critical absorption limit for zinc atoms, was reflected from (111) and ($\bar{1}\bar{1}\bar{1}$) polished surfaces. Differences in the intensity of the lines were noticed, which might, however, be due to difference in the degree of polish. Preliminary experiments using a cleavage plane also showed differences in the relative intensities. C. J. SMITHELLS.

Structure of cyanite, Al_2SiO_5. W. H. TAYLOR and W. W. JACKSON (Proc. Roy. Soc., 1928, **A**, **119**, 132—146).—The crystal structure of cyanite has been determined by a qualitative method, based on the estimation of the relative intensities of a large number of reflexions obtained in a series of single-crystal rotation photographs. The crystal belongs to the pinacoidal class of the triclinic system, the space-group being C_i^1, and has a 7·09, b 7·72, c 5·56 Å.; α 90° 5·5′, β 101° 2′, γ 105° 44·5′. There are four molecules in the unit cell. The structure is based on a slightly distorted cubic arrangement of close-packed oxygen atoms, the silicon and aluminium atoms being distributed uniformly among the interstices of the oxygen assemblage so that independent tetrahedral SiO_4 groups are formed, whilst each aluminium atom lies at the centre of an octahedron having an oxygen atom at each of the corners. The very perfect cleavage parallel to (100) is explained by the existence of widely-spaced planes, parallel to (100), densely packed with silicon, aluminium, and oxygen atoms; similarly, the less perfect but fairly distinct cleavage parallel to (010) is explained by the existence of sheets densely packed with silicon and aluminium atoms, widely spaced and parallel to (010). No such densely-packed layers can be distinguished parallel to (001), corresponding with the fact that no (001) cleavage occurs. The unusually large variation of hardness in different directions on the (100) face is attributed to

the existence of the cleavage parallel to (010). It should be possible to extend this explanation to include examples of hardness variation of much smaller amount. L. L. BIRCUMSHAW.

Crystal structure of the alkali metals and of strontium. F. SIMON and E. VOHSEN (Z. physikal. Chem., 1928, **133**, 165—187; cf. this vol., 223).—Lithium has a body-centred cubic lattice, the constant at 100° Abs. being 3·46 Å. The face-centred cubic lattice of strontium, stable at low temperatures, has a lattice constant at 100° Abs. of 6·03 Å. Powder measurements indicate the existence of a hexagonal form at lower temperatures. Calcium at the ordinary temperature exhibits the face-centred cubic lattice, whilst zinc and cadmium show one modification only both at the ordinary and at higher temperatures. H. F. GILLBE.

Crystal structure of lead phosphate and pyromorphite. F. ZAMBONINI and A. FERRARI (Atti R. Accad. Lincei, 1928, [vi], 7, 283—291).—From *X*-ray measurements by the rotating crystal and by the Debye-Scherrer method it is shown that these two substances have essentially the same type of structure, and that therefore they cannot have the complex ion structure assigned to them by Abegg, Bodlander, and Werner. R. W. LUNT.

Crystal structure of lithium iodide trihydrate. S. B. HENDRICKS (Amer. J. Sci., 1928, [v], **15**, 403—409).—The crystal structure of lithium iodide trihydrate has been determined by the use of Laue and spectrum photographs. The space-group and resulting atomic configuration are the same as those of the triethylammonium halides. The unit cell contains two molecules of lithium iodide trihydrate and has $d_{100}=7\cdot45$ Å. and $d_{001}=5\cdot45$ Å. F. J. WILKINS.

Molecular structure and scattering of *X*-rays. G. W. STEWART and M. MANNHEIMER (Z. anorg. Chem., 1928, **171**, 61—72).—Previous work on the diffraction of *X*-rays by organic liquids is summarised (cf. A., 1927, 1015; this vol., 224). R. CUTHILL.

New type of crystal fine structure. Crystal structure of hexamminecobaltic iodide. H. HENTSCHEL and F. RINNE (Ber. Sachs. Ges. Wiss., math.-phys. Kl., 1927, **79**, 3—4, 5—54; Chem. Zentr., 1928, i, 152).—The crystal structure of hexamminecobaltic iodide is a combination of the rock salt and fluorspar types. The elementary cell contains four molecules; $a=10\cdot91$ Å. The distance Co—N is 1·64—1·91 Å. The lattice is face-centred. A. A. ELDRIDGE.

Uncommon common salt. A. F. DUFTON and C. G. WEBB (Nature, 1928, **121**, 942).—Crystals of sodium chloride formed in a gel prepared by addition of sodium silicate to hydrochloric acid were cubes with hollow faces and bevelled edges, the form being (110). A. A. ELDRIDGE.

Constitution of silver subfluoride. II. E. BRODY and T. MILLNER (Z. anorg. Chem., 1928, **172**, 84—86; cf. this vol., 223).—Polemical. H. F. GILLBE.

Constitution of silver subfluoride. C. DEL FRESNO (Z. anorg. Chem., 1928, **172**, 256—264).—Theoretical. The possibility of the existence of silver subfluoride is demonstrated, but the process of addition of fluorine to the silver fluoride lattice, as described by Brody and Millner (this vol., 223), is not possible. H. F. GILLBE.

Crystal group of pentaerythritol; the tetrahedral carbon atom. A. SCHLEEDE and A. HETTICH (Z. anorg. Chem., 1928, **172**, 121—128).—By observations with the tube electrometer and study of the etching by methyl alcohol, it has been established that pentaerythritol belongs to the group of symmetry. It is thus not pyramidal but tetrahedral, in agreement with the classical stereochemistry of van 't Hoff and Le Bel. H. F. GILLBE.

Diffraction of de Broglie waves by crystal gratings. E. E. WITMER and L. ROSENFELD (Z. Physik, 1928, **48**, 530—540).—Mathematical. J. W. SMITH.

Magnesium; its etching and structure. H. B. PULSIFER (Amer. Inst. Min. Met. Eng., Tech. Pub., 1927, No. 42, 17 pp.).

Twinning in beryllium, magnesium, zinc, and cadmium. C. H. MATHEWSON and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 53, 8 pp.)

Twinning in copper and brass. A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 56, 10 pp.).

Cause of translation striæ and translation strain-hardening in crystals. M. J. BUERGER (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. **54**, 14 pp.).—The phenomenon of slipping by blocks in a deformed crystal of a "pure" metal is due to atoms of impurities which, scattered regularly through the space lattice, distort it, producing planes of varying degrees of weakness. When separation of distorted shearing planes occurs, during slip, more than atomic linkings will allow, cleavage occurs. CHEMICAL ABSTRACTS.

Characteristic infra-red vibrations of certain crystals of the rock-salt type. L. G. CARPENTER and L. G. STOODLEY (Phil. Mag., 1928, [vii], 5, 823—832).—Mathematical. Using the data of Lennard-Jones for the force fields of atoms and ions, the frequency of the characteristic infra-red vibration of sodium chloride and potassium chloride, bromide, and iodide, respectively, has been calculated. W. E. DOWNEY.

Optical properties of the highly refractive isostructural compounds of magnesium, calcium, strontium, and barium with oxygen, sulphur, selenium, and tellurium. M. HAASE (Z. Krist., 1927, 65, 509—587; Chem. Zentr., 1928, i, 10—11).—The following refractive indices are recorded: magnesium oxide (d 3·579+0·002), n_D 1·7366±0·001, n_{Tl} 1·7416+0·0005, n_C 1·7335±0·001; calcium oxide 1·838±0·002, n_{Tl} 1·845±0·003; strontium oxide n_{535} 1·880, n_{570} 1·875, n_{600} 1·8675, n_{630} 1·863, n_{656} 1·8565±0·001; barium oxide n_{520} 2·002±0·001, n_{557} 1·989±0·002, n_{589} 1·980±0·001, n_{650} 1·960+0·004; the value for beryllium oxide increases with rise of the temperature of preparation from the nitrate; magnesium sulphide n_D 2·26±0·07; calcium sulphide n_{520} 2·161, n_{589} 2·137, n_{633} 2·124,

n_{656} 2·120±0·002; strontium sulphide n_{540} 2·122, n_{570} 2·114, n_{595} 2·105±0·003, n_{656} 2·087±0·005; barium sulphide n_D 2·155±0·005; magnesium selenide n_D >2·42; calcium selenide n_{555} 2·292, n_{589} 2·274, n_{620} 2·261, n_{656} 2·245±0·002; strontium selenide n_{540} 2·252, n_{565} 2·236, n_{589} 2·220, n_{620} 2·208, n_{656} 2·190±0·003; barium selenide n_{560} 2·289, n_{589} 2·268, n_{620} 2·252, n_{675} 2·230; calcium tellurido n_D >2·51; strontium telluride n_D 2·408±0·004, n_C 2·367±0·005; barium telluride n_D 2·440±0·005, n_C 2·379±0·003 (lattice constant a 6·82±0·02 Å.). A. A. ELDRIDGE.

Crystallography, especially optical, of some organic compounds. S. RÖSCH (Z. Krist., 1927, **65**, 680—711; Chem. Zentr., 1928, i, 9).—A study of *p*-toluoylacetophenonenol, $C_6H_4Me·C(OH):CHBz$, and dibenzoylmethanol, CPh(OH):CHBz.

A. A. ELDRIDGE.

Crystallography of dicyanodiamide. E. BAIER (Z. Krist., 1927, **65**, 719; Chem. Zentr., 1928, i, 26).—Dicyanodiamide, monoclinic, has $a:b:c$= 1·0021 : 1 : 0·4854, β=90° 31′; axial plane (010), $n_{\beta D}$ 1·5492. A. A. ELDRIDGE.

Resistance to shear in metal crystals. G. I. TAYLOR (Trans. Faraday Soc., 1928, **24**, 121—125; cf. A., 1927, 1017).—*X*-Ray examination of compressed aluminium in which all the distortion was due to slipping parallel to a 111 plane (cf. Proc. Roy. Soc., 1926, **A, 111**, 529) showed that all parts of the material which had rotated through angles greater than 2° had rotated about the transverse direction in the plane of slip. This direction of rotation is the same as that which might be expected if the detached portions of the crystals acted as rollers between the slip planes. The theory of rotation of material in the neighbourhood of regions of stress concentration is discussed. L. F. GILBERT.

Pyrophoric lead. G. R. LEVI and A. CELERI (Atti R. Accad. Lincei, 1928, [vi], 7, 350—355).—Pyrophoric lead has been prepared by heating the tartrate, citrate, oxalate, and formate under paraffin; the product is purified by washing with benzene. The amount of active lead has been determined from measurements of the volume of hydrogen liberated when the substance is treated with hydrochloric acid; the highest concentration is reached in the product from lead formate. *X*-Ray measurements of pyrophoric lead have shown that its crystalline structure is identical with that of ordinary lead. R. W. LUNT.

Determination of mol. wt. of saturated vapours of pure liquids and their mixtures by the displacement method. M. S. VREVSKI (Z. physikal. Chem., 1928, **133**, 357—361).—See this vol., 18.

Resistance of sputtered films. R. S. BARTLETT (Phil. Mag., 1928, [vii], **5**, 848—859).—It is found that the ageing of sputtered films depends on the temperature to which the film is raised. The resistance of the film decreases to a minimum value and then increases as the temperature is further raised. Occluded gas is the main cause of the high specific resistance of new films and of the decrease with ageing brought about by outgassing. A state of tension in the film, produced by unequal coefficients of expansion of film and backing, opens or closes gaps in the film as the temperature changes, giving rise to the low or negative temperature coefficients of resistance found in the experiments. W. E. DOWNEY.

Disturbance of the superconductivity of mercury by a magnetic field. W. J. DE HAAS, G. J. SIZOO, and H. K. ONNES (Arch. Néerland., 1928, [iii], **A, 11**, 1—47).—The hysteresis effect in the disturbance of superconductivity which has already been found in the case of tin (cf. A., 1927, 11, 717) was also found for mercury. The effect was observed in all cases examined. Whilst the increase of resistance as the field was increased was regular in the majority of instances, the return to a state of superconductivity as the field was diminished occurred in a series of jumps, the number and extent of which varied for the different resistances used. It is supposed that the difference in the intensities of field when these discontinuities occur is due to the different orientation of crystals in relation to the field. The hysteresis effect, and also the discontinuities in the curve, were obtained both in transverse and in longitudinal fields, although the position of the discontinuities was different in the two cases. The area of the hysteresis diagram varies with temperature. The relationship between the temperature and the strength of the field when the resistance has been half restored can be expressed by a straight-line graph. It is also shown that when a superconductor is placed in a magnetic field of sufficiently great intensity the resistance curve shows no anomalies. A. J. MEE.

Influence of pressure on the electrical conductivity of gold up to 1000 atm. A. MICHELS and P. GEELS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 50—55).—A continuation of previous work (A., 1927, 99). A bridge method has been used for measuring resistances. Measurements have been made at temperatures between 15° and 40°, approximately, and at 50 atm. pressure intervals between 0 and 250 atm., but at 200 atm. intervals between 250 and 1000 atm. The results are tabulated. The tempering of hard-drawn wire for a considerable time at 40° appears to cause a marked reduction in the pressure effect. Bridgman's results are criticised (cf. A., 1926, 565). M. S. BURR.

Theory of electrostriction and its experimental control. G. BRUHAT and M. PAUTHENIER (Compt. rend., 1928, **186**, 1289—1291).—The isothermal and adiabatic electrostrictions have been calculated in terms of directly measurable quantities, and the agreement with the results obtained experimentally by means of the Lorentz-Lorenz formula has been shown to be fairly good in the few cases for which data are available. J. GRANT.

Electrical conduction from the viewpoint of wave mechanics. W. V. HOUSTON (Z Physik, 1928, **48**, 449—468).—Mathematical.

J. W. SMITH.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. CAU (Compt. rend., 1928, **186**, 1293—1295).—Determinations of the optical rotations and ellipticities of thin layers of iron of various thicknesses, formed on the walls of an evacuated glass container by distillation from an

electrically-heated iron wire, indicate the existence of a birefringence accompanied by dichroism, the principal directions of which are parallel and perpendicular, respectively, to that of the original wire. The effect ceases when the deposit is removed, and is due to the magnetic field of the heating current, in which the atoms of vapour tend to orient themselves in positions which are retained after deposition and are unaffected by a magnetic field placed parallel to the deposit. J. GRANT.

Refractive index and specific mass of liquid and of viscous sulphur. P. MONDAIN-MONVAL and P. SCHNEIDER (Compt. rend., 1928, **186**, 1356—1357; cf. this vol., 479).—r_L has been calculated from the values of n and d between 120° and 200°. At 160°, a change of slope was obtained on the r_L-temperature diagram, which was made up of two nearly straight lines. J. GRANT.

Extension of Dulong and Petit's law to gaseous compounds and mixtures. A. PRESS (Phil. Mag., 1928, [vii], **5**, 832—834).—Theoretical. It is shown that for gaseous compounds and mixtures the formula $2\alpha=C_vM(\gamma-1)$ holds, where α is a constant. W. E. DOWNEY.

Preliminary isotherms of ethylene. C. A. CROMMELIN and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1059—1061).—Isotherms for ethylene have been determined at 20·18°, 10·17°, 0·10°, and −1·36°. The observations have been represented by Onnes' empirical equation of state and values for the first three coefficients, A_A, B_A, and C_A, calculated, succeeding coefficients being neglected. The results are in good agreement with Amagat's values, but differ from those of Masson and Dolley (A., 1923, ii, 462). M. S. BURR.

Accurate measurements of the specific heat of solid substances between 0° and 1625°. II. Specific heat of platinum and tungsten. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1069—1088).—By a method previously described (this vol., 469), the specific heats of platinum between 0° and 1625° and of tungsten between 0° and 1300° have been determined. In the case of tungsten a correction had to be applied at the higher temperatures for the oxides formed. The values of the atomic heat of platinum at constant volume, calculated from those at constant pressure, increase practically linearly with temperature, although they have already reached a value $3R$ below 0°. Similar results are obtained in the case of tungsten, the value $C_v=3R$ being reached at about 400°. The results cannot be explained by any heat of transformation, since no allotropic modification is obtained in either case. The results seem to throw doubt on the theories postulating the existence of a limiting value of $3R$ for the atomic heat at constant volume, and they are not explained by any extension of these theories. M. S. BURR.

Relation between specific heat and temperature. A. DENIZOT (Bull. Soc. Amis Sci. Poznan, 1926, **2**, 1—3).—In the temperature range where the atomic heat is approximately 6, the specific heat of many elements is proportional to log T. CHEMICAL ABSTRACTS.

Latent heat of fusion and vibration frequency. W. HERZ (Z. anorg. Chem., 1928, **170**, 237—240).—Whilst among the non-metals the value of the quotient of the latent heat of fusion per g. by the vibration frequency may lie between 1×10^{-12} and 1×10^{-11}, the range of variation shown by the metals, with the exception of mercury, aluminium, and beryllium, which are abnormal, is only about $3·5—7·5\times10^{-12}$. The values for many salts also lie within this latter range, but calcium chloride and alkali metal salts give figures about twice as great. R. CUTHILL.

Evaporation of rhombic sulphur. G. AMINOFF (Z. Krist., 1927, **65**, 632—635; Chem. Zentr., 1928, i, 3).—Sulphur spheres were evaporated at 100°, and the surfaces formed were measured goniometrically. Plane evaporation surfaces are formed, corresponding with the principal crystal faces. A. A. ELDRIDGE.

Simplified formulæ for specific heats of gases and solids, especially of explosion products. N. YAMAGA (Proc. Imp. Acad. Tokyo, 1928, **4**, 102—105).—Using Eucken's formula for the specific heat of gases in a simplified form, $C_v=nR+m\varphi(\theta/T)$, the values of n, m, and θ have been deduced for the gaseous products of explosions at temperatures of 3000—4000°. The rotational specific heat of monatomic gases is taken as 0, for polyatomic gases the atoms of which are arranged linearly R, and for other gases $\frac{3}{2}R$, which determines n. θ is chosen to accord with observed specific heats. The specific heats of solids produced in explosions are deduced from the Nernst–Lindemann equation. C. J. SMITHELLS.

Two different liquid states of helium. W. H. KEESOM and M. WOLFKE (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 90—94).—The data for the variation of the various physical constants of helium with temperature seem to suggest that helium can form two different liquid phases. From the specific heat data of Dana and Onnes (A., 1927, 101), a heat of transformation of helium I to helium II of 0·13 g.-cal./g. may be deduced. The heating and cooling curves of liquid helium have been studied, and these show a slight halt at 2·3° Abs. at a pressure of 38 mm. No change in the appearance of liquid helium at this temperature was observed. Liquid helium II is stable at the lower temperature and has a lower density, a greater heat of vaporisation, and a smaller surface tension than liquid helium I. A triple point such as liquid I–liquid II–vapour has, previously, been observed only with more complex substances which have a mesomorphic phase. M. S. BURR.

Specific heat of carbon dioxide. Correction. W. H. MCCREA (Proc. Camb. Phil. Soc., 1928, **24**, 290).—The suggestion embodied in an equation of a previous paper (cf. A., 1927, 1122) that the molecule of carbon dioxide might exist in two forms is now shown to be untenable. C. J. SMITHELLS.

Measurement of the kinetic heat effect in air, hydrogen, and argon. K. RÜCKER (Ann. Physik, 1928, [iv], **85**, 831—865).—In the Gaede molecular pump an oriented motion is superimposed on the random motions of the molecules. Besides causing a high vacuum, the oriented motion causes a kinetic heat effect (Gaede effect). Accurate measurements

have now been obtained for the Gaede effect in air, hydrogen, and argon and the data have been interpreted theoretically (cf. Weber, Z. Physik, 1924, **24**, 267). R. A. MORTON.

Liquid state. W. HERZ (Z. anorg. Chem., 1928, **170**, 233—236).—For many liquids, both associated and non-associated, the values of $z/\gamma^{1.6}$ and $Z/B^{1.3}$, where z is the number of molecules per c.c., γ the surface tension, and B the internal pressure, vary very little with change in temperature.
R. CUTHILL.

Fundamental pressure-coefficient of helium. W. H. KEESOM and (MISS) VAN DER HORST (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 970—979).—The pressure coefficient of helium between 0° and 100° has been determined in two different gas thermometers of volume 108 c.c. and 355 c.c., respectively. The mean value, when all corrections are made, is 0·0036611, with a maximum possible uncertainty of 2×10^{-7}. This is in close agreement with the value deduced by Cath and Onnes (Arch. Neerland., 1922, [iii], **A**, **6**, 1) from the difference of the fundamental pressure coefficients for the international helium and hydrogen thermometers. M. S. BURR.

Vapour tensions of liquid ethylene. C. A. CROMMELIN and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1057—1058).—Determinations of the vapour pressure of liquid ethylene have been made between 7·90° and −69·27°. The error of the measurements is about 0·025%.
M. S. BURR.

Salt-like hydrides. III. M. PROSKURNIN and J. KASARNOVSKI (Z. anorg. Chem., 1928, **170**, 301—310; cf. A., 1927, 718; this vol., 595).—Densities of hydrides of the alkali metals have been determined as follows: sodium, 1·38±0·04; potassium, 1·47; rubidium, 2·60±0·07; cæsium, 3·42±0·1. From these figures it appears that combination with hydrogen is accompanied by a contraction of the metal lattice by an amount which increases with increase in the atomic volume of the metal; this effect is even more pronounced than with the hydrides of the alkaline-earth metals. The molecular volumes of both groups of hydrides approximate to those of the corresponding fluorides, and the lattices may consequently be assumed to be of the rock-salt type. On this basis, the radius of the H′ ion is calculated to be 1·45 Å. R. CUTHILL.

Physical properties of acetic anhydride and related substances and their constitutional significance. D. C. JONES (J.C.S., 1928, 1193—1200).—The mol. wt. of acetic anhydride in benzene and *cyclo*hexane has been determined cryoscopically. In the latter solvent the ratio M(found)/M(calc.) varied from 1·09 at a concentration of 0·355 g./100 g. of solvent to 1·54 at 2·947 g. %. At a concentration of 5·33 g. % the invariant point, 2·269°, is reached where solid *cyclo*hexane is in equilibrium with two liquid phases. In benzene, the mol. wt. is normal up to a concentration of 3·8% with a slight tendency to increase at higher concentrations. The values for the "association factor" in the case of aniline and acetic anhydride dissolved in *cyclo*hexane are very similar in solutions of about the same concentrations. On the assumption that the mol. wt. of acetic acid is 120, the values for the acid are much smaller than those for the anhydride in corresponding solutions. The determinations of the temperature coefficients of molecular cohesion and mol. surface energy by Walden and Swinne (A., 1913, ii, 299) for acetic acid, acetic anhydride, aniline, etc. confirm the conclusion reached from the f.-p. determinations, that acetic anhydride and aniline behave as "normal" liquids, whereas the acid gives about half the calculated values.

Values for the parachors of acetic, propionic, *n*-butyric, and *n*-valeric acids are calculated and compared with those observed. Acetic anhydride gives a mol. volume value which might be expected if it were a ketonic ester. A study of the effect of groups containing oxygen on the solubility in water of aliphatic compounds containing four atoms of carbon might lead to the view that acetic anhydride contains a carbonyl and an ester group. It is concluded that there must be a marked conjugation between the three atoms of oxygen in the molecule of acetic anhydride which does not behave as if a free carbonyl group were present. The parachor is known to be insensitive to structural changes which produce large effects on properties such as solubility or chemical reactivity. H. INGLESON.

Molecular and atomic volumes. XVIII. Volume of ammonia in crystalline ammonium salts. W. BILTZ and G. BALZ (Z. anorg. Chem., 1928, **170**, 327—341; cf. this vol., 572).—By a comparison of the molecular volumes of ammonium salts of inorganic acids with those of the corresponding isomorphous salts of the alkali metals, the volume of the ammonia molecule in these compounds is found to be about 20, and is thus equal to the zero volume. In the salts of several organic acids, also, the volume is 20, but in the salts of the higher fatty acids the volume may be about 28. With dibasic acids, the first molecule of ammonia taken up retains its zero volume, but in the case of the lower aliphatic dibasic acids the second molecule undergoes a contraction.
R. CUTHILL.

Density of sodium azide. E. MOLES (Anal. Fís. Quím., 1928, **26**, 133—135).—A correction and redetermination. Pure sodium azide has d_4^{24} 1·8473±0·0004.
R. K. CALLOW.

Internal pressure and thermal vibrations of solid substances. E. N. GAPON (J. Russ. Phys. Chem. Soc., 1927, **59**, 933—949).—The internal pressure of elements, binary compounds, salts, and complex compounds is discussed. Two formulæ for the internal pressure of solid substances are derived and applied to the calculation of the internal pressures of copper, cadmium, lead, magnesium, aluminium, thallium, gold, and carbon. The results are in fairly good agreement with those calculated by the formulæ of Traube and Richardson. The relationship between internal pressure and coefficients of expansion and compression of elements and binary compounds is obtained and it is shown that the latter can be evaluated if the internal pressure is known. From considerations of internal pressure and association in the solid state an expression is derived by

which the association can be calculated and by the application of which it is shown that the alkali metals are associated in the solid state. Six formulæ for the vibration of elements are deduced and verified.

A. Ratcliffe.

Free-space numbers. II. W. Herz (Z. anorg. Chem., 1928, **171**, 14—17; cf. A., 1925, ii, 185).—For a number of liquids the ratio of the excess of the critical volume over the zero volume to the product of the critical volume by the free-space number at the critical temperature has a value of about 0·87; the value rises slowly on ascending a homologous series. It thus appears that even at 0° Abs. there are spaces between the molecules.

R. Cuthill.

Vapour pressures of pure substances, and of binary mixtures. Vapour pressures of mercury and graphite. J. J. van Laar (Z. anorg. Chem., 1928, **171**, 42—60).—By applying the method of thermodynamic potential to the equilibrium between a liquid and its vapour, there are derived the equations $L=a_1/v_1+RT$ and $\log p=-L/RT-\log a_1/v_1^2$, where L is the total molecular heat of evaporation, a_1 is one of the constants in van der Waals' equation for the liquid, the molecular volume of the liquid, T the temperature, R the gas constant, and p the vapour pressure. By combining these relations there results the equation $\log p=-a_0/v_0RT+\log(a_0/v_0^2)-\alpha_0T$, where a_0, v_0, and are the values, extrapolated to $T=0$, of a_1, v_1, and the coefficient of expansion, respectively; if b in the equation of state is a function of v, the term $\log(a_0/v_0^2)$ becomes more complex. This equation is in satisfactory agreement with the experimental figures for p for mercury from −40° to 1480°, the critical temperature; the value 4·60 is deduced for the critical density and 1150 atm. for the critical pressure. Applying the above equations to graphite (cf. A., 1921, ii, 17), it appears that the b. p. is about 5300° Abs., the critical temperature about 8000° Abs., and the critical pressure about 1500 atm. Starting from the relation previously developed for the molar potentials of the components of a binary liquid mixture (A., 1925, ii, 866) an expression is derived for the vapour pressure of such a mixture. This is capable of accounting for Weissenberger's experimental data (cf. A., 1926, 465) without the assumption of compound formation; such deviations as occur seem to be attributable to association.

R. Cuthill.

Fundamental state of the helium atom. E. A. Hylleraas (Z. Physik, 1928, **48**, 469—494).—Mathematical.

J. W. Smith.

Compressibility isotherms of hydrogen, nitrogen, and a 3 : 1 mixture of these gases at temperatures between 0° and 400° and at pressures to 1000 atm. E. P. Bartlett, H. L. Cupples, and T. H. Tremearne (J. Amer. Chem. Soc., 1928, **50**, 1275—1288).—Compressibility data for the above gases are recorded. The additive volume rule holds fairly well at 300°, but not below, and the additive pressure rule holds within 2% if it is defined as follows: at constant temperature the pressure exerted by one constituent of a gaseous mixture equals the product of its mol. fraction and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture. Practical applications of the data recorded are given.

S. K. Tweedy.

Changes in refractive index and density in binary mixtures. L. Counson (Arch. Sci. phys. nat., 1928, [v], **10**, 136—141).—A theoretical deduction is given of Pulfrich's law (Z. physikal. Chem., 1889, 561) according to which the variations of density and refractive index are always in the same direction. The proof is more rigid than that of de Lattre (A., 1927, 616) and leads to the same expression, $(dD/D)/(dn/n)=6n^2/(n^2-1)(n^2+2)$, where dD and dn are, respectively, the variations in density and refraction. The right-hand side of this expression is always positive.

W. A. Richardson.

Viscosity isotherms of binary mixtures. G. Tammann and M. E. Pillsbury (Z. anorg. Chem., 1928, **172**, 243—255).—The four main types of binary viscosity isotherms are discussed, and new data are recorded for the viscosity of methyl alcohol–water mixtures at temperatures between 0° and 30°. The curves exhibit the normal maximum at about 41% of methyl alcohol, and by cooling this mixture to about −50° to −60° crystals of ice separate; no separation of a crystalline hydrate of methyl alcohol is observed. From the corresponding maximum-viscosity mixtures of acetic acid and water and of propionic acid and water, crystals of the single components separate on cooling, whereas ethyl alcohol–water mixtures containing from 34 to 43% of alcohol yield transparent crystals of a tetrahydrate.

H. F. Gillbe.

"Volume adjustment" in solutions. F. Wratschko (Pharm. Presse, 1927, **32**, 355—358, 399—402; Chem. Zentr., 1928, i, 292—293).—Tannin (15%) in aqueous solution has d 1·4373, in alcohol (30%) 1·3717, (60%) 1·3611, (90%) 1·3260. Differences in density for solids and their solutions are also recorded.

A. A. Eldridge.

Diffusion of zinc in copper and in copper–zinc mixed crystals at 350°. Diffusion in the solid state. W. Kohler (Zentr. Hütten- u. Walzwerke, 1928, **31**, 650—657; Chem. Zentr., 1928, i, 467).—Mean diffusion coefficients are: copper–zinc, 0 000033 cm.²/day; α-brass–zinc, 0·000039 cm.²/day; β-brass–zinc, variable.

A. A. Eldridge.

Hardness of alloys. A. Mallock (Nature, 1928, **121**, 827).—Curves correlating the hardness with the composition of alloys of lead with antimony, tin, and bismuth are recorded.

A. A. Eldridge.

Age-hardening of silver–aluminium alloys rich in aluminium. M. Hansen (Naturwiss., 1928, **16**, 417—419).—The hardening at 100°, 150°, 175° and the influence of time has been examined for 12 quenched alloys of aluminium containing 0·5—12% of silver. An alloy with 6% of silver shows the greatest percentage increase in hardness, whilst the most favourable temperature is about 150°.

R. A. Morton.

Reflective powers of some eutectic alloys in relation to their micro-structures. G. Ando (Mem. Coll. Sci. Kyoto, 1928, **A**, **11**, 43—84; cf. Chikashige and others, A., 1926, 896).—The reflective

powers of the binary alloys silver–copper, copper–cadmium, cadmium–tin, cadmium–bismuth, bismuth–tin have been investigated in their dependence on wave-length and composition. The reflective power is usually minimal at the eutectic point. When, however, the reflective powers of the two components differ considerably, the minimum tends to deviate towards the side of the weaker component.

J. S. Carter.

Significance of the crystal regions α, α+β, β in the system copper–zinc in the hot-working of alloys. W. Mayer (Metallbörse, 1927, **17**, 2357—2358, 2469—2470, 2525—2527; Chem. Zentr., 1928, i, 401—402).—All copper–zinc alloys of the regions α, α+β, β can readily be worked hot, except M 66 (66% Cu). The grain size is also of decisive significance. Copper–aluminium alloys are also considered.

A. A. Eldridge.

Interatomic forces in metals and alloys. R. F. Mehl (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 57, 16 pp.).—For elements of nearly equal atomic number the compressibilities vary inversely with the interatomic forces; the compressibility is independent of deformation and grain size. Data on the compressibility of alloys are tabulated and discussed. The theory that martensite consists largely of ferrite and finely-divided cementite is supported. The relation between the hardness, compressibility, and zinc content of brasses was studied. The atomic volume of an element in alloys is not constant. The electron distribution around the atom periphery produces some slip resistance.

Chemical Abstracts.

Manganese–copper alloys, and the improvement of their physical properties. F. Heusler [with E. Dönnges] (Z. anorg. Chem., 1928, **171**, 146—162).—The alloy of copper containing 9—10% of aluminium and 14% of manganese (B., 1923, 405) is too hard to be of much practical value, even when in the soft state. A much more useful product is obtained, however, if the amount of manganese is reduced to 4—5%, the tensile strength after rolling then being 74 kg./sq. mm., and the extension 15%; this alloy can also be hardened. Alloys of manganese and copper only, or alloys of copper containing 5—15% of manganese and only 4—5% of aluminium, contain between 20° and 600° only the characteristic α-crystals, and therefore cannot be improved. Alloys of copper with more than about 2% of manganese and more than 1% of silicon may be improved ("Isima bronzes"); these may be hardened immediately after being sand-cast without being first re-heated, and are never ferromagnetic. The changes in hardness, electrical conductivity, and volume of specimens of these bronzes and also of alloys of manganese, aluminium, and copper on ageing have been followed.

R. Cuthill.

Analysis by means of *X*-rays and crystal structure of alloys. Constitution of cadmium–magnesium alloys. G. Natta (Annali Chim. Appl., 1928, **18**, 135—188).—A summary is given of the work done so far on the *X*-ray investigation of metallic alloys. By means of the powder method, tempered alloys of cadmium and magnesium have been investigated, as well as alloys which have been heated and also those spontaneously transformed by long keeping at the ordinary temperature. In the tempered alloys there are two types of solid solution, viz., those of cadmium in magnesium and of magnesium in cadmium. In alloys which have been cooled rapidly the two types exist together for a very large range of composition, and in the 50% alloy the intensities of the lines of the two lattices are approximately equal. With the introduction of magnesium the cadmium lattice is deformed without following Vegard's law, the length of the unit cell increasing from 2·98 to 3·01 Å. as the magnesium varies from 0 to 40 at.-%, the axial ratio decreasing at the same time from 1·89 to 1·875. Similarly, the magnesium lattice is deformed by the introduction of cadmium atoms, the length of the unit cell decreasing from 3·22 to 3·155 Å. for 15 at.-% of cadmium.

By means of the Laue method, alloys containing not more than 50% of cadmium have been examined. Up to almost 30 at.-% of cadmium the alloys are ideal solid solutions; beyond this composition the alloys consist of solid solutions having regular distributions of the atoms and very large elementary cells with dimensions which are multiples of those of the magnesium lattice. The solid solutions of magnesium in the cadmium lattice containing a large percentage of magnesium also show lines which are not always in agreement with those of pure cadmium, indicating a regular arrangement of the magnesium atoms. The compound CdMg does not exist except as a solid solution in the magnesium lattice with the cadmium atoms arranged regularly.

O. J. Walker.

Miscibility relations of acetic anhydride. D. C. Jones and H. F. Betts (J.C.S., 1928, 1177—1192).—The mutual solubility of mixtures of acetic anhydride with carbon disulphide, *cyclo*hexane, and a saturated petroleum fraction, decane, respectively, has been studied. The mean-concentration curves were also determined by an independent method. For the *cyclo*hexane and petroleum mixtures the mean curves are linear, but for the carbon disulphide mixtures the mean diameter is slightly curved, the curvature not being due to impurities. The three systems show good agreement with the theory of corresponding states in the phase which is rich in the less polar constituent, but in the other phase the deviations are large at lower reduced temperatures. The effect of moderate amounts of acetic acid on the critical solution temperature is small in all cases, but it is possible to detect 0·1% of acetic anhydride in acetic acid from critical solution data. The position of acetic anhydride in the internal pressure series is discussed in the light of the solubility results. The critical solution temperatures for the mixtures with carbon disulphide, *cyclo*hexane, and petroleum are, respectively, 29·83°, 52·45°, and 85·50°, and the critical concentrations of acetic anhydride (weight %) are, respectively, 36·17, 47·33, and 52·11.

W. A. Richardson.

Dissolution velocity of oxygen in sodium hydroxide, sodium carbonate, and hydrochloric acid solution. S. Miyamoto (Bull. Chem. Soc. Japan, 1928, **3**, 98—101).—The velocity of dissolution of oxygen when air is passed into sodium hydroxide,

sodium carbonate, or hydrogen chloride solution has been calculated from the oxidation velocities of sodium hydroxide and stannous chloride. H. F. GILLBE.

Solubility of *m*-nitroaniline in water. J. H. WALTON and T. G. FINZEL (J. Amer. Chem. Soc., 1928, **50**, 1508—1510).—Previous results (cf. Carnelley and Thomson, J.C.S., 1888, **53**, 782; Sidgwick, *ibid.*, 1921, **119**, 1013) were probably vitiated by the presence of finely-divided solid matter. The solubility increases from 0·03% at 0° to 1·23% at 83·4°. Analysis of the solutions was effected by the sodium nitrite and titanium chloride methods.

H. E. F. NOTTON.

Solubility of chloropentamminerhodium dichloride in water and hydrochloric acid, and that of ammonium chloropalladate in ammonium chloride solution. S. F. SHEMTSCHUSHNI (Ann. inst. platine, 1927, **5**, 364—365).—Saturated (25°) aqueous chloropentamminerhodium dichloride contains 0·828% of salt; when the solvent is 2·61, 4·51, or 10·56% hydrochloric acid the values are 0·086, 0·021, and 0·007%, respectively. Saturated aqueous (28·22%) ammonium chloride dissolves 0·26% of ammonium chloropalladate. CHEMICAL ABSTRACTS.

Influence of alkali nitrates on the solubility of lead nitrate. I. G. MALQUORI (Gazzetta, 1928, **58**, 203—208).—In order to determine to what extent hydration of ions and formation of complex salts affect the solubility relations, the isotherms of the systems $LiNO_3$–$Pb(NO_3)_2$–H_2O and $CsNO_3$–$Pb(NO_3)_2$–H_2O at 25° have been studied. The results when combined with the data of Glasstone and Saunders (J.C.S., 1923, **123**, 2134) for sodium and potassium nitrates show that the solubility of lead nitrate increases in the order Li<Na<K<Cs. The most highly hydrated lithium ion lowers the solubility of the lead nitrate to the greatest extent. The tendency to form complex nitrates, which increases the solubility of lead nitrate, increases from lithium to cæsium, so that ion hydration and complex formation oppose one another in their effect on solubility.

O. J. WALKER.

Solubility of salts in saturated solutions of other salts. I. I. KRASIKOV and I. T. IVANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 561—563).—Solubility effects due to the influence of a common ion are of very frequent occurrence. Exceptional behaviour is shown by mercuric chloride, which is far more soluble in chloride solutions than in pure water, by chlorides, which have the same solubility in mercuric chloride solutions as in water, and by potassium and strontium nitrates, the solubilities of which in solutions of sodium and potassium nitrate, respectively, are the same as in water. In the absence of a common ion, a diminution in solubility is frequently met with, but the solubility for sodium, potassium, and barium nitrates in mercuric chloride solution is the same as in water. If the saturated solution of one salt lowers the solubility of another, the saturated solution of the second salt will similarly affect the solubility of the first.

R. TRUSZKOWSKI.

Dissolution of metals in molten salts. W. EITEL and B. LANGE (Z. anorg. Chem., 1928, **171**, 168—180).—From observations on the Tyndall effect and ultramicroscopic examination it appears that solutions of lead in molten lead chloride are not of colloidal but of molecular nature. A similar conclusion is also reached from a thermodynamical examination of surface tension data. It is very probable that dissolution occurs owing to the formation of compounds of the type $Pb_n,PbCl_2$, so that in the solutions there is very little free lead. The colour of the solutions is due to the free molecules of metal, as is also the colour which frequently appears when the pure chloride is melted. If the molten solutions are chilled, the free lead produced by dissociation of the compound may separate in particles of microscopic or ultramicroscopic dimensions. R. CUTHILL.

Effect of electrolytes on the distribution of acetic acid between benzene and water. R. MITTRA (J. Indian Chem. Soc., 1928, **5**, 209—219).—The influence of lithium, sodium, potassium, and barium chlorides, potassium nitrate, sodium oxalate, and lithium, sodium, and potassium sulphates on the partition of acetic acid between benzene and water has been investigated. *E.M.F.* measurements were made to determine the change in activity of the hydrogen ion on the addition of neutral salts. From the results obtained the relative effects of the neutral salts can be discussed only qualitatively. All the salts, except sodium oxalate and potassium sulphate, cause an increase in activity, which increases with concentration. The two exceptions produce a negative effect at lower concentrations. By vapour-pressure measurements, McBain and Kam (J.C.S., 1919, **115**, 1332) have shown that sodium sulphate also has a negative effect on the activity of the acetic acid molecule at still lower concentrations of the acid. It appears, therefore, that the negative effect decreases in the order, potassium sulphate, sodium sulphate, and lithium sulphate. It is probable that, at sufficiently low concentrations of the acid, the negative effect may be observed with all sulphates and is to be ascribed to the sulphate ion only. The cations have the power to produce positive activation in the order Li>Na>K. The hydrogen-ion activity decreases with increasing concentration of sulphate, which is contrary to the effect produced by the other salts examined. The formation of the HSO_4 ion probably plays a part. Potassium nitrate has little effect on either the acetic acid molecule or the hydrogen ion. The activating effect of the chlorides on the acetic acid molecule is again in the order Li>Na>K. Barium has much the same effect as potassium. The chlorides also increase the activity of the hydrogen ion. The activating effect of an electrolyte on the acetic acid molecule does not necessarily run parallel with its effect on the hydrogen ion. It is probable that the so-called agreement with the Debye equation is more or less fortuitous, the investigations quoted in support being too limited in scope. Factors such as the existence of undissociated molecules in aqueous solution, or the ion association of Bjerrum and the hydration of ions, are not negligible, even at concentrations of the order of 0·01*N*.

M. S. BURR.

Applicability of Chakravarti and Dhar's adsorption equation. M. N. Chakravarti and N. R. Dhar (Kolloid-Z., 1928, **45**, 12—21).—The authors' adsorption equation is applicable to the following cases of adsorption: silver salts by silver iodide, acids and alkali by humic acid, a number of acids and the arsenite ion by ferric hydroxide, hydrochloric acid by hide power, acetic acid by carbon, iodine in various solvents by wood charcoal, salts of various valencies by barium sulphate and by wood charcoal. Experimental curves obtained by other investigators in experiments on adsorption by barium sulphate and by wood charcoal are shown to be in agreement with the authors' adsorption equation, which is considered to fit the experimental data better than the general adsorption equation. The experiments with barium sulphate indicate that the adsorbed layer does not exceed one molecule in thickness, in agreement with Langmuir's theory. The equation requires a maximal adsorption, and this has been realised experimentally. The results show that the values of the adsorption coefficient, α, and the constant, K, depend on the chemical nature of the adsorbent and are independent of its method of preparation and age, whilst the maximal adsorption, A, decreases with age and also varies with the method of preparation. E. S. Hedges.

Adsorption of iodine by charcoal in some mixtures of organic solvents. J. Trividic (Compt. rend., 1928, **186**, 1358—1360).—The fixation of iodine by charcoal in the mixtures water–alcohol (80%), benzene–toluene (1 : 1), chloroform–carbon tetrachloride (1 : 3), and toluene–alcohol (1 : 3) follows Freundlich's rule (cf. this vol., 471). The results are not in agreement with the conclusions of Schilov and Pevsner (A., 1926, 238). J. Grant.

Relationship between the velocity of adsorption of hydrogen by palladium, iron, and nickel, and the orientation of the crystals. G. Tammann and J. Schneider (Z. anorg. Chem., 1928, **172**, 43—64).—The chemical as well as the elastic properties of metals are considerably influenced by cold working. The colour of gold–silver and gold–copper alloys tends to become more yellow as the metal is rolled, whilst the dissolution velocity of iron in acids diminishes. Further, the degree of working to which iron, palladium, or nickel is subjected influences very greatly the velocity with which gaseous and electrolytically evolved hydrogen is adsorbed, a great variety of effects being observed. Hard palladium does not adsorb hydrogen at 150°, whilst the electrolytically developed gas is adsorbed by the hard and soft metal with practically the same velocity. Iron and nickel, on the other hand, adsorb gaseous hydrogen at 200—300° much more rapidly and to a greater extent when hard than when soft; the reverse holds for electrolytic hydrogen. After α-iron has completely undergone the γ-transformation it no longer adsorbs gaseous hydrogen at 300°. The velocity of adsorption of gaseous hydrogen by palladium at 150° depends on the crystal orientation in the surface of the metal, being the greater the larger the number of icositetrahedral planes in the surface layer. The number of such planes decreases after heating to a higher temperature, and the adsorption velocity shows a corresponding diminution. The effect is less marked for the adsorption of electrolytic hydrogen. Similar circumstances influence the rate of adsorption on iron and nickel, the velocity being greatest for the octahedral planes. The velocity of adsorption by a palladium sheet which contains dissolved hydrogen is diminished by the action of air on the surface, but is unaffected if the sheet is free from hydrogen. The production of water molecules in the lattice is probably the cause of this phenomenon. H. F. Gillbe.

Rate of absorption of water by bakelite. H. G. Leopold and J. Johnston (J. Physical Chem., 1928, **32**, 876—878).—When the percentage increase in weight is plotted against the quotient time of immersion in water/(half-thickness of sheet)^2, a single curve is obtained for all the sheets of brown bakelite examined. The rate of penetration of water into this type of bakelite is negligible for ordinary atmospheric conditions. Yellow bakelite gained in weight for two days when immersed in water and then steadily lost weight, yielding phenol to the water in which it was immersed. L. S. Theobald.

Adsorption phenomena in solutions. XII. Electroendosmosis. (Frau) L. Orlova (Z. physikal. Chem., 1928, **134**, 345—352; cf. Schilov and Tschmutov, this vol., 581).—Further experimental support is given for the view suggested by Kruyt (A., 1918, ii, 289) that charged surfaces in contact with dilute electrolyte solutions first adsorb the ions of like charge and thereby increase their charge. The effect of increasing concentrations of acids, alkalis, and salts on electroendosmosis through negative kaolin diaphragms and positive alumina diaphragms has been investigated. The curves representing this effect for the negative diaphragms show a more or less distinct maximum, whilst for the positive diaphragms the curves show a minimum in several cases. The charge of the positive surface is more easily reversed in sign, and it is therefore more unstable. The characteristic shape of the curves can in general be explained by supposing that two types of adsorption are superimposed on one another, viz., a primary adsorption of ions, which gives rise to the charge on the surface and increases it, and a secondary adsorption of the oppositely charged ions, which manifests itself as molecular adsorption and decreases the primary charge on the surface. O. J. Walker.

Behaviour of magnesium hydroxide towards aqueous mercuric chloride solutions and salts of tervalent arsenic. M. Rakusin and E. Izkin (Trans. Sci. Chem.-Pharm. Inst., 1926, **16**, 109—114; Chem. Zentr., 1928, i, 93).—Magnesium hydroxide readily adsorbs mercuric chloride and Fowler's (arsenite) solution, and is thus an antidote; sodium cacodylate is not adsorbed. Aluminium hydroxide adsorbs Fowler's solution but not sodium cacodylate. A. A. Eldridge.

Action of caffeine on the water absorption of colloids. J. Szeloczey (Magyar Orvosi Arch., 1927, **28**, 626—638).—Caffeine lowers the temperature at which gelatin passes from the gel to the sol condition, increasing the quantity of free water and decreasing that of imbibed water. The decrease of

water absorption is not directly proportional to the concentration of caffeine; it depends on the p_H, but not on the concentration. CHEMICAL ABSTRACTS.

Active silicic acids (silica gel). E. BERL and H. BURKHARDT (Z. anorg. Chem., 1928, **171**, 102—125).—The properties of several silica gel preparations have been examined. Although considerable differences were shown by the various specimens in respect of the heat of wetting by water and by benzene, the adsorption curves for crystal-violet dissolved in "tetralin" were nearly all very closely similar (cf. A., 1925, ii, 507; Mecklenburg, *ibid.*, 530). From the adsorption isotherms for water vapour, it appears that the water content of the gels, as well as the size of their pores, plays an important part in their activity. By mixing solutions of sodium silicate and aniline hydrochloride, gels have been obtained which, in respect of the adsorption of water vapour, were much more active than the other preparations, which included a commercial product prepared by Patrick's method (B., 1919, 363). To obtain the best results, the reactants should be at considerable dilutions, excess of hydrochloric acid must be avoided, and the gel should not be washed until 24 hrs. after precipitation is begun. Contrary to the statements contained in B.P. 205,081 (B., 1925, 169), the activity of silica gels is diminished by subjecting them to high pressure. R. CUTHILL.

Effect of addition of small amounts of metals of alkalis and alkaline earths on the capillarity constant of mercury. F. OPPENHEIMER (Z. anorg. Chem., 1928, **171**, 98—101).—The surface tension of mercury is reduced by small amounts (0·005—0·05%) of sodium, calcium, or lithium, the depression increasing with increase in the concentration of foreign metal. The surface tension of bromoform, on the other hand, is raised by ethyl diazoacetate. It thus appears that there is some connexion between the surface tension and the velocities of the reactions studied by Fraenkel, Wengel, and Cahn (this vol., 717). R. CUTHILL.

Colloidal theory of surface tension. S. RAY (Kolloid-Z., 1928, **45**, 9—12).—Existing views of the nature of surface tension are criticised. A new theory of surface tension, adopting the concepts of charged particles in vogue in colloid chemistry, is evolved, according to which the rise of liquid in a capillary tube is due to the electrical attraction between the charged gas molecules and the charged liquid molecules. Depression of the liquid in a capillary (as in the case of mercury) indicates an electrical repulsion between the particles. The theory is applied to the behaviour of the capillary electrometer.

E. S. HEDGES.

Unimolecular films. S. E. SHEPPARD and R. L. KEENAN (Nature, 1928, **121**, 982).—When the thickness of the film of an aqueous solution of a substance on mercury is calculated by assuming that the density of the solute is the same as that of the substance in bulk and is plotted against the concentration, a point is reached at which the thickness becomes independent of the concentration. The value for cellulose nitrates from acetone is 3—5 Å., for stearic acid from ether at 25°, 22—24 Å., for oleic acid 11·2 Å., for elaidic acid 12·2 Å., and for *n*-decoic acid 13·6 Å. Thus the fatty acids are apparently oriented in unimolecular films, approaching closest packing, whilst the "high-molecular" substances appear to have a casual, porous, net-like structure, or a molecular dimension which cannot be the length of the molecule, but may be the thickness of a polymeric chain or sheet. The latter view is preferred. Proteins from water give values of the order 6—7 Å.

A. A. ELDRIDGE.

Surface layer of liquids and the size of molecules. S. G. MOKRUSCHIN (J. Physical Chem., 1928, **32**, 879—881).—Evidence supporting the author's view concerning the structure of the surface layers of liquids (A., 1927, 1128) and the formula for calculating molecular diameters (A., 1924, ii, 820) is advanced. The density of the surface layer should be less than that of the liquid in bulk.

L. S. THEOBALD.

Disinfectant action. II. Relations of phenols and amines to proteins. E. A. COOPER and J. MASON (J. Physical Chem., 1928, **32**, 868—875; cf. A., 1927, 203).—Adsorption effects predominate in the aqueous systems picric acid–serum-albumin, salicylsulphonic acid–gelatin or albumin, ethylamine–gelatin, and aniline–gelatin, the ratio of the acid or amine taken up to that remaining in solution decreasing in all cases when the initial concentration of the solution increases. Hydrazine hydrate is not absorbed by gelatin and hydroxylamine hydrochloride shows a maximum absorption at low concentrations with egg-albumin. Germicidal and inhibitory power are not definitely related to the solubility in or adsorption by proteins in the colloidal state, but when the latter are not in the sol condition, bactericidal action and adsorption (or solubility) run parallel. Adsorption data are given. L. S. THEOBALD.

Influence of some colloidal substances on the rate of absorption of carbon dioxide by neutral sodium carbonate solutions. P. RIOU and L. LORTIE (Compt. rend., 1928, **186**, 1543—1546; cf. A., 1927, 311).—Increasing additions of peptone, pepsin, soluble starch, or gelatin to solutions of sodium carbonate ($3·7\times10^{-2}$—$14·8\times10^{-8}$ g.-mol./100 c.c.) rapidly decrease the rate of absorption of carbon dioxide at 20° up to a concentration of about 0·125%, after which there is usually no change. The viscosity is therefore not the only factor affecting the rate of absorption. J. GRANT.

Selective permeability of membranes. Influence of the mobility of the ions on the polarisation. (MLLE.) CHOUCROUN (Compt. rend., 1928, **186**, 1548—1551; cf. A., 1927, 931).—If unequally concentrated solutions of the same electrolyte are separated by a "charged" membrane (*e.g.*, prepared from an acid or alkaline solution of gelatin) the membrane shows appreciable polarisation only when the ion having the same sign has a mobility almost equal to or greater than that of the other ion involved. The polarisation is measured by the difference in the *P.D.* for the liquid couple with and without the membrane.

J. GRANT.

Osmosis of ternary liquids. Experimental. I and II. F. A. H. SCHREINEMAKERS and B. C. VAN B. WALTER (Proc. K. Akad. Wetensch. Amster-

dam, 1928, **31**, 113—124, 169—178).—I. A system of two ternary liquids in osmotic contact with one another through a membrane permeable by each of the three substances, previously discussed theoretically (this vol., 233), has been investigated experimentally. The liquids taken were aqueous solutions of sodium carbonate and sodium chloride, respectively, and for the membrane both parchment and pig's bladder were used. The results are tabulated and the direction of real and apparent osmosis is indicated.

II. The apparent osmosis of systems VI—XII, made up of $Na_2S_2O_6+BaS_2O_6+H_2O$, is discussed. The experimental data are given for a collodion membrane alone, a parchment membrane, and a collodion membrane with a deposit of copper ferrocyanide. The sodium dithionate in these systems behaves in the same way as the sodium chloride in the systems I—V previously examined. The change of barium dithionate in the system VI is the only example of an abnormal change of concentration in the systems I—XII. M. S. BURR.

Equilibria between double sulphates and aqueous sulphuric acid. I. C. MONTEMARTINI and L. LOSANA (Notiz. chim.-ind., 1927, **2**, 551—556; Chem. Zentr., 1928, i, 175).—The curves which represent the expansion of solutions of aluminium sulphate, aluminium and sodium sulphates, chromium and potassium sulphates, and aluminium chloride on heating show breaks at 73°, 66°, 77°, and 63°, respectively; the cooling curves are below the former, and are uniform. For solutions of aluminium nitrate, chromium nitrate, ferric sulphate, and ferric and potassium sulphates both sets of curves show points of inflexion. The *E.M.F.* of the cell $Al_2(SO_4)_3$ (dissolved cold)|Al or Pt|$Al_2(SO_4)_3$ (boiled) reaches zero after 1 month. The viscosity of heated aluminium sulphate and potassium chromium sulphate solutions is still not constant after 25 days. In the presence of increasing quantities of sulphuric acid the points of inflexion of the dilatation curves are shifted towards lower temperatures. The solubility of aluminium sulphate in sulphuric acid solutions differs according as the solution is saturated at 12·5° or is saturated at 100° and maintained at 12·5° for 4 days.

A. A. ELDRIDGE.

Physical properties of aqueous hydroxybenzene solutions. L. E. SWEARINGEN (J. Physical Chem., 1928, **32**, 785—793).—The density, viscosity, index of refraction, and surface tension of aqueous solutions of phenol, pyrocatechol, resorcinol, quinol, and pyrogallol have been measured at 25°. The densities can be represented by the equation $D=mC+D_0$, where C is the molar concentration. The value of m is 0·0075, 0·0230, 0·0210, 0·0210, and 0·0350 for the substances in the above order. Excepting surface tension, the number and position of the hydroxyl groups have no marked influence on the physical property concerned. The lowering of the surface tension diminishes from phenol to pyrogallol.

L. S. THEOBALD.

Preparation of chloride-free colloidal ferric oxide from ferric chloride. C. H. SORUM (J. Amer. Chem. Soc., 1928, **50**, 1263—1267).—Stable ferric hydroxide sols, free from chloride and nitrate ions, were prepared by dropping ferric chloride solution into boiling water and dialysing the product for some days in water at 90—97°. Dialysis for 5 weeks failed to induce coagulation. S. K. TWEEDY.

Slow hydrolysis of ferric chloride. E. HEYMANN (Z. anorg. Chem., 1928, **171**, 18—41).—The nature of the changes which occur in solutions of ferric chloride on keeping has been examined. With a freshly-prepared solution, the whole of the products of hydrolysis pass through an ultrafilter, but the degree of dispersity decreases with increasing age, the proportion of the iron finally in the colloidal state increasing with rise in temperature and with decrease in salt concentration. That this quantity may correspond with an actual equilibrium appears possible from the fact that if a chloride solution is heated at 80° for 45 min., whereby the hydrolysis is almost completed, and then aged at 20° or 37°, the amount of colloid ultimately approximates to that corresponding with the final temperature. On the other hand, there is less chlorine in the colloid produced at 80° than in those produced at the lower temperatures, and the amount does not change on cooling. The increase in conductivity of the chloride solutions with age runs parallel with the colloid content except immediately after the solution has been prepared, when the conductivity increases the more rapidly, as would be expected in view of the initial high degree of dispersity of the products of hydrolysis. The micelles themselves possess a measurable conductivity, but although with increasing age of the solution they increase in quantity their relative contribution to the conductivity of the system diminishes. This may be due in part to changes in dispersity, yet chemical changes are also involved, since the amount of chlorine falls at the same time, the composition of the final product of slow hydrolysis corresponding, not with a hydroxide, but with an oxychloride. It appears likely that the first product of hydrolysis is an oxychloride of the type $FeCl_3,nFe(OH)_3$, where n is probably less than 9. The molecules of this compound tend to associate, *i.e.*, coagulate, and react with water with elimination of hydrogen chloride and formation of secondary oxychlorides which increase in complexity until their molecules attain colloidal dimensions. The original equilibrium is consequently disturbed, and more and more ferric chloride is hydrolysed. In this way, the present results receive a satisfactory explanation; they are definitely in conflict, however, with the views of Wagner (A., 1914, ii, 349). R. CUTHILL.

Ferrous hydroxide. E. DEISS and G. SCHIKORR (Z. anorg. Chem., 1928, **172**, 32—42).—Ferrous hydroxide sol cannot be prepared by direct dialysis of ferrous chloride solution, as little hydrolysis appears to take place. By passing gaseous ammonia into ferrous chloride solution in complete absence of oxygen a pure white, pulverulent precipitate is obtained, resembling in appearance calcium hydroxide. By repeated centrifugal separation and washing of the precipitate with air-free water a stable sol is obtained which is colourless by reflected and red by transmitted light, the concentration being about 4 g./litre. A stable sol cannot be obtained by the use of aqueous

ammonia solution. The colloidal particles are positively charged, and the coagulating powers of a number of anions have been determined. The brown liquid obtained by mixing ferrous and ferric hydroxide solutions rapidly changes to a green colour, and finally turns black with complete precipitation of the colloid. The green substance probably results from the combination of one molecule of ferrous hydroxide with one of ferric hydroxide, but attempts to isolate the compound have been unsuccessful.

H. F. GILLBE.

Colloidal barium sulphate. W. A. LOTT (J. Amer. Pharm. Assoc., 1928, **17**, 454—456).—Three methods for the preparation of barium sulphate in the form of a reversible colloid are described. The following gives the best preparation: 60 g. of barium hydroxide are mixed with water to a paste and glacial acetic acid is added until neutral to phenolphthalein; 16·2 g. of 96% sulphuric acid are diluted with 65 g. of alcohol and cooled to 0° and the mixture is added to the concentrated barium acetate solution at 65° while stirring rapidly. The resulting colloidal solution is dried in a vacuum desiccator at 60°. The dried barium sulphate is readily peptised with water and the colloidal solution passes completely through a No. 5 Whatman filter and remains stable for several days. A small excess of soluble barium salt is present in the colloid and is necessary for its formation, but the product is no more toxic to white mice or guinea-pigs than ordinary precipitated barium sulphate. The colloid is peptised by the adsorbed barium ions and without them the particles are immediately agglomerated.

E. H. SHARPLES.

Preparation of a lead selenide hydrosol. J. BROOKS (J. Physical Chem., 1928, **32**, 698—708).—Lead selenide sols have been prepared by the passage of hydrogen selenide into a solution of lead acetate and gelatin (5%), and into a suspension of lead carbonate in the acetate and gelatin, with the addition of sodium hydrogen carbonate in both cases to neutralise the acetic acid formed. With the first method, the percentage conversion into hydrosol decreases as the initial concentration of lead acetate is increased above a certain limit, an effect which is attributed to the presence of the acetate ion or acetic acid during the process of formation. The velocity of growth of nuclei is unaltered whilst the rate of formation of nuclei is decreased, and this aspect is treated quantitatively. The rate of stirring in the first method has little effect on the yield of colloid, but in the second method the yield is decreased at rapid rates. Addition of the hydrogen carbonate in this case also coagulates a small amount of the colloid formed. The sols can be concentrated by long boiling, or preferably by the precipitation of the lead and gelatin with a saturated solution of ammonium sulphate, removal of this reagent by washing in the cold, and the subsequent redispersion of the sols in warm water.

L. S. THEOBALD.

Conductivity of copper hydrosols. H. D. MURRAY (J.C.S., 1928, 1235—1239).—Measurements have been made of the conductivity of copper sols (prepared by Bredig's method) with the addition of various electrolytes. The copper particles behave as if coated with cupric hydroxide, which saturates the dispersion medium, giving a solution which is too concentrated to permit of the study of the ion equilibrium at the surface of the particles.

W. A. RICHARDSON.

Colloidal clay. A. DEMOLON and G. BARBIER (Rev. gen. Colloid., 1928, **6**, 29—31).—The colloidal elements of soils may be classified as those which determine its texture, and those which determine its buffering and adsorbing powers etc. Removal of electrolytes from brick-clay induces complete dispersion of the argillaceous material. The rate of flow of a clay suspension is connected with the concentration of the clay by a hyperbolic curve, and the addition of an electrolyte to a completely peptised colloidal solution increases the viscosity considerably, the chloride and nitrate of a particular metal having the greatest effects. These increments may be correlated with the permeability of the corresponding coagulum and indicate the production of aggregates of varying sizes, of which those due to flocculating salts are the largest and most rigid, and have maximum permeability. Adsorption by clay follows the laws of true adsorption, and is characterised by equilibria which depend on the final p_H value. The amount of metallic cations fixed increases with the final p_H value independently of their nature. The ionic exchanges peculiar to zeolitic silicates also depend on the colloidal structure. The chemical composition of alluvial clay is similar to that of halloysite.

J. GRANT.

Examination of sols produced by peptisation of oxides of iron with silicic acid sol. A. FODOR and A. REIFENBERG (Kolloid-Z., 1928, **45**, 22—31; cf. A., 1927, 620).—Ignited ferric oxide is peptised by silicic acid sol to a brick-red sol which scatters light strongly. The sol bears a negative electrical charge and is partly coagulated by hydrochloric acid, whilst the coagulation by aluminium chloride is in accordance with an "irregular series." Ferrous oxide is also peptised by colloidal silicic acid to a green sol, which is oxidised slowly in the air and rapidly by hydrogen peroxide to a yellow ferric oxide sol. The particles of this sol are negatively charged, but the sol differs from the preceding one in relative viscosity and alkali-fixing capacity; the sol is readily coagulated by hydrochloric acid and the irregular series phenomenon is shown with aluminium chloride. A third sol, prepared by direct admixture of ferric hydroxide sol and colloidal silicic acid, is negatively charged, but differs from the preceding sols in size of the particles, in relative viscosity, and in its coagulation, the irregular series being exhibited with both hydrochloric acid and aluminium chloride. In all three cases, the ferric hydroxide can be separated from the silicic acid by addition of sodium hydroxide or neutral salts.

E. S. HEDGES.

Influence of mercaptan on the life-period of colloidal solutions of sulphur. E. IWASE (Kolloid-Z., 1928, **45**, 31—36).—The stability of colloidal sulphur dispersed by the non-electrolyte ethyl mercaptan has been examined. Sols were prepared by pouring 10 c.c. of a solution of sulphur in alcohol into a series of vessels each containing 90 c.c. of aqueous ethyl mercaptan in progressively increasing

concentration. On keeping it was found that the preparations containing either insufficient or an excess of ethyl mercaptan settle more rapidly than those containing intermediate quantities. The stability curve thus passes through a maximum, and the life-period of colloidal sulphur at the maximum position is at least three times that of colloidal sulphur containing no ethyl mercaptan. Differences between the dispersion of sulphur by electrolytes and by ethyl mercaptan are pointed out and discussed.

E. S. HEDGES.

Role of dielectric constants, polarisation, and dipole moment in colloid systems, especially in non-aqueous dispersoids. I. WO. OSTWALD (Kolloid-Z., 1928, **45**, 56—82).—Recent work is discussed and the data for about 250, mainly organic, liquids are recorded. The different values obtained for dipole moments by different methods of measurement and the deviations of these from the requirements of the various theories are also considered. "Single moments," obtained in the vapour state or dilute solution, are differentiated from "mass moments," obtained from the massive liquid. Consideration of the relation between polarisation values, dipole moments, and chemical nature leads to the following conclusions. Simple hydrocarbons show little orientation polarisation or only small permanent dipole moments. Halogenated hydrocarbons give large dipole moments. For simple alcohols, the moment rises with increasing number of CH_2 groups, thus varying antibatically with the dielectric constant. Aldehydes and ketones have very high moments, whilst ethyl ether has a middle value somewhat greater than 1. Amines and other nitrogenous bases have high dipole moments. Fatty acids, although incompletely investigated, give values greater than 1. In the three chloroacetic acids, the moment decreases with increasing number of chlorine atoms. The dipole moments of esters lie mostly between 1 and 2, and an increase is observed when the acid radicals form a homologous series. The moments of highly associated liquids (water, nitrobenzene, acetone) vary greatly with the method of determination, but the values are mainly high. The highest values are obtained with nitro-compounds (nitrobenzene 3·8, *o*-dinitrobenzene *ca.* 6, 2 : 5-dinitrotoluene *ca.* 4·5, dinitronaphthalene *ca.* 6). Various polarisation values are treated statistically and graphically as functions of the dielectric constant and for most of them, and more particularly for the dipole moment, a maximum is obtained for medium values of the dielectric constant. This result does not seem to be connected with the association of liquids of high dielectric constant. E. S. HEDGES.

Relation of some colloids to iodine and possible application to the titration of colloids. W. ENGELHARDT (Kolloid-Z., 1928, **45**, 42—46).—Colloidal gold (prepared by fourteen different methods) is rapidly dissolved by a solution of iodine in potassium iodide with formation of the complex salt $KAuI_2$. With potassium iodide, colloidal gold dissolves slowly and with alcoholic iodine solution it forms a dark precipitate. The behaviour of a number of other colloids with these reagents was examined and gave the following general results. Colloidal gold, silver, copper, mercury, cadmium, zinc, lead, bismuth, antimony, arsenic, and tellurium react readily with iodine in potassium iodide. Colloidal selenium reacts slowly under these conditions, and only when the iodine is in large excess. Colloidal boron, carbon, sulphur, platinum, palladium, rhodium, manganese, and iron do not react with iodine. When these elements are arranged in their positions in the periodic table, a nearly straight line can be drawn, separating those elements which are affected in the colloidal state by iodine from those which are not so affected. Most colloidal metal hydroxides do not react with iodine, whilst the majority of colloidal metal sulphides do so. It is suggested that colloids which do not contain reducing matter may be titrated by adding excess of iodine and titrating back with sodium thiosulphate. E. S. HEDGES.

Formation of filaments of ferric oxide by evaporation of colloidal solutions. P. BARY (Compt. rend., 1928, **186**, 1539—1541).—The residue from the evaporation at 50—60° of colloidal solutions of the compound nFe_2O_3,Fe_2Cl_6,aq. obtained by prolonged dialysis of ferric chloride solution, takes the form of filaments of ferric oxide oriented radially and concentric with the base of the vessel. The actual pattern depends on the conditions of the experiment, and is due to the capillary action of the walls on the supposedly rod-shaped colloidal particles.

J. GRANT.

Optical examination of substances with powder- or thread-like structure. G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1928, **45**, 1—7).—The optical properties of substances having a powder- or thread-like structure are discussed from a theoretical point of view, and spectro-photometric observations with light normally reflected from a number of disperse systems are recorded. The dispersion media (air, water, glycerol, anisole, and carbon disulphide) were so chosen that they absorb light almost equally but have different refractive indices. The disperse phases were chalk, powdered glass, mica, filter-paper, and talc. The experimental results are in agreement with the theory, and it is considered that the procedure may be developed so as to provide a general method for the optical characterisation of heterogeneous substances. E. S. HEDGES.

Structure formation in colloidal solutions. H. ZOCHER (Collegium, 1928, 203—208).—Concentrated vanadium pentoxide sols form spiral-shaped drops. There are two phases, one of which appears in polarised light and under the microscope to consist of spiral drops with their axes mainly in one direction. This phase is referred to as the "tactosol," and the second phase as the "atactosol." The structure of benzopurpurin "tactosol" is similar, but that of ferric hydroxide "tactosol" shows layers surrounded by cylindrical drops of the unarranged sol. The "tactosol" consists of alternate layers of colloid particles and water. D. WOODROFFE.

Colloidal state and cohesion at the time of solidification. J. ERRERA (Trans. Faraday Soc., 1928, **24**, 162—164; cf. A., 1925, ii, 362).—For frequencies less than 10^6 the dielectric constant of

solids produced from liquids having permanent dipoles rises sharply to a maximum near the point of fusion, after which it falls. The existence of colloidal structures in solids in the neighbourhood of the point of fusion is suggested (cf. Joffe, Rept. Physical Inst. Leningrad, 1926).

This hypothesis is in accordance also with the observation that the rise of dielectric constant, which is believed to be due to the polarisation of colloidal particles, becomes less and less as the frequency is increased, suggesting that the conditions do not provide sufficient time for the relaxation of the particles. L. F. GILBERT.

Photophoresis in liquids. S. RAY (Kolloid-Z., 1928, **45**, 7—9).—A description is given of experiments with emulsions of oil in water and with suspensions of sulphur in which streaming of the particles was caused by illumination of the system from one side. E. S. HEDGES.

Physico-chemical study of gum-arabic. A. W. THOMAS and H. A. MURRAY, jun. (J. Physical Chem., 1928, **32**, 676—697).—The base-combining capacity, the osmotic pressure, and viscosity of solutions of gum-arabic purified by precipitation with alcohol and electrodialysis have been studied in their dependence on p_H. The equivalent weight of the arabic acid found by titration with sodium and barium hydroxides is 1200 approximately, and 1000 when varying concentrations of alkali and acid are used in measuring base-combining capacity. The nature of the titration curve and this agreement between equivalent weights indicate that arabic acid is a relatively strong acid. The osmotic pressure–p_H curves for sodium and barium arabates show maxima at p_H 4·25 and 3·35, respectively, with no evidence of an isoelectric point. Viscosity is lowered by the addition of neutral salts. The Donnan theory of membrane equilibrium accounts qualitatively for the results obtained in the measurements of osmotic pressure and viscosity. L. S. THEOBALD.

Viscosity and hydratation. IV. Properties of liquid formed during syneresis and the theory of syneresis. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 467—483).—The liquid which separates in the syneresis of geranin and of benzopurpurin gels contains small quantities of these dyes which are present as single and double molecules respectively. The remaining gel is composed of hydrated colloidal particles of geranin, every molecule of which is bound with 2043 mols. of water. Addition of sodium chloride to geranin solutions diminishes the solubility of the latter, but increases the proportion of colloidal particles of the dye in solution, as a result of which the viscosity of the solution increases. Thus the action of this electrolyte is first to induce aggregation of molecules into colloidal particles, which, as the concentration of sodium chloride is increased, are then coagulated as a hydrated gel.

R. TRUSZKOWSKI.

Acid fixation and swelling of fibrin. I. E. VOIT. **II. Swelling of native fibrin in dilute hydrochloric acid.** F. SCHULDENZUCKER. **III. Water- and acid-fixing power of fibrin coagulated by boiling in water.** F. LOCHMÜLLER (Z. Biol., 1928, **87**, 269—278, 279—291, 292—306).—I. General review.

II. The quantity of hydrochloric acid which combines with fibrin immersed in a fixed volume of solution increases rapidly at first with increase in the concentration of acid, then more slowly, and finally approaches a limit. The maximum swelling of the fibrin increases with increase in the amount of acid absorbed, but reaches a maximum and then decreases and finally approaches a limiting value. Under the conditions of the experiment some hydrolysis is caused by the acid and this must be considered in interpreting the results. It is concluded that acid fibrin has a swelling power nine times as great as that of neutral fibrin.

III. Fibrin denatured by boiling with water behaves very similarly to native fibrin when it is placed in contact with hydrochloric acid in respect of the amount of acid with which it combines, the chief difference being that the fixation of acid increases more slowly with concentration of acid. On the other hand, the maximum amount of swelling is much less, being only one seventh of that of native fibrin. Hydrolysis of the protein takes place to some extent and has a maximum value at that concentration of acid at which maximum swelling occurs. Experiments on the uptake of water by quartz sand, talc, and starch are described as well as some properties of purified fibrin. W. O. KERMACK.

Deaminised gelatin. Z. C. LOEBEL (J. Physical Chem., 1928, **32**, 763—778).—The behaviour of a gelatin deaminised by Hitchcock's method (A., 1923, i, 1244) has been compared with that of isoelectric, ash-free gelatin prepared according to Loeb. The isoelectric point of the deaminised product lies at p_H 4·0. The optical rotation, viscosity, surface tension, and foaming have been studied as functions of p_H. The viscosity–p_H curves at 10°, 25°, and 50° of solutions prepared at 50° and 75° are all similar in shape. Each curve shows minima at p_H 4·0 and 7·3, and maxima at p_H 2·9, 6·5, and 7·9. The rise on the alkaline is greater than that on the acid side of the isoelectric point. The corresponding curves for 25° and 50° for solutions of ordinary gelatin prepared at 75° show that a minimum occurs at the isoelectric point, that the rise on the acid side is greater than on the alkaline, and that deamination shifts the isoelectric point to the acid side. The optical rotation at 10°, and the foaming of deaminised gelatin at the ordinary temperature, are at a maximum at p_H 4·0, whilst surface tension is at a minimum. The last results agree with those recorded by Bogue (A., 1922, i, 782) and Johlin (A., 1925, ii, 388), and conform to the theory of an adsorption film. The titration curves of gelatin and of the deaminised product with sodium hydroxide indicate that the hydroxyl groups which replace the amino-groups in deamination are acidic. A change in slope for deaminised gelatin at p_H 7·5 corresponds with one for gelatin at p_H 7·7, the second point of abrupt change in the properties of gelatin. Further, the difference in base-combining capacity of the two substances is equivalent to their difference in nitrogen content, and the value of the former for deaminised

gelatin is indicated to be $9 \cdot 7 \times 10^{-4}$ equiv./g., the larger value accounting for the greater viscosity on the alkaline side of the isoelectric point. The second point of abrupt change in properties is discussed.

L. S. THEOBALD.

Double refraction of caoutchouc in the deformed and undeformed state. M. KRÖGER (Kolloid-Z., 1928, **45**, 52—56).—Crude caoutchouc becomes doubly refractive on keeping. Lateral extension gives rise to biaxial positive double refraction. Vulcanisation produces uni- or bi-axial positive double refraction, whilst lamellar deformation results in weak biaxial negative double refraction.

E. S. HEDGES.

Properties of "pure" cellulose as a colloid. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **8**, 21—39).—See this vol., 474.

Relation between elastic properties and structure of organic fibres. R. O. HERZOG (Naturwiss., 1928, **16**, 420—421).—For amorphous materials, $D\eta = \alpha\Phi\delta^2/6$, in which D is the coefficient of "inner" diffusion, η is the viscosity of the gel, and α a constant for a given material, δ is the diameter of the colloid particle, and Φ the torsion modulus. An attempt has been made by comparing the fibre diameter of various natural and artificial fibres to test the relation and to decide whether the elastic properties are to be ascribed to the crystallites or to the crystallite aggregates (secondary particles). Although further investigation is needed the latter alternative is probably to be preferred.

R. A. MORTON.

Equilibrium of nitrogen and hydrogen with ammonia in a corona discharge. G. L. WENDT and J. E. SNYDER (J. Amer. Chem. Soc., 1928, **50**, 1288—1292).—At 28·5° and 733 mm. 4·1% by vol. of ammonia exists in the equilibrium mixture. According to calculation, the same conditions are realised thermally at 270° and possibly at 2500°. Corona discharge thus appears to activate various molecular species with an enormous increase in the reaction velocity.

S. K. TWEEDY.

Equilibria relations for the water-gas reaction in the temperature interval 300—1000°. B. NEUMANN and G. KÖHLER (Z. Elektrochem., 1928, **34**, 218—237).—The reaction $CO + H_2O \longrightarrow CO_2 + H_2 + 10090$ g.-cal. has been investigated from 300° to 1000° using an alloy of 94% Co, 5% Al, and 1% K as catalyst. Down to 355° complete equilibrium is attained, whereas at 295° it is incomplete. At temperatures below 500° it is necessary to employ a catalyst having the composition 94% Fe, 5% Al, and 1% K in order to hinder side reactions, principally methane formation. Equilibrium in these circumstances can be obtained at temperatures down to 400°, being incomplete at 365°. At 310° higher hydrocarbons make their appearance. Above 400° the equilibrium constants determined for the two opposing reactions are in very close agreement. A new expression calculated for the reaction isochore yields curves which correspond well with those derived from the experimental data. The integration constant I calculated from the equilibrium constants shows almost perfect agreement with the sum of the chemical constants of the vapour-pressure equation obtained by taking I_H as 3·685; the agreement is less satisfactory if Fried's value of 3·385 be employed. Combination of the integration constants for the formation of water vapour and of carbon dioxide yields for that of the water-gas reaction the value $0 \cdot 82 \pm 0 \cdot 12$, which approximates closely to that determined experimentally, viz., $+0 \cdot 84 \pm 0 \cdot 04$. If the water-gas constant be calculated from the water vapour and carbon dioxide constants by means of Hofmann's or Eastman's expressions no agreement exists with the experimental value. Furthermore, calculation from the data for the system iron–oxygen–hydrogen, assuming the correctness of Eastman's data for the system iron–oxygen–carbon, yields a curve which agrees with the experimental figures except for the iron oxide–iron equilibria.

H. F. GILLBE.

Equilibrium in the reaction, $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$. R. N. PEASE and P. R. CHESEBRO (J. Amer. Chem. Soc., 1928, **50**, 1464—1469).—Equilibrium has been approached from both sides at 505°, using a nickel–thorium catalyst. The mean experimental value, $K_{p(\mathrm{atm.})} = 0 \cdot 037$, agrees closely with that calculated from the free energy equation for this reaction (Lewis and Randall, "Thermodynamics"). The presence of about 1% of carbon monoxide in the effluent gases is shown to be accounted for by the reactions $CH_4 + H_2O \rightleftharpoons CO + 3H_2$, and $CO_2 + H_2 \rightleftharpoons CO + H_2O$ (cf. Neumann and Jacob, A., 1925, ii, 532).

H. E. F. NOTTON.

Cryoscopic study of benzene solutions. J. M. PETERSON and W. H. RODEBUSH (J. Physical Chem., 1928, **32**, 709—718).—The f.-p. depressions of dilute solutions of methyl alcohol, ethyl alcohol, water, toluene, acetic acid, and benzoic acid in benzene have been measured by a new and more accurate method. The vapour densities of the solutes have been calculated from the f.-p. data by means of a thermodynamic relation. Excepting methyl alcohol and acetic acid, the f.-p. depression is a linear function of concentration for dilute solutions. The apparent mol. wt. of water and ethyl alcohol are independent of concentration and are, respectively, 18·1 and 46·4. Some association is indicated in the case of ethyl alcohol, and acetic acid behaves as a typical associated vapour. Except for benzoic acid, Henry's law may be assumed to hold in the more dilute solutions and further, where the f.-p. depression indicates polymerisation, an abnormal vapour density actually exists, which is shown to be a necessary consequence of the first conclusion. The interpretation of f.-p. data in connexion with the question of association is discussed.

L. S. THEOBALD.

Cryoscopic mol. wt. determination of glycogen in liquid ammonia. L. SCHMID, E. LUDWIG, and K. PIETSCH (Monatsh., 1928, **49**, 118—121).—Determination of the mol. wt. of various samples of glycogen by cryoscopic measurements in liquid ammonia, using a platinum resistance thermometer to measure the depression of the f. p., have been made. The mean value of the mol. wt. is 180.

J. W. BAKER.

Molecular association regarded as a phenomenon of molar concentration. G. G. LONGINESCU and (MLLE.) G. CHABORSKI (Bul. Soc. Romane Stiin., 1928, **30**, 3—29).—It is suggested that the various phenomena usually ascribed to the existence of association, *e.g.*, abnormally small f.-p. depressions, are not so much a consequence of an actual polymerisation of the molecules as of a particularly high value of the molar concentration, C_m, *i.e.*, the number of g.-mol. of the substance per litre. From the density data for a large number of organic liquids and solids, it appears that normal non-associated liquids have a value of about 10 for C_m. If, then, the degree of association of a particular liquid is taken as given by the quotient of its molar concentration by 10, the resulting values are in satisfactory agreement with those calculated from other physical properties, *e.g.*, surface tension. Instances of abnormally large f.-p. depressions where no electrolytic dissociation can possibly occur are readily accounted for by C_m being less than normal, without it being necessary to postulate the existence of a non-electrolytic dissociation (cf. Walden, A., 1911, ii, 97). R. CUTHILL.

Refraction and dissociation of electrolytes. I. In water. E. SCHREINER (Z. physikal. Chem., 1928, **133**, 420—430).—From measurements of the molecular refraction at 18° in respect of the sodium *D* line and the hydrogen *C* and *F* lines of aqueous solutions of trichloroacetic acid and its sodium and lithium salts, the degree of dissociation of the acid has been calculated, the results being in satisfactory agreement up to concentrations of about 2 g.-mol./litre with the values obtained from conductivity data, when these are corrected for interionic forces and viscosity. For both hydrogen chloride and lithium chloride in aqueous solution the molecular refraction decreases with increasing concentration, the relation between these quantities being so similar in the two cases as to suggest that if the salt is completely ionised so also is the acid. In any case, the experimental data are not such as to permit of a calculation of the degree of dissociation of the acid. It seems probable that in respect of refraction molecules formed by association of ions behave like a mixture of the free ions. R. CUTHILL.

Calculation of electrolytic dissociation constants from electrical conductivity. W. NERNST (Sitzungsber. preuss. Akad. Wiss., 1928, 4—8).—The alkali halides are said to be only partly ionised and it is shown that the fraction of non-ionised molecules may be calculated with considerable accuracy from the change of molecular conductivity with concentration. H. F. GILLBE.

Condition of silver chloride and other sparingly soluble substances in gelatin. A. C. CHATTERJI and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 175—181).—Experiments on the electrical conductivity of silver chloride, formed in gelatin solutions by the interaction of silver nitrate and potassium chloride, indicate that only a very small proportion exists as ions, so that, instead of forming a supersaturated solution, the greater part of it is present in the colloidal state. Similar conclusions may be reached with regard to silver chromate. From the experimental results of Bolam and MacKenzie with silver chromate in gelatin (A., 1926, 678), there appears to be no definite relationship between the amount of silver present in the non-ionic condition and the quantity of gelatin present. Their *E.M.F.* measurements show that the amount of silver present in the ionic condition for silver chromate in gelatin is, in most cases, below 40%. The hydrogen ions present in gelatin promote the dissolution of silver chromate, but not of silver chloride. Hence the amount of free silver ions present in the case of silver chloride is much less than in that of silver chromate. M. S. BURR.

Complex formation in solutions of stannous chloride and of stannous bromide. M. PRYTZ (Z. anorg. Chem., 1928, **172**, 147—166).—The normal potential of $Sn/Sn^{\cdot\cdot}$, determined from measurements with stannous perchlorate solutions, is 0·1359 volt. Measurements of the potential in 0·01*M*-stannous chloride and bromide solutions indicate that the activity of the stannous ion decreases rapidly as that of the halogen ion increases. The following constants have been calculated: $[SnCl^{\cdot}]/a_{Sn^{\cdot\cdot}}[Cl']=32$; $[SnCl_2]/[SnCl^{\cdot}][Cl']f'^2=5{\cdot}5$; $[SnCl_3']/[SnCl_2][Cl']=0{\cdot}6$; $[SnCl_4'']f''/[SnCl_3'][Cl']f'^2=0{\cdot}3$; $[SnBr^{\cdot}]/a_{Sn^{\cdot\cdot}}[Br']=13$; $[SnBr_2]/[SnBr^{\cdot}][Br']f'^2=5$; $[SnBr_3'][SnBr_2][Br']=0{\cdot}44$. From these figures the molar percentages of the various stannous complexes present in solutions containing halogen ions at increasing concentrations have been calculated. The concentration of the complex ions $SnCl_3'$ and $SnBr_3'$ increases over a certain concentration range at a rate roughly proportional to the halogen-ion concentration; Goldschmidt's conclusion, viz., that these complex ions are the true reducing agents in acid solutions, is therefore supported. The results of the measurements are not incompatible with Young's figures for the conductivities of similar solutions. H. F. GILLBE.

Relation between the hydrolysis equilibrium constant of esters and the strengths of the corresponding acids. R. J. WILLIAMS, A. GABRIEL, and R. C. ANDREWS (J. Amer. Chem. Soc., 1928, **50**, 1267—1271).—The equilibrium constants for the hydrolysis of some methyl and ethyl esters were determined by the direct method. For esters which are not too dissimilar, those of the stronger acids appear to be more completely hydrolysed under like conditions than those of the weaker acids. The constants, however, vary with the conditions, and their relation with the acid strength seems to be very complex. S. K. TWEEDY.

Activity coefficients of ions in aqueous solutions of non-electrolytes. J. N. BRONSTED and J. W. WILLIAMS (J. Amer. Chem. Soc., 1928, **50**, 1338—1343).—The effect of variation in the dielectric constant of the solvent on activity coefficients has been studied by measuring the solubilities of croceo- and luteo-tetranitrodiamminocobaltates in sodium chloride solutions containing ether or varying quantities of sugar. The requirements of the Debye–Huckel theory are confirmed, even when the solvent is a mixed one. S. K. TWEEDY.

Activity coefficients of hydrogen chloride in ethyl alcohol. J. W. Woolcock and (Sir) H. Hartley (Phil. Mag., 1928, [vii], 5, 1133—1144).—The activity coefficients of hydrogen chloride in ethyl alcohol have been determined from measurements of the *E.M.F.* of the cell $H_2|HCl|AgCl|Ag$ at 25° over the concentration range 0·0003—1·2*M*. The values of the *E.M.F.* obtained are in good agreement with those of Danner (A., 1924, ii, 117) and are lower than those of Harned and Fleysher (A., 1925, ii, 538). The activity coefficient over the range 0·0003—0·004*M* is given by $-\log f=3{\cdot}40C^{1/2}$, the value being greater than that required by the Debye theory. The discrepancies are attributed to the incomplete ionisation of the hydrogen chloride.

A. E. Mitchell.

Activity of cadmium iodide in aqueous solution. F. H. Getman (J. Physical Chem., 1928, **32**, 940—946; cf. this vol., 241).—The activity coefficients of cadmium iodide at concentrations down to 0·005*M* have been calculated from measurements at 25° of the *E.M.F.* of the cells $Cd|CdI_2(M)|AgI|Ag$, $Cd|CdI_2(M)|PbI_2|Pb\text{–}Hg$, and $Pt\text{–}H_2(1\text{ atm.})|HI(M)|PbI_2|Pb\text{–}Hg$. The values derived from the first two cells show good agreement. The variation of the activity coefficient with concentration is similar for cadmium chloride, bromide, and iodide. The coefficients for aqueous solutions form a progressive series in which the values are in the order given above, and they differ from each other more widely than do the corresponding values for the alkali halides. The divergence of the curve obtained by plotting the activity coefficient against the logarithm of concentration from the corresponding conductivity ratio curve is greatest in the case of cadmium iodide.

L. S. Theobald.

Entropy of dilute solutions. A. Landé (Z. anorg. Chem., 1928, **171**, 143—145).—Planck's expression for the entropy of a dilute solution has been derived by a method in which, instead of supposing that the temperature is raised and the pressure lowered until the solution is in the state of an ideal gas, these variables are kept constant, and the validity of the gas laws for the solutes is utilised. R. Cuthill.

Application of the third law of thermodynamics to some organic reactions. G. S. Parks and K. K. Kelley (J. Physical Chem., 1928, **32**, 734—750).—Previous investigations (Gibson, Latimer, and Parks, A., 1920, ii, 586) have only approximately confirmed the validity of the third law of thermodynamics for organic reactions. The law has now been tested using the reaction $CHMe_2{\cdot}OH_{liquid}=COMe_{2\,liquid}+H_{2\,gas}$. The heat capacities of *iso*propyl alcohol and acetone have been measured by the method previously described (A., 1926, 232) from 70° to 293° Abs., and the heats of fusion at the m. p. found are 21·08 and 23·42 g.-cal./g. respectively. From these data ΔS_{298° has been calculated on the assumption of the third law. From the equilibrium constants for this reaction in the gaseous phase, measured with copper as catalyst over the range 184—218°, the values of ΔF_{298° and ΔH_{298° have been calculated for the reaction involving the liquid alcohol and ketone, and the value of ΔS_{298° thereby obtained agrees well with that derived from the thermal data. The data of Lange (A., 1925, ii, 96), Conant and Fieser (A., 1923, ii, 727), and Schreiner (A., 1925, ii, 978) for the reaction $C_6H_4(OH)_{2\,solid}=C_6H_4O_{2\,solid}+H_{2\,gas}$ provide confirmation of the validity of the third law. L. S. Theobald.

Theory of fusion and of specific heat of liquid metals. A. Magnus (Z. anorg. Chem., 1928, **171**, 73—81).—Assuming that the movements of the atoms of a liquid element are governed by the quantum laws, and that the frequency, ν, *i.e.*, the reciprocal of the average interval between two successive impacts of an atom, is proportional to the *n*th power of the temperature, *T*, the equation $dU/dT-n(U-U_0)/T$ $(1-n)E(\nu,T)$ is obtained. Here *U* is the total energy, and $E(\nu,T)$ represents the Einstein function. Taking the value 2 for *n*, this equation agrees fairly well with the available data for the specific heat of mercury at higher temperatures, but below about 100° there are considerable deviations. These might appear to indicate that *n* is a function of *T*, but they can be accounted for satisfactorily by supposing that *n* does not vary, but that at lower temperatures the liquid is associated. It thus appears probable that when a solid melts fragments of the lattice persist in the liquid, and gradually disappear only as the temperature rises further and further above the m. p. The energy of a gas may be assumed to consist of a portion which relates to the period in which the atom is actually in collision, and is given by the above equation, and a portion, 1·5*R*, which is calculated from purely kinetical considerations, and relates to the intervals between collisions. The lower the pressure the smaller is the former quantity, so that there is a continuous transition to an ideal gas.

R. Cuthill.

Enantiotropy, monotropy, and pseudomonotropy. I. N. Nagasako (Bull. Chem. Soc. Japan, 1928, 3, 90—95).—Thermodynamic relationships are discussed, and pseudo-equilibria are considered.

H. F. Gillbe.

One-component system SiO_2–catalysts for the slow transformations. C. J. van Nieuwenburg and C. N. J. de Nooijer (Rec. trav. chim., 1928, **47**, 625—634).—Fenner (A., 1913, ii, 133) fixes the stability regions of the modifications of silica as quartz, up to 870°, tridymite, 870—1470°, and cristobalite from 1470° to 1710°, the true stable m. p. Since as a rule Fenner employed a very large excess (200%) of catalyst (sodium tungstate) to accelerate the rates of the changes, he investigated a part of the three-component system SiO_2–WO_3–Na_2O. An attempt has been made to obtain a more satisfactory catalyst. In all, results from 44 catalysts are given. The silica used was a pure miocene quartz sand from Lommel (Belgium), 99·9% SiO_2, the small amount of impurity consisting chiefly of rutile, hæmatite, zircon, and staurolite. The washed, ignited sand was graded (between 20 and 30 mesh per cm.), mixed with 1% of catalyst, and heated in a carbon resistance furnace up to 1300° in $1\frac{3}{4}$—2 hrs. and maintained at 1300°±15° for 1 hr. After removal from the furnace the density was determined. The original sand had *d* 2·64(5). On being heated

alone to 1300° the value fell to 2·62(5). The percentages converted by the catalysts are calculated on the assumption that the density of the completely converted product should be 2·30 (the mean between those of tridymite and cristobalite, 2·27 and 2·33). Fenner's catalyst (1% of sodium tungstate) causes 23% inversion, whilst the most effective examined, lithium carbonate, converts 98%. Sodium and potassium carbonates and sodium fluosilicate are also very effective catalysts. Phosphoric oxide and boron trioxide recommended by Rebuffat and Parravano were found to give poor results. The effect of grain size on the rate of transformation under otherwise comparable conditions is emphasised.

The possible technical value of using such catalysts as alkali carbonates in the manufacture of silica bricks is mentioned. H. INGLESON.

Vapour pressures of binary systems. A. W. PORTER (Trans. Faraday Soc., 1928, **24**, 343—347; cf. A., 1921, ii, 377).—It follows from the law of Duhem and Margules that equations connecting the vapour pressure with the concentration should not violate the condition that each side of the equation must be symmetrical with respect to the molar fractions (μ_1 and μ_2) of the constituents, each of which is supposed to be of the same molecular type as the substance in the vapour state. The application of Perman's data for aqueous solutions of sugar shows that Raoult's law does not hold, even in the most dilute regions, and satisfactory equations representing the data are derived for both constituents. From the data for potassium chloride solutions at 80°, general considerations relating to true, colloidal, and immiscible solutions, and to systems in which solvent is absorbed on the solute, are advanced. The equations are also applied to the determination of equilibrium constants in terms of vapour pressures instead of masses or molar fractions, and it is pointed out that the so-called activity coefficients are not constants but functions of μ_1 and μ_2 and of a term representing the mutual action between the components present. A solution may be almost "ideal" for the solvent in the presence of a small quantity of solute, but it is then by no means ideal from the point of view of the latter. The conditions are more complex for ternary systems. J. GRANT.

Crystals of β-brass. VON GOLER and G. SACHS (Naturwiss., 1928, **16**, 412—416).—The gradual transformation of β-brass over the temperature range 300—470° is not accompanied by any change in the Laue pattern large enough to indicate a new lattice. The increase in temperature causes the weaker interferences to disappear and the stronger ones are reduced in intensity. The relation between the temperature effect and recrystallisation is discussed. The effective slip planes have been studied from tensile tests. R. A. MORTON.

Equilibrium diagram of the copper-rich side of the copper-tin system. T. MATSUDA (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 141—161).—The existence of a transformation at 590° in copper-tin alloys containing 15—26·5% of tin has been confirmed by thermal analysis and by electrical resistance measurements. It is attributed to a eutectoid change, the eutectoid containing 26% of tin. The existence of a eutectoid transformation at 520° was also confirmed. Apart from these changes the equilibrium diagram for alloys containing 0—40% of tin agrees with that of Bauer and Vollendruck. Drop forging tests show that alloys containing 18—22% of tin become malleable above 520°. These alloys show a reduction in Brinell hardness when quenched from above 590°. C. J. SMITHELLS.

Tin-bismuth and tin-cadmium alloys in the solid state; assumption of stable equilibria at various temperatures. M. LE BLANC, M. NAUMANN, and D. TSCHESNO (Ber. Sachs. Ges. Wiss., math.-phys. Kl., 1927, **79**, 71—106; Chem. Zentr., 1928, i, 401).—In the system tin-bismuth there is on the bismuth side a small homogeneous region extending to 1·5 at.-% Sn (micrographical observation) or 3·5 at.-% Sn (electrical observations). On the tin side at about 13 at.-% Bi a compound (? $BiSn_7$) appears, forming a homogeneous system with excess of tin. In the system tin-cadmium at 130° with 20 at.-% Cd a compound, probably $CdSn_4$, is formed, yielding a heterogeneous system with excess of cadmium. With excess of tin at 2·5 at.-% of cadmium a single homogeneous phase is formed. A. A. ELDRIDGE.

Thermochemical study of the system cadmium-mercury. T. W. RICHARDS, H. L. FREVERT, and C. E. TEETER, jun. (J. Amer. Chem. Soc., 1928, **50**, 1293—1302).—The negative heats of dissolution in mercury of cadmium amalgams containing 16—33% Cd increase on ageing, due to the gradual disappearance of the traces of liquid phase present owing to the phenomenon of "coring." This preliminary segregation of the components may be prevented by chilling at −190°, and fresh samples so chilled give the same heats of dissolution as aged amalgams. The solidus point is defined as the point at which melting begins when the solid phase is completely homogeneous; it can be found exactly only by successive thermochemical determinations on quenched samples. The results agree with those of Bijl (A., 1903, ii, 6). S. K. TWEEDY.

Heusler's alloys. Manganese-aluminium-copper. O. HEUSLER (Z. anorg. Chem., 1928, **171**, 126—142).—The constitution of the ferromagnetic alloys of manganese, aluminium, and copper has been studied, and the m.-p. diagrams are reproduced. Since the range of composition for which the alloys are magnetic corresponds with the region of existence of ternary β mixed crystals it appears probable that these give rise to the magnetic property. In order to confirm this view, differential heating curves have been obtained with an alloy containing 14·0% of manganese and 10·5% of aluminium, and quenched from 700° and then aged at various temperatures. The results show that the thermal effect of the magnetic transformation vanishes if the β-mixed crystals are decomposed by ageing. This accords with the theory (cf. A., 1927, 502) that the ferromagnetic state results from the association of the atoms in the homogeneous solid solution to magnetic molecules. It has not been possible, how-

ever, to ascertain the composition of the magnetic substance. R. CUTHILL.

Thermal dissociation of cadmium nitrate. G. MALQUORI (Gazzetta, 1928, **58**, 217—222).—A more detailed description of results already published (this vol., 593). O. J. WALKER.

Solution equilibria between crystalline zinc hydroxide and sodium hydroxide. R. FRICKE (Z. anorg. Chem., 1928, **172**, 234—242).—The solubility of rhombic zinc hydroxide in sodium hydroxide solution is independent of the relative quantities of the substances present. For solutions containing 7—42% of sodium hydroxide, equilibrium is attained at 30° in less than 2·5 hrs., but with concentrations greater than 30% the zinc hydroxide is converted into oxide. Monosodium zincate may be prepared by saturating a hot 44% solution of sodium hydroxide with zinc oxide, filtering from residue with exclusion of carbon dioxide, and keeping the solution in a closed vessel at the ordinary temperature. After about 2 days long needles commence to separate, and by gentle shaking a thick mass of crystals is obtained. H. F. GILLBE.

Equilibrium in binary systems containing carbamide as one component. N. A. PUSCHIN and D. KONIG (Monatsh., 1928, **49**, 75—82).—The binary systems formed by carbamide (B) with trichloroacetic acid, resorcinol, quinol, phenol, guaiacol, α-naphthol, naphthalene, and diphenyl (A) have been investigated by the method of thermal analysis. In the first three cases equimolecular *compounds* of the type AB, m. p. 80°, 101°, and 130°, respectively, are formed, whilst with phenol a *compound* of the type A_2B, m. p. 59°, is formed. Guaiacol and α-naphthol yield only mechanical mixtures. With naphthalene and diphenyl two liquid layers are formed, the mutual solubilities of carbamide and the hydrocarbons being very small. The eutectic temperatures in the other cases are, respectively, 59° and 27°, 90° and 84°, 110° and 125°, 36°, 24·5°, and 65°, the corresponding mol. percentages of the component A being 37 and 75, 30 and 75, 20 and 63, 93·5, 94 and 67, respectively. J. W. BAKER.

X-Ray investigation of the decomposition of complex iron cyanides. R. BRILL and H. MARK (Z. physikal. Chem., 1928, **133**, 443—455).—When ammonium ferrocyanide is heated in a vacuum at 320°, the product appears, from its *X*-ray diagram, to be ferrous ferrocyanide. If this is decomposed further by heating in a current of nitrogen and hydrogen in the proportion of 1 : 3, lines which appear to correspond with α-iron soon appear in the diagram, and ultimately pure α-iron remains. At certain stages of the reduction, intermediate products, probably carbides and nitrides, can also be detected. R. CUTHILL.

Causticisation of sodium carbonate by ferric oxide. XI. Heat of dissolution of sodium carbonate. M. MATSUI, S. NAKATA, K. AKIYAMA, and K. BITO (J. Soc. Chem. Ind. Japan, 1928, **31**, 140—147).—The heat of dissolution of sodium carbonate in water was measured by means of a constant-temperature calorimeter with an electric heating device, and found to be Na_2CO_3[s]+aq.[1000 mol.]=Na_2CO_3[aq.]+5606·7±22·1 g.-cal. at 25°. S. OKA.

Decomposition of orthoclase. O. K. BOTVINKIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 1029—1031).—Observations on the decomposition of orthoclase by water vapour at 115°, 315°, and 318° and by water saturated with carbon dioxide at 75, 90, 95, and 120 atm. show that orthoclase is very stable towards water and aqueous solutions of carbon dioxide; the stability decreases slightly with rise of temperature and of pressure. A. RATCLIFFE.

Solubility of cadmium sulphide in hydrochloric acid. M. AUMERAS (Compt. rend., 1928, **186**, 1541—1543).—The application of the author's method for the study of equilibria in ionised systems (A., 1927, 1141) has shown that the solubility at 16° of cadmium sulphide in hydrochloric acid can be represented by [HCl]=970[H_2S][$CdCl_2$] for dilute solutions. This corresponds with complete dissociation of hydrochloric acid and of cadmium chloride and with the single-stage dissociation H_2S $HS'+H^{\cdot}$. To avoid oxidation, the experiments were performed in an atmosphere of nitrogen. J. GRANT.

Equilibria of sulphides and silicates in slags. W. JANDER and K. ROTHSCHILD (Z. anorg. Chem., 1928, **172**, 129—146).—The reversible equilibria in the systems lead silicate–ferrous sulphide, cuprous silicate–ferrous sulphide, nickelous silicate–ferrous sulphide, lead silicate–cuprous sulphide, cuprous silicate–nickelous sulphide, nickelous silicate–lead sulphide, and sodium silicate–lead sulphide have been investigated. The simple mass action law is not applicable to these systems, but by use of an approximation equation derived from the Lorenz modified mass action law the constants 1·12, 1·44, 2·25, 10·01, 1·02, and 1·64, respectively, are obtained. In the sodium silicate–lead sulphide system the experimental error is too large to admit of a satisfactory constant being obtained, since the reaction proceeds nearly to completion. From the constants for any two systems, that for a third may be calculated with considerable accuracy. The affinity relationships of the various metals towards sulphur and oxygen alter considerably at higher temperatures. H. F. GILLBE.

Quaternary system, water–sodium nitrate–sodium chloride–sodium sulphate from below 0° to above 100°. A. CHRETIEN (Caliche, 1927, **9**, 248—259).—The eutectic points and the composition of the solid and liquid phases have been determined. CHEMICAL ABSTRACTS.

Reciprocal pair: $2NaCl + Ba(ClO_3)_2 = 2NaClO_3 + BaCl_2$. C. DI CAPUA and A. BERTONI (Gazzetta, 1928, **58**, 249—253).—The isotherms of the four systems $NaClO_3$–$NaCl$–H_2O, $NaCl$–$BaCl_2$–H_2O, $BaCl_2$–$Ba(ClO_3)_2$–H_2O, $Ba(ClO_3)_2$–$NaClO_3$–H_2O have been studied at 20° and the triangular diagrams constructed. The stable pair is found to be $Ba(ClO_3)_2$–$NaCl$. The composition of the solutions in equilibrium with the two stable triads $Ba(ClO_3)_2+NaCl+NaClO_3$ and $Ba(ClO_3)_2+NaCl+BaCl_2$ as solid phases has also been determined. O. J. WALKER.

Vapour pressure and heat of dilution of aqueous solutions. V. Activity. E. P. PERMAN (Trans. Faraday Soc., 1928, **24**, 330—336).—See this vol., 368.

Properties of metallic hydrides. A. SIEVERTS and A. GOTTA (Z. anorg. Chem., 1928, **172**, 1—31).—The heats of formation of cerium, praseodymium, and lanthanum hydrides are 42,260, 39,520, 40,090 g.-cal./g. of hydrogen respectively, whilst the densities of the hydrides are 5·55, 5·56, and 5·83, respectively. The heats of formation differ very little from those of calcium, barium, and lithium hydrides, but whereas these substances have considerably greater densities than the corresponding metals, the reverse is true of the rare-earth hydrides investigated and of titanium, zirconium, and vanadium hydrides. In several ways, the rare-earth halides resemble those of the elements of the titanium and vanadium groups of the periodic classification, and are by their semi-metallic nature sharply differentiated from the salt-like hydrides formed by the elements of the first and second groups, and from the metallic hydrides of iron, cobalt, nickel, and platinum. H. F. GILLBE.

Accuracy of Stohmann's thermochemical data. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1928, **47**, 606—618).—Swientoslawski's method (A., 1920, ii, 470) of correcting the older thermochemical data to the basis of the international thermochemical standard of 1922 (heat of combustion of benzoic acid 6324 g.-cal.$_{15}$/g., weighed in air) consists in comparing values A_1, A_2, A_3, etc. obtained by the earlier worker with values A_1', A_2', A_3' found later under the same conditions but using the international standard. The series of the earlier worker are regarded by Swientoslawski as homogeneous if the ratios α_1, α_3, etc. vary only within 0·1—0·15%. The mean of the values is used by him to correct the earlier data.

The heats of combustion of about 40 substances previously determined by Stohmann have been redetermined. The factors required to bring Stohmann's data to the international basis vary from 1·0031 to 0·9892, but lie mainly between the limits 0·994 and 1·002. Stohmann's results do not fall into two homogeneous groups as stated by Swientoslawski and Pillich, but constitute a very heterogeneous group. It is impossible to apply any correction to the data of Stohmann which could reduce them to the present international standard. Probably the error of Swientoslawski and Pillich arises from the use of too few comparison substances. H. INGLESON.

Absolute determination of heat of combustion of benzoic acid. W. A. ROTH, O. DOEPKE, and H. BANSE (Z. physikal. Chem., 1928, **133**, 431—442).—A redetermination of the heat of combustion of benzoic acid has given the value of 6323 g.-cal.$_{15}$/g.
R. CUTHILL.

Heat of formation of molecular hydrogen. F. R. BICHOWSKY and L. C. COPELAND (J. Amer. Chem. Soc., 1928, **50**, 1315—1322).—Direct determinations give 105,000$\pm$3500 g.-cal. at constant pressure. S. K. TWEEDY.

Valve oscillator for use in conductivity measurements. J. W. WOOLCOCK and D. M. MURRAY-RUST (Phil. Mag., 1928, [vii], **5**, 1130—1133).—Describes the construction, from commercial standard components, of a valve oscillator of the type described by Ulich (A., 1925, ii, 671). The apparatus has been employed in the measurement of the conductivities of dilute non-aqueous solutions.
A. E. MITCHELL.

Conductivity measurement by means of an oscillating valve circuit. E. F. BURTON and A. PITT (Phil. Mag., 1928, [vii], **5**, 939—943).—The plate-grid coil and grid-filament coils of a valve-oscillating circuit are arranged round a tube which is to contain the specimens to be examined. The oscillations in the circuit are rectified in a second valve circuit and passed through a galvanometer. The steady current through the galvanometer is balanced by means of a contra-current from a potentiometer arrangement. If, with the circuits so arranged, a slightly conducting liquid is placed in the tube, a deflexion of the galvanometer is obtained. For example, a change in conductivity of water from 10·5 to 11·5$\times 10^{-6}$ produced a galvanometer deflexion change of 32·2—33·7. W. E. DOWNEY.

Voltage effect in the conductivity of electrolytes in weaker fields. M. WIEN (Ann. Physik, 1928, [iv], **85**, 795—811).—In an earlier paper (A., 1927, 940) a voltage effect in the form of a deviation from Ohm's law for electrolytic resistances was recorded for moderate and strong fields. An extension of the Debye theory of electrolytic conduction has been made by Joos and Blumentritt (Physikal. Jahrb., 1927, **28**, 836) but it is restricted to weaker fields. A method of measuring the voltage effect with weak fields has now been devised and applied to a series of ferro- and ferri-cyanides and other salts in different concentrations. The voltage effect in weak fields is in accord with the expression $\Delta\lambda_v = AX^2(1-BX^2)$, A and B being constants and X the applied field in volt/cm. A is approximately proportional to the square of the product of the valencies (z) of the ions, and approximately proportional to the root of the conductivity: the expression $A=5{\cdot}5\times z_1^2z_2^2(\kappa_0/\kappa)^{\frac{1}{2}}\times 10^{-13}$, in which κ_0 is the conductivity 0·001, is empirically valid. A also depends to some extent on the nature of the ions. The B term likewise increases as the product of the valencies increases, but the rate of increase of A is much greater than that of B. As the concentration decreases B increases; on an average B is three times as great with a concentration corresponding with conductivity $\kappa=0{\cdot}000125$ as $\kappa=0{\cdot}001$.

Experiments with solutions of cobalt chloride and of potassium iodide in acetone show results of the same general type, but A is greater and B smaller than in aqueous solutions under the same conditions.
R. A. MORTON.

Behaviour of dilute electrolytes in high field strengths. M. BLUMENTRITT (Ann. Physik, 1928, [iv], **85**, 812—830).—A satisfactory theoretical basis for the experimental results of Wien (cf. preceding abstract) has been evolved in terms of the Debye-Hückel theory. The equation $\Delta\lambda=AX^2(1-BX^2)$ requires A to be approximately given by $[1/(D\eta)^{\frac{1}{2}}]g(z)$, in which η is the equivalent concentration per litre, and $q(z)=z^{3{\cdot}5}$ for binary electrolytes with ions having

equal viscosity constants. It is shown that the initial effect $\Delta\lambda = AX^2$ depends on concentration, dielectric constant, and the valencies of the ions, in exactly the manner found in Wien's experiments. The second term BX^2 requires B to vary as $D/\eta \, . f(z)$, $f(z)$ being equal to z for binary electrolytes with ions showing equal viscosity constants. B varies as found by Wien. Such discrepancies as arise occur with 1—3 and 1—4 valencies in the electrolytes, and are probably due to departures from the Debye–Hückel theory. The application of Onsager's modification of the theory should clarify the position but the calculations are likely to prove more complicated.

R. A. MORTON.

Contact potentials. I. Calculation of contact potential from kinetics of diffusion. E. DENINA (Gazzetta, 1928, 58, 160—177).—The theory of electrode–electrolyte potentials is developed from the kinetics of diffusion, and it is shown that the Nernst expression $E = (RT \log P/p)/nF$ can be regarded as a special case of a more general equation. The potential at the interface of two non-miscible solutions and the Soret effect are discussed in relation to the new theory.

R. W. LUNT.

Anomalies of the *E.M.F.* relationships of palladium in hydrogen chloride solutions. F. MULLER (Z. Elektrochem., 1928, 34, 237—240).—The anomalous behaviour of palladium when used as an indicator electrode in oxidation–reduction reactions is connected with the presence of hydrogen chloride in the solutions. The difference in the behaviour of this metal compared with that of the others of the same group is ascribed to the existence of a sparingly soluble film of unknown nature on the surface of the electrode.

H. F. GILLBE.

Determination of the ζ-potential on cellulose. Method. D. R. BRIGGS (J. Physical Chem., 1928, 32, 641—675).—A method for the determination of the ζ-potential on cellulose materials by means of measurements of the streaming potential is described. Preliminary experiments showed that substitution of κ_s, the specific conductance of the liquid in the diaphragm, for κ_D, that of the liquid in bulk, gives values of the ratio $H\kappa_s/P$, where H is the streaming potential under a hydrostatic pressure P, which are more nearly independent of the tightness of packing of the cellulose material. κ_s can now be accurately measured by the method described and absolute values of ζ can be obtained from the streaming potential equation $\zeta = 4\pi\eta\kappa_s H/P\epsilon$. ζ varies with the source and history of the cellulose used; approximate values for two samples of a rag pulp and for a wood pulp are 0·214, 0·016, and 0·0083 volt, respectively. The effect of ions on the ζ-potential of cellulose is studied. The literature and development of the streaming potential equation are reviewed.

L. S. THEOBALD.

Overvoltage. IV. Measurement of minimum overvoltage from the current–voltage curve. V. Relationship between minimum overvoltage and current density. T. ONODA (Z. anorg. Chem., 1928, 172, 87—108, 109—120).—IV. The hydrogen overvoltage at gold, platinum, copper, nickel, and mercury electrodes has been determined from the current–voltage curves. This method shows the influence on the overvoltage of the mode of storage of the electrodes, and also the attainment of a minimum value after anodic polarisation. The minimum values in volts obtained at 30° in $2N$-sulphuric acid solution are: platinum 0·0061, gold 0·0084, nickel 0·084, copper 0·091, and mercury 0·855, in good agreement with the earlier measurements (cf. A., 1926, 941).

V. The anodic polarisation of a gold electrode at a current density greater than 0·3 coulomb/cm.² results in a certain minimum overvoltage, expressed by the equation $\pi_m = \pi_0 I^b$, where π_m is the minimum overvoltage, b is a constant dependent only on the metal employed, and π_0 is the minimum overvoltage when the current density I is 1 milliamp./cm.² The overvoltage is not influenced by a film of oxide on the electrode nor by adsorbed oxygen, but is concerned solely with the gold electrode.

H. F. GILLBE.

Electrochemical behaviour of silicate glasses. III. Cathode and anode gases. IV. Solid electrolytic deposits. M. J. MULLIGAN, J. B. FERGUSON, and J. W. REBBECK (J. Physical Chem., 1928, 32, 779—784, 843—851; cf. A., 1926, 31; this vol., 245).—III. Additional evidence of the formation and disappearance of cathode gas during the electrolysis of various glasses and of the permeability of glass to various ions is advanced. The disappearance of gas on current reversal may be due to the sodium from the hydroxide film entering the glass, and the re-formation of water which is adsorbed; in support of this, it is found that hydrogen disappears only in the presence of sodium hydroxide. Cathode gas has now been obtained with Schott glasses and with Cavalier glass. Replacement of the sodium in the soda–lime glass by silver in one case prevented the formation of cathode gas, but other experiments indicated that silver does not always uniformly replace the sodium. The movement of water into or out of glass under the influence of an electric current is also indicated. Anode gas is formed with soda–lime glass at 275° and possibly at lower temperatures. This is accompanied by the formation of a deposit insoluble in water but soluble in nitric acid; traces of such deposits are formed at 100°. The results are in general agreement with those of Le Blanc and Kerschbaum (A., 1910, ii, 481) except for the lower temperatures now observed, a difference which may be ascribed to differences in the composition of the glasses used.

IV. Solid deposits are formed near the surface when the glasses are electrolysed with mercury first as anode and then as cathode. The deposit consists mainly of silicon, probably produced by the action of sodium on the silicates. Silver has also been deposited. The formation of these deposits appears to result from a puncturing of the anodic glass layers, and the dielectric strength of these layers depends partly on the nature of the ions which reach them.

L. S. THEOBALD.

Theory of passivity. II. Relation between passivation current density and time. W. J. MÜLLER and O. LÖWY (Monatsh., 1928, 49, 47—74).—On the basis of the theory of passivity previously enunciated (Müller and Konopicky, this vol., 247) it

is shown that the smaller the current density employed the thicker is the protective film, and a formula for the relationship between the passivation time (t_p) and the current density (i_0/F_0) is deduced. This formula $t_p=B(i_0/F_0)^{-m}$, where B is a constant and m is an exponential obtained from the experimental data, represents a straight line, $\log t_p=\log B-m \log (i_0/F_0)$ when the logarithms of time and current density are employed. The values of i_0 calculated from this equation are found to be in good agreement with the observed values in the results previously obtained for iron, nickel, zinc, and chromium, and also with fresh data for iron in various electrolytes at 20°, in N-sulphuric acid, and in sulphuric acid containing ferrous and ferric sulphates. The earlier suggestion (*loc. cit.*) that the protective film consists of stable hydrated sulphates is confirmed by photomicrographic investigations of the surface of the iron electrodes on which, when passivity has been produced, a crystalline layer of ferrous sulphate heptahydrate can be detected. The behaviour of protected, unprotected, and rotating electrodes has been studied and the results are those which would be expected from the theory. In electrolytes saturated with ferrous sulphate the minimum current density at which passivity can be produced has a higher value in the case of the unprotected electrode than in the case of the protected electrode, and a still higher value when a rotating electrode is used. With relatively high current densities (above 0·31 amp./cm.^{2}) the passivation time is approximately the same with both the protected and the unprotected electrodes, but at lower current densities the time is very much longer in the latter case. With a rotating electrode the time increases rapidly with decrease in current density at values of the latter below 0·54 amp./cm.^{2} At the same current densities the same passivation time is observed both with polished electrodes and with electrodes which have been covered with an oxide film by immersion in potassium chromate solution (Evans, A., 1927, 619). The oxide film is completely dissolved in the acid solutions used and hence any theory of passivity based on the protective oxide film is excluded.

J. W. BAKER.

Effect of superposed alternating current on the deposition of zinc–nickel alloys. H. C. COCKS (Trans. Faraday Soc., 1928, **24**, 348—358).—The variations in the average deposition potential and in the composition of the zinc–nickel alloys deposited cathodically from 0·1N-acid sulphate solutions with variations in *D.C.* density and in the ratio *A.C* : *D.C.* are recorded. In the apparatus used, although a leak of *A.C.* into the *D.C.* circuit and *vice versa* occurred, the readings of the hot wire and moving-coil ammeters in series with the cathode indicated only the *D.C.* and *A.C.* passing through the electrolytic cell. With rise of *D.C.* density the reaction-resistance to nickel deposition and the hydrogen evolution increase; at the same time, the hydrogen overvoltage rises, and zinc deposition increases until it becomes the main process. As the density of the *D.C.* component of the pulsating current is increased (the ratio *A.C* : *D.C.* being constant), the composition of the deposits above the critical *D.C.* density follows the curve for *D.C.* alone. The phenomena attending the deposition of zinc and nickel together and separately are outlined, and an explanation is given of the effects of superposed *A.C.* based on its known depolarising effect on irreversible electrode processes and on the assumed net result of the periodic increases in current density above that of the *D.C.* component (cf. Allmand and Cocks, A., 1926, 912).

J. GRANT.

Theory of electrolytic deposition of chromium from chromic acid solutions. Y. KATO and T. MURAKAMI (J. Soc. Chem. Ind. Japan, 1928, **31**, 124—128).—The current efficiency for the electrolytic deposition of chromium is very low, being less than 30% in most cases, but it increases with increasing current density. The authors assume that hydrogen overvoltage is due to accumulation of monatomic hydrogen and apply Nernst's formula to the calculation of the concentration of the monatomic hydrogen. On this assumption, the values of the concentration of the monatomic hydrogen at different densities are calculated from the overvoltage. When these concentrations and the amount of chromium deposited are plotted against the current density the resulting curves are found to be nearly parallel, and from this it is inferred that the electrolytic deposition of chromium from chromic acid solution does not result directly by the loss of electrons from CrO_4'' or Cr_2O_7'', but indirectly by the reducing action of the monatomic hydrogen on the film (consisting of chromium oxides) which is formed on the cathode. Superposition of alternating current on direct current makes the current efficiency very low, and this fact favours the above theory. The lowering of the current efficiency with rising temperature is also in accord with the theory.

K. KASHIMA.

Theory of electrodialysis. R. BRADFIELD (Naturwiss., 1928, **16**, 404—408).—Electrodialysis has the advantage of removing electrolytes from colloidal solutions more quickly than ordinary dialysis. The colloidal solution is placed between two membranes outside of which are electrodes dipping into running water. With the application of an electric field, the anions pass through the anode membrane and appear as acid, whilst the cations appear in the cathode chamber as hydroxide. With most membranes, the ions diffuse unequally and excess of one kind may seriously modify the properties of the colloid in the middle chamber. The defects of electrodialysis are minimised by using very small currents, but in so doing the advantage of rapidity is lost. If suitable negative cathode membranes and positive anode membranes could be obtained it would be possible to conserve both speed and neutrality. A stable positive membrane can be made by treating a collodion film with a 2% solution of hæmoglobin. Experiments with a parchment membrane on the cathode side and collodion, parchment, or hæmoglobin membranes on the anode side indicate that the latter is much the best, since after electrodialysis the solutions in the middle chamber show the smallest departures from neutrality with the new membrane. The efficiency of the electrodialysis (E=[acid+base]/coulombs) is, moreover, higher for the hæmoglobin membrane than for the other membranes; *e.g.*, for sodium chloride it is 0·71 as against 0·41 and 0·46. For the salts of weak

acids E is considerably greater than unity, in apparent contradiction with Faraday's law. An explanation of this phenomenon is given. R. A. MORTON.

Region of existence of unimolecular reactions. L. S. KASSEL (J. Amer. Chem. Soc., 1928, **50**, 1344—1352).—Previously recorded experimental data confirm the theoretical prediction (cf. this vol., 372) that unimolecular reaction rates decrease at low pressures. The typical decomposition of a polyatomic molecule will be bimolecular at high pressures (due to collision reactions), with a negligible unimolecular part (due to spontaneous decomposition of activated molecules); as the pressure is lowered the latter part gains in importance until it dominates and obscures the bimolecular part. At still lower pressures the unimolecular reaction rate decreases until it merges into a second order rate having a constant higher than that for the high-pressure bimolecular reaction. In the latter stage nearly all the activated molecules decompose, since deactivation collisions become infrequent. The decomposition of acetaldehyde represents a transition from the high-pressure bimolecular to the unimolecular stage, and the decomposition of azomethane, a transition from the unimolecular to the low-pressure bimolecular stage. Possible methods of deciding which of several types of bimolecular reaction dominates a given reaction are outlined. Unimolecular reaction rates vary over a wider range than Dushman's formula allows (A., 1921, ii, 315).
S. K. TWEEDY.

Irregular mode of spherical propagation of flame. T. TERADA and K. YUMOTO (Proc. Imp. Acad. Tokyo, 1928, **4**, 98—101; cf. A., 1926, 1106).—The corrugated surface of the nearly spherical flame front previously observed when mixtures of hydrogen and oxygen were ignited by a spark is attributed to shrinkage of the gas due to condensation of water vapour. The presence of anti-knock materials in the gas reduced the effect. C. J. SMITHELLS.

Effects of anti-detonants in the vapour phase. AUBERT, DUMANOIS, and PIGNOT (Compt. rend., 1928, **186**, 1298—1299; cf. Moureu and Dufraisse, this vol., 180, 251).—The effect of 5% of an anti-detonant in a mixture of air and pure hexane in the wt.-ratio 17·52 : 1 is to increase the duration of combustion. In particular, with lead tetraethyl the maximum pressure is attained by a series of steps (instead of by an apparently continuous, rapid rise) which are supposed to represent successive stages of increasing complexity in the oxidation of the hydrocarbon, the complete evolution of which is ensured by the presence of the anti-detonant. J. GRANT.

Limits of inflammability of gases and vapours. H. F. COWARD and G. W. JONES.—See B., 1928, 392.

Explosions in closed vessels. Correlation of pressure development with flame movement. O. C. DE C. ELLIS and R. V. WHEELER.—See B., 1928, 392.

Flammability of mixtures of methyl and ethyl chlorides and bromides [with air]. G. W. JONES.—See B., 1928, 428.

Neutral salt action in ionic reactions. Temperature coefficients of neutral salt action. A. VON KISS and (FRL.) I. BOSSANYI (Rec. trav. chim., 1928, **47**, 619—626; cf. A., 1927, 632, 945).—The reaction taking place between persulphate and iodine ions has been studied at seven temperatures from 0° to 75°. The temperature coefficient is unaffected by the presence of neutral salts, *e.g.*, magnesium sulphate or potassium nitrate. The temperature coefficient has the normal value which falls with rise of temperature. H. INGLESON.

Velocity of decolorisation of potassium permanganate by oxalic acid and the influence of other substances in the solution. M. BOBTELSKY and D. KAPLAN (Z. anorg. Chem., 1928, **172**, 196—212).—The occurrence and nature of induction are discussed especially in relationship to the electrical condition of the reacting system. The influence of added substances on the velocity of reduction of potassium permanganate solutions by oxalic acid has been investigated. In dilute solution the influence of ions which are unable to undergo oxidation or reduction is very small, whereas in concentrated solution the action is extremely variable, zinc, cadmium, aluminium, and chlorine ions accelerating the reaction very considerably. Other ions exert specific accelerative influences, and the suggestion is made that a method for the determination of such ions could be based on this effect. H. F. GILLBE.

Equilibrium in salt solutions. "Activity theory of reaction velocity." W. F. K. WYNNE-JONES (J.C.S., 1928, 1230—1233).—A criticism of Soper's results (cf. this vol., 24, 26). F. J. WILKINS.

Equilibrium in electrolyte solutions and the reaction-velocity equation. F. G. SOPER (J.C.S., 1928, 1233—1235).—A reply to Wynne-Jones (see preceding abstract). The evaluation of the free energy change of the medium (J. Physical Chem., 1928, **32**, 67) is amended. F. J. WILKINS.

Action of nitrous acid on amino-compounds. I. Methylamine and ammonia. T. W. J. TAYLOR (J.C.S., 1928, 1099—1105).—Nitrous acid solutions stabilised according to a method previously described (A., 1927, 943) were used. They were prepared from barium nitrite and sulphuric acid, without separation of the barium sulphate. The velocity of reaction with methylamine is proportional to the product $[CH_3{\cdot}NH_3^{\cdot}][NO_2'][HNO_2]$. It is suggested, therefore, that the reaction occurs between undissociated molecules of methylamine nitrite and nitrous acid. The reaction is retarded by potassium chloride and strong acids. Ammonia behaves in exactly the same way and the reaction mechanisms are therefore probably identical. F. J. WILKINS.

Kinetics of oxidation of organic compounds by bromine. I. Action of bromine on oxalic acid. E. JÓZEFOWICZ (Rocz. Chem., 1928, **8**, 123—151).—The reaction between bromine and $N/80$—$N/20$ oxalic acid at 20° proceeds according to the equation $dx/dt=k_0(a-x)^2/x^2$. The hydrogen bromide produced has a retarding effect on the velocity; in the presence of excess of hydrogen bromide $dx/dt=k_0(a-x)^2/(c+x)^2$. Strong acids such as hydrochloric or nitric acid also exert an inhibiting influence, which is, however, one fifth of that for hydrogen bromide; the velocity

equation is in this case $dx/dt=k_0(a-x)^2/(0{\cdot}2c+x)^2$, whilst in the presence of bromides a greater retardation takes place, dx/dt being $k_0(a-x)^2/(0{\cdot}6c+x)^2$. Chlorides do not affect the reaction, which is accelerated by raising the p_H. The temperature coefficient of the reaction is 4·52. The reaction of oxidation of acid oxalates proceeds according to the same equation as for oxalic acid, but with a velocity three times as great, whilst neutral oxalates react so rapidly as to render the analysis of the reaction impossible. The above results indicate that hypobromous acid appears transiently in the reaction mixture and oxidises the oxalate anion. R. TRUSZKOWSKI.

Reaction of bromine with aliphatic acids. II. Relative speeds of bromination of acetyl bromide and acetyl chloride. H. B. WATSON (J.C.S., 1928, 1137—1141).—The view that the bromination of aliphatic acids (A., 1925, i, 1232) proceeds mainly through the acid bromide, the speed of bromination of which is proportional to the concentration of the halogen, is supported by experiments on the bromination of acetyl bromide in the absence of atmospheric moisture. Small amounts of ferric chloride or sulphuric acid do not accelerate the reaction, but iodine bromide does so. Bromine reacts with acetyl chloride more slowly than with acetyl bromide. Interaction of the type $R{\cdot}CO_2H+R'{\cdot}COBr \rightarrow R{\cdot}COBr+R'{\cdot}CO_2H$ between acetic acid and bromoacetyl bromide takes place to the extent of 80% in 1 hr. at 25°. A. A. ELDRIDGE.

Saponification of fats in heterogeneous systems. L. LASCARAY (Rev. gén. Colloïd., 1928, 6, 32—44).—The saponification reaction of fats in a heterogeneous system occurs exclusively at the interface of the phases and is explainable, together with its anomalies, by the Harkins–Langmuir theory of the structure of the interface. The rate of saponification depends on the degree of dispersion of the fat and is directly and inversely proportional to the amount of emulsifier in the system and to the proportion of unsaturated glycerides in the fat, respectively. The glyceryl radical, which tends to dissolve in water, is attached to 1, 2, or 3 fatty acid radicals in the fat layer, according as it comes from a mono-, di-, or tri-glyceride, respectively. For comparative studies of the rate of saponification in which a very stable emulsion, unaffected by outside influences, is required, the fat may be mixed well with a concentrated neutral soap solution and the emulsion warmed to 100°. Since the soap acts only as an emulsifier, reaction occurs between fat and water only, and is one of non-catalytic hydrolysis. An alcohol–water mixture exists in which the rate of saponification is minimal owing to the fact that the solubilities of fats and soaps in such mixtures decrease with an increase in the relative amount of water, whilst the emulsifying powers increase. J. GRANT.

Effect of neutral salts on the velocity of saponification of ethyl acetate by sodium hydroxide. I. S. D. WILSON and (MISS) E. M. TERRY (J. Amer. Chem. Soc., 1928, 50, 1250—1254).—The influence of sodium chloride, acetate, or nitrate (0·02—0·5M) on the rate of saponification of 0·008M-ethyl acetate by 0·01M-sodium hydroxide is recorded. The equations given in the preceding paper (this vol., 718) hold in the case of sodium chloride. S. K. TWEEDY.

Decomposition of diacetone alcohol by sodium hydroxide in water mixtures of organic solvents. G. ÅKERLÖF (J. Amer. Chem. Soc., 1928, 50, 1272—1275).—The decomposition velocity of diacetone alcohol with 0·1N-sodium hydroxide solution as catalyst was measured at 25° in mixtures of some alcohols with water. Contrary to Goldschmidt's rules for ester formation (A., 1927, 208), the velocity in pure primary alcohols increases with increasing mol. wt. of the solvent; it decreases as the number of hydroxyl groups increases, and, in the case of isomeric alcohols, is greatest in that alcohol with the most compact alkyl group. In some of the pure alcohols the reaction velocity is largely influenced by traces of water, this influence decreasing with decreasing mol. wt. of the alcohol or with increasing number of hydroxyl groups. S. K. TWEEDY.

Velocity measurements of intramolecular changes in arylacylhalogenoamines. (MISS) C. C. J. FONTEIN (Rec. trav. chim., 1928, 47, 635—667).—An extension of the work of Blanksma (A., 1903, ii, 137) on the conversion of phenylacetylchloroamine into *p*-chloroacetanilide. In carrying out the velocity determinations use is made of the fact that the unchanged chloroamine reacts with potassium iodide (in the presence of hydrochloric acid), liberating iodine. The effect of changes in the acyl, halogen, and aryl groups on the reaction velocity has been studied. The following groups increased the reaction velocity in the order benzoyl>acetyl>formyl>butyryl>propionyl. The bromine atom in phenylacetylbromoamine migrates very much more readily than does the chlorine atom in the corresponding chloroamine. The introduction of the groups methyl, chlorine, and bromine into the *m*-position increases the reaction velocity, the effect of the halogens being approximately twice that of the methyl group. All the reactions studied are unimolecular and are catalysed by hydrochloric acid and by sunlight. For equivalent concentrations of the organic solvents used, the reaction velocity is greatest in acetic acid, intermediate in ethyl alcohol, and least in methyl alcohol. The addition of water to the solvent reduces the velocity. H. INGLESON.

Influence of the alcohol group of amino-acid esters on the rate of formation of 2 : 5-diketopiperazines and on the formation of guanidino-compounds by the action of guanidine on the various amino-acid esters. E. ABDERHALDEN and S. SUZUKI (Z. physiol. Chem., 1928, 176, 101—108).—The preparation and properties of the *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, *n*-amyl, and benzyl esters of glycine and their hydrochlorides are described. The rate of conversion of these esters and the methyl and ethyl esters of glycine into 2 : 5-diketopiperazines in sealed tubes at 18° and 37° has been measured; the velocity is greatest with the methyl ester and least with the benzyl ester. The same gradation occurs, the methyl ester giving the greatest velocity, when the action of guanidine on the ester hydrochlorides is measured by the amount of ammonia formed. A. WORMALL.

Rate of reactions between two liquid phases. W. FRAENKEL, E. WENGEL, and L. CAHN (Z. anorg. Chem., 1928, **171**, 82—97).—The experiments previously carried out on the rate of dissolution in acids of metals dissolved in mercury (A., 1924, ii, 475) have been repeated and extended to amalgams of beryllium, magnesium, aluminium, cæsium, rubidium, and zinc. It now appears that if the acid concentration is not too high, the relation between the reaction velocity and the time is the same for all the amalgams. At first, hydrogen is evolved at a constant rate, but when the amount of metal falls below about 0·0005—0·001 g.-equiv./100 g. of mercury the rate becomes proportional to the concentration of the amalgam; this latter stage is not observed if the acid concentration is too high. The velocity coefficient of the second part of the reaction is directly proportional to the area of the surface at which reaction occurs, and decreases with increase in the relative amount of amalgam. The initial velocity, on the other hand, is almost independent of the volume of the amalgam, but is very nearly proportional to the acid concentration, and also increases linearly with increase in the rate of stirring; the rate of evolution of hydrogen may also be considerably influenced by the overvoltage. For the alkali metals, the constant initial velocities are in the order of the normal electrode potentials as derived from measurements with molten salts, whilst with the other metals it is the velocity coefficients of the second part of the reaction period which are in this order. The reaction between an aqueous solution of an acid and a bromoform solution of ethyl diazoacetate follows the unimolecular law at all concentrations, the velocity coefficient being independent of the hydrogen-ion concentration of the acid, but approximately proportional to the rate of stirring.

R. CUTHILL.

Intensive drying. R. H. PURCELL (J.C.S., 1928, 1207—1215).—Intensive drying had no effect on the reduction of silver and mercury oxides by carbon monoxide, the rate of reduction of copper oxide by hydrogen, or the rate of oxidation of mercury, but the temperature required for the reduction of copper and bismuth oxides was raised by carbon monoxide to 425°. Quantitative experiments on the reduction of copper oxide by carbon monoxide showed that the rate of reaction depended on the temperature and concentration of water vapour. When little or no water vapour was present the reduction ceased to be autocatalytic. The influence of a dry third substance on the same reaction has also been studied. Alcohol, benzene, and ether catalysed the reduction somewhat less efficiently than water, whilst sulphur dioxide and bromine were without effect. F. J. WILKINS.

Velocity of formation of anhydrous calcium sulphate from gypsum. P. P. BUDNIKOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 880—889).—The velocity of formation of the insoluble anhydrous salt was determined from conductivity measurements of solutions containing finely-powdered, chemically pure synthetic gypsum that had been heated at 140°, 160°, 200°, or 220° for 2, 5, 17, 24, and 40 hrs. The results show that the amount of the insoluble anhydrous salt formed depends on the temperature and duration of heating. A. RATCLIFFE.

Determination of the degree of tarnishing of a metallic surface by its reflective power. G. ANDO (Mem. Coll. Sci. Kyoto, 1928, A, **11**, 85—93).—The reflective power of a metal surface is determined directly after polishing and also after keeping the polished surface for a given time in an atmosphere containing known amounts of moisture and carbon dioxide. The ratio of the two reflective powers is a measure of the degree of tarnishing. The method has been applied to several alloys. J. S. CARTER.

Corrosion of metals as affected by time and by cyclic stress. D. J. MCADAM, jun. (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 58, 38 pp.).—Various alloys were subjected to corrosion at cyclic stresses from zero to the corrosion-fatigue limits for various times and at various cycle frequencies, and then subjected to fatigue in air.

CHEMICAL ABSTRACTS.

Acid and salt effects in catalysed reactions. XIII. Inert salt effects in the catalytic action of acids. XIV. Influence of inert salts on the catalytic catenary for acetic acid–acetate mixtures. H. M. DAWSON and A. KEY (J.C.S., 1928, 1239—1248, 1248—1257).—XIII. Measurements have been made of the velocity of the iodine–acetone reaction when catalysed by hydrochloric, dichloroacetic, monochloroacetic, and acetic acids in solutions of sodium chloride (0·1—4·0*M*). The reaction velocity is greater than in solutions free from sodium chloride. It is not clear whether this increase in the case of hydrochloric acid solutions is due to the presence of a minute quantity of the highly active undissociated strong acid or to the stimulating action of the sodium chloride on the catalytic activity of the hydrogen ion. Both factors may be operative. The inert salt effects of weaker acids, however, seem to involve some new cause. Assuming that for hydrochloric acid the second factor only is operative, it is shown that the ionisation constant of a weak acid is first increased by the added salt and then diminished at higher salt concentrations. Similar results were obtained with lithium and potassium chlorides. The maximum values for the ionisation constants are greatest for lithium and least for potassium chloride (cf. Harned, A., 1925, ii, 538).

XIV. The influence of catalytically inert salts on the velocity of iodination of acetone when catalysed by weak acids either in the presence or absence of the corresponding salt has been investigated, and the results demonstrate that the catalytic phenomena described in the previous papers of this series are not affected to any great extent by the changes in ionic environment which are associated with the replacement of water as the solvent by solutions of catalytically inert salts. Whilst the replacement of water by 0·1—4·0*M*-sodium chloride solutions has a considerable effect on the catalytic activity of the hydrogen ion and the degree of ionisation of the acetic acid, it scarcely influences the catalytic activity of the acetic acid molecule and acetate ion. The v—p_H curves in all cases approximate to a true catenary. F. J. WILKINS.

Catalytic activity of hydrochloric acid and of potassium and sodium hydroxides in aqueous solution. (Miss) E. M. Terry (J. Amer. Chem. Soc., 1928, 50, 1239—1250).—On certain assumptions it is deduced that for ester hydrolysis catalysed by hydrogen or hydroxyl ions, $K_{obs.}(\gamma_{KOH}/\gamma_{HCl})=K'd$, where K' is the coefficient of the reaction when the catalytic influence is proportional to the molality of the catalyst, and $d=\gamma_{H'}/(\gamma_{HCl}/\gamma_{KOH})=\gamma_{OH'}/(\gamma_{KOH}/\gamma_{HCl})$. Experimental results are quoted demonstrating that $K'd$ is a constant for ester hydrolyses in acid and alkaline solution, and also in the presence of sodium and potassium chlorides, although it is not constant for sucrose inversion, in which some other, undefined, variable appears to play a part. Interpretation of the expressions is discussed. S. K. Tweedy.

Inhibition of esterification by pyridine. K. C. Bailey (J.C.S., 1928, 1204—1206).—Experiments on the inhibition of the reaction between acetic acid and ethyl alcohol by pyridine indicate that esterification occurs partly on the walls of the containing vessel and partly in the liquid phase. F. J. Wilkins.

Autoxidation and antioxygenic action. XXVII. Action of different catalysts on the autoxidation of furylethylene. C. Moureu, C. Dufraisse, and J. R. Johnson (Bull. Soc. chim., 1928, [iv], 43, 586—590; cf. A., 1922, i, 250; 1923, i, 91; 1925, i, 362, 363; 1927, 465).—The resinification of furylethylene, required for conversion into furylacetylene, is largely prevented by the use of an antioxygenic agent. The capacity of furylethylene for absorbing oxygen is greater than that of styrene, acraldehyde, or benzaldehyde. The course of the oxidation of furylethylene in the presence of phloroglucinol, resorcinol, quinol, α-naphthol, pyrogallol, thiophenol, iodoform, and potassium xanthate as catalysts was studied. Of the phenols, quinol showed the most intense antioxygenic action, the addition of 1 in 10^3 remarkably retarding the rapidity of oxidation. R. A. Pratt.

Oxidation catalytic action of iron. H. Handovsky (Z. physiol. Chem., 1928. 176, 79—88).—The following iron compounds do not effect the oxidation of leucine when the iron compound and a 0·5—1% solution of leucine are shaken with air or oxygen: ferrous sulphate, magnetic iron oxide, colloidal ferric hydroxide sols, and a mixture of metallic iron and iron oxide prepared by heating iron oxalate. Metallic iron, however, prepared by heating iron oxide in a stream of hydrogen effects the oxidation of leucine with the production of carbon dioxide, ammonia, and *iso*valeraldehyde (isolated as the *p*-nitrophenylhydrazone). Glycine, alanine, valine, tyrosine, histidine, formyl-leucine, and glycyl-leucine are similarly oxidised by the reduced iron, yielding substances which give a positive fuchsine–sulphurous acid reaction. The oxygen uptake with leucine is never more than 19% of that required for complete combustion and the oxidation is inhibited by hydrocyanic acid. When the heated reduced iron is cooled in nitrogen a black iron powder is obtained which has no oxidising action on leucine, but if the inactive iron is reheated for some time and subsequently cooled in hydrogen the oxidising power is regenerated. The conclusion is reached that it is not the iron but the hydrogen dissolved in it which effects the oxidation of amino-acids and that the "active" hydrogen reacts with oxygen to give hydrogen peroxide which is catalytically decomposed on the surface of the iron. Similarly, animal charcoal loses its power to catalyse the oxidation of leucine when heated and cooled in nitrogen but regains this power when reheated and cooled in hydrogen. A. Wormall.

Theory of centres of activity in heterogeneous catalysis. F. H. Constable (Proc. Camb. Phil. Soc., 1928, 24, 291—306).—Previous work bearing on the theory of catalytic action is reviewed, and it is concluded that the experimental facts dealing with adsorption and catalysis can be explained quantitatively on the assumption of strong specific fields of force that emanate from special configurations of atoms on the catalyst surface. C. J. Smithells.

Method of generalising the law of mass action for heterogeneous surface reactions. F. H. Constable (Proc. Camb. Phil. Soc., 1928, 24, 307—314).—Assuming the theory of centres of activity (see preceding abstract) the absorption of the reactants on the centres of activity is introduced as a further condition in homogeneous systems. The surface is treated as if it were homogeneous, reaction taking place as if those centres on which the heat of activation is smallest were alone responsible for chemical change. The general equation is worked out in terms of the rate of bombardment and the mean lives of the molecules on the surface. The general solution is impracticable, so the special cases of irreversible synthesis and decomposition are considered and results are obtained. C. J. Smithells.

Theory of wall reactions. M. Pólanyi (Chem. Rund. Mitteleuropa Balkan, 1927, 4, 160—161; Chem. Zentr., 1928, i, 285).—For the specific case of the catalytic acceleration of the formation of diatomic from monatomic hydrogen at glass walls Frenkel's relation $q=15T$ g.-cal., where q is the adsorption potential, is applied. The average value of q for moist glass is 1500—4000 g.-cal., for dry glass and quartz >4500 g.-cal., and for metal 40,000 g.-cal. A. A. Eldridge.

Catalysis under reduced pressure. V. Grignard (Bull. Soc. chim., 1928, [iv], 43, 473—491).—A lecture.

Syntheses under high pressure. Interaction of carbon monoxide and hydrogen. G. T. Morgan, R. Taylor, and T. J. Hedley.—See B., 1928, 439.

Synthesis of alcohols higher than methyl alcohol from carbon monoxide and hydrogen. P. K. Frolich and W. K. Lewis.—See B., 1928, 397.

Reaction between atmospheric oxygen and strongly acid iodide solutions in presence and absence of arsenic acid. F. L. Hahn (Z. anal. Chem., 1928, 73, 412—413; cf. Ditz, this vol., 263; Bottger, *ibid.*).—The so-called "oxygen effect" is catalysed by minute quantities of metal salts, especially by those of iron. The catalytic effect of iron is repressed in presence of phosphates, arsenites, and arsenates and hence the "oxygen error" is negligible

in the iodometric determination of arsenic. The replacement of starch by benzene as an indicator is recommended in iodometric determinations involving the presence of acid. J. S. CARTER.

Synthesis of water over nickel and copper catalysts. Mixture effect and promoter action. F. E. SMITH (J. Physical Chem., 1928, **32**, 719—733; cf. Larson and Smith, A., 1925, ii, 563).—The catalytic effect in the synthesis of water between 75° and 180°, with an oxygen concentration of 2·4%, of the following catalysts, prepared by reduction of the precipitated hydroxides, has been investigated: copper, nickel, copper–nickel mixtures, a mixture of copper and alumina. A sample of copper prepared by reduction of the fused oxide was also used. The results are represented graphically and show that, in the final steady-state synthesis, the most efficient catalysts are those which form the greatest amounts of oxide during catalysis and undergo the least change in physical structure, especially shrinkage, on reduction and later heat treatment. Precipitated copper which shrinks most during its preparation is the worst catalyst. The order of decreasing catalytic efficiency is copper–alumina (19 : 1), copper from the fused oxide, nickel, nickel–copper (1 : 3), copper–nickel (1 : 7·5), and copper from the precipitated hydroxide. No mixture effect occurs in the copper–nickel series as regards catalytic efficiency, but such an effect becomes evident when the amounts of oxide formed are compared. Heating to 444° is accompanied by marked shrinkage of the catalysts, a decrease in oxide-forming capacity, and, except in the case of nickel, a corresponding decrease in catalytic efficiency. These effects were slight with the copper–alumina catalyst and large with the precipitated copper. The behaviour of the nickel may be explained by the changes in physical properties accompanying the transition temperature at 360°. The results show that the physical nature of the catalyst surface, as well as its chemical properties, is of prime importance in determining catalytic activity, and they agree with Taylor's theory of a catalytic surface (A., 1926, 365). The probable mechanism appears to consist of the interaction of hydrogen molecules and activated oxygen molecules or atoms, in the form of an oxide, at points of greatest activity on the surface of the catalyst. Contrary to the theory of Benton and Emmett (A., 1926, 482), the stable oxide formed plays little part in the synthesis. It is formed by an unavoidable side reaction which ultimately results in a partial poisoning of the catalyst.

L. S. THEOBALD.

Preparation of hydrogen bromide in the presence of charcoal. V. N. BOSHOVSKI and P. DANILITSCHENKO (J. Russ. Phys. Chem. Soc., 1927, **59**, 851—858).—Hydrogen bromide is easily obtained from bromine in presence of charcoal. Experiments were first carried out at the ordinary temperature in an aqueous solution. The reaction takes place according to the equation $Br_2+H_2O \rightleftharpoons H^{\cdot}+Br'+HBrO$. In absence of light the equilibrium is reached very slowly. The presence of activated charcoal increases the rate of the reaction. When water vapour and bromine were passed through a quartz tube containing activated and brominated charcoal at 500° all the bromine was converted into hydrogen bromide and the reaction is represented by the equation $Br_2+H_2O \longrightarrow 2HBr+O$. Oxygen combines with carbon, forming carbon monoxide or carbon dioxide, and the heat of combustion gives the 33,610 g.-cal. necessary for the above reaction.

A. RATCLIFFE.

Precipitation of vanadic acid on asbestos fibre. N. N. EFREMOV and A. ROSENBERG (J. Russ. Phys. Chem. Soc., 1927, **59**, 701—714).—The catalytic action of vanadated asbestos depends on the ease with which the reaction $2V_2O_4+O_2 \leftarrow 2V_2O_5$ takes place. The asbestos fibre is soaked in a dilute sulphuric acid solution of vanadyl sulphate, $V_2O_2(SO_4)_2$, which is obtained by the reduction of a boiling solution of ammonium vanadate with ammonium hydrogen sulphite. At 40—50° the solution is made alkaline with a concentrated solution of ammonia, an excess of which must be avoided. The solution is evaporated nearly to dryness and the fibre is then spread on asbestos sheets and dried. The precipitate formed on the asbestos after drying consists chiefly of the compounds $(NH_4)_2VO_3$ and V_2O_4,H_2O. The process is repeated if necessary. To convert the quadrivalent vanadium into the quinquevalent form the asbestos is heated at 500—600°. A. RATCLIFFE.

Hydrogen electrode. S. SEKINE (Z. Elektrochem., 1928, **34**, 250—253).—The hydrogen electrode in conjunction with a lead dioxide electrode has been investigated, using *N*-sulphuric acid as electrolyte. On closing the circuit through a variable rheostat and milliameter, Ohm's law is valid if palladium be employed in the hydrogen electrode. With platinum, however, on decreasing the resistance the current at first increases and then decreases sharply. Quantitative measurements of this effect have been made, together with the influence of the time factor. It is suggested that the current decrease is due to the formation, at high current density, of an adsorbed film of oxygen on the platinum electrode, the escape of hydrogen being thereby inhibited. H. F. GILLBE.

Electro-deposition of thallium. O. W. BROWN and A. MCGLYNN.—See B., 1928, 451.

Influence of the cathode on the electro-deposition of chromium. H. S. LUKENS.—See B., 1928, 414.

Behaviour of plating baths and anodes during electro-deposition of chromium. R. SCHNEIDEWIND and S. F. URBAN.—See B., 1928, 450.

Effect of tervalent chromium and iron on chromic acid chromium plating baths. R. SCHNEIDEWIND, S. F. URBAN, and R. C. ADAMS, jun.—See B., 1928, 450.

Electrochemical oxidation of solutions of cerous salts. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 61—67).—Both cerous sulphate and cerous nitrate may be completely oxidised by electrolysis of the acid solution with an anode of sheet platinum, the cathode being immersed in a 20% solution of sulphuric acid or nitric acid, as the case may be, contained in a porous pot. The current yield for the nitrate is about four times as great as it is for the

sulphate, and for either salt decreases with increase in the current density at the anode. Dilute acid solutions of ceric nitrate or ceric sulphate may be kept for 30 days without undergoing any change.

R. CUTHILL.

Decomposition of carbon monoxide in the corona due to alternating electric fields. E. OTT (J.C.S., 1928, 1378).—A reference to previous work (A., 1925, ii, 579; cf. Lunt and Venkateswaran, A., 1927, 531). F. J. WILKINS.

Electrocatalytic reduction of carbon monoxide. G. FESTER and M. SCHIVAZAPPA (Z. anorg. Chem., 1928, **171**, 163—167).—By cathodic reduction of carbon monoxide, using as electrode copper gauze coated with powdered nickel, and a sulphuric acid solution of vanadic acid as electrolyte, small amounts of formaldehyde may be obtained. R. CUTHILL.

Periodic electrolytic oxidation of formic acid. E. MULLER and S. TANAKA (Z. Elektrochem., 1928, **34**, 256—264).—The electrolytic oxidation of formic acid takes place in two stages, an intermediate compound being formed on, and remaining attached to, the anode. The velocity of the second stage is dependent on the rate at which this compound breaks up into adsorbed hydrogen and carbon dioxide. The periodic phenomena are probably due to the existence of a metastable limiting concentration of the intermediate substance. H. F. GILLBE.

Photochemical ozonisation and its relation to the polymerisation of oxygen. O. R. WULF (Proc. Nat. Acad. Sci., 1928, **14**, 356—358).—The fact that in gaseous oxygen at high pressure ozone is formed at wave-lengths 2090 and 2530 Å., whilst the molecule O_2 does not absorb in this region, can be explained by assuming that there exists in oxygen a molecular form of the element other than the molecule O_2. Evidence is put forward to show that this is the polymeride O_4. The new absorption cannot be due to the influence of molecular impacts on the absorption of the molecule O_2, as has been supposed, for reasons concerning the position of the absorption, its behaviour on alteration of temperature and pressure, and the characteristics of the ultra-violet absorption of oxygen. A. J. MEE.

"After-effect" in certain photochemical reactions. II. B. K. MUKERJI and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 203—208; cf. A., 1926, 366).—A continuation of previous work. If the following photochemical reactions are allowed to proceed, first in the light and then in the dark, the velocity coefficient is larger, for a short time after the removal of the light, than when there has been no exposure to light: oxidation of ferrous sulphate, oxalic acid, sodium nitrite, sodium malate, and sodium lactate, respectively, by iodine; the bleaching of dicyanin; the decomposition of Fehling's solution in presence of ferric chloride; the decomposition of potassium manganioxalate, and the reduction of copper sulphate by ammonium oxalate in the presence of ferric chloride. The last reaction does not take place at all in the dark unless the reactants have been previously exposed to light. The phenomenon of "after-effect" may be explained by supposing that the life-period of the activated molecules is considerably prolonged by the action of light, and these molecules revert only slowly to the inactive state in the dark. M. S. BURR.

Photolysis of benzaldehyde. M. DE HEMPTINNE (Compt. rend., 1928, **186**, 1295—1297).—The suggestion of Henri and Wurmser (A., 1927, 946) that the photolysis of benzaldehyde into benzene and carbon monoxide is due to the total absorption portion of the spectrum of its vapour, whilst the other portions are responsible only for molecular excitation, is confirmed by the fact that only rays of wave-lengths less than 2600 Å. produce photolysis at the ordinary temperature. At 0·2 mm. and 208°, the absorption spectrum of the vapour is greatly modified, the fine bands between 2966 and 2610 Å. becoming continuous, whilst rays of wave-lengths greater than 2700 Å. will produce photolysis. In the absence of illumination, benzaldehyde vapour is decomposed into benzene only above 400°. These phenomena have passed unnoticed when benzaldehyde has been used in solution. J. GRANT.

Mechanism of formation of the latent photographic image. F. C. TOY (Nature, 1928, **121**, 865).—For very thin layers of silver bromide the three curves representing, respectively, the relative photoconductivity effects, the relative photographic effects, and the relative light absorptions, each plotted against the wave-length for equal incident intensity, are closely similar; hence the primary stage of the photographic mechanism is probably intimately connected with that producing conductivity changes on illumination.

A. A. ELDRIDGE.

Additivity of photographic densities. G. TICHOV (Bull. Acad. Sci. Leningrad, 1927, 511—532; Chem. Zentr., 1928, i, 464).—A study of the intensity of blackening of a photographic plate in relation to the additivity of the light sources.

A. A. ELDRIDGE.

Activation of hydrogen by the catalytic action of metals. M. U. POLJAKOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 847—849).—See this vol., 459.

A. RATCLIFFE.

Formation of crystalline gold. G. I. COSTEANU (Bul. Soc. Romane Stiin. 1928, **30**, 35—37).—Minute hexagonal plates of metallic gold have been obtained by the slow evaporation of a mixed solution of stannic bromide and auric bromide. R. CUTHILL.

Experiments on transmutation. J. A. N. FRIEND (J.C.S., 1928, 1321—1324).—Specimens of gold, silver, and barium sulphate exposed to radium emanation gave no spectroscopic evidence of transmutation. The coloration of quartz glass by emanation is discussed. F. J. WILKINS.

Bleaching powder. VIII. Decomposition of calcium hypochlorite by carbon dioxide. S. URANO (J. Soc. Chem. Ind. Japan, 1928, **31**, 53—60).—Carbon dioxide decomposes calcium hypochlorite in presence of water: $3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2$; it also decomposes aqueous calcium hypochlorite and chloride: $Ca(OCl)_2+CaCl_2+2CO_2=2CaCO_3+2Cl_2$. Although the formation of chlorate or the evolution of chlorine, respectively, is caused by heat only, carbon

dioxide accelerates these reactions, since the liberated hypochlorous acid exerts an oxidising action. As carbon dioxide expels almost all the chlorine from bleaching powder, Lunge assumed the chemical constitution of bleaching powder to be Ca(OCl)Cl; a mixture of hypochlorite and chloride, however, also loses all its chlorine by the action of carbon dioxide. Even calcium chloride itself is decomposed by carbon dioxide in presence of oxidising agent, *e.g.*, potassium permanganate. The chemical constitution of bleaching powder cannot therefore be deduced from the action of carbon dioxide. K. KASHIMA.

Hydrates of cadmium, zinc, and magnesium nitrates. G. MALQUORI (Gazzetta, 1928, **58**, 209—216).—Results already published (this vol., 480) are given in more detail. Of the nitrates mentioned above, cadmium nitrate is the only one which can be completely dehydrated by nitric acid at the ordinary temperature. The heat of hydration of anhydrous cadmium nitrate is +11·52 kg.-cal. The structure of the hydrated nitrates of bivalent metals is discussed and the views of Lembert (A., 1923, ii, 313) are supported. O. J. WALKER.

Formation and properties of mercuric ammonium chloride. F. G. GERMUTH (Amer. J. Pharm., 1928, **100**, 285—293).—In the determination of magnesium the addition of ammonium chloride to a solution of magnesium chloride in which freshly-precipitated mercuric oxide is suspended greatly accelerates the rate of formation of magnesium oxide. When a mixture of magnesium chloride and mercuric oxide with an excess of ammonium chloride is gently heated in a vacuum the sublimate formed contains mercuric ammonium chloride, $HgCl_2,2NH_4Cl,2H_2O$, m. p. 210—212°, subl. 220—223°/755 mm. The compound, which appears to crystallise in the same system as the hydrate $CuCl_2,2NH_4Cl,2H_2O$, is also produced from an aqueous mixture of the two chlorides. It seems probable that the accelerating effect of the ammonium chloride in the determination of magnesium is due to the formation of the salt. H. INGLESON.

Samarium subhalides. W. PRANDTL and H. KOGL (Z. anorg. Chem., 1928, **172**, 265—272).—The so-called samarium subchloride has been prepared in a pure state, and free from oxychloride, as follows: the hexahydrated trichloride is precipitated by passing hydrogen chloride into a solution of the samarium oxide in hydrochloric acid solution, dehydrating this substance by melting in a current of dry oxygen-free hydrogen chloride, and reducing by pure hydrogen. The product is of a deep brownish-red colour, and is transparent only in thin layers. Samarium subbromide, prepared, although with greater difficulty, in a precisely analogous manner, is opaque and almost black. On heating the sub-salt at about 1000° in an atmosphere of hydrogen in a gold vessel, the corresponding trihalide volatilises and the surface becomes coated with a gold–samarium alloy. The subhalides thus behave as molecular compounds or solid solutions of samarium and samarium trihalide.

H. F. GILLBE.

Substances analogous to graphite. II. R. CIUSA (Gazzetta, 1928, **58**, 222—223; cf. A., 1925, i, 1083).—A graphite, $(C_6)_n$, has been obtained from hexaiodobenzene by heating it first in a closed tube and then in an open tube in a current of nitrogen. The graphite obtained at 770° has a resistivity of 0·11 and *d* 2·25. These values are very nearly equal to those obtained for Ceylon graphite.

O. J. WALKER.

Influence of the "conversion" yield and the temperature of condensation on the purity of the product and on the "condensation yield" in the synthesis of carbonyl chloride. F. GIORDANI.—See B., 1928, 446.

Influence of iron oxide on the properties of glass. S. ENGLISH, H. W. HOWES, W. E. S. TURNER, and F. WINKS.—See B., 1928, 404.

Liquid silicate immiscibility. J. W. GREIG (Amer. J. Sci., 1928, [v], **15**, 375—402).—Polemical against Tanton (*ibid.*, 66; cf. Greig, B., 1927, 440; this vol., 132). F. J. WILKINS.

Occurrence of titanium tetrachloride in commercial disilicon hexachloride. F. S. KIPPING and R. A. THOMPSON (J.C.S., 1928, 1377).—Evidence of the presence of titanium tetrachloride in commercial disilicon hexachloride was indicated by reactions with hydrogen peroxide and with thymol and sulphuric acid. Addition of ether caused the separation of a yellow compound, probably $TiCl_4,Et_2O$. Complete removal of the tetrachloride was effected only by five or six fractional distillations.

F. J. WILKINS.

Hydrogenation of tin salts at high temperatures and pressures. V. N. IPATIEV and V. I. NIKOLAEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 331—338).—The reduction of aqueous solutions of stannic hydroxide and sulphate and stannic chloride was studied at various temperatures and pressures. Stannic hydroxide is the most readily reduced to the metallic state and the presence of anions such as sulphate and chloride ions has an inhibiting influence.

A. RATCLIFFE.

Oxidation of the mixture of stannous hydroxide and sodium sulphite in sodium carbonate solution with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 95—98).—A mixture of stannous hydroxide and sodium sulphite in sodium carbonate solution is oxidised very slowly by air, since the oxidation of stannous hydroxide inhibits that of sodium sulphite. H. F. GILLBE.

Action of phenylhydrazine on metallic oxides and salts. II. [Preparation of] lead suboxide. E. PUXEDDU (Gazzetta, 1928, **58**, 224—231; cf. A., 1916, i, 292).—Phenylhydrazine reduces lead monoxide and dioxide and triplumbic tetroxide to lead suboxide, which is obtained as a brown or black powder of composition satisfying the formula Pb_2O (which is not the case with preparations from lead oxalate). The reaction temperature is maintained at 80—150°; above this, metallic lead is also formed. For the reduction of lead dioxide the phenylhydrazine is employed in ethereal solution, as otherwise the reaction is violent.

Mercuric or mercurous chloride is reduced by phenylhydrazine to mercury. This is used for the determination of the latter. The test-tube containing the

reagents is warmed at first gently and then at 80°; the mercury is washed with acidified water and with alcohol, and is dried in a potassium hydroxide desiccator containing mercury. E. W. WIGNALL.

Monobasic, polybasic, and polymonobasic acids and their differentiation. E. WEITZ and H. STAMM (Ber., 1928, **61**, [*B*], 1144—1155; cf. A., 1925, ii, 1147).—The solubility of ammonium and alkali salts of polybasic acids is generally diminished by addition of ammonia, frequently in a very marked manner, whereas that of the salts of monobasic acids is either increased or only slightly diminished. The observed effect may be regarded as the algebraic sum of two distinct tendencies, the competition of ammonia and the salt for water and the effort to form ammines. Exceptions are encountered with hydrofluoric and periodic acids, which are known to exhibit marked tendency towards polymerisation, and persulphuric and dithionic acids. The two last-named acids differ structurally from most inorganic polybasic acids in that their molecules contain two distinct monobasic acid groups, and for such compounds the term "polymonobasic" is suggested. The ions may be arranged in order of increasing tendency towards the formation of ammines in the sequence PO_4''', IO_5''', SO_4'', F', S_2O_6'', Cl', NO_3'', Br', ClO_3', S_2O_8'', I', CNS', ClO_4'. The relationships with organic acids are less obvious. The monocarboxylic compounds mainly resemble the monobasic inorganic acids. The polycarboxylic acids of the fatty series, although containing two separated carboxyl groups, behave as polybasic. Phthalic and terephthalic acids are definitely polybasic, whereas *iso*phthalic, trimesic, and benzene-*m*-disulphonic acids are polymonobasic. Hofmeister's lyotropic sequence for the ions is arranged in the opposite order to that given above, so that the tendency of anions towards union with ammonia is the reverse of their tendency towards combination with water. Further regularities are observed with regard to solubility, since the barium compounds of monobasic acids are soluble in water, whereas those of polybasic acids are insoluble or sparingly soluble; this rule is maintained intact only by regarding iodic, hydrofluoric, and periodic acids as polybasic and persulphuric, dithionic, and the polythionic acids as monobasic. The rule holds generally for organic acids; barium *iso*phthalate and *m*-benzenedisulphonate are soluble in water, whereas barium phthalate and terephthalate are sparingly soluble. A less trustworthy criterion is the solubility in aqueous or anhydrous alcohol; the ammonium and alkali salts of monobasic inorganic acids are usually appreciably more soluble than those of polybasic acid. In this instance, the polymonobasic acids behave as monobasic acids. Great caution must be observed in reaching conclusions as to the basicity of acids from the solubility of their ammonium or alkali salts in water alone. The influence of the ions on the coagulation of dialysed ferric chloride solution has been examined. The unique position of the polymonobasic acids and their inclination towards the monobasic acids is clearly displayed in their colloid-chemical action. Whereas, however, a fairly sharp differentiation of inorganic acids into mono- and poly-basic compounds is possible on the basis of the effects of ammonia and solubility of the barium salts, this is not possible on colloid-chemical grounds. An intermediate group appears to exist comprising polymonobasic acids, acids apparently polybasic on account of polymerism, and the majority of organic acids.

The inability of polymonobasic acids to yield hydrogen salts is due to the independence of the two acidic groups and the consequent absence of a marked difference in the first, second, etc. dissociation constants; a step-wise neutralisation appears therefore improbable. H. WREN.

Fluoride of bivalent uranium. A. SIEVERTS (Z. anorg. Chem., 1928, **170**, 191—192).—The statement, which appears in some of the literature, that a fluoride of bivalent uranium was isolated by Giolitti and Agamennone is erroneous, the formula $UF_2,2H_2O$ in the original paper (Atti R. Accad. Lincei, 1904, [v], **14**, i, 165) clearly being a misprint for $UOF_2,2H_2O$. R. CUTHILL.

Univalent manganese. II. W. MANCHOT and H. GALL (Ber., 1928, **61**, [*B*], 1135—1140; cf. A., 1927, 220; Grube and Brause, this vol., 29).—The *salt*, $Na_5Mn(CN)_6$ is obtained as a colourless, microcrystalline powder, very sensitive to oxidising agents when a solution of sodium manganocyanide is reduced by aluminium and sodium hydroxide; the resulting solution is filtered into a solution of sodium hydroxide and sodium cyanide saturated with sodium acetate. The precipitated compound is centrifuged and the residue treated similarly with concentrated sodium hydroxide solution, saturated sodium acetate, and finally with alcohol. If sodium cyanide is omitted in the above preparation, salts similar to the compound $Na_5Mn(CN)_6$ are obtained which contain a much smaller proportion of sodium. The *potassium* salt, $K_5Mn(CN)_6$, may be prepared similarly from potassium manganocyanide, but a preferable method consists in reducing the sodium compound (as above) and adding the filtered solution to a solution of potassium hydroxide and potassium cyanide saturated with potassium chloride. Variations in the procedure afford similar salts containing a smaller proportion of potassium, and the existence of a compound, $K_2Mn(CN)_3$, is highly probable. If, however, potassium cyanide is used in the final washing of the precipitates, the salt $K_5Mn(CN)_6$ is invariably obtained. Grube and Brause's claim of the isolation of a salt, $K_3Mn(CN)_4$, appears arbitrary; repetition of their experiments yields the pentapotassium compound. H. WREN.

Ruthenium chlorides. H. REMY and A. LÜHRS (Ber., 1928, **61**, [*B*], 917—925).—Ruthenium chloride soluble in water (cf. Remy and Wagner, A., 1927, 328) does not differ in composition from the variety insoluble in water. Analyses show that it is free from hydrogen and hence undoubtedly contains tervalent ruthenium. When titrated by the amalgam method (Remy, A., 1921, ii, 209) it requires exactly one equivalent of hydrogen to yield a solution of maximal blue intensity. This amount is also required by the so-called "aquopentachlororuthenate" of Howe (A., 1904, ii, 490), the composition of which, therefore, corresponds with the formula $2K_2RuCl_5,3H_2O$ advanced by Briggs (A.,

1926, 926). The compound obtained by the action of hydrochloric acid on ruthenium tetroxide contains quadrivalent but not tervalent metal as previously assumed, since when titrated to a blue solution it requires two equivalents of hydrogen as maximum. The double salt, $K_4[Ru_2OCl_{10}]$, obtained as a well-defined compound by various other methods, is readily prepared from its solutions; this compound, which likewise contains quadrivalent ruthenium, replaces the previous so-called "brown or α-pentachlororuthenates." The blue solutions obtained by the complete reduction of ruthenium salts by sodium amalgam contain the bivalent metal. The green coloration, formed intermediately during the reduction exclusively of quadrivalent ruthenium salts in solution strongly acidified with hydrochloric acid, is due to compounds of tervalent ruthenium. H. WREN.

Action of concentrated sulphuric acid on metallic rhodium. S. F. SHEMTSCHUSHNI (Ann. inst. platine, 1927, **5**, 361).—With mechanical stirring, rhodium dissolves in hot concentrated sulphuric acid. CHEMICAL ABSTRACTS.

Osmium. III. E. FRITZMANN (Z. anorg. Chem., 1928, **172**, 213—233).—A summary of the work of Tschugaev. H. F. GILLBE.

Spectrum analysis of minerals. F. LOWE (Fortschr. Min. Kryst. Pet., 1927, **12**, 220—227; Chem. Zentr., 1928, i, 825).

Centrifugal separation of solid phases. F. VON WOLFF (Fortschr. Min. Kryst. Pet., 1927, **12**, 93—95; Chem. Zentr., 1928, i, 825).—Purification and quantitative separation of minerals are effected with a centrifuge; the tube contains a short pipette with the heavy liquid in which the powdered mineral is placed. An electrically heated centrifuge for use with fusible salts is described. A. A. ELDRIDGE.

Quantitative analysis of cations without the use of hydrogen sulphide. D. STROHAL (Arh. Hemiju, 1928, **2**, 77—85).—A system for the quantitative analysis of cations which does not involve the use of hydrogen sulphide is described.

R. TRUSZKOWSKI.

Smooth platinum wire for electrometric titrations in neutralisation reactions. S. POPOFF and M. J. McHENRY (Ind. Eng. Chem., 1928, **20**, 534—538).—Using a smooth platinum wire as an air electrode, acidities and basicities can be determined with considerable precision even in presence of oxidising agents, *e.g.*, permanganate. Acidities can be determined with accuracy in presence of phenol, cresols, or varnishes. The method is particularly adapted to the determination of alkaloids and yields results which are more trustworthy than those obtained using the hydrogen or quinhydrone electrodes. The procedure is identical with that customarily followed in making hydrogen electrode measurements, except that the hydrogen stream is replaced by a stream of air free from carbon dioxide. An electrode of tungsten wire may be used, but the change in *E.M.F.* at the end-point is not so pronounced as with platinum.

J. S. CARTER.

Quinhydrone electrode in amyl alcohol solutions. Determination of neutralisation numbers of petroleum products. H. SELTZ and D. S. McKINNEY (Ind. Eng. Chem., 1928, **20**, 542—544).—The neutralisation numbers of petroleum products can be determined potentiometrically with considerable precision, using as solvent amyl alcohol saturated with lithium chloride and containing 0·04% of quinhydrone. The alkali used for titration is a solution of potassium or lithium hydroxide in amyl alcohol. The titration vessel is a wide-mouthed bottle closed by a stopper containing holes for an electrode, the burette jet, nitrogen inlet, and outlet tubes, and the reference electrode. The reference electrode is a test-tube having a small hole near the closed end. The lower portion of the test-tube is occupied by an agar-agar–lithium chloride gel, which functions as a bridge. Above this are the amyl alcohol solvent and an electrode. The electrodes are bright platinum. Using this arrangement, the *E.M.F.* passes through zero during the titration and the leads to the potentiometer must be reversed. This may be avoided by adding benzoic acid to the reference electrode, but this is not recommended. In the determination of neutralisation numbers of mineral oils, 10 g. of oil are dissolved in about 125 c.c. of solvent. A larger amount of oil is not advisable since the conductivity, and hence the sensitivity, of the cell is considerably reduced. J. S. CARTER.

Adjustment of the reaction of indicator solutions and its importance in determining the hydrogen-ion concentration of slightly buffered solutions. W. H. PIERRE and J. F. FUDGE (J. Amer. Chem. Soc., 1928, **50**, 1254—1262).—A critical study of the various methods of preparing and adjusting certain indicator solutions is described. A simple method of adjustment is given, although the quinhydrone electrode is satisfactory for this purpose. Indicator solutions should be adjusted to a p_H value midway between the extreme values for which they are used, and not to neutrality. S. K. TWEEDY.

Ionocolorimeter; its use in the determination of ionic acidity of solutions. CAILLE (Bull. Soc. Chim. biol., 1928, **10**, 590—601).—A modified colorimeter is described in which the light travels through a fixed length of the liquid under examination, containing a known amount of an indicator such as methyl-red or bromothymol-blue which has different colours at different p_H values, by one optical path and through two baths, containing solutions of the indicator at the same concentration and at the p_H values which completely liberate the two differently coloured isomerides, by the other. A device controlling the movement of the two dipping glasses in the latter path ensures that the liquid path in that case is always equal to the length of the liquid under examination. Compensating absorption glasses equalise the intensities of the two components of the light. The calibration curves for most indicators follow the straight-line law.

G. A. C. GOUGH.

Determination of chlorine ions. U. N. SLAVIANOV (J. Russ. Phys. Chem. Soc., **60**, 355—359).—The errors arising in the gravimetric and volumetric determination of chlorine ions are discussed and a method based on that of Volhard, but with elimination of most of the errors, is described. A. RATCLIFFE.

Determination of chlorine, bromine, and iodine in organic compounds. H. TER MEULEN (Rec. trav. chim., 1928, **47**, 698—700; cf. A., 1924, ii, 55).—The method of determination of these halogens by hydrogenation of the organic compound in the presence of gaseous ammonia is satisfactory only when precautions are taken to prevent the loss of the ammonium halide which is produced. In the new procedure the exit gases pass over strongly-heated barium carbonate and thus any halogen present in them is retained as the barium salt. In certain cases the use of a hydrogenating catalyst is necessary. For this purpose a roll of heated nickel foil is recommended. Results obtained by this method agree well with the theoretical. H. INGLESON.

Determination of very small quantities of iodides. J. T. DUNN.—See B., 1928, 402.

Micro-determination of iodine in potable waters. III. Oxidation method. M. SETTIMJ.—See B., 1928, 466.

Rapid determination of gases in metals, especially oxygen in steel. W. HESSENBRUCH and P. OBERHOFFER.—See B., 1928, 409.

Sulphur dioxide and its aqueous solutions. I. Analytical methods, vapour density, and vapour pressure of sulphur dioxide. Vapour pressure and concentrations of the solutions. C. E. MAASS and O. MAASS (J. Amer. Chem. Soc., 1928, **50**, 1352—1368).—If commercially pure sulphur dioxide is passed over phosphorus pentoxide and condensed, and the liquid repeatedly distilled in a vacuum, a very pure gas is obtained. Sulphurous acid may be accurately determined by rendering the solution strongly alkaline and titrating with acidified iodine solution in presence of a little sugar. Iodine solution may be standardised against gaseous sulphur dioxide, weighed directly, by this method. The vapour densities of sulphur dioxide were measured from −6° to 30° and an equation is deduced, involving the apparent mol. wt., which enables the weight of gas removed from a known volume to be calculated from the initial and final pressures. The following vapour pressures are recorded: pure sulphur dioxide (1—27°), aqueous solutions (10—27°), two-phase water–sulphur dioxide system (10—27°). In the latter system the saturated water phase has a constant pressure, which can be read off from the graph, and its composition (solubility of sulphur dioxide) determined by extrapolating the vapour-pressure curve for aqueous solutions. The concentration of water in the sulphur dioxide phase may be calculated by Raoult's law, but a method is given whereby its partial pressure may be measured directly. A method of separating a portion of a liquid phase from a liquid–liquid–gas phase without disturbing the equilibrium is described.

S. K. TWEEDY.

Micro-determination of nitrogen in cellulose nitrate. D. KRÜGER.—See B., 1928, 400.

Electrometric titration of the nitrite ion with potassium permanganate. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 69—71).—Permanganate may be titrated electrometrically at 45° with $0{\cdot}1M$-potassium nitrite, using a platinum electrode, but the titration as a method of determining nitrite is subject to the same errors as Lunge's method.

R. CUTHILL.

Ceric salts as oxidising agents in electrometric titration. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 73—76).—If an acid solution of ceric sulphate is titrated electrometrically with $0{\cdot}1M$-potassium nitrite, using a platinum electrode, there is a point of inflexion on the titration curve corresponding with the reaction of 2 mols. of sulphate with 1 mol. of nitrite. The presence of an alkali metal persulphate interferes. R. CUTHILL.

Modification of Ridsdale's method for determining phosphoric acid. A. S. DODD.—See B., 1928, 445.

Protein reactions of various metaphosphates. D. BALAREV (Z. anal. Chem., 1928, **73**, 411—412).—The relative minimal concentrations of Tammann's tri- and tetra-metaphosphates, and the metaphosphates obtained by heating sodium ammonium hydrogen phosphate and by dissolution of phosphorus pentoxide in water required to cause coagulation of a solution of protein are 1, 0·083, 0·016, and 0·0071, respectively. The protein reaction may be used as a means for the identification of metaphosphates.

J. S. CARTER.

Zinc spot in the Marsh test. H. B. ARBUCKLE and O. J. THIES, jun. (J. Elisha Mitchell Sci. Soc., 1927, **43**, 50—54).—The reaction $Zn+2HCl=ZnCl_2+H_2$ is reversible. Deposition of zinc may take place when hydrochloric but not sulphuric acid is used in the Marsh test. CHEMICAL ABSTRACTS.

Test for borates. A. GABRIEL and H. G. TANNER (J. Amer. Chem. Soc., 1928, **50**, 1385).—The alkaline solution is evaporated nearly to dryness, the residue treated with 1 c.c. of concentrated sulphuric acid and then, after cooling, with 2 c.c. of methyl alcohol. The vapours are blown through a long capillary tube into a Bunsen flame, which is coloured green by methyl borate. S. K. TWEEDY.

Application of Desgrez's apparatus for the determination of total carbon to alkalimetric microanalysis. L. LESCŒUR and T. TUROBINSKI (Bull. Soc. Chim. biol., 1928, **10**, 606—616).—The solution under examination is oxidised under the conditions described by Nicloux (A., 1927, 436) at the ordinary pressure in a stream of air free from carbon dioxide, and the gaseous products, after removal of traces of chlorine by passage over dry potassium ferrocyanide, are absorbed in barium hydroxide. Since the gases contain other acidic substances besides carbon dioxide, the barium carbonate is removed and determined gravimetrically or preferably volumetrically. G. A. C. GOUGH.

Volumetric determination of carbon dioxide. L. LESCŒUR and (MLLE.) S. MANJEAN (Bull. Soc. Chim. biol., 1928, **10**, 523—536).—The gas containing carbon dioxide is circulated through $0{\cdot}02N$-barium hydroxide (containing 5% of barium chloride) and the loss of alkalinity determined by slow titration with $0{\cdot}02N$-hydrochloric acid. Correction is made for the carbon dioxide present in the air in the apparatus.

G. A. C. GOUGH.

Determination of potassium. S. MORGULIS and A. PERLEY (J. Biol. Chem., 1928, **77**, 647—649).—The factor 0·071 given by Kramer and Tisdall (A., 1921, ii, 412) for calculation of the amount of potassium from the result of the final titration is not constant for different reagents and different amounts of potassium; each new reagent should therefore be standardised against known different amounts of potassium. Phosphorus does not interfere with the determination of potassium by this method. C. R. HARINGTON.

Effect of silica dishes in the determination of potassium. L. D. HAIGH (J. Assoc. Off. Agric. Chem., 1928, **11**, 219—220).—In the determination of potassium by the official method, the evaporation and ignition of the potassium residues in silica dishes tend to render part of the potassium insoluble when phosphates are present. T. M. A. TUDHOPE.

Ceric sulphate as a volumetric oxidising agent. I. Determination of calcium. II. Determination of iron. III. Titration of iodide. IV. Determination of arsenic. V. Determination of antimony. VI. Volumetric determination of cerium. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1928, **50**, 1322—1334, 1334—1338, 1368—1371, 1372—1376, 1376—1378, 1379—1385).—I. Ceric sulphate solution, conveniently prepared by dissolving impure cerium dioxide in sulphuric acid (d 1·5), may be standardised against sodium oxalate in presence of hot sulphuric, perchloric, or hydrochloric acid. The end-point may be determined electrometrically or visually (colourless to yellow), although in the latter case the burette reading must be corrected slightly. The reverse titration proceeds quantitatively in hot solutions in presence of sulphuric, perchloric, or nitric acid. Exactly the same conditions hold for the determination of ferrous iron (Someya, this vol., 146). The oxalate titration with ceric sulphate proceeds quantitatively at the ordinary temperature in the presence of a little iodine chloride (catalyst); methylene-blue may then be used as an internal indicator, provided the conditions are suitable for a rapid end-point equilibrium being attained. Calcium may be determined by precipitating it from solution as oxalate and titrating the solution of the latter in hydrochloric acid with ceric sulphate.

II. Iron may be accurately titrated with ceric sulphate after reduction with stannous chloride in hydrochloric acid (followed by addition of mercuric chloride) or with zinc or aluminium in sulphuric acid. Neither arsenious acid nor manganese interferes with the titration. The end-point may be determined electrometrically or by using less than 0·8 c.c. of 1% diphenylamine or diphenylbenzidine solution as internal indicator. The former is preferable in the analysis of iron ores. The oxidation of ferrous iron due to atmospheric oxygen introduces a constant error which may be eliminated either by applying a small correction factor or by standardising the ceric sulphate against iron of known purity (cf. Furman, this vol., 499).

III. Alkali iodide in sulphuric acid solution may be electrometrically titrated by ceric sulphate solution; moderate amounts of bromide may be present. In hydrochloric acid solution, the results are about 0·5% too low owing to loss of iodine. The former titration may be reversed and may then be used for determining cerous cerium after a bismuthate oxidation (Metzger, A., 1909, ii, 620).

IV. Arsenious acid in hydrochloric acid solution may be titrated electrometrically at 80° with ceric sulphate solution. Potassium bromide may be used as a catalyst, less salt being required the higher are the temperature and the acid concentration. The titration may be carried out at the ordinary temperature in presence of iodine chloride; methylene-blue is a suitable indicator. When determining arsenic the ceric sulphate solution should be standardised against arsenious oxide of known purity, or else the normality factor obtained by oxalate titration should be multiplied by 1·003.

V. Antimonious chloride may be titrated electrometrically at the ordinary temperature in presence of iodine chloride. No correction factor is required.

VI. Cerium, in presence of other rare earths, is oxidised with ammonium persulphate in presence of silver nitrate (catalyst) and then titrated with either potassium iodide (a blank correction is necessary), sodium nitrite (the end-point equilibrium is attained slowly), or ferrous sulphate. Sodium nitrite solution may be standardised by oxidation in acid solution with silver bromate, the precipitated silver bromide being collected and weighed, or else by electrometric titration with potassium permanganate solution.

S. K. TWEEDY.

Titrimetric determination of calcium and magnesium carbonates in limestone. J. S. PIERCE, W. C. SETZER, and A. M. PETER.—See B., 1928, 402.

Micro-determination of metallic elements. I. Micro-chemistry of potassium ferrocyanide. [Micro-determination of zinc.] R. NAKASEKO (Mem. Coll. Sci. Kyoto, 1928, **A**, **11**, 95—112).—The minimum quantity of iron detectable with potassium ferrocyanide is 1 in 3×10^6 of solution, the optimum acidity being about $0{\cdot}1N$ (strong acid). When solutions of ferric chloride are added to dilute solutions of ferrocyanides the presence of neutral salts or of acidity retards the development of the blue colour.

A method for the micro-determination of zinc is outlined. The solution, which should be free from iron and manganese, is evaporated and the residue ignited. The residue is treated with 2 c.c. of water, 1 c.c. of $6N$-hydrochloric acid, and 1 c.c. of $5N$-ammonium chloride, and $0{\cdot}02N$-potassium ferrocyanide added dropwise from a burette until the granular precipitate becomes colloidal (formation of $Zn_3K_2[Fe(CN)_6]_2$). The whole is diluted to 10 c.c., inserted in a water-bath at 60—70°, and kept in the dark for 30 min., when it is centrifuged. The excess of ferrocyanide in the supernatant liquor is determined with the aid of a reference table by observing the time required for the development of the blue colour when 0·05 mg. of iron (1 drop of a standard solution) is added to 5 c.c. The amount of zinc in the sample analysed is $(a-500b)\times0{\cdot}47$ mg., where a is the number of c.c. of $0{\cdot}02N$-ferrocyanide added and b the normality of the excess of ferrocyanide.

Acid solutions of potassium ferrocyanide undergo rather rapid decomposition when exposed to daylight and deposit Prussian blue. On long keeping, dilute neutral solutions are slowly hydrolysed with deposition of ferrous cyanide. J. S. CARTER.

Solubility influences and quantitative analysis. I. E. WENDEHORST (Z. angew. Chem., 1928, **41**, 567—568).—The fact that the normally negligible solubilities of certain substances are often not inconsiderable in presence of neutral salts is responsible for a number of errors in gravimetric determinations. Experiments in which known quantities of zinc and cadmium were precipitated by sodium carbonate and ammonium carbonate, respectively, from media containing varying amounts of sodium, potassium, or ammonium salts show that under these conditions the amount of oxide finally weighed may be slightly greater, or considerably less, than the theoretical amount. In presence of considerable amounts of ammonium chloride no zinc was precipitated. J. S. CARTER.

Colorimetric determination of lead. A. D. PETROV (J. Russ. Phys. Chem. Soc., **60**, 1928, 311—316).—The reaction whereby lead peroxide gives with *p*-tetramethyldiaminodiphenylmethane in presence of acetic acid an intense blue colour has been applied to the detection and determination of lead. The analysis is easily carried out and gives sufficiently accurate results. Iron and other impurities reduce the accuracy of the method. A. RATCLIFFE.

Deposition of metals on copper from cyanide solutions. I. Separation and determination of small amounts of lead. B. S. EVANS.—See B., 1928, 449.

Volumetric determination of small quantities of thallium. J. PROSZT (Z. anal. Chem., 1928, **73**, 401—404).—To the solution of thallous salt are added 3—4 drops of hydrochloric acid (*d* 1·19) for each mg. of thallium present. Saturated bromine water is then added dropwise until a yellow colour persists. The excess of bromine is removed by treating with a few c.c. of a 5% solution of phenol and a little potassium iodide. The liberated iodine is titrated with 0·01 or 0·02*N*-thiosulphate solution, using a microburette. The small variation of the thallium factor of the thiosulphate solution with the quantity of thallium involved must first be determined by trial measurements, using known small amounts of thallium. J. S. CARTER.

Electrolytic deposition of traces of metals and their characterisation by spectrum analysis. E. BAYLE and L. AMY (Bull. Soc. chim., 1928, [iv], **43**, 604—624; cf. A., 1912, ii. 821; 1925, ii. 1208).—The authors claim to have increased the sensitiveness of the methods of Hartley and Moss, and of Jolibois and Bonnet. A detailed account of their electrolytic deposition apparatus is given. A glass electrolytic cell is used, having the anode of platinum, which need not necessarily be pure, and the cathode of copper, or of copper-free zinc for copper determinations. The nature of the electrolytic bath varies according to the metal to be deposited. Several media exist for each metal, and by appropriate choice, two metals could be deposited simultaneously or separately. Details are given for the deposition of gold, silver, copper, lead, antimony, chromium, manganese, cobalt, and nickel. By spectrum analysis, the authors detect 10^{-3} to 10^{-7} mg. of substance dissolved in any volume. The sensitiveness of the deposition method varies with the electrode used and the metal under investigation. The following limits (g.) are given: (*a*) with a copper electrode: gold 10^{-6}, silver 10^{-8}, lead 10^{-10}, antimony 10^{-4}, cobalt 10^{-5}, nickel 5×10^{-7}, iron 10^{-7}, copper 10^{-8}, manganese 10^{-10}, and zinc 10^{-8}: (*b*) with a zinc electrode: silver 10^{-6}, copper 10^{-7}. The presence of marked amounts of the salts of alkali or alkaline-earth metals, and of ammonium salts does not alter the sensitiveness. The number of lines on the spectrogram allows a partial evaluation of the amount of metal present if it alone is deposited. The sensitiveness of the results obtained with the ten elements already referred to is compared with the sensitiveness of some of their respective characteristic chemical reactions. R. A. PRATT.

Determination of minute amounts of mercury. A. STOCK and W. ZIMMERMANN (Z. angew. Chem., 1928, **41**, 546—548).—A method for the determination of quantities of mercury of the order 10^{-3}—5×10^{-5} mg. and for the detection of amounts of the order 7×10^{-6} mg. is described. The initial stages are similar to those already described (A., 1926, 703, 814), save that deposition on a copper wire is effected in evacuated apparatus and at 50—60°. The sublimate obtained on distillation is dissolved in 0·25 c.c. of chlorine water and excess of chlorine expelled by air. The solution is treated with a drop of a cold, saturated solution of carbamide and diluted to 0·5 c.c. in the cell of a microcolorimeter. The blue colour produced on addition of a drop of a saturated, alcoholic solution of diphenylcarbazone is observed in a darkened room by yellow light. Comparative tests are made with solutions of pure mercuric chloride under identical conditions. J. S. CARTER.

Systematic detection of the rare elements. T. KATO (J. Soc. Chem. Ind. Japan, 1927, **30**, 658—670).—A systematic method of separation and detection of all rare-earth metals except germanium and radium is worked out, and is described in a tabular form. S. OKA.

Electrometric titration of lanthanum, cerium, and thorium as ferrocyanides. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 51—59).—A 0·005—0·007*M*-solution of lanthanum nitrate in 30% alcohol may be titrated electrometrically with 0·1*M*-potassium ferrocyanide, using a platinum electrode, the point of inflexion on the titration curve corresponding with the formation of the salt $KLaFe(CN)_6$. The end-point is less definite if about 10% of alkali metal salts is present. The titration of thorium nitrate must be carried out at about 70°, but the presence of alcohol is not necessary; the end-point is reached when an equimolecular amount of ferrocyanide has been added. In presence of 10% of ammonium or potassium chloride this titration is impossible. R. CUTHILL.

Potentiometric determination of iron with permanganate by a new method. T. HECZKO (Z. anal. Chem., 1928, **73**, 404—411).—The electrodes

are two platinum wires. The free end of one is in contact with the bulk of the solution of ferrous salt, whilst the free end of the other is wrapped round the upper portion of a short rod of pumice. Connexions are made to a galvanometer. Before commencing a titration the pumice is completely immersed in the solution and then partly withdrawn. The well-stirred solution is now titrated with permanganate, the throw of the galvanometer being observed after each addition. The end-point is reached when the ratio throw/c.c. of permanganate is maximal. The pumice should be immersed for a short period when the end-point is approached. The method depends on the establishment of an *E.M.F.* as a result of the difference between the ferrous-ion concentrations in the pumice and the bulk of the solution. J. S. CARTER.

Gravimetric separation of iron and mercury. G. SPACU (Bul. Soc. Stiinţe Cluj, 1927, **3**, 394—397; Chem. Zentr., 1928, i, 825).—Pyridine is added dropwise to the solution of the metals, containing ammonium thiocyanate, until the dark red colour becomes yellowish-brown. The precipitate is washed with hot water and ignited to ferric oxide, whilst the mercury is determined in the filtrate as sulphide.

A. A. ELDRIDGE.

Micro-determination of metallic elements. II. Micro-detection of iron with dimethylglyoxime. R. NAKASEKO (Mem. Coll. Sci. Kyoto, 1928, **A**, **11**, 113—117).—The tint and depth of colour produced on mixing solutions of iron, hydrogen sulphide, ammonia, and dimethylglyoxime vary with the order of mixing, but are constant under constant conditions. For the colorimetric determination of iron the test solution is first treated with a freshly-prepared, saturated solution of hydrogen sulphide to reduce ferric salts. The mixture is then treated with dimethylglyoxime (1% alcoholic solution) and finally with ammonia. The foregoing and the thiocyanate method are about equally sensitive. J. S. CARTER.

Determination of ferrous oxide in rocks. E. SALVATORE and A. SQUEO (Z. Krist., 1927, **66**, 162—166; Chem. Zentr., 1928, i, 825).—An electrically heated platinum dish containing the rock with hydrofluoric acid is covered by a greased cover-glass; a stream of dry carbon dioxide and a platinum wire stirrer are provided. A. A. ELDRIDGE.

Determination of iron in iridium sponge. O. E. ZVJAGINTSEV (Ann. inst. platine, 1927, **5**, 361).—The material is fused with sodium carbonate, the mass is extracted with water, and most of the ferric oxide removed from the iridium oxide by means of hydrochloric acid. CHEMICAL ABSTRACTS.

Determination of iron in red lead. H. HEINRICHS.—See B., 1928, 456.

Determination of iron and aluminium in the presence of calcium, magnesium, and phosphoric acid. A. J. PATTEN and O. B. WINTER (J. Assoc. Off. Agric. Chem., 1928, **11**, 202—208).—The method described by Patten (*ibid.*, 1923, **6**, 418) has been investigated and found trustworthy. The method is specially applicable to the analysis of plants. The ferric iron and the aluminium are precipitated as phosphates by the addition of an excess of ammonium acetate to the solution, which is slightly acid to thymol-blue. The ammonium acetate, acting as a buffer, maintains the solution below p_H 5·4. Iron and aluminium phosphates are precipitated at p_H 5·0—5·4, whereas calcium phosphate is not precipitated below p_H 6·5. A micro-method for the determination of the iron and aluminium is described. After the separation of the iron and aluminium as phosphates, they are determined colorimetrically, the iron by means of thiocyanate, and the aluminium by means of the ammonium salt of aurintricarboxylic acid (aluminon). T. M. A. TUDHOPE.

Determinative mineralogy. III. [Microchemical tests.] P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (Amer. J. Sci., 1928, [v], **15**, 423—430; cf. this vol., 267).—A study has been made of the sensitivity of, and the effect of the presence of other metals on, the microchemical tests for iron, gallium, indium, and palladium. A new test for palladium, which is dependent on the formation of palladium dimethylglyoxime, is described.

F. J. WILKINS.

Detection of cobalt by means of diphenylthiocarbazone. H. FISCHER (Wiss. Veroff. Siemens-Konzern, 1928, **6**, [2], 147—149).—The addition of a solution of diphenylthiocarbazone in 10% ammonia containing a little hydrazine sulphate as stabiliser to a feebly ammoniacal solution of a cobalt salt produces a violet coloration when more than 1 μg. of cobalt per c.c. is present. The reaction will detect 0·1% Co in nickel if the solution is kept until the green nickel compound has flocculated. Zinc under the same conditions gives a purplish-red colour. To detect cobalt in presence of zinc the reaction is carried out in *N*-sodium hydroxide solution and the colour of the test compared with that produced by a zinc solution free from cobalt; under these conditions, the cobalt colour rapidly disappears and a grey precipitate of cobalt sulphide and sulphur separates.

A. R. POWELL.

Electrometric titration of uranyl ion with potassium ferrocyanide. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 77—81).—In order to titrate uranyl acetate electrometrically with 0·1*M*-potassium ferrocyanide using a platinum electrode, the acetate solution must contain 35% of alcohol and be at 70°. There is then an abrupt change in potential corresponding with the formation of uranyl ferrocyanide. Uranyl nitrate cannot be titrated in this way. R. CUTHILL.

Potentiometric stannometry. E. MULLER and J. GÖRNE (Z. anal. Chem., 1928, **73**, 385—400).—Potentiometric measurements involving stannous chloride should be carried out in an atmosphere of nitrogen. In presence of sufficient hydrochloric acid the following reactions may be followed potentiometrically: $Sn^{\cdot\cdot}+I_2\longrightarrow Sn^{\cdot\cdot\cdot\cdot}+2I'$; $2Fe^{\cdot\cdot\cdot}+Sn^{\cdot\cdot}\longrightarrow 2Fe^{\cdot\cdot}+Sn^{\cdot\cdot\cdot\cdot}$ (75°); $2HCrO_4'+14H^{\cdot}+3Sn^{\cdot\cdot}\longrightarrow 2Cr^{\cdot\cdot\cdot}+8H_2O+3Sn^{\cdot\cdot\cdot\cdot}$: $2Fe(CN)_6'''+Sn^{\cdot\cdot}\longrightarrow 2Fe(CN)_6''''+Sn^{\cdot\cdot\cdot\cdot}$; $2Au^{\cdot\cdot\cdot}+3Sn^{\cdot\cdot}\longrightarrow 2Au+3Sn^{\cdot\cdot\cdot\cdot}$; $Pt^{\cdot\cdot\cdot\cdot}+2Sn^{\cdot\cdot}\longrightarrow Pt+2Sn^{\cdot\cdot\cdot\cdot}$ (75°). Where no desirable temperature is indicated the reactions may be followed at the ordinary temperature. With solutions of gold and platinum it is advisable to add chlorine

water and potassium bromate, respectively, to ensure that the metals are in their highest state of oxidation before titration with stannous chloride. The titration curve will then show two breaks. The first break corresponds with the removal of the excess of oxidising agent and the commencement of the reaction indicated above. It is perhaps advisable to replace the usual platinum electrode by a graphite rod during the first stage of the platinum titration. When solutions of stannous sulphate containing sulphuric acid are titrated at 75° with a solution of mercuric perchlorate the first break in the curve corresponds with the completion of the reaction $Hg^{\cdot\cdot}+Sn^{\cdot\cdot}\longrightarrow Hg+Sn^{\cdot\cdot\cdot\cdot}$, and the third break with $Hg+Hg^{\cdot\cdot}\longrightarrow 2Hg^{\cdot}$. The intermediate break is probably a result of the reaction $2Sn^{\cdot\cdot\cdot\cdot}-Hg^{\cdot\cdot}+Hg\longrightarrow Hg_2^{\cdot\cdot}Sn_2^{\cdot\cdot\cdot\cdot}$. The presence of antimony ($Sb^{\cdot\cdot\cdot}$) does not interfere. The reaction between permanganate and stannous sulphate, $2MnO_4'+5Sn^{\cdot\cdot}+16H^{\cdot}\longrightarrow 2Mn^{\cdot\cdot}+5Sn^{\cdot\cdot\cdot\cdot}+8H_2O$, can be followed at the ordinary temperature in presence of sulphuric acid. J. S. Carter.

Iodometric determination of vanadium in special steels and in ferrovanadium. K. Roesch and W. Werz.—See B., 1928, 409.

Analysis of platinum ores by fusion with lead. S. F. Shemtschushni (Ann. inst. platine, 1927, 5, 364).—The ore (1 g.) is fused with lead (25 g.) at 1250—1300° in a graphite crucible for 2·5 hrs., the metal is dissolved in nitric acid, the lead being precipitated as sulphate and the excess of sulphuric acid removed with barium chloride. The insoluble residue is dissolved in aqua regia (only iridium remains undissolved) and the mixed solutions are analysed in the usual way. Chemical Abstracts.

Separation of rhodium from iridium by potassium iodide. V. V. Lebedinski (Ann. inst. platine, 1927, 5, 364).—A boiling aqueous solution of potassium iodide is added to a boiling neutral solution of the chlorides, ebullition being continued for 3—4 min. The rhodium iodide is collected and washed with dilute aqueous potassium iodide, and the separation repeated after dissolution in aqua regia and evaporation to dryness. The iodide is reduced by heating in hydrogen, and the residual metal washed with hot water. The iridium in the filtrate is determined by reduction with zinc.

Chemical Abstracts.

Analysis of iridium. O. E. Zvjagintsev (Ann. inst. platine, 1927, 5, 189—192).—The metal (1—2 g.) is fused under borax with silver (10—20 g.) and the mass digested with nitric acid; the process is repeated and the platinum and palladium are determined in the solutions. The ignited residue of iridium with some rhodium is weighed, and the difference regarded as base metals. To test for iron and ruthenium, 2—3 g. are fused with sodium carbonate, and the mass is extracted with water; ruthenium is precipitated from the extract with nitric acid, whilst the insoluble residue contains iron. For the final analysis, the sample (7—10 g.) is heated in hydrogen and cooled in carbon dioxide, the loss representing oxygen and volatile compounds; the metal is heated with barium dioxide (3 pts.) in a nickel crucible for 2 hrs., the product extracted with hot water and dissolved in aqua regia, the treatment being repeated until all the iridium is dissolved. The excess of nitric acid is removed by evaporation and the solution diluted to 1 litre; the barium is removed with the correct quantity of sulphuric acid, and sodium nitrate added to the hot solution, with stirring, until it becomes yellow. A slight excess of sodium carbonate is then added, and iron, nickel, etc. are precipitated as hydroxides by boiling. The filtrate is acidified with hydrochloric acid, and platinum, rhodium, ruthenium, etc. are precipitated as sulphides by addition of sodium sulphide to the hot solution. After evaporation of the filtrate with hydrochloric acid most of the iridium is precipitated as potassium or ammonium chloroiridate, and the remainder with magnesium.

Chemical Abstracts.

Physical methods in chemical laboratories. I. Introduction. F. Paneth (Z. angew. Chem., 1928, 41, 507—508).—An introductory discussion.

J. S. Carter.

Physical methods in chemical laboratories. IV. Significance of spectroscopy in chemical investigations. I. E. Rabinowitsch (Z. angew. Chem., 1928, 41, 555—561).—Energy-levels and term-systems are briefly explained, and the methods whereby heats of ionisation and dissociation are deduced from spectroscopic evidence are indicated.

J. S. Carter.

Physical methods in chemical laboratories. II. Vacuum technique. K. Peters (Z. angew. Chem., 1928, 41, 509—515).—Modern methods of evacuation, measurement of pressure, and investigation of in-leaking are reviewed and the scope of the application of vacuum methods to analytical, photochemical, preparative, and other problems is briefly outlined. A number of diagrams and references are given. J. S. Carter.

Manometer for vacuum distillation. F. Friedrichs.—See B., 1928, 429.

Design of fractionating columns. D. B. Keyes, R. Soukup, and W. A. Nichols, jun.—See B., 1928, 429.

Extraction apparatus especially suitable for liquids. P. H. Prausnitz (Chem. Fabr., 1928, 324—325).—A continuous extractor can be used equally as well as a Soxhlet even when of considerable cross-section if the condensed extracting liquid is prevented from falling in one place. This is effected by widening the lower end of the condenser and drawing it out into a large number of points. Extraction is more rapid than with a Soxhlet apparatus. The same device is applied to Wagenaar's apparatus for extracting a solute from a lighter liquid with a heavier one. A glass filter is of no use as a distributor in these two cases, but is serviceable in the extraction of a heavier liquid with a lighter one. C. Irwin.

Apparatus for carrying out filtrations, precipitations, etc., in absence of air. P. Dickens (Chem. Fabr., 1928, 323—324).—A conical flask with side tube closed by a glass tap and narrowed at the top is united by a funnel to a similar but inverted flask. Suitable ground-glass joints are provided for the funnel. C. Irwin.

Adiabatic calorimeter for high temperatures. W. KANGRO (Z. Elektrochem., 1928, **34**, 253—256).—A new adiabatic calorimeter for use at 800—900° is described. An electric oven containing a pure silver block and platinum resistance thermometer is surrounded by a similarly equipped cylindrical oven; the two thermometers are connected in a bridge in such a manner that a change of temperature in the inner oven results in an equal and almost simultaneous change of that of the outer oven. H. F. GILLBE.

Electrical methods in hygrometry. P. W. BURBIDGE and N. S. ALEXANDER (Proc. Physical Soc., 1928, **40**, 149—155).—The possibility of applying electrical methods to the measurement of humidity is investigated. The two methods considered depend on (1) the change in resistance of organic materials when exposed to water vapour and (2) the change in mobility of ions due to water vapour. In neither case is the method suitable for general use, although each could be applied in special cases. C. J. SMITHELLS.

Optics of the total radiation pyrometer. H. MIETHING (Wiss. Veroff. Siemens-Konz., 1928, **6**, (2), 135—146).—The absorption of heat radiations by the glass and quartz lenses of the ardometer (a total radiation pyrometer) has been determined graphically for black-body conditions between 700° and 2000° and the calculations have been confirmed by experiment. It is shown to be impossible to measure the radiation energy of selectively radiating bodies by means of an ardometer with glass lenses, as high results are obtained with bodies (*e.g.*, metals) the emissive power of which decreases, and low results with bodies the emissive power of which increases in the infra-red with rise of temperature.
A. R. POWELL.

Photographic examination of moving flames. A. G. WHITE (J.C.S., 1928, 1159—1161).—A new method is described for the examination of moving flames which is independent of their luminosity, and takes advantage of the fact that the progress of the flame causes an abrupt change in the optical properties of the medium through which it passes. It gives better definition and better resolution than the ordinary direct photographic method.
F. J. WILKINS.

Relationship between chemical composition and the resistance of glasses to the action of chemical reagents. II. Glasses containing iron oxides. V. DIMBLEBY and W. E. S. TURNER.—See B., 1928, 404.

Instrument to record the carbon dioxide content of a gaseous mixture. R. GORDON and J. F. LEHMANN.—See B., 1928, 391.

Simple, automatic control of vacuum. S. P. MILLER and P. V. MCKINNEY (Ind. Eng. Chem., 1928, **20**, 552).—The vacuum is controlled by a valve to the atmosphere. The valve is a fine, capillary opening in contact with a rubber stopper mounted on the arm of an electro-magnet. The latter is operated by platinum contacts in the mercury of the manometer. A vacuum reduced to 5 mm. is controlled within 0·3 mm. J. S. CARTER.

Vacuum resistance vessel for conductivity measurements and conductometric analyses. I. A. REMEZOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 925—931).—A vessel for conductivity measurements has been devised in which owing to its complete isolation from the influence of the surroundings it is possible to maintain a constant temperature for 18—20 min. after switching on the current. Measurements with an accuracy of ±0·05—0·01% have been made with this instrument. When used for conductometric analyses a micro-burette is ground into the lid of the vessel. Good results were obtained for the neutralisation of a series of acids and alkalis by this method. A. RATCLIFFE.

Method of determination of m. p. with electrical signal. G. WICK and G. BARCHFELD (Chem. Fabr., 1928, 281).—The substance is packed in the bottom of a glass tube and above it rests a narrow glass rod on which rests a contact arm. The tube is placed in a heated block and when liquefaction occurs the rod and arm fall, closing an electric circuit.
C. IRWIN.

New microcolorimeter and its use. H. KLEINMANN (Chem. Fabr., 1928, 263—264, 278—279).—The colorimeter is similar in principle to the Duboscq instrument and consists of a pair of vessels of 1 c.c. capacity, dipping rods, lamps, scales, and eyepiece. For accurate results careful filtration of the solutions is necessary and air bubbles must not be allowed. Errors then should not exceed 1%. The instrument is suitable in conjunction with a micro-Kjeldahl apparatus for the determination of nitrogen by Nessler reagent. Quantities as small as 5×10^{-6} mg. can be determined, the principal difficulty being, not of manipulation, but in obtaining reagents sufficiently free from ammonia. C. IRWIN.

High-frequency vacuum furnace for laboratory use. E. W. FELL (Arch. Eisenhüttenw., 1927—1928, **1**, 659—661; Stahl u. Eisen, 1928, **48**, 661—662).—A 3·6-kw. high-frequency induction furnace working in a large evacuated glass bell-jar is described and figured. The bell-jar rests on a ground-glass plate, from which it is separated by a soft rubber washer. In the centre of the plate on a thick insulating slab of asbestos is the induction coil of water-cooled copper tube surrounding a refractory crucible which is surmounted by a refractory radiation shield. The connexions to the vacuum pump are made through an opening in the top of the bell-jar which also carries a small periscope in which the behaviour of the mass may be observed. The tubes for cooling water and the electrical connexions are passed through holes in the glass plate which are then rendered gas tight with a suitable plastic cement. Means are also provided for dropping small quantities of metal or flux on to molten charge during an experiment.
A. R. POWELL.

Report on metallography. H. C. BOYNTON and others (Proc. Amer. Soc. Testing Materials, 1928, **27**, i, 597—599).—Nickel-silver is best etched with boiling ferric ammonium sulphate solution. Etching reagents for identifying carbides etc. in alloy steels are discussed. CHEMICAL ABSTRACTS

Geochemistry.

Electrical conductivity and refractive index of peat-bog waters. I. A. Smorodincev and A. N. Adova (J. Russ. Phys. Chem. Soc., 1928, 60, 497—505).—Changes in the mineral content of peat-bog water may be followed by electrical conductivity measurements. Where the content of organic matter is high, as in sphagnum waters, no strict parallelism exists between the solid content and the electrical conductivity. Sedge-grass waters, which have low refractive indices, possess an electrical conductivity four to five times as great as that of sphagnum waters. The refractive index varies, up to a certain point, proportionally to the organic content.

R. Truszkowski.

Spectrochemistry of Portuguese mineral waters; that of Gerez. A. P. Forjaz (Compt. rend., 1928, 186, 1366—1367).—A water from a porphyroid granitic formation in the north of Portugal was examined spectrographically after concentration and removal of the alkaline-earth metals. In addition to the elements already detected in these structures (*ibid.*, 1921, 173, 1170) germanium, cæsium, silver, and lead were found. The role of germanium as an indicator of geological age and origin is mentioned.

J. Grant.

Base exchange and the formation of petroleum. M. Stuart (Nature, 1928, 121, 940; cf. Taylor, this vol., 612).—It is questioned whether in Nature solid fats could be a sedimentary deposit in water and accumulate as such together with sand; further, a study of the effect of the bacterial decomposition in sea water under anaerobic conditions by *Microspira aestuarii* (van Delden) of protoplasm and of vegetable oils incorporated as sediments in clay is suggested.

A. A. Eldridge.

Helium and the genesis of petroleum. C. C. Farr and M. N. Rogers (Nature, 1928, 121, 938).—The formation of higher hydrocarbons from methane by α-particles observed by Lind and Bardwell (A., 1926, 769, 1077) may account for the genesis of petroleum, in view of the fact that in the mid-United States of America the regions in close proximity to oil-fields are also regions in which the natural gases have a high helium content. Tentative calculations suggest that the formation of 1 cu. ft. of helium would produce nearly 2 tons of liquid hydrocarbon. A. A. Eldridge.

Thermal instability of the earth's crust. H. H. Poole and J. H. J. Poole (Phil. Mag., 1928, [vii], 5, 662—667).—The published physical data on solid and liquid basalts lead to the result that the adiabatic temperature gradient of the earth's crust is 0·75° per kilometre at the surface and decreases with increasing depth. On similar grounds, the m.-p. gradient is 3° per kilometre at a depth of 40 kilometres. The two gradients should be equal at a depth of about 200 kilometres. At depths less than 200 kilometres, it is improbable that the adiabatic could be steeper than the m.-p. gradient. These results lead to the conclusion that, in the absence of infusible continental masses, a deep layer of magma the radioactivity of which is at all comparable with that of surface specimens of basic or ultra-basic rocks would undergo periodic changes of state possibly accompanied by corresponding changes in the temperature gradient in the crust. In the presence of continental masses, however, resolidification of the underlying basaltic magma would be prevented, and the present solidity of the magma underlying the continents is best explained by Joly's assumption that tidal effects in the liquid magma produce lateral displacements of the continents and thus allow the escape of accumulated heat. A. E. Mitchell.

Geochemical inertia of the elements of the triads. P. Vinassa de Regny (Atti R. Accad. Lincei, 1928, [vi], 7, 23—25; cf. this vol., 267).—Further consideration leads to the conclusion that, as a rule, simple or compound substances, whether natural or artificial, organic or inorganic, have even molecular numbers. Almost the whole of the earth's mass is composed of substances with atomic numbers up to 28, *i.e.*, lying within the first triad. The geochemical inertia of the elements of the triads is to be attributed to the number and arrangement of the electrons corresponding with a condition of equilibrium. T. H. Pope.

Quantitative mineralogical and chemical classification of igneous rocks. E. T. Hodge (Univ. Oregon Pub. [Geol. Series], 1927, 1, 133—200).—Rocks are classified mineralogically in four classes, based on the content of felspars and felspathoids; the classes are subdivided into 19 orders, based on the ratio of orthoclase (and orthoclase equivalents) to the other felspars. The classes and orders are divided into seven ranges, based on the law of saturation, the ranges passing through every class and order. The arrangement is such that the mineralogical composition gives the chemical composition.

Chemical Abstracts.

Allochromy, morphotropy, and formation of minerals, particularly gem stones. R. Klemm (Fortschr. Min. Kryst. Petr., 1927, 12, 47—48; Chem. Zentr., 1928, i, 894).—Change in habit on entry of colouring elements is considered; formation of mixed crystals is postulated. A. A. Eldridge.

Synthetic spinel. F. Rinne (Fortschr. Min. Kryst. Petr., 1927, 12, 68—69; Chem. Zentr., 1928, i, 894).

Rock-forming alkali hornblendes. W. Kunitz (Fortschr. Min. Kryst. Petr., 1927, 12, 49—50; Chem. Zentr., 1928, i, 896).—The end components of the series syntagmatite–arfedsonite correspond with the formulæ $HCa_3Al_3Fe_5Si_6O_{25}$ and $HNa_3Fe_5Si_9O_{25}$. Becke's series gastaldite–riebeckite was confirmed, the first and last formulæ being $H_2(NaAl)_2Mg_4Si_9O_{27}$ and $H_2(NaFe)_2Mg_4Si_9O_{27}$. It is believed that the whole of the iron was originally ferrous. A. A. Eldridge.

Change of the green colour of beryl into blue. J. Kurbatov and W. Kargin (Zentr. Min. Geol., 1927, *A*, 361—362; Chem. Zentr., 1928, i, 481).—When ordinary beryl is heated at 450—500° for 30

min., it becomes bluish; the change is apparently due to the presence of iron. A. A. ELDRIDGE.

Rosterite and other beryls. F. ZAMBONINI and V. CAGLIOTI (Gazzetta, 1928, **58**, 131—152).—Following a description of the chemical and crystallographic analysis of the beryl rosterite the composition of this substance is discussed with reference to that of other beryls. It is suggested that all beryls consist of mixed crystals of the general formula $R_2SiO_3,R_2Al_2Si_2O_8$, where R_2 may denote one or more of: Li_2, Na_2, K_2, Cs_2, Rb_2, Be, Ca, or Mg. R. W. LUNT.

Thomsonite from the basalt of Disko, Greenland. H. R. VON GAERTNER and F. MACHATSCHKI (Zentr. Min. Geol., 1927, *A*, 365—366; Chem. Zentr., 1928, i, 482).—The crystals of thomsonite contained SiO_2 41·64, Al_2O_3 29·96, CaO 11·24, Na_2O 3·50, K_2O 0·49, H_2O 13·14%. A. A. ELDRIDGE.

Rare-earth elements. N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 515—544).—A number of rare-earth minerals are discussed, and in certain cases analysed, the results obtained confirming those of other authors. The methods used for the separation of the individual elements from each other are reviewed in detail, and a combination of fractional crystallisation and precipitation methods is proposed for the separation of yttrium from erbium and ytterbium. R. TRUSZKOWSKI.

Occurrence and detection of the platinum metals in Norwegian rocks. II. G. LUNDE and M. JOHNSON (Z. anorg. Chem., 1928, **172**, 167—195).—The amounts of platinum metals, gold, and silver in a number of Norwegian rocks have been determined by methods similar to those described in the previous paper (A., 1927, 439). Results are given also for the quantities of these metals present in the ordinary analytical reagents. H. F. GILLBE.

Chlorite-schists from the Tatra Mts. S. JASKÓLSKI (Bull. Acad. Polonaise, 1928 for 1927, **A**, 703—717).—The chlorite-schists of the Tatra Mts. grade into and have been derived from amphibolites and amphibolite-biotite-schists. Analyses of these rocks show a similarity in composition to diorites, from which the amphibolites were no doubt derived. Two analyses are also given of the chlorite isolated from these rocks, and their composition is compared with that of celadonite. L. J. SPENCER.

Nature of clay, and its significance in the weathering cycle. G. W. ROBINSON (Nature, 1928, **121**, 903—904).—Evidence is adduced in support of the view that the primary residual product of the chemical weathering of silicates is a mixture of kaolinite and nontronite, or of hydrated silicates having the same silica/sesquioxide ratio (2·0). A. A. ELDRIDGE.

Variation of the refractive indices of sphalerites and their iron contents. S. NISHIO (J. Fac. Eng. Tokyo, 1928, **17**, 183—189).—By the immersion method in fused mixtures of sulphur and selenium, determinations for different wave-lengths were made of the refractive indices of blende from several Japanese localities, and the results are plotted on curves. The extreme values for sodium light are 2·370 (with 1·16% Fe) and 2·428 (with 10·35% Fe). L. J. SPENCER.

Constituents and genesis of a few minerals produced from hot springs and their vicinities in Japan. III. Calcium carbonate minerals deposited from effervescent springs. I. SUGANUMA (Bull. Chem. Soc. Japan, 1928, **3**, 87—89).—A high temperature is not necessary for the production of aragonite, in contradiction to Meigen's views. H. F. GILLBE.

Organic Chemistry.

Oleic, palmitic, and stearic acids as parents of petroleum. N. D. ZELINSKI and K. P. LAVROVSKI (Ber., 1928, **61**, [*B*], 1054—1057; cf. B., 1927, 865).—Decomposition of oleic acid in the presence of 30% of aluminium chloride commences at the ordinary temperature and is very vigorous at 150°, giving carbon dioxide, inflammable gases which decolorise permanganate solution, and liquid products. The hydrocarbons of lowest b. p. are somewhat similar to analogous fractions obtained by the condensation of ethylene. The fractions of intermediate and highest b. p. do not contain hexahydroaromatic derivatives, but are rich in paraffin and *cyclo*paraffin hydrocarbons which have not been fully elucidated but probably contain derivatives of *cyclo*pentane. It is remarkable that aluminium chloride transforms oleic acid into liquid paraffin hydrocarbons but not into *cyclo*hexane hydrocarbons or solid paraffins. Stearic and palmitic acids decompose more readily than oleic acid in the presence of aluminium chloride, giving carbon dioxide and reducing gases. Palmitic acid yields a small liquid distillate, b. p. 70—130°, and a solid paraffin, (?)$C_{30}H_{62}$, m. p. 79·5°, mean mol. wt. 412. Stearic acid gives small liquid fractions, b. p. 130—190° and 100—140°/15 mm., respectively, and 60% of a solid paraffin hydrocarbon, (?)$C_{34}H_{70}$, m. p. 80·5°, mol. wt. 511.

It is not improbable that palmitic and stearic acids are the parents of petroleums rich in solid paraffins. H. WREN.

Oxidation of *n*-hexane. M. BRUNNER and E. K. RIDEAL (J.C.S., 1928, 1162—1170).—The oxidation of hexane is shown to be very similar to the autoxidation of benzaldehyde, there being a period of induction during which peroxide molecules are formed which can react with hexane. When the concentration of the peroxide rises to a certain value there is probably a chain mechanism of excitation of peroxide molecules and rapid combustion sets in. The temperature of initial combustion is not characteristic of the hydrocarbon (cf. Lewis, A., 1927, 851). The induction period can be shortened by a rise in temperature or an increase of oxygen pressure. Aniline exerts a marked inhibiting effect on the oxidation and pumice causes

slow combustion accompanied by a slight decrease in pressure due to the formation of aldehydes and polymerised products from the decomposition of peroxide molecules. B. W. ANDERSON.

Synthesis of Δ^{α}-butene. H. J. LUCAS and R. T. DILLON (J. Amer. Chem. Soc., 1928, **50**, 1460—1464).—The methods of obtaining Δ^{α}-butene are reviewed. Its preparation in 43 g. lots from allyl bromide and magnesium methyl bromide at 70° (cf. Kirrmann, A., 1926, 934) and purification by washing and fractional distillation are detailed. H. E. F. NOTTON.

Preparation and physical properties of α-, β-, and *iso*-butylenes and *n*- and *iso*-butanes. C. C. COFFIN and O. MAASS (J. Amer. Chem. Soc., 1928, **50**, 1427—1437).—α-Butylene (*a*) is prepared from butyl iodide and alcoholic potassium hydroxide, β-butylene (*b*) from butyl alcohol in presence of phosphoric acid at 250—280° (King, J.C.S., 1919, **115**, 1404), *iso*butylene (*c*) from *iso*butyl alcohol (cf. A., 1927, 851), and *n*- (*d*) and *iso*- (*e*) butanes from the appropriate butylene and hydrogen using a nickel catalyst at 150—200°. All were purified by repeated fractionation. A large number of measurements of physical properties are recorded over the following temperature ranges. Vapour pressure: (*a*) —3·7° to —77·5° (*e.g.*, 811·4 mm., —4·4°; 83·3 mm., —52·3°); (*b*) 20·4° to —66·8° (707·4 mm., —1·0°; 79·6 mm., —47·1°). Density: (*a*) 9·8° to —46·0° ($d^{-0·5}$ 0·6170; 0·6528); (*b*) 17·8° to —42·4° ($d^{0·9}$ 0·6303, $d^{-30·4}$ 0·6638); (*d*) 32·5° to —34·4° ($d^{18·8}$ 0·5805, $d^{-30·2}$ 0·6318); (*e*) 25·3° to —27·8° (d^{20} 0·5591, $d^{-27·8}$ 0·6131). Surface tension: (*a*) 20° to —55° (13·85 at 10°); (*b*) 20° to —50° (14·82 at 10°); (*d*) 29·7° to —36·1° (13·64 at 10·1°); (*e*) 23·3° to —36·3° (11·61 at 9·8°). The following constants are tabulated and compared with those obtained (A., 1921, i, 489) with the corresponding lower homologues; m. p.; b. p. (*a*) —6·1°, (*b*) 1·0°, (*c*) —6·6°, (*d*) —0·5°, (*e*) —10·2°; critical temperature; Ramsay and Shields' constant; Trouton's constant; surface tension at the b. p. (*a*) 15·95, (*b*) 16·78, (*c*) 15·72, (*d*) 14·90, (*e*) 14·10; total surface energy; mol. vol. at the b. p., and mol. vol. at the m. p. H. E. F. NOTTON.

Polymerisation. XI. Polymerisation and depolymerisation of amylenes under the influence of silicates. S. V. LEBEDEV and I. A. VINOGRADOV-VOLZYNSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 441—452).—A mixture of amylenes, consisting of trimethylethylene and methylethylethylene, yielded when heated with floridin (a silicate activated by heating at 300—350°) diamylene, b. p. 37—39°. This product when heated at 150—160° with floridin yielded gaseous and liquid products. The former consist of 8·25% of methane and 91·4% of a mixture of *iso*- and butylenes, with possibly traces of propylene. The liquid products consisted of *iso*propylethylene, *iso*pentane, trimethylethylene, *γ-methyl-Δ^{β}-pentene*, b. p. 67—69°, heptylene, octylene, and nonylene. R. TRUSZKOWSKI.

Polymerisation of acetylene. I. C. FUJIO (J. Soc. Chem. Ind. Japan, 1928, **31**, 77—86).—When purified acetylene is passed through a glass tube filled with a catalyst and heated at 400—700°, the yield and nature of the tar produced depend on the temperature, rate of passing acetylene, and the nature of the catalyst; the maximum yield was about 82% by passing 5 litres of the gas per hour over clay heated at 650°. The tar fraction b. p. below 175° consisted of benzene and other aromatic hydrocarbons and the fraction b. p. 175—250° mostly of naphthalene. The yield of the "gas oil" fraction of the tar was greatest with charcoal as catalyst. When a metal tube was used instead of glass, the decomposition of acetylene into carbon, hydrogen, and other gaseous substances took place more abundantly than the polymerisation. The tar thus produced differed from that obtained by using a glass tube; the fraction of b. p. 100—250° was large and that of b. p. 175—250° contained only a trace of naphthalene. A porcelain tube, however, behaves like glass in the polymerisation of acetylene. K. KASHIMA.

Activity of halogen derivatives of the propyl series. B. V. TRONOV and A. J. GERSEVIC (J. Russ. Phys. Chem. Soc., 1927, **59**, 727—739).—The connexion between the number and position of halogen atoms in the molecule and their reactivity was investigated from the viewpoint of Lowry's theory of alternate polarity and the electronic conception of double linkings for compounds of the ethyl series, both saturated and unsaturated.

The activity, both "ionic" and "molecular," of the halogen atoms was estimated by the rate of reaction with pyridine and sodium methoxide, respectively. A second halogen atom if in the α-position to the first decreases the ionic activity, but increases it if in the β-position, in accordance with the theory of alternate polarity, whereas in both cases the activity towards sodium methoxide is increased. In monosubstituted α-derivatives, the halogen atom is much more active in ionic and slightly more active in molecular reactions than in β-derivatives. An adjacent double linking always greatly enhances the activity, whilst a hydroxyl group has the same effect as a second halogen atom. M. ZVEGINTZOV.

Reaction of the Grignard reagent with γ-chloropropyl *p*-toluenesulphonate; a method of lengthening carbon chains by three carbon atoms. S. S. ROSSANDER and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 1491—1496).—In equimolecular proportions Grignard reagents and γ-chloropropyl *p*-toluenesulphonate give only small yields of the desired product (cf. Gilman and Beaber, A., 1923, i, 453). Thus, magnesium butyl halides give only the corresponding γ-chloropropyl halides; magnesium *n*-heptyl bromide gives *n*-decyl chloride (11·4%); magnesium *n*-hexyl bromide, *n*-nonyl chloride (14%); magnesium benzyl chloride, δ-phenylbutyl chloride (42%), and magnesium δ-phenylbutyl chloride, η-phenylheptyl chloride (25%). Volatile sulphur compounds and substances of high b. p. are also formed. An improved yield of the derivative with three additional carbon atoms is obtained from 1 mol. of a Grignard reagent containing six or more carbon atoms and 2 mols. of γ-chloropropyl *p*-toluenesulphonate. In this way γ-phenylbutyl chloride (50% of the theoretical yield), γ-phenylpropyl chloride (62%), *n*-amyl chloride (23%), *n*-nonyl chloride (52%), *n*-pentadecyl chloride (30%), γ-*cyclo*hexylpropyl

chloride (62%), η-phenylheptyl chloride (44%), and *n*-decyl chloride (50%) were formed together with considerable quantities of the corresponding γ-chloropropyl halide. Magnesium benzyl chloride (1 mol.) yields with 1 mol. of *n*-butyl *p*-toluenesulphonate, mainly amylbenzene with butyl chloride and toluene, and with 2 mols. an increased yield of the first two.

H. E. F. NOTTON.

Oxonium compounds. D. McINTOSH (Proc. Nova Scotian Inst. Sci., 1927, **16**, 96—103).—See A., 1926, 144.

Colour reactions of some alcohols. L. EKKERT (Pharm. Zentr., 1928, **69**, 289—296).—The colour reactions obtained by treating very dilute solutions of the aliphatic alcohols (propyl to octyl) in ethyl alcohol (96%) containing small amounts of furfuraldehyde, various aromatic aldehydes, or sucrose with concentrated sulphuric acid are recorded. These reactions, which are to a great extent specific, may be used to distinguish between small amounts of isomeric alcohols.

G. A. C. GOUGH.

Rate of oxidation of alcohols by chromic and nitric acids in aqueous solution. B. V. TRONOV, B. F. UDODOV, and M. J. TSCHISHOVA (J. Russ. Phys. Chem. Soc., 1927, **59**, 1149—1156).—The rate of oxidation by chromic acid (0·3*N*) and nitric acid (39% and 67%) of methyl, ethyl, *n*- and *iso*-propyl, *iso*- and *tert*.-butyl, γ-methylbutyl, propylenyl, and benzyl alcohols, *cyclo*hexanol, methyl glycol, and glycerol was measured at 17—19° in equimolecular solution, by determining from time to time the amount of acid used. Owing to the complex nature of the products, esterification and partial insolubility of some of the alcohols, only the first few values were used for comparison. The rate of oxidation of the saturated monohydric primary alcohols increased with the length of the carbon chain. Secondary alcohols are more easily oxidised by nitric acid, but less easily by chromic acid, whilst *tert*.-butyl alcohol is not effected. The unsaturated alcohols are more reactive than the saturated.

M. ZVEGINTZOV.

Rate of oxidation of alcohols, ethers, and esters by potassium permanganate and chromic anhydride under various conditions. B. V. TRONOV and A. A. LUKANIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 1157—1172; cf. preceding abstract).—The behaviour of ethyl alcohol, ether, and acetate, *n*- and *iso*-propyl alcohols, propaldehyde, and propyl acetate towards both acid and alkaline potassium permanganate and chromic anhydride (both with and without an excess of sulphuric acid) was investigated, in order to elucidate certain difficulties encountered in previous investigations. The bimolecular velocity coefficient for the oxidation reaction was determined at 19—21°, the compound to be oxidised being present in equimolecular proportions, or in excess. The primary alcohols with permanganate and all the alcohols and ethers with chromic anhydride give satisfactory coefficients. *iso*Propyl alcohol does not, whilst the esters are hydrolysed by chromic anhydride. The rate of oxidation is always greatly increased by excess of acid or alkali, and the alcohols are much more readily oxidised than the other compounds. All the earlier observations (cf. *loc. cit.*) are confirmed.

M. ZVEGINTZOV.

Rate of oxidation of alcohols by potassium permanganate. B. V. TRONOV, A. A. LUKANIN, and J. J. PAVLINOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1173—1197; cf. preceding abstracts).—The rate of oxidation by 0·03*N*-potassium permanganate in equimolecular proportions in neutral solution at 16°, 18°, 21°, and 24° of the following alcohols was investigated: Methyl, *n*-propyl, *iso*propyl, trimethylcarbinol, ethyl, *n*-butyl, *iso*butyl, *iso*amyl, heptyl, cetyl, *sec*.-butyl, *cyclo*hexanol, *tert*.-amyl, pinacol, ethylene glycol, propylene glycol, glycerol, erythritol, adonitol, mannitol, allyl, and benzyl. The first four were also oxidised in alkaline solution. In neutral solution the primary alcohols and ethylene glycol only give a satisfactory bimolecular velocity coefficient.

All the monohydric alcohols (except allyl alcohol) reduce neutral potassium permanganate as far as quadrivalent manganese, whilst with the others the reduction is more complete. In alkaline solution (in which oxidation is always many times more rapid than in neutral) the velocity coefficient falls rapidly up to 10—20% of available oxygen, and is then steady up to 40—50%.

The saturated polyhydric alcohols are the more readily oxidised the greater is their number of hydroxyl groups. Of the monohydric alcohols the secondary are slightly more active than the primary, whilst the tertiary are almost inactive. Activity increases with the length of the chain. The benzene nucleus, and especially unsaturated linkings, very greatly increase the rate of oxidation.

M. ZVEGINTZOV.

Catalytic oxidation with air of ethyl, *iso*propyl, and *n*-butyl alcohols. R. M. SIMINGTON and H. ADKINS (J. Amer. Chem. Soc., 1928, **50**, 1449—1456).—The catalysts used include copper, silver, platinum, nickel, alloys of copper with silver, zinc,* bismuth, cadmium, palladium, platinum, nickel, manganese, and silicon, and of silver with gold, zinc, bismuth, and palladium, also mixtures of copper oxide with oxides of molybdenum,* uranium, iron, vanadium,* and tungsten * (* with all except these, the reaction proceeded without external application of heat). Gauze, pellets, strip, and wire catalysts were equally efficient. The yields of carbon monoxide and dioxide, saturated and unsaturated hydrocarbons, aldehyde or ketone, and acid are tabulated for some 12 catalysts. The maximum yields of aldehyde and ketone were: ethyl alcohol 76·0% (using an alloy of Cu 90%, Ag 10%), *iso*propyl alcohol 76·1% (silver pellets), *n*-butyl alcohol 72·5% (Cu 80%, Zn 20%) and 72·0% (silver). The yield of hydrogen was small except with catalysts containing zinc. Alloys containing 99% of silver or copper did not differ catalytically from the pure metals, so that probably a large proportion of the surface is active. Plated catalysts are ineffective on account of the rapid dissolution of the plating in the underlying metal. With any self-heating catalyst the mol. ratio of the carbon dioxide formed from equal mols. of alcohol is ethyl, 3 : *iso*propyl, 2 : *n*-butyl, 1.

H. E. F. NOTTON.

***iso*Propylacetylenylcarbinol and two stereoisomeric forms of di*iso*propylbutinenediol.** V. KRESTINSKI and V. MARJIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 1135—1140).—See A., 1927, 1052.

Alkali compounds of polyhydric alcohols and carbohydrates. L. SCHMID, A. WASCHKAU, and E. LUDWIG (Monatsh., 1928, **49**, 107—110).—Carefully-purified ethylene glycol, glycerol, dextrose, lævulose, glycogen, and chitin form definite *monosodium compounds* when treated with sodium in pure, anhydrous liquid ammonia solution (cf. Schmid and Becker, A., 1925, i, 1386), the compound in each case being isolated and analysed. In the case of the inulin compound the inulin was recovered unchanged in rotation by decomposition with water.
J. W. BAKER.

Configuration of α-glycols formed by oxidation of ethylene derivatives. J. BÖESEKEN (Rec. trav. chim., 1928, **47**, 683—693).—The evidence for the configuration of the diols obtained by the oxidation of various open-chain and cyclic olefine derivatives by alkaline potassium permanganate or peracids is summarised and an attempt at correlation is made. In the case of open-chain derivatives the evidence is not conclusive, the only proved case being the oxidation of maleic acid (*cis*) exclusively to meso-tartaric acid, and of fumaric acid (*trans*) to racemic acid. In the cyclic series *cyclo*pentene, 1-methyl- and 1-phenyl-*cyclo*pentene, indene, *cyclo*hexene, 1-methyl-*cyclo*hexene, and tetrahydronaphthalene-1 : 2-diol when oxidised with potassium permanganate yield exclusively, or almost exclusively, the *cis*-1 : 2-diols. Evidence for the configuration of the diols is based (1) on the possibility of optical resolution of the *trans*-isomeride, (2) the formation of complexes with boric acid and borates, with resulting increase in electrical conductivity, and (3) the formation of cyclic condensation products with acetone. Thus oxidation by permanganate takes the expected course and it is suggested that intermediate products of the type $\begin{matrix}-\underset{|}{C}-O \\ \quad\; O\end{matrix}\!\!>\mathrm{Mn}<$ are formed which, by hydrolysis, yield the *cis*-diols. On the other hand, oxidation by means of peracids usually takes the opposite course. Perbenzoic acid yields the ethylene oxide, whilst peracetic acid yields the monoacetate of the diol, each product being smoothly hydrolysed to the same diol. Thus *cyclo*pentene, 1-methyl*cyclo*pentene, *cyclo*hexene, and 1-methyl*cyclo*hexene yield exclusively the *trans*-diol, whilst indene and 1-phenyl*cyclo*hexene yield a mixture of *cis*- and *trans*-diols. In the former case the proportion of the two forms depends largely on the acidity or alkalinity of the medium and on the temperature, the *cis*-form preponderating in acid media. In the latter case in 0·05*N*-sulphuric acid at low temperatures the *cis*- and *trans*-diols are formed in approximately equimolecular proportions. Thus the presence of a phenyl group on the ethylenic carbon atom causes the formation of a large quantity of the *cis*-form. Confirmation of this is found in the oxidation of stilbene and *allo*-stilbene with peracetic acid. Decomposition of butan-β-ol with phosphoric acid at 200° yields mainly *cis*-Δ^{β}-butene, since the latter on oxidation with peracetic acid yields racemic butane-βγ-diol.
J. W. BAKER.

Preparation of αδ-dihydroxy-*n*-butane (tetramethyleneglycol) and αδ-dibromo-*n*-butane. A. MÜLLER (Monatsh., 1928, **49**, 27—30).—αδ-Dihydroxy-*n*-butane [phenylurethane, m. p. 183—183·5° (corr.), 163—164° on remelting; Hamonet, A., 1905, i, 403, gives 180—181°] is readily prepared in 54% yield by reduction of ethyl succinate with sodium and absolute alcohol, followed, after removal of the alcohol by steam distillation in the usual manner, by distillation of the product with superheated steam. The aqueous distillate is distilled in a vacuum and an aqueous distillate passes over, leaving behind almost pure tetramethylene glycol, which is again distilled in a vacuum. When the glycol is treated with a current of dry hydrogen bromide at 80° for 5 hrs. a 70% yield of αδ-dibromo-*n*-butane is obtained.
J. W. BAKER.

Pinacolin transformation of a βγ-butylene glycol. T. TAIRA (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 46—48).—When βγ-butylene glycol is distilled with 25% sulphuric acid, some methyl ethyl ketone is produced. CHEMICAL ABSTRACTS.

Dimethyl peroxide. A. RIECHE [with W. BRUMSHAGEN] (Ber., 1928, **61**, [*B*], 951—956).—*Dimethyl peroxide*, b. p. 13·5°/740 mm., *d* 0·8—0·85, is prepared by the action of potassium hydroxide on a mixture of hydrogen peroxide and methyl sulphate in an indifferent atmosphere. The gaseous substance is very freely soluble in alcohol and ether, freely soluble in water. Its constitution is established by its reduction to methyl alcohol. Its oxidising action is not profound; iodine is liberated slowly from acidified potassium iodide solution, whereas quinol and hydrazobenzene are not oxidised. Almost quantitative reaction ensues when its ethereal solution is shaken with aqueous titanium trichloride. It is extremely explosive, particularly when in the gaseous state, being unusually sensitive to shock; light appears to have little effect on it. Formaldehyde is produced by its explosive decomposition. H. WREN.

Synthesis of partly acylated glycerides. II. B. HELFERICH and H. SIEBER (Z. physiol. Chem., 1928, **175**, 311—315; cf. this vol., 44).—By the action of *p*-nitrobenzoyl chloride on glycerol αγ-ditrityl ether in dry pyridine at 0° is obtained the β-p-*nitrobenzoate*, m. p. 188° (corr.), which by hydrolysis with hydrogen bromide in acetic acid yields *glycerol*-β-p-*nitrobenzoate*, m. p. 120—121° (corr.). The structure of this is proved by its ready conversion by the action of benzoyl chloride in pyridine into glyceryl αγ-dibenzoate β-*p*-nitrobenzoate (Bergmann, Brand, and Dreyer, A., 1921, i, 444). *Glyceryl* αγ-*ditrityl ether* β-*palmitate*, m. p. 70—72° (corr.), is similarly obtained from the αγ-ditrityl ether and palmityl chloride. J. W. BAKER.

Polymerisation and condensation. II. Products of interaction of potassium acetate and epichlorohydrin. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1928, **77**, 685—696).—Epichlorohydrin was heated with anhydrous potassium acetate (*a*) for 24 hrs. at 120° rising to 150°, (*b*) for 48 hrs. at 125° rising to 155°. By fractional distillation of the product there was obtained in the first case unchanged epichlorohydrin, glycidol acetate, diacetin, and *diacetylglycerylglycidol*, b. p. 110—114°/0·1 mm., m. p. 125°, and in the second case the above compounds together with impure *triacetyldiglycerol*, b. p.

155—168°/0·05 mm.; the distillation residue appeared to consist of polymerides of glycerol of high mol. wt.

C. R. HARINGTON.

Chloromethyl sulphate. V. GRIGNARD, C. TOUSSAINT, and J. CAZIN (Bull. Soc. chim., 1928, [iv], **43**, 537—542).—An account of work carried out prior to the investigation of Fuchs and Katscher (this vol., 43). Chloromethyl ether (1 mol.) and fuming sulphuric acid (60%; 1 mol.) in the cold afford a fraction, b. p. 82—83°/22 mm., of the approximate composition $3SO_3,2(CH_2Cl)_2O$, probably a mixture of maximum b. p., and identical with the liquid obtained by Houben and Arnold (A., 1907, i, 1000). If the temperature is allowed to rise to 160° until 4 mols. of sulphur trioxide are taken up, the products are a little chloromethyl sulphate, fractions of the approximate composition $2SO_3,(CH_2Cl)_2O$ and $3SO_3,(CH_2Cl)_2O$, and a solid residue, m. p. about 150°, probably methylene sulphate. With 1 mol. of sulphur trioxide after several hrs. at 160° a little chloromethyl sulphate is formed accompanied by chloromethyl pyrosulphate, $2SO_3,(CH_2Cl)_2O$. Chloromethyl sulphate, b. p. 100—103°/12—13 mm., $d^{1\cdot}$ 1·634, 1·453, is obtained in 26% of the theoretical yield by distilling sulphur trioxide (1 mol.) into 1 mol. of chloromethyl ether, at 105°, raising the temperature to 200°, adding 0·5 mol. of chloromethyl ether, and heating for ½ hr. at 200°; at 180° the yield is only 14·3%. Equimolecular quantities heated in a sealed tube at 180—200° for 50 min. give a 31% yield of chloromethyl sulphate. Hydrolysis with dilute sodium hydroxide affords sulphuric and hydrochloric acids, formaldehyde, and formic acid, the last-named being formed by the action of the alkali on the formaldehyde. Attempts to chloromethylate aniline, phenol, and benzene with this reagent were unsuccessful.

R. BRIGHTMAN.

Preparation and properties of ββ′-dicyanodiethyl sulphide. V. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 921—924).—Ethylenecyanohydrin, prepared by the action of potassium cyanide on the chlorohydrin, when treated at 0° with thionyl chloride in chloroform solution, yields β-chloropropionitrile, which reacts vigorously with anhydrous sodium sulphide in the presence of methyl alcohol to give -*dicyanodiethyl sulphide*, m. p. 24—25°, possessing none of the toxic properties of "mustard gas." On warming with acids and alkalis, thiodipropionic acid is obtained quantitatively.

M. ZVEGINTZOV.

Spectrochemical investigation of esters of selenious and selenic acid. W. STRECKER and W. DANIEL (Annalen, 1928, **462**, 186—194).—An investigation to discover the existence or otherwise of the selenium analogues of the unsymmetrical "sulphites," $R{\cdot}SO_2{\cdot}OR$. Whilst, however, symmetrical ethyl sulphite and the isomeric unsymmetrical ester are respectively converted by magnesium phenyl bromide into diphenyl sulphoxide and phenyl ethyl sulphone (cf. A., 1910, i, 532), the products of the interaction of alkyloxides and selenyl chloride on the one hand and of silver selenite and alkyl halides on the other give rise to selenium when similarly treated. Optical examination of the selenious esters prepared by the two different methods fails to reveal any difference between them.

Methyl selenite, prepared by adding selenyl chloride to a well-cooled ethereal suspension of sodium methoxide, has b. p. 69°/15 mm., $d_4^{20\cdot1}$ 1·7890, 1·48078. When prepared at a low temperature from methyl iodide and silver selenite in ethereal suspension, it has d_4^{20} 1·761, $n^{16\cdot3}$ 1·48058. Ethyl selenite from selenyl chloride has b. p. 82—83°/14·5 mm., d_4^{20} 1·500, $n_\alpha^{20\cdot1}$ 1·46247, that from silver selenite having b. p. 83—84°/15 mm., d_4^{20} 1·492, $n_\alpha^{16\cdot8}$ 1·46125. n-*Propyl selenite* from selenyl chloride has b. p. 109°/15 mm., d_4^{20} 1·349, ^{6} 1·46166, whilst that from the silver salt has b. p. 111°/16·5 mm., d_4^{20} 1·343, $n_\alpha^{16\cdot6}$ 1·46086.

The difficulties encountered by Meyer and Wagner (A., 1922, i, 620) when purifying selenic esters have been overcome and pure specimens of three esters have now been examined: methyl selenate, b. p. 68—68·5°/3 mm., d_4^{20} 1·750, $n_\alpha^{19\cdot5}$ 1·44103; *ethyl selenate*, b. p. 76°/3 mm., d_4^{20} 1·498, $n_\alpha^{19\cdot9}$ 1·43942; n-*propyl selenate*, b. p. 83—84°/3 mm., d_4^{20} 1·335, $n^{19\cdot3}$ 1·45308. Details are given for the preparation of these esters from silver selenate. The esters can be kept indefinitely in sealed vessels.

When sodium methylsulphonate is heated with phosphorus selenide, P_2Se_5, a 30% yield of dimethyl selenide and a 38% yield of dimethyl diselenide (calculated on the phosphorus selenide) result (cf. Jackson, 1875). Hochwalt's directions (cf. B., 1926, 513) for diminishing the production of the diselenide were found unsatisfactory. Dimethyl selenide has b. p. 54—55°/753 mm., d_4^{20} 1·401, 1·47990, whilst the b. p. (hitherto unrecorded) of the diselenide is 150—151°/745 mm. Attempts to prepare dimethyl selenoxide by oxidation of the selenide proved abortive. The densities at other temperatures and refractive indices for other wave-lengths are recorded.

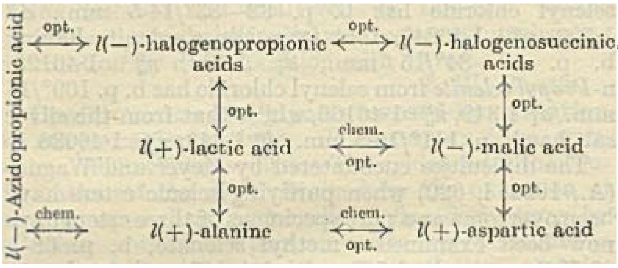
E. E. TURNER.

Reaction of bromine with aliphatic acids. II. Relative speeds of bromination of acetyl bromide and acetyl chloride. H. B. WATSON.—See this vol., 716.

Periodic electrolytic oxidation of formic acid. E. MULLER and S. TANAKA.—See this vol., 720.

Steric series. IX. Configuration of the monosubstituted propionic and succinic acids. K. FREUDENBERG and A. LUX (Ber., 1928, **61**, [*B*], 1083—1089; cf. this vol., 153).—Comparison of the optical properties of derivatives of *l*-bromosuccinic acid with those of *l*(−)-malic and *l*(−)-bromopropionic acid shows the adherence of lævorotatory bromosuccinic acid to the *l*-series. If the work of Kuhn and Wagner-Jauregg (this vol., 506) is also taken into account, the following series may be regarded as established, natural *l*(+)-lactic, *l*(−)-halogenopropionic acids, *l*(+)-alanine, *l*(−)-malic, *l*(−)-monohalogenosuccinic, and *l*(+)-aspartic acids. Review of the results afforded by optical and chemical methods of determining the configuration of active compounds shows that α-hydroxy-, amino-, and halogeno-fatty acids of the same configuration almost universally suffer similar change in rotation under the influence of the same substituents provided that the use of solvents is avoided and all dipolar and associ-

ating groups (carboxyl, hydroxyl, amino-) are masked. Clough's method appears to give trustworthy results within the individual groups, but it is not suitable for comparison of substances belonging to different groups. In the subjoined table the abbreviations "opt." and "chem." denote the determination of configuration by optical and chemical methods :



The following data are recorded : *l*(—)-bromosuccinic acid, m. p. 179°, $[\alpha]_D^{20}$ —70·2° ; l(—)-*bromosuccinyl chloride*, b. p. 56°/1 mm., d^{22} 1·796, $[\alpha]_D^{22}$ —58·4° ; methyl *l*-bromosuccinate, b. p. 79°/1 mm., d^{19} 1·513, $[\alpha]_D^{19}$ —65·3° ; *propyl* l-*bromosuccinate*, m. p. 108°/1 mm., d^{23} 1·279, $[\alpha]_D^{23}$ —41·5° ; dl-*bromosuccinbisdimethylamide*, m. p. 79° (obtained also from the active chloride) ; methyl *l*(—)-chlorosuccinate, $[\alpha]_D$ —42·3° ; ethyl *l*(—)-chlorosuccinate, $[\alpha]_D^{20}$ —32·7° ; *l*(—)-methoxysuccinyl chloride, d^{23} 1·341, $[\alpha]_D$ —44·6° ; l(—)-*acetylmalyl chloride*, b. p. 118°/14 mm., d^{22} 1·377, $[\alpha]_D^{22}$ —13·1°. H. Wren.

Esters of α-bromobutyric acid. V. Deulofeu (Bull. Soc. chim., 1928, [iv], **43**, 549—551).—The *propyl*, b. p. 190·5—194° (50%), iso*propyl*, b. p. 179—182° (30%), and *allyl*, b. p. 189—193° (25%), esters of α-bromobutyric acid have been prepared in the yield indicated, using sulphuric acid as catalyst (cf. Michael, A., 1902, i, 69). R. Brightman.

Components of unsaturated acids of chrysalis oil. W. Kimura (J. Soc. Chem. Ind. Japan, 1927, **30**, 858—865).—The unsaturated acids were separated from the saturated acids by means of the lead salt–alcohol method and brominated. They were found to consist of oleic, linoleic, and linolenic acids as formerly reported by other investigators, but the content of linoleic acid was not so small as formerly reported. The same conclusion was reached from the identification of the products of the oxidation of the mixed acids by potassium permanganate. The oxidation products were found to be dihydroxystearic acid, α- and β-sativic acid, and linusic acid. S. Oka.

Soya-bean oil. I. Component fatty acids. II. Isolation of dipaltmitolein. K. Hashi (J. Soc. Chem. Ind. Japan, 1927, **30**, 849—855, 856—858).—I. The fatty acids of soya-bean oil were separated into a solid (10·6%) and a liquid (85·4%) part by means of Twitchell's lead salt–alcohol method. The solid fatty acids were esterified with methyl alcohol and the esters fractionated. They were found to consist of much palmitic acid, an appreciable amount of stearic acid, and a little arachidic acid. Bromination of the liquid fatty acids shows the presence of linolenic acid, 2·9% ; linoleic acid, 51·5% ; oleic acids, 35·6% ; and solid fatty acids, 11·1%.

II. The dipalmitolein was extracted with acetone from soya-bean oil and purified by ten recrystallisations from the same solvents. S. Oka.

Reduction of α-elæostearic acid. ($\Delta^{\iota\lambda}$-Linoleic acid and Δ^{κ}-oleic acid.) J. Boeseken and J. van Krimpen (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 238—240).—By an improvement in the hydrogenation method previously employed (A., 1927, 1169), the first reduction product of ethyl α-elæostearate has been obtained pure and octodecadienic acid, m. p. 28·5°, n_D^{70} 1·4639, has been separated from it and shown by ozonisation to have double linkings at ι and λ. For the ethyl ester n_D^{70} is 1·4746, mol. refraction 96·87 (calc. 95·28), and iodine value 109 (calc. 180). These facts point to the existence of a conjugated system. If this ester is hydrogenated with two thirds of the calculated amount of hydrogen, the product hydrolysed, and the acid recrystallised, the largest fraction has m. p. 38·5°, n^{70} 1·4432, yields hexoic and sebacic acids on ozonisation, and gives no lowering of m. p. when mixed with Bertram's vaccenic acid (Chem. Weekblad, 1927, **24**, 226). M. S. Burr.

Separation of glycerides. IV. Oil of silkworm pupa. B. Suzuki and Y. Yokoyama. **V. Cod-liver oil.** B. Suzuki and Y. Masuda (Proc. Imp. Acad. Tokyo, 1928, **4**, 161—164, 165—168).—IV. Bromination of oil of silkworm pupa by the method previously described (this vol., 152) gives *dioleo-linolenin bromide*, m. p. 86°, yielding, on hydrolysis with hydrochloric acid, hexabromo- and dibromo-stearic acids, two iso*linoleo-dilinolenin bromides*, m. p. 133° and 154° (hydrolytic products, hexabromostearic acid and *iso*linoleic acid tetrabromide), trilinolenin bromide, m. p. 172° (cf. *loc. cit.*), *triolein bromide* (hydrolytic product, dibromostearic acid), *palmito-oleo-linolenin bromide* (hydrolytic products, hexabromostearic, dibromostearic, and palmitic acids), and *palmito-diolein bromide* (hydrolytic products, dibromostearic and palmitic acids).

V. From cod-liver oil, there were obtained *stearidono-diclupanodonin bromide*, m. p. 125°, hydrolysed by hydrochloric acid to *octabromostearic acid* (I), m. p. 200° (decomp.), and decabromobehenic acid, *diarachidono-clupanodonin bromide*, m. p. 112° (hydrolytic products, decabromobehenic and octabromoarachidic acids), *diclupanodono-linolenin bromide*, m. p. 118° (hydrolytic products, hexabromostearic and decabromobehenic acids), *clupanodono-stearidono-zoomarin bromide*, m. p. 220° [hydrolytic products, (I), dibromopalmitic and decabromobehenic acids], *clupanodono-arachidono-zoomarin bromide*, m. p. 105° (hydrolytic products, decabromobehenic, octabromoarachidic, and dibromopalmitic acids), *clupanodono-stearidono-arachidonin bromide*, m. p. 240° (decomp.); [hydrolytic products, (I), decabromobehenic and octabromoarachidic acids], two *linoleno-dizoomarin bromides* (hydrolytic products, hexabromostearic and dibromopalmitic acids), and *linoleo-diazoomarin bromide* (hydrolytic products, tetrabromostearic and dibromopalmitic acids).

[With Y. Yokoyama.]—Debromination of (I), followed by catalytic reduction of the unsaturated acid,

$C_{18}H_{28}O_2$ (stearidonic acid), produced, gives stearic acid. H. BURTON.

Influence of the ring oxygen atom on the rate of reaction of certain lactones. E. HOLLO (Ber., 1928, **61**, [*B*], 895—906).—Measurements are recorded of the rates of hydrolysis and lactonisation of ethylene glycollate, α-hydroxypropionate, α-hydroxy- -butyrate, α-hydroxy*iso*butyrate, δ-valerolactone, and α-methyl-δ-valerolactone in 50 vol.-% aqueous acetone at 25° (±0·1°) in the presence of hydrogen chloride as catalyst, the course of the change being followed by titration with barium hydroxide at 0° in presence of phenolphthalein. Alkyl groups in the α-position retard hydrolysis and lactonisation, their effect being more pronounced in the first process; their sequence of activity is $Me<Et<Me_2$. With the ether-lactones investigated, the presence of a cyclic oxygen atom depresses the rate of hydrolysis to about 56—57% and that of lactonisation to about 39—41% of that of the usual δ-lactones.

Ethylene glycollate, m. p. 31°, b. p. 213—214°/747·6 mm., d_4^{15} 1·2521, is prepared in 70—80% yield by the action of chloroacetic acid on the monosodium compound of ethylene glycol in the presence of ethylene glycol. Excess of solvent is removed at as low a temperature as possible or by means of acetone and the sodium β-hydroxyethoxyacetate is decomposed with hydrochloric or phosphoric acid; the liberated acid is distilled, whereby anhydrisation occurs for the main part. Slowly when preserved, immediately under the influence of hydrogen ions, the monomeric form passes into a *polymeride*, m. p. 66—68°, b. p. 216—220°, from which it is regenerated by distillation. Analogous methods are used in the preparation of *ethylene α-hydroxypropionate*, b. p. 100—101°/17 mm., *ethylene α-hydroxy*-n-*butyrate*, b. p. 104·5—105°/20 mm., and *ethylene α-hydroxy*iso-*butyrate*, b. p. 120—128°/20 mm., which could not be caused to solidify and are found by analysis to contain a small proportion of the corresponding hydroxy-acids. δ-Valerolactone, b. p. 116—118°/25 mm., is obtained in 60—70% yield by heating sodium δ-iodovalerate in a vacuum; it slowly passes into a colourless polymeride. *α-Methyl-δ-valerolactone* has b. p. 116—117°/16 mm. H. WREN.

Configurational relationships of α-hydroxyvaleric and lactic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1928, **77**, 555—562).—*d*-α-Hydroxy-*n*-valeric acid, $[\alpha]_D^{20}$ +1·5° (*barium* salt, $[\alpha]_D^{20}$ −4·9°), was converted into *ethyl α-hydroxy*-n-*valerate*, b. p. 81°/20 mm., $[\alpha]_D^{20}$ −5·05°, which gave, on reduction, l-*pentane-αβ-diol*, b. p. 78—81°/1 mm., $[\alpha]^{20}$ −9·8° in alcohol (*diphenylcarbamate*, m. p. 110—113°, $[\alpha]_D^{20}$ −12·2° in alcohol). *α-Chloropentan-β-ol*, b. p. 59—62°/14 mm., obtained by the action of chloroacetaldehyde on magnesium propyl bromide, was oxidised to *chloromethyl propyl ketone*, b. p. 55—57°/15 mm.; this was converted into *hydroxymethyl propyl ketone*, b. p. 62—64°/18 mm., which, on treatment with actively fermenting yeast, gave d-*pentane-αβ-diol*, b. p. 97—99°/13 mm., $[\alpha]_D^{20}$ +16·62° in alcohol (*diphenylcarbamate*, m. p. 107—110°, $[\alpha]_D^{20}$ +16·5° in alcohol); this, with hydrogen bromide, gave d-*α-bromopentan-β-ol*, b. p. 72—74°/18 mm., $[\alpha]_D$ +10·5°, which, on reduction, gave d-*methylpropylcarbinol*, $[\alpha]_D^{20}$ +14·3° in alcohol (*α-naphthylcarbamate*, m. p. 94—96°, $[\alpha]_D^{20}$ +17·7°). It follows that *d*-α-hydroxyvaleric acid is configuratively related to *d*-γ-hydroxyvaleric acid (since the latter gives *d*-pentane-αβ-diol on reduction) and hence to *d*-lactic acid (A., 1926, 1024). C. R. HARINGTON.

Synthesis of trimethyl*cyclo*homotetronic acid. R. ANSCHUTZ and H. QUITMANN (Annalen, 1928, **462**, 97—104).—β-Acetoxy-αα-dimethylbutyric acid is converted by thionyl chloride into β-acetoxy-αα-dimethylbutyryl chloride, b. p. 101°, which reacts with methyl sodiocyanoacetate to give *methyl β-acetoxy-αα-dimethylbutyrylcyanoacetate*, $OAc\cdot CHMe\cdot CMe_2\cdot CO\cdot CH(CN)\cdot CO_2Me$, b. p. 108°/0·5—1 mm. (*ammonium* salt, hygroscopic; *silver* salt). The corresponding *ethyl* ester has b. p. 110—112°/0·5—1 mm. (*silver* salt). Either ester is converted by concentrated hydrochloric acid into *trimethyl*cyclo*homotetronic acid*, $\begin{array}{l}CMe_2\cdot CO\cdot CH_2\\ CHMe\cdot O\cdot CO\end{array}$ (also +1 or $2H_2O$), m. p. 106·5°, b. p. 116—117°/0·5—1 mm. (*silver* salt described), also obtained by the action of sodium hydroxide at 50° on *methyl trimethyl*cyclo*homotetronic acid carboxylate*, $\begin{array}{l}CMe_2\cdot CO\cdot CH\cdot CO_2Me\\ CHMe\cdot O\cdot CO\end{array}$, b. p. 112—114°/0·5—1 mm., which is formed when methyl sodiomalonate reacts with β-acetoxy-αα-dimethylbutyryl chloride. The tetronic acid condenses with formaldehyde in aqueous solution to give the *methylenebis*-derivative, $\left[\begin{array}{l}CMe_2\cdot CO\cdot CH\cdot\\ CHMe\cdot O\cdot CO\end{array}\right]_2 CH_2$, m. p. 191°, with chloral similarly to give the *trichloroethylidenebis*-derivative, m. p. 143° (decomp.), and with paraldehyde in dilute aqueous acid solution to give the *ethylidenebis* compound, m. p. 154° (decomp.). E. E. TURNER.

History of the isomerism of fumaric and maleic acids. R. ANSCHUTZ [with O. SCHARFENBERG, P. TRUMMEL, A. VON VOLBORTH, and O. NEUHAUS] (Annalen, 1928, **461**, 155—191).—Partly historical, partly polemical against Kuhn and Ebel (A., 1925, i, 780), and for the rest mainly a publication of results recorded in Bonn theses since 1888. The object of the present paper is to decide between the two possible formulæ (I and II) for maleic acid and its derivatives:

$$\text{(I.)}\quad \begin{array}{l}H\cdot C\cdot CO_2H\\ \quad\Vert\\ H\cdot C\cdot CO_2H\end{array} \qquad\qquad \begin{array}{l}H\cdot C—C(OH)_2\\ \quad\Vert\quad\;\; >O\\ H\cdot C—CO\end{array}\quad\text{(II.)}$$

It is concluded that there are two main tendencies at work: that for the formation of symmetrical molecules (as I) and that for the formation of five-membered rings (as II). The results obtained appear to show that the salts, esters, and amic acid are of type (I) for maleic acid itself, whilst alkyl- and phenyl-maleic acids give derivatives of type (II). When more than one alkyl group is present, the ammonium salts of the amic acids closely resemble ammonium carbamate, a fact which is put forward as evidence in favour of the above contention. A number of new substances are described, as below.

Citraconamic acid, $\begin{array}{l}CH—C(NH_2)\cdot OH\\ \Vert\qquad\;\; >O\\ CMe\cdot CO\end{array}$, has m. p.

124—125° (*silver* salt; *methyl* ester, m. p. 84—85°). The *ammonium* and *silver* salts and the *methyl* (m. p. 126—127°) and *ethyl* (m. p. 158°) esters of citraconanilic acid (as I or II) are described. *Citracon*-p-*toluidic acid*, from *p*-toluidine and citraconic anhydride in ether, has m. p. 170—171° (*methyl* and *ethyl* esters, m. p. 105° and 168—169°, respectively; *ammonium* and *silver* salts). *Citracon*-p-*tolil*, m. p. 114—115°, is formed from the last-named acid or esters by boiling with water. *Citraconsemiphenylhydrazide* has m. p. 108·5°.

Ethyl hydrogen ethylfumarate, $CO_2H{\cdot}CH{:}CEt{\cdot}CO_2Et$, has m. p. 88°, whilst its isomeride, $CO_2Et{\cdot}CH{:}CEt{\cdot}CO_2H$, has m. p. 53°. *Ammonium ethylmaleamate* is described, as are also *ethylmaleimide*, m. p. 141°, and *ethylmaleanilic acid*, m. p. 106—107°. The last-named is converted by boiling water or by acetyl chloride into the *anil*, m. p. 129—130°, which is steam-volatile. The *methyl* ester, m. p. 118—119°, and *ammonium* salt of ethylmaleamic acid are described.

Dimethylmaleic acid, prepared from the *cyanohydrin*, b. p. 127—128°/13 mm., d_4^{25} 1·0549 (*acetyl* derivative, b. p. 148—149°/18 mm.), of ethyl acetoacetate by Michael's method, was converted through the anhydride into *ammonium dimethylmaleamate* (corresponding *silver* salt and *methyl* ester, m. p. 57—58°, described). Both ammonium ethyl- and dimethyl-maleamates behave like ammonium carbamate towards hydrochloric acid. The free amic acids are incapable of existence, the acid therefore producing ammonium chloride and the corresponding anhydride. Evaporation of a solution of ammonium dimethylmaleate gives the imide, m. p. 113°. Addition of ethereal ethylamine to an ethereal solution of dimethylmaleic anhydride gives *ethylammonium dimethylmaleamate*, converted by hydrochloric acid into dimethylmaleic anhydride. *Ammonium dimethylmaleanilate* and the corresponding *silver* salt and *methyl* ester, m. p. 69—70°, are described. *Dimethylmale*-p-*toluidic acid* has m. p. 74—77° (*ammonium* and *silver* salts; the *methyl* ester, from the silver salt and methyl iodide, passes on recrystallisation into the p-*tolil*, m. p. 110°).

Ammonium diethylmaleamate, m. p. 136—137°, and the corresponding *silver* salt are described. *Phenylammonium diethylmaleanilate* has m. p. 52—53° and the corresponding p-*toluidine* derivative m. p. 57°. *Diethylmaleanil*, m. p. 62—63°, is obtained when the aniline salt is boiled with water.

Ammonium diphenylmaleamate has m. p. 147—148° (*silver* salt). p-*Methylphenylammonium diphenylmale*-p-*toluidate*, m. p. 119—120°, is convertible into *diphenylmale*-p-*tolil*, m. p. 194°.

Ammonium and *silver bromocitraconamate* are described. *Phenylammonium bromocitraconanilate*, m. p. 127—128°, is convertible into bromocitraconanil, m. p. 144°. The *ammonium* and *silver* salts of bromocitraconanilic acid are described. p-*Methylphenylammonium bromocitracon*-p-*toluidate* and the corresponding *ammonium* and *silver* salts are described. *Bromocitracon*-p-*tolil* has m. p. 135·9—136°.

Bromofumaryl chloride, b. p. 93°/14 mm., is converted by aniline into the *chloride-anilide*, $NHPh{\cdot}CO{\cdot}CH{:}CBr{\cdot}COCl$, m. p. 154° (corresponding *methyl ester–anilide*, m. p. 126°; the *dianilide*, m. p. 162°). *Anilidofumardianilide* has m. p. 194° and *anilidomaledianilide*, m. p. 175°. *Bromofumaryl chloride*-p-*toluidide* has m. p. 159°, the *di*-p-*toluidide*, m. p. 184°, and *bromofumar*-p-*toluidic acid*, m. p. 169° (*methyl* ester, m. p. 105—106°). *Bromofumar*-β-*naphthylamide chloride* has m. p. 160° and the *di*-β-*naphthylamide* m. p. 234°. *Bromofumar*-β-*naphthylamic acid* has m. p. 176—177° (indef.) (*methyl* ester, decomp. 116—117°). The *silver* salt and *methyl* ester, m. p. 122°, of bromomaleanilic acid are described. *Bromomale*-p-*toluidic acid* has m. p. 162°, the *methyl* ester, m. p. 92°, and the p-*tolil*, m. p. 144—145°. *Bromomale*-β-*naphthylamic acid*, m. p. 173°, *methyl* ester, m. p. 112°, and the corresponding β-*naphthylimide*, m. p. 208°, are described.

Fumaryl bromide has b. p. 113—115°/32 mm., *fumaryl chloride methyl* ester b. p. 83°/17 mm., *fumaryl chloride ethyl* ester b. p. 84°/17 mm., *benzyl fumarate* m. p. 60—61°, and *benzyl hydrogen fumarate* m. p. 98°. *Benzyl hydrogen citraconate*, m. p. 86°, gives benzyl alcohol and citraconic anhydride when distilled at 13 mm. *Benzyl mesaconate* has b. p. 160—165°/0·5 mm. and *benzyl hydrogen mesaconate* (α compound) m. p. 71·5°. E. E. TURNER.

Cleavage of ethyl αα′-dibromoadipate by diethylamine. R. C. FUSON (J. Amer. Chem. Soc., 1928, **50**, 1444—1449).—It is suggested that ethyl 1-diethylamino*cyclo*butane-1 : 2-dicarboxylate is first formed and then decomposes into (*a*) ethyl acrylate, which gives with diethylamine ethyl β-diethylaminopropionate, and (*b*) ethyl α-diethylaminoacrylate, which is hydrolysed by dilute acid to ethyl pyruvate. This mechanism is confirmed by the observation that the product regarded by von Braun (A., 1926, 1128) as ethyl α-diethylaminopropionate is actually the β-diethylamino-derivative (Flürscheim, A., 1904, i, 19), and that in absence of water or acid, the reaction product contains, in addition to the β-diethylamino-ester, a second ester of the same b. p. which is converted by acid into ethyl pyruvate.

H. E. F. NOTTON.

Reduction of polybasic α-hydroxy-acids under the simultaneous influence of catalysts. V. N. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1083—1086).—See A., 1927, 1054.

Effect of hydrogen at high pressures and temperatures on solutions of substituted hydroxysuccinic acids in the presence of alumina and nickel oxide as catalysts. G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1071—1076; cf. A., 1926, 1124).—The behaviour of the sodium salts of α-hydroxy-α′-methylsuccinic, α-hydroxy-αα′-dimethylsuccinic, and α-hydroxy-α-methyl-α′-ethylsuccinic acids at 250° and 60—80 atm. in the presence of hydrogen, with alumina and nickel oxide as catalysts, was investigated, in order to verify the mechanism suggested (*loc. cit.*) for the condensation of sodium lactate into sodium succinate, under the same conditions, by way of the formation and decomposition of α-hydroxy-αα′-dimethylsuccinic acid. In all cases, a yield of 25—30% of methylsuccinic acid was obtained, together with quantities varying from 18 to 45% of formic and acetic acids, as well as traces

of the higher fatty acids. In the case of α-hydroxy-α-methyl-α′-ethylsuccinic acid, 30% of butyric acid was formed. M. ZVEGINTOV.

Condensation of α-hydroxy- and α-keto-acids under the simultaneous influence of catalysts. V. N. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1077—1081).—See A., 1927, 1053.

Lactone formation of cellobionic and glucoarabonic acids, and its bearing on the structure of cellobiose. P. A. LEVENE and M. L. WOLFROM (J. Biol. Chem., 1928, **77**, 671—683).—Cellobionic acid forms one lactone with a 5-membered ring, whilst glucoarabonic acid forms two lactones with 4- and 5-membered rings, from which it follows that in cellobiose the reducing sugar is substituted in the δ-position (cf. Zemplen, A., 1926, 822; Haworth and others, this vol., 47). *Cellobiose oxime*, m. p. 122—123°, has been obtained crystalline; other modifications of the work of Zemplen (*loc. cit.*) are described. C. R. HARINGTON.

α-Chloro- and α-bromo-α-sulphopropionic acids and their resolution. H. J. BACKER and H. W. MOOK (Bull. Soc. chim., 1928, [iv], **43**, 542—549).—*α-Chloro-α-sulphopropionic acid* ($+H_2O$), m. p. 93—94° [*potassium, thallium*, and *barium* ($+3H_2O$) salts], is obtained in 50% yield by the action of 1 mol. of sulphuric anhydride on 1 mol. of α-chloropropionic acid at 120—170°, or in 70% yield by heating barium α-sulphopropionate with 100% excess of barium chlorate and hydrochloric acid in a sealed tube at 100°. *α-Bromo-α-sulphopropionic acid* ($+H_2O$), m. p. 105—110° [*potassium, thallium*, and *barium* ($+3H_2O$) salts], is similarly prepared. With barium α-sulphopropionate a temperature of 140—175° is required for bromination. Both acids have been resolved by decomposition of their sodium salt with strychnine acetate. l-*α-Chloro-α-sulphopropionic acid* (*strychnine* salt; *sodium* salt, $[\alpha]_D$ —0·73°) has $[\alpha]_D$ —0·20°, l-*α-bromo-α-sulphopropionic acid* (*strychnine* salt, sodium salt, $[\alpha]_D$ —0·33°), $[\alpha]_D$ —0·03°. Both the active acids and their salts are stable at temperatures up to 100°, and the presence of alkali effects hydrolysis and not racemisation (cf. A., 1925, i, 359, 632). R. BRIGHTMAN.

Silver xanthate. A. REYCHLER (Bull. Soc. chim. Belg., 1928, **37**, 165—167).—Silver xanthate is prepared by the action of potassium xanthate on silver nitrate, chloride, bromide, or iodide. It is a yellow, crystalline substance, unaffected by boiling dilute hydrochloric and sulphuric acids, but is decomposed by a mixture of nitric and hydrochloric acids forming silver chloride. It is not acted on by dilute alkalis, but is decomposed by concentrated alkalis. It is soluble in alkali cyanide solutions, from which it is reprecipitated by acidification, but it does not dissolve in sodium thiosulphate solution. If potassium xanthate is added to a sodium thiosulphate solution of a silver salt, silver xanthate is precipitated. H. BURTON.

Action of zinc on mixtures of polyhalogenated hydrocarbons with ketones and aldehydes. I. CUCULESCU (Bul. Soc. Romane Stiin., 1928, **30**, 39—41).—When metallic zinc acts on a mixture of a polyhalogenated paraffin hydrocarbon with an aldehyde or ketone, the metal combines with the halogen, and the resulting halide may form a molecular compound with the aldehyde or ketone, and at the same time hydrocarbons are evolved; in no case is an organo-metallic compound produced. The mixtures containing an aldehyde react more readily than those containing a ketone. R. CUTHILL.

Application of the Merling reaction to aldehydes. Synthesis of *iso*propylacetylenylcarbinol. V. KRESTINSKI and F. SOLODKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 1141—1147).—See A., 1927, 1052.

Synthesis with diazomethane. IV. Reaction between aldehydes and diazomethane. F. ARNDT and B. EISTERT (Ber., 1928, **61**, [*B*], 1118—1122).—Chloral in ethereal solution is slowly converted by diazomethane into *ααα-trichloropropylene βγ-oxide*, b. p. 44—45°/13 mm. (together with a small proportion of methyl dichloroacetate), and not trichloroacetone as stated by Schlotterbeck (A., 1907, i, 185, 478; 1909, i, 553). The constitution of the compound follows from its indifference towards *o*-nitrophenylhydrazine and semicarbazide and its conversion by concentrated hydrochloric acid into *β-hydroxy-αααγ-tetrachloropropane*, b. p. 95—96°/17 mm. (non-crystalline *benzoyl* derivative), and by acetic anhydride and ferric chloride into *βγ-diacetoxy-ααα-trichloropropane*, b. p. 126—128°/16 mm.

m-Nitrobenzaldehyde and diazomethane afford exclusively *m*-nitroacetophenone, whereas *p*-nitrobenzaldehyde gives a mixture of *p*-nitroacetophenone and *p*-nitrophenylethylene oxide. It appears that the production of substituted ethylene oxides is to be expected, particularly from those aldehydes which have a pronounced tendency towards the formation of hydrates. H. WREN.

Nierenstein reaction. M. NIERENSTEIN (Nature, 1928, **121**, 940).—Polemical concerning the reaction between diazomethane and acyl chlorides. A. A. ELDRIDGE.

Catalytic condensation of methyl ethyl ketone. A. PETROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 485—489).—Methyl ethyl ketone when heated to 380—400° under 80—100 atm. pressure in the presence of a clay catalyst gives a small yield of condensation products, consisting of mesityl oxide, triethylbenzene, and homo*iso*phorone. Where sodamide is used as the catalyst, the yield of condensation products is considerably higher; these consist of a mixture of isomeric homo*iso*phorones, which on hydrogenation yield a mixture of cyclic hydrocarbons, $C_{12}H_{24}$. R. TRUSZKOWSKI.

Action of phosphorus pentachloride on ethyl *tert.*-butyl ketone. Transformation of β-hydroxy-δδ-dimethylpentan-γ-one (trimethylacetylmethylcarbinol) into acetyl-*tert.*-butylcarbinol. V. VASSILIEV (Bull. Soc. chim., 1928, [iv], **43**, 563—567).—Ethyl *tert.*-butyl ketone with 1 mol. of phosphorus pentachloride (slight excess) at 70° affords *β-chloro-δδ-dimethylpentan-γ-one* (α-chloroethyl *tert.*-butyl ketone), b. p. 84°/53 mm., d_0^{20} 0·9814, which when heated with 3 mols. of potassium formate in

methyl alcohol at 150° for 10 hrs. gives mainly *acetyl-*tert.*-butylcarbinol*, b. p. 108—111°/100 mm., d_4^{20} 0·9352 (*semicarbazone*, m. p. 188°), together with a little *δδ-dimethylpentane-βγ-diol*, m. p. 54°, the formation of the glycol being due to the reducing action of the potassium formate. Under these conditions the trimethylacetylmethylcarbinol (β-hydroxy-δδ-dimethylpentan-γ-one, first formed (cf. Favorsky and Achmarine, A., 1913, i, 12), b. p. 103—108°/100 mm. (semicarbazone, m. p. 133—134°), is almost entirely converted into the isomeric acetyl-*tert.*-butylcarbinol, the conversion not being, however, quite complete, since with magnesium phenyl bromide the product affords, in addition to *β-phenyl-δδ-dimethylpentane-βγ-diol*, m. p. 82·5°, traces of *γ-phenyl-δδ-dimethylpentane-βγ-diol*, m. p. 94°. The keto-alcohol prepared from β-bromo-δδ-dimethylpentan-γ-one is also a mixture, and in either case complete conversion into acetyl-*tert.*-butylcarbinol is obtained by heating in a sealed tube at 120° for 5—6 hrs. with a little sulphuric acid. With magnesium methyl bromide acetyl-*tert.*-butylcarbinol gives βδδ-trimethylpentane-βγ-diol, m. p. 64·5—65° (crystallographic measurements for the two forms are given), oxidised by 4% potassium permanganate to β-hydroxy-αα-dimethyl-β-*tert.*-butylethylene oxide, and identical with the glycol obtained by Prileschaeff (A., 1904, i, 795).

R. BRIGHTMAN.

Transformation of oxoctenol into acetylmethyl-*tert.*-butylcarbinol. (MLLE.) A. I. OUMNOV (Bull. Soc. chim., 1928, [iv], **43**, 571—573).—When heated in a sealed tube for 8 hrs. at 120° with alcoholic sulphuric acid β-hydroxy-αα-dimethyl-β-*tert.*-butylethylene oxide (oxoctenol) is converted into *acetylmethyl-*tert.*-butylcarbinol*, b. p. 176—178°/746 mm., d_0^{20} (*semicarbazone*, m. p. 190—190·5°), oxidised by chromic acid and potassium hydrogen sulphate to pinacolin and acetic acid, together with some trimethylacetic acid (by oxidation of pinacolin).

R. BRIGHTMAN.

Transformation of *iso*butyryldimethylcarbinol into acetylmethyl*iso*propylcarbinol. (MLLE.) A. I. OUMNOV (Bull. Soc. chim., 1928, [iv], **43**, 568—571).—*iso*Propyl α-bromo*iso*propyl ketone with 20% potassium carbonate gives a ketone alcohol, b. p. 161—162°, d_0^{20} 0·9132 (*semicarbazone*, m. p. 178—179°), isomeric with that obtained when the corresponding chloro-ketone is used (A., 1913. i, 12). With magnesium phenyl bromide the new product affords *γ-phenyl-βδ-dimethylpentane-βγ-diol*, m. p. 75—76°, oxidised by chromic anhydride and potassium hydrogen sulphate to acetone and phenyl *iso*propyl ketone. The new ketone alcohol is thus iso*butyryldimethylcarbinol*, and when warmed with alcoholic sulphuric acid for 8 hrs. at 120° is converted into the isomeride previously prepared (*loc. cit.*). With magnesium phenyl bromide this isomeride affords *β-phenyl-γδδ-trimethylpentane-βγ-diol*, b. p. 153—155°/14 mm., oxidised to acetophenone and methyl *iso*propyl ketone, the latter being further oxidised to acetic acid and acetone. The isomeride is thus *acetylmethyl-*iso*propylcarbinol* and not *iso*butyryldimethylcarbinol, as originally stated (*loc. cit.*), the latter undergoing transformation under the experimental conditions, probably with intermediate formation of an oxide alcohol. The presence of traces of such an intermediate compound may explain the low yields (up to 70%) obtained in preparation of the semicarbazones, and of variations in density and b. p. of the ketone alcohol prepared from the chloroketone and by transposition.

R. BRIGHTMAN.

Carbohydrates and polysaccharides. XIII. Properties of γδ-dihydroxycarbonyl derivatives and their bearing on the polymerisation of polysaccharides. H. HIBBERT and C. P. BURT (J. Amer. Chem. Soc., 1928, **50**, 1411—1416).—*Δ^β-Hepten-ζ-one*, b. p. 150—152°, synthesised from crotonaldehyde by way of Δ^{β}-buten-α-ol, α-bromo-Δ^{β}-butene, and *ethyl Δ^{β}-butenylacetoacetate*, b. p. 135—139°/46 mm., is oxidised by barium permanganate to *methyl γδ-dihydroxyamyl ketone*, b. p. 139—143°/10 mm. In presence of a trace of sulphuric acid at 90° this loses 1 mol. of water, giving a resinous polymeric *anhydride*, mol. wt. 553—590 in benzene. The corresponding product from methyl γδ-dihydroxybutyl ketone (cf. A., 1924, i, 16) has mol. wt. 395—445 in phenol and 3706 in camphor. The nature of these anhydrides and their relation to cellulose are discussed. When the next higher homologue, βγ-dihydroxy-β-methylheptan-ζ-one (Harries, A., 1902, i, 345), is heated with or without traces of sulphuric acid, β-methyl-Δ^{β}-heptenone βγ-oxide is formed without notable polymerisation.

H. E. F. NOTTON.

Ring structure and optical relationships in the mannose–rhamnose–lyxose series of sugars. Isolation of a new form of lyxose. W. N. HAWORTH and E. L. HIRST (J.C.S., 1928, 1221—1230).—The additive principle of optical superposition as used by Hudson (cf. A., 1926, 714) in ascribing a 1 : 4 ring structure to α-methylglucoside and 1 : 5 and 1 : 4 ring structures to α- and β-mannose, respectively, is adversely criticised. Crystalline *β-lyxose*, m. p. 117—118°, $[\alpha]_D$ −70°, was prepared by treatment of calcium galactonate with hydrogen peroxide and ferric acetate. The new sugar shows rapid mutarotation to $[\alpha]_D$ +14°, the equilibrium value for α-lyxose, to which it bears the same relation as does β-mannose to α-mannose. The connexion between the *cis*- and *trans*-nature of the hydroxyl groups and the relative solubilities of the α- and β-forms of the sugars is discussed.

B. W. ANDERSON.

Decomposition of sugars by the action of very dilute alkalis. F. FISCHLER and A. F. LINDER (Z. physiol. Chem., 1928, **175**, 237—247).—In extension of the work on dextrose (A., 1927, 449) the decomposition of various monoses (lævulose and galactose) and bioses (lactose and maltose) by very dilute alkali has been studied, similar results being obtained in each case. The yield of methylglyoxal is diminished when no sodium sulphite is added, and reaches its maximum when the distillation is carried out in a current of carbon dioxide, with 0·04—0·02*N*-sodium carbonate and with the addition of sodium sulphite. With varying concentration of alkali the yield reaches a maximum value with 0·1*N*-potassium hydroxide or 0·1—0·01*N*-sodium carbonate solutions, and decreases when larger or smaller concentrations are employed. The rotation of the sugar is reduced almost to zero after heating for 1—2 hrs. under these

conditions. Diminution in the reducing power of the sugar or of dihydroxyacetone is the greater the stronger is the alkali concentration, the values obtained with all hexoses being of the same order, and those with bioses forming a second series similar amongst themselves, but differing somewhat from the monose values. The production of acidity by the action of various concentrations of alkali has also been studied. The maximum quantity of acid (1·35—2 equiv./mol. of hexose) is produced by the action of $0·1N$-potassium hydroxide, smaller, and approximately equal amounts being produced by the action of $0·5N$- and $0·01N$-alkali solutions; the same values are obtained either in the presence or absence of oxygen. Similar results are obtained with dihydroxyacetone. These results, therefore, confirm the authors' view (*loc. cit.*) that the primary degradation product of all hexoses is dihydroxyacetone (2 mols.) (bioses being first converted into hexoses), the production of acid products being due to the action of oxygen liberated from the sugar molecules themselves. J. W. BAKER.

Sugars. VIII. H. KILIANI (Ber., 1928, **61**, [*B*], 1155—1169; cf. A., 1926, **51**, 940).—The double lactone of *l*-mannosaccharic acid appears to differ from all analogously-constituted compounds of the sugar group by its pronounced ability to reduce Fehling's solution. Similar properties have been attributed by Peirce (A., 1916, i, 18) to the double lactone of *d*-αα-manno-octaric acid; this compound is identical with the α-galaoctanehexol-di-acid of Kiliani and Wingler (A., 1922, i, 321), which has no reducing properties. The action of Peirce's compound is probably due to the presence of traces of aldehydic or ketonic acids frequently left after oxidation of carbohydrates with nitric acid. It is emphasised, however, that Fehling's solution frequently shows abnormal reactions with acids or lactones unless they have previously been neutralised by alkali. The sensitiveness of the dilactone to Fehling's solution must therefore be ascribed to the production of an aldehydic or a ketonic group. The formation of the former is improbable, since it involves a terminal carboxyl group. Fission of the dilactone by potassium hydroxide can occur in only two ways, between either the αβ or the ββ' carbon atoms; if potassium cyanide is added to the mixture and the resulting nitrile is hydrolysed, the enantiomorphous form of the acid obtained by Dull (cf. A., 1926, 940) by the oxidation of lævulosecarboxylic acid must result in the former case, whereas the production of two previously unknown tricarboxylic acids is possible in the latter case. Actually, the *calcium* salt, $(C_7H_7O_{10})_2Ca_3,9H_2O$, and the corresponding basic *copper* salt, $(C_7H_7O_{10})_2Cu_3,Cu(OH)_2,18H_2O$, differ completely from the corresponding compounds of Düll's αβγο-tetrahydroxybutane-ααδ-tricarboxylic acid; fission therefore occurs between the ββ' carbon atoms. The fate of the two hydrogen atoms lost by the mannosaccharic acid molecule during ketonisation remains undecided; the production of methylamine during the change could not be detected.

Precautions necessary for the successful oxidation of *l*-mannonolactone are described and a new, rapid method for the preparation of the double lactone of *l*-mannosaccharic acid is described in detail.

Pure lævulose is readily converted into the crystalline cyanohydrin, which is extraordinarily unstable (the presence of impurities in crude lævulose appears to render the product more stable), so that a process is described whereby the sugar is transformed into "lævulosecarboxylic" acid without isolation of the cyanohydrin. The acid is isolated as the crystalline *brucine* salt (*tetrahydrate*; anhydrous, m. p. 162°), from which it is prepared by the successive use of barium hydroxide and oxalic acid; it is oxidised by nitric acid to αβγδ-tetrahydroxybutane-ααδ-tricarboxylic acid (*tetrahydrated potassium* salt).

The use of oxalic in place of sulphuric acid is recommended for the determination and precipitation of barium in salts of organic acids. H. WREN.

Effect of borate on oxidation of dextrose and other sugars. M. LEVY and E. A. DOISY (J. Biol. Chem., 1928, **77**, 733—751).—The oxidation of dextrose, lævulose, galactose, lactose, and maltose by any alkaline copper reagent is more or less inhibited by the presence of borate, probably owing to formation of a boric ester of the sugar; acid oxidising agents such as Barfoed's reagent are not affected in this way. The oxidation of the aldehydic group of aldoses by hypoiodite is also decreased by borate except in the case of lactose. Boric acid should therefore not be used as a preservative for biological specimens required for investigation of carbohydrate metabolism. C. R. HARINGTON.

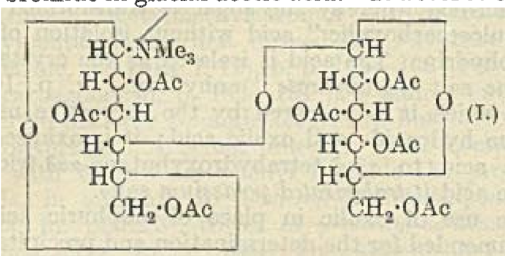
Carbohydrate oxidation. VIII. Action of potassium hydroxide on lævulose. W. L. EVANS and J. E. HUTCHMAN (J. Amer. Chem. Soc., 1928, **50**, 1496—1503).—The action of various concentrations of aqueous potassium hydroxide on lævulose at 25°, 50°, and 75° has been studied. The amounts of lactic acid, pyruvaldehyde, and acetic and formic acids obtained are shown graphically. The results are, in general, the same as those obtained both with dextrose and with glyceraldehyde (cf. this vol., 397; A., 1926, 1228), which indicates that both sugars are in equilibrium (although the equilibrium mixtures are not quantitatively identical) with a large proportion of γδ-"enediol," which is subsequently degraded to glyceraldehyde. The curves for formic acid indicate the formation of some αβ-"enediol." Although the quantities are different in each case, the maximum yield of pyruvaldehyde is obtained at the same alkali concentration from both lævulose and glyceraldehyde, and the same is true of the yield of formic and acetic acids from dextrose and lævulose.

H. E. F. NOTTON.

Synthesis of sucrose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1928, **11**, 436—442).—A more detailed account of work already published (see this vol., 510).

Action of trimethylamine on acetobromocellobiose and acetobromomaltose. G. ZEMPLÉN, Z. CSÜROS, and Z. BRUCKNER (Ber., 1928, **61**, [*B*], 927—937; cf. Karrer, Widmer, and Staub, A., 1924, i, 713).—The action of a solution of trimethylamine in ethyl alcohol on acetobromocellobiose at 85—95° yields *hepta-acetylcellobiosidotrimethylamine* (I), m. p.

205—206° (decomp.), $[\alpha]_D$ −11·07° in chloroform, which very closely resembles Karrer's "cellal acetate" in properties. When hydrolysed by sodium methoxide in chloroform it gives homogeneous cellobiose in 50% yield. It does not react with hydrogen bromide in glacial acetic acid. It absorbs one atom of



(I.)

bromine in chloroform solution, giving *hepta-acetylcellobiosidotrimethylammonium bromide*, $C_{29}H_{44}O_{17}NBr$, m. p. 148—149°, $[\alpha]_D^{18}$ −7·53° in chloroform. Treatment of the bromo-compound with silver carbonate in absolute methyl alcohol or aqueous acetone, with silver acetate in anhydrous benzene, or with aqueous sulphurous acid leads to removal of the added bromine atom with regeneration of the original material.

Acetobromomaltose and trimethylamine solution at 70° give *hepta-acetylmaltosidotrimethylamine*, $C_{29}H_{41}O_{17}N$, m. p. 165°, decomp. 208°, $[\alpha]_D^{11}$ +65·59° in chloroform; it gives a non-crystalline *bromo*-derivative from which it is re-formed by the action of sulphurous acid. Acetobromomaltose and trimethylamine at 90—95° afford trimethylammonium bromide and hepta-acetylmaltose. H. WREN.

Acetolysis of mannocellulose. Production of two new sugars, a tetra- and a penta-mannoholoside. G. BERTRAND and J. LABARRE (Bull. Soc. chim., 1928, [iv], 43, 311—321).—See this vol., 157.

Starch. H. PRINGSHEIM and P. MEYERSOHN (Z. physiol. Chem., 1928, **173**, 211—219).—The results and conclusions of Peiser (A., 1927, 136) cannot be confirmed. Starch prepared, as by Peiser, by precipitation from starch paste with alcohol and washing with alcohol and ether, the alcohol and ether being removed rapidly in a vacuum over sulphuric acid, yields on acetylation a small amount of an acetate which has the acetyl content given by Peiser; if the alcohol and ether are removed by drying in the air, however, no hardening of the starch occurs, and the product is more readily acetylated, yielding an acetate with a slightly higher acetyl content and a significantly higher rotation ($[\alpha]_D^{17}$ +220° and 222·5°, compared with $[\alpha]_D^{17}$ +178—180° and +191—196° for acetates obtained from the hornified starch). Hydrolysis of the acetate by hot sodium hydroxide yields a non-reducing "starch," as claimed by Peiser, but this is due to the destruction of the reducing groups by the hot alkali. Hydrolysis in the cold yields products which have reducing powers of 4—5% of that of maltose, or 8% of that of maltose when the acetate with the highest acetyl content and rotation is employed. Peiser's acetylation is accompanied by the formation of dextrins which account for the high acetyl values, and the results are not inconsistent with the conception of the starch molecule as an aggregate of small molecules. A. WORMALL.

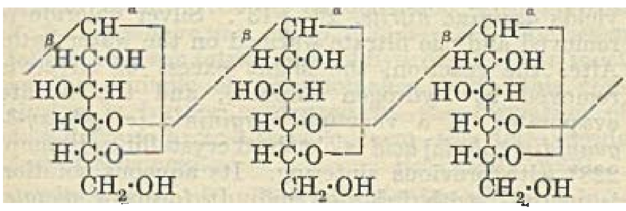
Methylation of starch. L. SCHMID and M. ZENTNER (Monatsh., 1928, **49**, 111—117).—Potato starch after 27 methylations with diazomethane yields a methylated starch containing 21·5% of methoxyl (unchanged by further methylation). This methylated starch was hydrolysed with 1% methyl-alcoholic hydrogen chloride and the product extracted with acetone (*A*, 35·3% OMe), the acetone extract precipitated with ether (*B*, 25·23% OMe) and extracted with methyl alcohol (*C*, 20·01% OMe). Fraction *A* after hydrolysis with 5% hydrochloric acid yields a product of methoxyl content 29·7%, $[\alpha]_D$ + 83·58°, corresponding with a dimethylglucose. This, by oxidation with nitric acid (*d* 1·2), yields an acid the methyl ester of which contains only three methoxyl groups, and hence one of the methylated hydroxyl groups in the dimethylglucose is probably in position 6. J. W. BAKER.

Inulin. VI. H. PRINGSHEIM and I. FELLNER (Annalen, 1928, **462**, 231—239).—In view of the many diverse opinions held as to the mol. wt. of inulin and its derivatives, further determinations have been made by the cryoscopic method in water. Inulin has *M* 1091—1172 in 0·8—1·1% solution. "Inulin" obtained by hydrolysing the products of heating inulin acetate in presence of tetrahydronaphthalene at various temperatures has *M* as follows: from acetate heated at 250°, 576—635 in 0·6—0·9% solutions (cryoscopic); from acetate heated at 260°, 457—461 in 0·8—1·36% solutions (cryoscopic); from acetate heated at 290°, 339—316 in 0·6—1·7% solutions (cryoscopic) (331—329 in 0·65—1·9% solutions, ebullioscopic determination). It is noted that the mol. wt. of molecules corresponding with 7, 4, 3, and 2 fructose anhydride units, respectively, are 1134, 648, 486, and 324. E. E. TURNER.

Behaviour of cellulose when heated under pressure with water. E. BERL and A. SCHMIDT (Annalen, 1928, **461**, 192—220).—The products of the action of water, at temperatures from 150° to 350° and correspondingly high pressures, on pure cotton cellulose were examined as falling into one of the three groups: (*a*) water-insoluble, (*b*) water-soluble, and (*c*) gaseous products. The initial action of water under such conditions is hydrolytic in nature, this effect being greater as the hydrogen-ion concentration of the water increases, viz., with rise of temperature. Acids produced similarly accelerate hydrolysis. Dextrose appears as the first recognisable product, and this then undergoes charring—a fact elicited by control experiments with pure dextrose. Water-soluble, highly polymerised humalic acids are formed at this stage, these passing later into water-insoluble humic acids which are soluble, however, in ammonia. From the dextrose, hydroxymethylfurfuraldehyde is formed, and this undergoes scission through the functioning of 2 mols. of water to give lævulic acid and formic acid.

Debye–Scherrer diagrams obtained for the original cellulose and for cellulose after treatment as above are given. E. E. TURNER.

Lignin and cellulose. VI. Methylcellulose. K. FREUDENBERG (Annalen, 1928, **461**, 130—131).—If the conclusions of Sponsler and Dore (cf. B., 1927, 934) are correct and are applied to Freudenberg's cellulose formula (this vol., 399), the latter becomes that annexed:



E. E. TURNER.

Isolation of lignin. L. KALB and T. LIESER [with R. HAHN, F. NEVELY, and H. KOCH] (Ber., 1928, **61**, [*B*], 1007—1022).—Exact information concerning the carbohydrates present in lignin obtained by incomplete treatment of wood can be obtained only by methods which permit the isolation of the carbohydrates in substance. Treatment of such lignin with chlorine dioxide and sodium sulphite, followed by characterisation of the carbohydrates by hydrolysis or fermentation with *Saccharomyces cerevisiæ* or *Schizosaccharomyces Pombe*, indicates the absence from them of galactose and presence of the components of the "skeleton substance" according to Schmidt's nomenclature. The chlorine dioxide–acetone process yields a greater quantity of carbohydrate than the sulphite method, the difference being probably due to the presence of hemicelluloses or dextrin-like products from the skeleton substance (due to the preliminary treatment with hydrochloric acid). The nature and mode of isolation of the carbohydrates from lignin permit the conclusion that they are residues of saccharifiable components of wood, mainly cellulose. This hypothesis is supported by the observation that they can be extracted (without destruction of the lignin) by ammoniacal copper oxide solution, from which they are precipitated, mixed with a little lignin, by acid. Hydrolysis and fermentation of the carbohydrates thus obtained proves their qualitative and approximately quantitative identity with those derived by the sodium sulphite process. During the extraction with ammoniacal copper oxide, the lignin does not acquire nitrogen or suffer oxidative degradation, since the process increases the methoxyl content to the characteristic value, 15—16%, of Willstatter's lignin, which can be raised by further methylation to about 30%. The observations further indicate that "hydrochloric acid lignin" is an individual substance approximating closely to native lignin and not a condensation product of a hypothetical "pure lignin" and carbohydrate. Comparison of the hydrolytic and chlorine dioxide–sodium sulphite processes (the latter is preferred to the acetone or ammoniacal copper oxide method, since it yields purer carbohydrates) for the determination of carbohydrate associated with lignin shows that the results obtained by the first method are invariably somewhat higher than those of the second, but the differences are very small when the carbohydrate content is low. Even after very prolonged hydrolysis a small amount of carbohydrate remains with the lignin; preparations which do not show more than 0·3% of carbohydrate by the chlorine dioxide–sodium sulphite process are, however, readily obtained and are regarded as "practically free from carbohydrate." Systematic experiments are recorded on the hydrolysis of wood by hydrochloric acid according to the procedure of Willstatter and Zechmeister (A., 1913, i, 955) and Willstatter and Kalb (A., 1922, i, 989). Modifications are introduced by diminishing the period of "main hydrolysis" with hydrochloric acid (d^0 1·222) to 2 hrs. and initiating the process at a lower temperature. After "subsequent hydrolysis" with rather more dilute acid, lignin "practically free from carbohydrates" is obtained. A variant of the method consists in replacing the "subsequent hydrolysis" by extraction with ammoniacal copper oxide, which yields a carbohydrate-free lignin provided that the primary hydrolysis has extended over 2—2½ hrs. Extraction of wood by ammoniacal copper oxide alone does not yield a pure lignin. It is doubtful if the more thorough shielding of the lignin by avoidance of the secondary hydrolysis compensates for the extra difficulty caused by the alkaline extraction.

H. WREN.

True lignin. I. Acetylation of pine wood. W. FUCHS (Ber., 1928, **61**, [*B*], 948—951).—Pine meal, uniformly moistened with water, is gradually added to an ice-cold mixture of acetic anhydride and concentrated sulphuric acid. The temperature is gradually raised to 55—60°. The reaction mixture is diluted with benzene, filtered, and the product washed successively with benzene and alcohol. The yield is about 150% of the wood, whilst the original 2·7% of acetyl is increased to 41% by a single treatment; subsequent treatment increases this value only slightly. Pentosans, hexosans, etc. are almost completely absent from the acetylated wood, which consists to the extent of about 97% of lignin, cellulose, and acetic acid. The methoxyl content of the wood remains unchanged. Acetylated wood appears to consist almost exclusively of cellulose triacetate and an acetyl-lignin with about 33% of acetyl. Attempts to extract the former compound by means of solvents were unsuccessful. Treatment of the acetylated wood with chlorine and sodium sulphite affords a cellulose acetate with somewhat varying acetyl content approximating to that of cellulose triacetate; the product is sparingly and incompletely soluble in chloroform and insoluble in acetone. When hydrolysed with alcoholic potassium hydroxide it gives homogeneous, lignin-free cellulose. When the acetylated wood is treated with methyl-alcoholic hydrogen chloride under pressure, about half the lignin remains undissolved, whilst the remainder can be almost completely precipitated from the solution by addition of water.

H. WREN.

Lignin acetals. II. E. HAGGLUND and H. URBAN (Cellulosechem., 1928, **9**, 49—53; cf. A., 1927, 753; this vol., 277).—"Hydrochloric acid lignin," "phosphoric acid lignin," and "alkali lignin" all partly dissolve, forming semiacetals, after prolonged boiling with ethyl or amyl alcohol and hydrogen chloride, up to 80% of "hydrochloric acid lignin" being thus dissolved by amyl alcohol. The alcoholysis

of lignins is not dependent on a tautomeric hydroxyl group, since methylated lignins react similarly; *e.g.*, a methylated lignin formed, with amyl-alcoholic hydrogen chloride, a light brown *substance*, m. p. 70°. Experiments with carefully purified material now indicate that lignin has M = about 400 and has the composition $C_{22}H_{20}O_{7-8}$ or $C_{19}H_{11}O_2(OMe)_2(OH)_2CHO$. B. W. ANDERSON.

αβ-Dialkylhydroxylamines. R. T. MAJOR and E. E. FLECK (J. Amer. Chem. Soc., 1928, **50**, 1479—1481; cf. A., 1914, i, 1167; Neuffer and Hoffman, A., 1925, i, 891).—Alkylation of hydroxyurethane in alkaline solution with 2·1 mols. of methyl or ethyl sulphate yields the αβ-dialkyl and a little of the α-monoalkyl derivatives (cf. Jones, A., 1898, i, 174; Hecker, A., 1914, i, 256). The dialkyl derivatives are hydrolysed and decarboxylated to the corresponding αβ-dialkylhydroxylamines by refluxing with 50% alcoholic potassium hydroxide. αβ-Diethylhydroxylamine forms a constant-boiling mixture, b. p. 74°, with water. H. E. F. NOTTON.

Influence of the alcohol group of amino-acid esters on the rate of formation of 2 : 5-diketopiperazines and on the formation of guanidino-compounds by the action of guanidine on the various amino-acid esters. E. ABDERHALDEN and S. SUZUKI.—See this vol., 716.

Preparation of ethyl aminomalonate. R. LOCQUIN and V. CERCHEZ (Compt. rend., 1928, **186**, 1360—1362).—Reduction of ethyl oximinomalonate with magnesium or aluminium amalgam gives a 65% yield of *ethyl aminomalonate*, b. p. 116—118°/12 mm. The following derivatives have been prepared: *ethyl ureidomalonate*, m. p. 167°, *aminomalondiamide*, m. p. 196°, *ethyl benzamidomalonate*, m. p. 161°, and an *oxalate*, $NH_2\cdot CH(CO_2Et)_2,(CO_2H)_2$, m. p. 138°. E. A. LUNT.

Jaffe's reaction for creatinine. IV. Compound of creatinine, picric acid, and sodium hydroxide. I. GREENWALD (J. Biol. Chem., 1928, **77**, 539—546).—Addition of alcohol to the solution resulting from treatment of creatinine with picric acid and sodium hydroxide yields a precipitate, $2C_4H_7ON_3,C_6H_3O_7N_3,3NaOH,3H_2O$; treatment of the aqueous solution of this substance with basic lead acetate yields an analogous compound with lead hydroxide in place of the sodium hydroxide; on dissolution in boiling dilute acetic acid, creatinine picrate is obtained. Treatment with mineral acids causes destruction of the picric acid. The substance is not itself responsible for the red colour characteristic of Jaffé's reaction. C. R. HARINGTON.

Isolation and function of phosphocreatine. C. H. FISKE and Y. SUBBAROW (Science, 1928, **67**, 169—170).—Calcium is used instead of barium in the isolation of phosphocreatine, the product having the composition $C_4H_8O_5N_3PCa,4H_2O$, and the constitution probably $PO(OH)_2\cdot NH\cdot C(:NH)\cdot NMe\cdot CH_2\cdot CO_2H$. This is the first substance containing phosphorus attached to nitrogen to be isolated from natural sources. The second dissociation constant of phosphocreatine is about $2{\cdot}5\times10^{-5}$; one of its functions in muscle is that of neutralising a considerable part of the lactic acid formed during muscular contraction. A. A. ELDRIDGE.

Deamination of arginine. K. FELIX and H. MÜLLER (Z. physiol. Chem., 1928, **174**, 112—118).—Arginine hydrochloride when treated with rather more than the equivalent quantity of silver nitrite yields *arginine nitrite*, α^{20} +13°. Silver chloride is removed and the filtrate warmed on the water-bath. After the reaction, the slight excess of silver is removed by hydrogen sulphide, and the filtrate evaporated in a vacuum. *Argininic* [*α-hydroxy-δ-guanidinovaleric*] *acid* is obtained crystalline, decomp. 228° with previous sintering. Its aqueous solution is neutral, with $[\alpha]^{20}$ −12·5°. It forms a *picrate*, m. p. 145°, decomp. 205°; the *picrolonate* darkens at 223°, decomp. 227—228°. On boiling argininic acid with aqueous barium hydroxide, carbamide and α-hydroxy-δ-aminovaleric acid are produced. Evaporation of the original argininic acid solution at the ordinary pressure causes decomposition (loss of carbon dioxide). H. D. KAY.

Synthesis of diethyl β-methyl-αγ-dicyanoglutaconate. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, **3**, 103—105; cf. A., 1927, 345, 1059; this vol., 158).—Ethyl orthoacetate, ethyl cyanoacetate, and acetic anhydride react to form ethyl β-ethoxy-α-cyanocrotonate, m. p. 74—75° (cf. Haller, A., 1900, i, 372). This compound condenses with ethyl sodiocyanoacetate to form ethyl α-sodio-αγ-dicyano-β-methylglutaconate, which is converted by dilute acid into ethyl αγ-dicyano-β-methylglutaconate. A. MCGOOKIN.

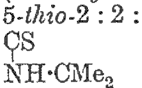
Preparation of guanidine derivatives starting from S-methylisothiocarbamide sulphate. V. PIOVANO (Gazzetta, 1928, **58**, 245—249).—*S*-Methylisothiocarbamide sulphate in boiling aqueous solution reacts with propylamine, evolving methylmercaptan and giving a 70% yield of *propylguanidine sulphate*, m. p. 220° (decomp.) [*picrate*, m. p. 177—178°; *chloroaurate*, m. p. 200° (decomp.); *chloroplatinate*, m. p. 195° (decomp.)]. With piperazine, *piperazine-guanidine sulphate*, m. p. 288—290° (decomp.), is obtained [*picrate*, m. p. 260—270° (decomp.); *chloroaurate*, m. p. 243° (decomp.); *chloroplatinate*, m. p. 265—268° (decomp.)]. E. W. WIGNALL.

Addition of ethyl sodiomalonate to aliphatic thiocarbimides. D. E. WORRALL (J. Amer. Chem. Soc., 1928, **50**, 1456—1459; cf. A., 1924, i, 208; 1925, i, 244).—The following *dicarbethoxythioacetalkylamides*, $NHR\cdot CS\cdot CH(CO_2Et)_2$, are obtained by treating ethyl sodiomalonate with alkylthiocarbimides and decomposing the enolic sodio-derivatives with acid: *methyl*, m. p. 49—50°; *ethyl*, m. p. 51—52°; *propyl*, m. p. 11°, and oily *butyl*, and the following *dicarbomethoxythioacetalkylamides* from methyl sodiomalonate: *propyl*, m. p. 42—43°; *butyl*, m. p. 62—63°, and *amyl*, m. p. 52—53°. With warm acids or alkalis these are completely hydrolysed, but with cold sodium hydroxide they give the following *sodium* salts, $NHR\cdot CS\cdot CH_2\cdot CO_2Na$, of *carboxythioacetalkylamides*: *ethyl*, decomp. 148—149°; *propyl*, decomp. 155—156°; *butyl*, decomp. 156—157°, and *amyl*, decomp. 157—158°. *Carboxythioacetbenzyl-*

amide, m. p. 95—96°, with formation of *thioacetbenzylamide*, m. p. 62—63°, is prepared similarly.
H. E. F. NOTTON.

Composition and structure of the polymeride of hydrocyanic acid. E. GRISCHKEVITSCH-TROCHIMOVSKI (Rocz. Chem., 1928, 8, 165—174).—The polymeride of hydrocyanic acid formed from 4 mols. of the latter gives on condensation with glyoxal 2 : 3-*dicyanopyrazine*, m. p. 132·5—133°. It hence follows that the tetrameride of hydrocyanic acid must be the dinitrile of diaminomaleic acid; this conclusion is further supported by the formation of 4 : 5-dicyano-1 : 2 : 3-triazole from the tetrameride and nitrous acid. R. TRUSZKOWSKI.

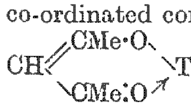
Interaction of hydrogen sulphide with amino- and imino-acid nitriles. E. GATEWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1928, 50, 1422—1427).—The course of the reaction with a given nitrile cannot be predicted, but the products are of three types: (*a*) dithiopiperazines (cf. A., 1911, i, 696, 712), (*b*) iminonitriles (from aminonitriles), and (*c*) thiodeoxyhydantoins, a new class of substances. Thus, α-amino*iso*butyronitrile or α-iminodi*iso*butyronitrile in aqueous-alcoholic ammonia yields with hydrogen sulphide a *substance*, m. p. 153—155° (*mercury* salt, m. p. 175°), provisionally regarded as 5-*thio*-2 : 2 : 4 : 4-*tetramethyl*-2-*deoxyhydantoin*,



This shows acidic and basic properties, is not desulphurised by mercuric oxide, and is hydrolysed by acids to α-amino*iso*butyric acid. α-Amino-α-methylbutyronitrile, α-amino-α-ethylbutyronitrile, and α-iminodipropionitrile are not attacked by hydrogen sulphide under these conditions. α-Aminopropionitrile yields α-iminodipropionitrile with an unstable, oily by-product, whilst iminodiacetonitrile yields mainly *iminodiacetothioamide*, m. p. 124°, with (?) 5-*thio*-2-*deoxyhydantoin*, m. p. 186°, and an amorphous *substance*.
H. E. F. NOTTON.

Action of cyanogen bromide on dimagnesium acetylene dibromide. A. S. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1927, 59, 915—919).—See A., 1927, 1051.

Chelate compounds of thallium dialkyl. R. C. MENZIES, N. V. SIDGWICK, E. F. CUTCLIFFE, and J. M. C. FOX (J.C.S., 1928, 1288—1291).—By double decomposition of thallium dialkyl halides with thallous acetylacetone and corresponding compounds or by the action of thallium dialkyl ethoxide or carbonate on the appropriate diketone, the following were prepared: *thallium dimethyl acetylacetone*, m. p. 214—215° (some decomp.); *thallium diethyl acetylacetone*; *thallium dimethyl benzoylacetone*, m. p. 128—129°; *thallium diethyl benzoylacetone*, m. p. 116—118°; *ethyl thallium diethyl acetoacetate*, m. p. 88—90°, and *thallium dimethyl salicylaldehyde*, decomp. 200°. These are crystalline compounds which can be sublimed under reduced pressure and are soluble in benzene and hexane, and thus appear to be chelate co-ordinated compounds of the type



In water, however, they form ionised solutions of alkaline reaction, in which the thallium dialkyl can be titrated quantitatively.
B. W. ANDERSON.

Complex salts of β-methyltrimethylenediamine with bivalent platinum. F. G. MANN (J.C.S., 1928, 1261—1263; cf. this vol., 157).—A solution of β-methyltrimethylenediamine hydrochloride in aqueous sodium hydroxide when refluxed with aqueous potassium chloroplatinite yielded a solution which, after treatment with sodium bromide, yielded *bis*-β-*methyltrimethylenediamineplatinous dibromide*, $[Pt\{CHMe(CH_2{\cdot}NH_2)_2\}_2]Br_2$, m. p. 266—268° (decomp.). The corresponding *di-iodide*, m. p. 263—264° (decomp.), and *dinitrate* (deflagrates) were similarly obtained, and from the di-iodide the *di*-d-*camphor*-β-*sulphonate monohydrate*, m. p. 279—281° (decomp.), [α] +15°, *di*-d-α-*bromocamphor*-π-*sulphonate*, slow decomp. 278—285°, [α] +69·2°, and *ditartrate* were prepared. The above six compounds, although highly crystalline, showed no sign of *cis-trans*-isomerism; moreover, the last three mentioned could not be resolved into optically active forms; the observed rotations were due solely to the sulphonate ions. B. W. ANDERSON.

Complex compounds of platinum and palladium with organic sulphides. E. C. FRITZMANN (Ann. inst. platine, 1926, No. 4, 55—179).—Unpublished work by Tschugaev and Ilyin is reported. The *compound* $2CMe_2(CH_2SEt)_2,2PtCl_2$, rose, changes at 114—116° to a yellow *modification* (monomeric), m. p. 218—219°. The *compound* $C(CH_2SEt)_4,PtCl_2$, decomp. 235°, when heated yields the *compound* $C(CH_2SEt)_4,2PtCl_2$, yellow, m. p. <100°. The *compound* $2(EtSHC{:}CHSEt)_2,2PtCl_2$ and a monomeric *form* are recorded. In unpublished work by Tschugaev and Ivanov, the following *compounds* are recorded: $PdCl_2,2Et_2S$, yellow, m. p. 82°; $PdBr_2,2Et_2S$, m. p. 100°; $PdI_2,2Et_2S$, m. p. 104°; $PdCl_2,(CH_2SEt)_2$, m. p. 180°; $PdBr_2,(CH_2SEt)_2$, m. p. 159°; $PdI_2,(CH_2SEt)_2$, m. p. 154°. In unpublished work by Tschugaev and Malchevski the transition from the non-conducting type $[Pt,2Et_2S,Cl_2]$ to the electrolyte $[Pt,4Et_2S]Cl_2$ is traced. Tschugaev and Vladimirov (unpublished) have shown that compounds of the type $[Pt,2R_2S,X_2]$ existing in two isomeric forms show negligible conductivity in methyl alcohol, further addition of thioether yielding $[Pt,4R_2S]Cl_2$, the two compounds being in equilibrium. CHEMICAL ABSTRACTS.

***cyclo*Pentane derivatives. Preparation of 1 : 2-dimethyl*cyclo*pentane.** G. CHAVANNE and (MLLE.) L. DE VOGEL (Bull. Soc. chim. Belg., 1928, 37, 141—152).—Magnesium methyl iodide converts *cyclo*pentanone into 1-*methyl*cyclo*pentanol*, b. p. 135·6°/760 mm., m. p. 36° (*allophanate*, m. p. 157°), dehydrated by *p*-toluenesulphonic acid to 1-*methyl*-Δ^1-cyclo*pentene*, b. p. 75·5—76°/760 mm., m. p. —127·2°, d_4^0 0·7979, n_D^{15} 1·4347. When this hydrocarbon is treated with monochlorocarbamide (cf. Detœuf, A., 1922, i, 236, 327) there are formed at least two *chlorohydrins* having b. p. about 75°/10 mm., d_4^{20} 1·1039, n_D^{20} 1·4785, and m. p. 35—37°, respectively. The mixture of chlorohydrins is converted by treatment with potassium hydroxide into

1-*methyl*-Δ^1-cyclo*pentene oxide*, b. p. 110·8—111°/760 mm., m. p. −80·5°, $d_4^{13.5}$ 0·9266, n_D^{15} 1·4311, which reacts with excess of magnesium methyl iodide to give the same stereoisomeric mixture of 1 : 2-dimethyl*cyclo*pentanols as that obtained from 2-methyl*cyclo*pentanone (van Rysselberge, A., 1926, 1238). When the theoretical quantity of the Grignard reagent is used and the reaction product is not distilled under reduced pressure the main product is 1 : 2-dimethyl*cyclo*pentene, together with a small amount of 2-methyl*cyclo*pentanone.

Catalytic reduction of 1 : 2-dimethyl*cyclo*pentene in acetic acid using platinum-black affords 1 : 2-dimethyl*cyclo*pentane, b. p. 94—99°/760 mm., d_4^{20} 0·764, n_D 1·417 (cf. van Rysselberge, *loc. cit.*).

H. BURTON.

Catalytic action of mercury and bismuth [in nitration]. J. B. MENKE (Rec. trav. chim., 1928, **47**, 668—672).—The nitration of benzene by metallic nitrates under varying conditions has been studied. When a mixture of benzene vapour and nitrogen oxides is heated in an atmosphere of mercury vapour or is passed over bismuth oxide at 400—500°, nitrobenzene and nitrophenol are formed. The formation of organo-metallic compounds which occurs when mercury is used is avoided by the second procedure, and in this case also, much less nitrobenzene is formed. Benzene is nitrated to nitrobenzene by a mixture of acetic anhydride and cupric, aluminium, ferric, cobalt, or nickel nitrate at 80°. Similar results are obtained with mercuric or mercurous nitrate, but in addition a little *o*-nitrophenol and (different) mercury compounds are obtained in these cases. When bismuth nitrate is used similar results are obtained but no metal complex compounds are formed. Thiophen is similarly nitrated by the action of aluminium nitrate and acetic anhydride at 60—65°. When acetic acid is substituted for its anhydride no nitration occurs except when the mercury or bismuth salts are used, and then only to a small extent, complex mercury compounds also being produced. Since phosphoric acid destroys its catalytic activity, bismuth cannot be used to replace mercury in the ordinary Kjeldahl or Gunning processes, nor in the oxidation of naphthalene to phthalic acid.

J. W. BAKER.

Comparative effects of the nitro-, carboxyl, and sulphonic acid groups on the hydrolysis of aryl halides. W. DAVIES and E. S. WOOD (J.C.S., 1928, 1122—1131).—The comparative activity of the chlorine atom in chlorobenzenes substituted in the 4-, 2 : 4-, and 2 : 4 : 6-positions by nitro-, carboxyl, and sulphonic acid groups, respectively, shows that the order of activation of the chlorine atom is $NO_2 > SO_3H > CO_2H$. The activity due to the nitro-group is, however, enormously (about 10^5 times) greater than that due to the other groups; the sulphinic acid group has an influence comparable with these latter. A nitro-group in the *o*-position also greatly increases the effect of a carboxyl or sulphonic acid group introduced into the *p*-position. The following compounds were prepared : *diphenylamine*-2 : 4 : 6-*trisulphonanilide*, m. p. 227° (decomp.); the *potassium* salts of chlorobenzene-2 : 4 : 6-trisulphonic acid and 1-chloro-2-nitrobenzene-4-sulphonic acid, respectively, and the *ammonium* salt of chlorobenzene-*p*-sulphinic acid.

B. W. ANDERSON.

Action of magnesium on *p*- and *m*-dibromobenzenes. J. S. SALKIND and P. V. ROGOVINA (J. Russ. Phys. Chem. Soc., 1927, **59**, 1013—1018).—An experimental refutation of older theories that only one halogen atom in an aromatic dibromo-compound reacts with magnesium in a Grignard synthesis.

m- and *p*-Dibromobenzenes were allowed to react with twice the theoretical quantity of magnesium; the products were hydrolysed, and the extent of the reaction was determined by dissolving the metal remaining and measuring the hydrogen evolved, and also by titrating the ionisable bromine. In each case, about 66—75% of the dihalogen magnesium derivative was formed.

The main product was tar, only about 23—31% of the theoretical yield of benzene being obtained.

M. ZVEGINTZOV.

Oxidation reactions. II. Oxidation of toluene with nitric acid and oxides of nitrogen in presence of oxygen. P. ASKENASY, E. ELOD, and C. TROGUS (Annalen, 1928, **461**, 109—130; cf. A., 1927, 635).—When toluene is boiled with nitric acid (*d* 1·4 ?) for 100 hrs., benzoic and *p*-nitrobenzoic acids are the main products, together with some *o*-nitrotoluene and carbon dioxide and traces of picric acid. Contrary to the statement of Fittig (Annalen, 1861, **117**, 192; **120**, 222), who probably used impure toluene, no hydroxybenzoic acids are formed. The absence of *p*-nitrotoluene is due to the comparatively ready oxidation of this substance by dilute nitric acid at a high temperature. On the other hand, *o*-nitro-toluene and -benzoic acid readily react with hydroxylamine formed during the heating process, to give *o*-toluidine and anthranilic acid, which undergo conversion into diazo-compounds in presence of nitrous acid. This would appear, at any rate, to be a source of, *e.g.*, nitrogen and phenol and thus of the picric acid actually identified.

Oxidation of toluene with nitric acid under considerable pressures (cf. Sachse, G.P. 216091) has also been investigated in detail. Oxidation proceeds in definite stages and the time interval between the beginning of reaction and the point when the toluene layer sinks to the bottom and begins to disappear with simultaneous evolution of nitric oxide has been plotted against temperature. Pressure as such has little effect on the reaction, but in so far as it leads to the attainment of a higher-boiling mixture it has a great effect. Reaction becomes explosive at temperatures above 200°. Increase in concentration of the nitric acid from 5 to 30% causes increase in yield of total products, in the amount of carbon dioxide formed, and in the nitrogen content of the products. The rate of reaction increases also, 30% acid reacting violently. A number of tables are given showing the effect of different conditions on the reactions under investigation (temperature, pressure, catalysts, etc.).

E. E. TURNER.

Arylsulphonyl chlorides. II. E. GEBAUER-FULNEGG, E. RIESZ, and S. ILSE (Monatsh., 1928, **49**, 41—46; cf. A., 1927, 139).—The action of sodium iodide on *p*-toluenesulphonyl chloride in acetone

solution yields sodium *p*-toluenesulphinate, di-*p*-tolyldisulphone (Kohler and MacDonald, A., 1899, i, 904), and di-*p*-tolyldisulphoxide (Otto and Troger, A., 1891, 718), iodine being liberated. The mechanism of formation of these compounds is discussed. The action of sodium iodide on *p*-diphenylsulphonyl chloride (obtained from the acid, which is produced in 90% yield by sulphonation with concentrated sulphuric acid at 50° in the presence of nitrobenzene as a diluent) similarly yields sodium *p*-diphenylsulphinate and di-diphenyldisulphone. J. W. Baker.

Alternating effect in carbon chains. XXV. Mechanism of aromatic side-chain substitution. XXVI. Nitration of ω-chloro- and ω-bromo-*p*-xylene. C. K. Ingold and E. Rothstein (J.C.S., 1928, 1217—1221, 1278—1280).—XXV. The side-chain bromination of nitro-*p*-xylene yields at least 76% of 3-*nitro*-p-*xylyl bromide*, m. p. 76°, showing that the reaction must proceed by preliminary attraction of potential bromine cations by electrons. The above bromide yielded the same 3-*nitro*-p-*xylyl*-ω-*trimethylammonium picrate*, m. p. 138°, as was obtained through the corresponding quaternary *chloride*, from the known 3-nitro-*p*-xylyl chloride (m. p. 48°).

XXVI. In the nitration of ω-chloro- and ω-bromo-*p*-xylene substitution occurs chiefly in the position *ortho* to the methyl group. These results are of importance in the development of the theory of anionotropy. A mixture, b. p. 120°/3 mm., of 2- and 3-*nitro*-4-*methylbenzyl ethyl ethers* was incidentally obtained during the investigation.

B. W. Anderson.

[Preparation of] styrene. T. W. Abbott and J. R. Johnson (Org. Syntheses, 1928, **8**, 84—86).

Aromatic compounds containing a *tert.*-butyl group. A. E. Tschitschibabin, S. Elgasine, and V. A. Lengold (J. Russ. Phys. Chem. Soc., 1928, **60**, 347—354).—See this vol., 404.

Production of condensed ring systems by catalytic dehydrogenation. II. Activated charcoal as reducing agent. N. D. Zelinski and M. V. Gaverdovskaja (Ber., 1928, **61**, [*B*], 1049—1053; cf. A., 1927, 47).—Triphenylcarbinol is converted by platinised charcoal at 150—180° into the labile form of triphenylmethane, m. p. 81°, and by activated charcoal at 300° into carbon dioxide and the stable variety of the hydrocarbon, m. p. 92°. Phenyldi*cyclo*hexylcarbinol, m. p. 77°, in contact with platinised charcoal affords 9-*phenylfluorene*, m. p. 145°, whereas with activated charcoal at 300° it gives *phenyldi*cyclo*hexylmethane*, b. p. 210—212°/20 mm., d_4^{20} 0·9890. Under similar conditions, diphenylmethylcarbinol yields 9-*methylfluorene*, m. p. 46°, and diphenylethane, b. p. 268—269°, d_4^{20} 0·9875, respectively, whilst diphenylethylcarbinol affords 9-*ethylfluorene*, m. p. 108°, and diphenylpropane, b. p. 278—279°/759 mm. Dimethylbenzylcarbinol is converted into *iso*butylbenzene, b. p. 170°/756 mm., d_4^{20} 0·8628, in presence of either catalyst. *Phenylmethylbenzylcarbinol*, b. p. 179°/14 mm., m. p. 51°, in contact with platinised charcoal gives 9-*methylphenanthrene*, m. p. 94°, whereas with activated charcoal it suffers reduction to αβ-*diphenylpropane*, b. p. 278°/751 mm., d_4^{20} 0·9807. Methylethylbenzylcarbinol appears to be reduced only to β-*benzylbutane*, b. p. 113—115°/11 mm., d_4^{20} 0·868; the formation of a condensed system is not observed. *tert.*-Amyl alcohol is converted into pentane, b. p. 30—30·5°, d_4^{20} 0·6281. Phenol is converted into benzene by repeated passage over activated charcoal at 300°. In general reduction of oxygenated organic compounds in presence of activated or platinised carbon occurs at notably lower temperatures than are required with other forms of carbon. H. Wren.

Synthesis of two hydrocarbons of high mol. wt., derivatives of fluorene and methane. K. Dziewoński and M. Panek (Bull. Acad. Polonaise, 1927, A, 745—751).—The action of methylal on fluorene in presence of phosphorus pentoxide in boiling chloroform solution yields 2 : 2′-*difluorylmethane*, m. p. 201—202°. *Dinitro*-2 : 2′-*difluorylmethane*, m p. 256—257°, is obtained by nitration, and oxidation by sodium dichromate in acetic acid yields 2 : 2′-*difluorenone ketone*, m. p. 297—298° [*triphenylhydrazone*, m. p. 203° (decomp.)]. Fusion of the ketone with potassium hydroxide yields at 200—210° an *acid*, $C_{27}H_{20}O_7$, m. p. 262—265°, and at 260—270° diphenyl-2 : 4′-dicarboxylic acid. The formation of the last proves the constitution of the foregoing compounds. As a by-product in the first condensation there is formed *di*(*fluorylmethylfluoryl*)*methane*, $[C_6H_4\underset{CH_2}{\bigtriangledown}C_6H_3\cdot CH_2\cdot C_6H_3\underset{CH_2}{\bigtriangledown}C_6H_3]_2CH_2$, m. p. 246—247°. This yields on oxidation *di*(*fluorenonylmethylfluorenonyl*) *ketone*, $[C_6H_4\underset{CO}{\bigtriangledown}C_6H_3\cdot CH_2\cdot C_6H_3\underset{CO}{\bigtriangledown}C_6H_3]_2CO$ m p 324—326°, which is decomposed by fusion with potassium hydroxide at 280° to give an *acid*, $C_{27}H_{20}O_7$.

R. K. Callow.

Closure of the fluorene ring in the di-α-naphthylmethane series. O. Magidson (Trans. sci. chem.-pharm. Inst., 1926, [16], 32—48; Chem. Zentr., 1928, i, 58).—See A., 1925, i, 384.

Dissociation of phenanthrene by heat in the presence of hydrogen under pressure. N. A. Orlov (J. Russ. Phys. Chem. Soc., 1927, **59**, 895—902).—See A., 1927, 1060.

Photodecomposition of triphenylmethyl. S. T. Bowden and W. J. Jones (J.C.S., 1928, 1149—1158).—The region of the visible spectrum in which triphenylmethyl shows the strongest absorption, viz., the greenish-blue (5300—4000 Å.), is the most active in effecting its decomposition, ultra-violet light having little or no effect. The first products of the photochemical change are probably triphenylmethane and phenyldiphenylenemethyl, the latter then undergoing association to diphenylbisdiphenylene-ethane. The behaviour of the triphenylmethyl radical is shown to be different from that of the triphenylmethyl ion, since the latter (in liquid sulphur dioxide) is not photochemically reactive. The slight decolorisation noticed in "solid triphenylmethyl" exposed to sunlight is thought to be due to the presence of adsorbed solvent. B. W. Anderson.

Hydrogenation of tetraphenylmethane and *p*-hydroxytetraphenylmethane under pressure. V. N. Ipatiev and B. N. Dolgov (J. Russ. Phys. Chem. Soc., 1927, **59**, 1087—1091).—See this vol., 163.

Odour and constitution among the mustard oils [thiocarbimides]. III. G. M. Dyson (Perf. Ess. Oil Rec., 1928, **19**, 171—174; cf. this vol., 283, 514).—The odours of aromatic thiocarbimides containing both halogen and methyl substituent groups together are described. The results agree with the generalisation previously described. The nature of the odour is dependent more on orientation than on the nature of the substituent group, and where chlorine and methyl groups occur together in the same compound the effect of the chlorine is more strongly marked than that of the methyl group. The following substituted phenylthiocarbimides and their odours are described: 3-*chloro*-4-*methyl*-, b. p. 274°; 4-*chloro*-3-*methyl*-, m. p. 22°; 2-*chloro*-5-*methyl*-, b. p. 269°; 5-*chloro*-2-*methyl*-, b. p. 272°; 2-*chloro*-4-*methyl*-, m. p. 23°; 4-*chloro*-2-*methyl*-, m. p. 34°; 2-*bromo*-4-*methyl*-, m. p. 18°, and 4-*bromo*-2-*methyl*-, m. p. 32°. s-*Di*-(2-*bromo*-4-*methyl*)- and s-*di*-(4-*bromo*-2-*methyl*)-*thiocarbamides*, m. p. 192° and 178°, are described. *o*-, *m*-, and *p*-Nitrophenylthiocarbimides and four of the nitrotolylthiocarbimides have been prepared. With the exception of that of *p*-nitrophenylthiocarbimide, their odours are very faint.

E. H. Sharples.

2-Methyl-5-*iso*propylanilides of some higher fatty acids. R. M. Hann and G. S. Jamieson (J. Amer. Chem. Soc., 1928, **50**, 1442—1443).—*Lauryl*-, m. p. 82—83°; *myristyl*-, m. p. 88—89°; *palmityl*-, m. p. 90—91°; *stearyl*-, m. p. 93—94°; *arachidyl*-, m. p. 81—82°, and *lignoceryl*-, m. p. 84—85°, 2-*methyl*-5-iso*propylanilides* have been prepared from the appropriate acid chlorides and cymidine.

H. E. F. Notton.

Molecular dissymmetry dependent on restriction of rotation about a single linking. Optically active benzenesulphonyl-8-nitro-1-naphthylglycine. W. H. Mills and K. A. C. Elliott (J.C.S., 1928, 1291—1302).—Benzenesulphonyl chloride reacts with 8-nitro-1-naphthylamine in pyridine, yielding 8-*nitro*-1-*benzenesulphonamidonaphthalene*, m. p. 198—199° (*dibenzenesulphonamido*-derivative, m. p. 199°), which is converted by ethyl bromoacetate in presence of sodium ethoxide into *ethyl* N-*benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate*, m. p. 173°. Hydrolysis of this with dilute acetic and sulphuric acids gives N-*benzenesulphonyl*-8-*nitro*-1-*naphthylglycine*, $NO_2{\cdot}C_{10}H_6{\cdot}N(SO_2Ph){\cdot}CH_2{\cdot}CO_2H$ (I), m. p. 214°. If the rotation of the $PhSO_2{\cdot}N{\cdot}CH_2{\cdot}CO_2H$ grouping is obstructed by the nitro-group (cf. Mills, Chem. and Ind., 1926, **45**, 884) it is probable that (I) will exist in two enantiomorphous modifications. When equivalent quantities of (I) and brucine are mixed in acetone solution *brucine* l-*benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate* ($+H_2O$), m. p. 195—196°, is formed. This salt exhibits mutarotation in chloroform solution, the average period of half change at 15·5° being 5 min. When this salt is decomposed in chloroform solution with dilute sulphuric acid, the resulting chloroform solution of the *l*-acid is strongly lævorotatory, and the time of half change at 14·9° is 17 min. A solution of the brucine *l*-acid salt in boiling methyl alcohol gives, on cooling, *brucine* d-*benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate* ($+3H_2O$), which is strongly dextrorotatory in chloroform solution, the rotation falling gradually to the final value of the brucine *l*-acid salt. If a chloroform solution of (I) is treated with a chloroform solution of brucine the initial lævorotation falls gradually to an equilibrium value. Decomposition in the usual way indicates the formation of the brucine *d*-acid salt, since the acid obtained shows dextrorotation.

In order to demonstrate that the optical activity found was not due to the asymmetric tervalent nitrogen atom, *benzenesulphonyl*-1-*naphthylglycine*, m. p. 188—189° (*ethyl* ester, m. p. 89°), was examined. The *quinine* salt of this acid exhibited no mutarotation under the conditions employed.

H. Burton.

Oxidation of arylthiolarylides. E. Gebauer-Fülnegg and E. Riesz (Monatsh., 1928, **49**, 31—40; cf. A., 1927, 1060).—4-Chloro-2-nitro-1-chlorothiolbenzene has been condensed with *o*-aminophenol, *o*- and *p*-phenylenediamines, and *as*-dimethyl-*p*-phenylenediamine, and the action of oxidising agents on the resulting chloronitrophenylthiolanilides has been investigated. Condensation with *o*-aminophenol in ether yields 4-*chloro*-2-*nitrophenylthiol*-o-*hydroxyanilide*, m. p. 143°, which, on oxidation with sodium dichromate and acetic acid, or with hydrogen peroxide, yields 4-*chloro*-2-*nitrophenyl*-o-*benzoquinonethiolimine*, $C_6H_3Cl(NO_2){\cdot}S{\cdot}N{:}C_6H_4{:}O$, m. p. 134—135°. Similarly, *p*-phenylenediamine yields *bis*-4′-*chloro*-2′-*nitrophenylthiol*-p-*phenylenediamine* (I), m. p. 212°. This is converted by various oxidising agents or by heating with acetone or acetic acid into a red *substance*, m. p. 264—270°, which by chlorination with chlorine in chloroform suspension yields 4-chloro-2-nitrobenzenesulphonyl chloride, also obtained by the direct chlorination of (I). *o*-Phenylenediamine yields *bis*-4′-*chloro*-2′-*nitrophenylthiol*-o-*phenylenediamine*, m. p. 181°, together with 2:3-diaminophenazine hydrochloride. The former, by oxidation, yields a red *substance*, m. p. 172°. *as*-Dimethyl-*p*-phenylenediamine condenses to yield p-*dimethylamino*-4′-*chloro*-2′-*nitrophenylthiolanilide*, m. p. 152°, which by oxidation with concentrated nitric acid yields 4′-*chloro*-2′-*nitrophenyl*-p-*benzoquinonethiol*-*iminedimethylimmonium nitrate*, $C_6H_3Cl(NO_2){\cdot}S{\cdot}N{:}C_6H_4{:}NMe_2{\cdot}NO_3$, m. p. 102°, from which the free *base*, m. p. 186°, is obtained by the action of alcoholic ammonia. The base is also obtained when hydrogen peroxide replaces nitric acid as the oxidising agent, the corresponding *chromate* being obtained when chromic acid is used.

J. W. Baker.

Preparation and constitution of thiocarbamides of fluorene. L. Guglialmelli, A. Novelli, C. Ruiz, and C. Anastasi (Anal. Asoc. Quím. Argentina, 1927, **15**, 337—362; cf. this vol., 629).—Fluorene derivatives are considered to show properties characteristic of 2:2′-disubstituted diphenyl derivatives, and may possess a configuration analogous to that proposed by Kaufler for diphenyl. The behaviour of 2:7-diaminofluorene as an *o*-diamine in thiocarbamide formation and the difficulty

of thiocarbamide formation by 2-amino-derivatives (*loc. cit.*) owing to steric hindrance may be explained on this basis.

By reaction with thiocarbonyl chloride in boiling toluene 2 : 7-diaminofluorene, m. p. 162°, yielded 2 : 7-*fluorylenethiocarbamide*, m. p. above 300°, for which an alternative bimolecular formula is possible, accompanied by (?) 7 : 7′-*diaminodi*-2 : 2′-*fluorylthiocarbamide*, which yielded an *azo-dye* on diazotisation and treatment with β-naphthol. Similarly 1 : 2-diaminofluorene (2 : 3-diaminofluorene, cf. Eckert and Langecker, this vol., 521) yielded 1 : 2(or 2 : 3)-*fluorylenethiocarbamide*, insoluble, m. p. above 300°; 1(or 3)-nitro-2-aminofluorene yielded 1 : 1′(or 3 : 3′)-*dinitro*-2 : 2′-*fluorylthiocarbamide*, m. p. above 330°, also prepared by reaction with carbon disulphide in presence of pyridine and iodine; 2-nitro-7-aminofluorene yielded 2 : 2′-*dinitrodi*-7 : 7′-*fluorylthiocarbamide*, m. p. above 330°. R. K. CALLOW.

Action of cuprous hydride on diazonium salts. Combined Sandmeyer–Gattermann reaction. P. NEOGI and A. K. MITRA (J.C.S., 1928, 1332—1333).—Treatment of diazo-solutions at 0° with moist cuprous hydride and halogen acid yields halogenobenzenes as the main products, together with small quantities of the corresponding hydrocarbons. Crystalline cuprous halide is formed during the reaction. From diazonium sulphates, the main products are phenols, but small amounts of hydrocarbons are formed also. H. BURTON.

Mechanism of the rearrangement of diazoaminobenzene into aminoazobenzene. II and III. N. YOKOJIMA (J. Soc. Chem. Ind. Japan, 1928, **31**, 100—108, 109—116).—II. Rearrangement of diazoaminobenzene into aminoazobenzene in the absence of aniline could not be effected by heating alone, by heating with paraffin wax, by heating the hydrochloride in either an open or a sealed tube, or by mixing diazoaminobenzene and hydrochloric acid in alcoholic solution. By the addition of aniline and hydrochloric acid in alcoholic solution, part of the diazoaminobenzene changed into aminoazobenzene, the yield increasing with the amount of aniline added.

III. The mechanism of rearrangement of diazoaminobenzene into aminoazobenzene is explained as follows. In the aniline solution, hydrochloric acid combines with diazoaminobenzene, forming a yellow salt, NPh:N·NHPh,HCl. The hydrogen chloride intensifies the basic property of the amino-group and accelerates the separation of the diazo-group from it. Aminoazobenzene is formed by the direct attack of the separated diazo-compound on the *p*-position of the aniline nucleus. S. OKA.

Spectrochemical studies of hydroxyazo-compounds. VI. T. UEMURA and S. TABEI (Bull. Chem. Soc. Japan, 1928, **3**, 105—107; cf. A., 1927, 1124).—The absorption curves of azobenzene and its *p*-amino- and *p*-acetamido-derivatives show that the auxochromic effect of the amino-group is diminished by acetylation. The two absorption bands of *m*-acetamido-*o*-hydroxyazobenzene are due to the hydroxyl group alone. A. MCGOOKIN.

[Free] acyl radicals. J. LORENZO (Anal. Fís. Quím., 1928, **26**, 98—117).—An account of work already abstracted on the decomposition of acetyl-, phenylacetyl-, and diphenylacetyl-azotriphenylmethane (Wieland and others, A., 1927, 237). The m. p. 137—138° is recorded for acetyltriphenylmethane. R. K. CALLOW.

Manufacture of halogen-substituted tertiary aromatic amines. I. G. FARBENIND. A.-G.—See B., 1928, 441.

New quaternary ammonium compounds from halogen-substituted tertiary aromatic amines. I. G. FARBENIND. A.-G.—See B., 1928, 361.

Manufacture of 2 : 5 : 6-trichloro-*m*-toluidine-4-sulphonic acid. I. G. FARBENIND. A.-G.—See B., 1928, 440.

Azo-dyes soluble in non-aqueous solvents. C. E. MAY and H. HUNT.—See B., 1928, 398.

Action of nitric acid on phenol in dilute aqueous solution. I. Mechanism of nitration of phenol. II. A. V. KARTASCHOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 819—832, 833—845).—I. The action of dilute nitric acid on phenol was investigated under different conditions to discover the factors which determine respectively the oxidation and nitration effects. Nitric acid of d <1·060 (9% HNO_3) does not give any dinitrophenols, so acids of d 1·045, 1·030, 1·020, 1·015, and 1·010 (*i.e.*, 8·13%, 5·5%, 3·7%, 2·8%, and 1·9% HNO_3) were used. Acid of d 1·010, even in large excess and on boiling, had no effect. With more concentrated acids, on boiling, violent oxidation took place, with formation of tar and separation of carbon. Increased acid concentration lowered the initial reaction temperature, with a consequent diminution of the oxidation and an increase in the nitration reactions. Excess of nitric acid has a much more marked effect on the lowering of the initial reaction temperature than its concentration. Easily oxidised impurities in the phenol, such as pyrocatechol, benzaldehyde, formaldehyde, and lævulose, have a similar effect, and, further, strongly catalyse the oxidation reaction at the expense of the nitration.

II. A mechanism for the action of dilute nitric acid on phenol is suggested and tested. The initial reaction is oxidation, reducing the nitric acid to nitrous acid, which forms nitrosophenol, which, in turn, is oxidised to nitrophenol. By testing various reaction mixtures of phenol and nitric acid with Liebermann's reagent, blue and green colorations are obtained, indicating various quantities of nitrosophenol. Addition of free nitrous acid or nitrosophenol catalyses the reaction. Nitrosophenol itself is easily oxidised by nitric acid in the cold to nitrophenol, which, itself, is incapable of oxidation, any further reaction being one of nitration. M. ZVEGINTZOV.

Halogenated *o*-anisidines. M. KOHN and R. KRAMER (Monatsh., 1928, **49**, 146—159).—Bromination of 4-chloro-*o*-anisidine (Reverdin and Eckhard, A., 1900, i, 28) with bromine in acetic acid solution yields 4-*chloro*-3 : 5-*dibromo*-o-*anisidine*, m. p. 113°, from which by removal of the amino-group by diazotisation and subsequent demethylation are obtained, successively, 4-chloro-3 : 5-dibromoanisole (Kohn and Domotor, A., 1927, 51) and 4-chloro-

3 : 5-dibromophenol (*benzoate*, m. p. 132°). Hence no wandering of the *p*-chlorine atom into the *ortho*-position occurs as in the case of the corresponding bromo-compound (Kohn and Karlin, A., 1927, 1182). 4-Chloro-3 : 5-dibromo-2 : 6-dinitroanisole (obtained by nitration of 4-chloro-3 : 5-dibromoanisole with a mixture of sulphuric and fuming nitric acids) when heated with pyridine is converted into the *N*-methylpyridinium salt of 4-chloro-3 : 5-dibromo-2 : 6-dinitrophenol. 4-Chloro-2 : 6-dinitroanisole is similarly demethylated to the corresponding phenol. Nitration of the *acetyl* derivative of 4-chloro-3 : 5-dibromo-*o*-anisidine yields the 6-*nitro*-compound, decomp. 215°, which by hydrolysis yields 4-*chloro*-3 : 5-*dibromo*-6-*nitro*-o-*anisidine*, m. p. 82°. Demethylation of 2 : 4-dichloro-6-nitroanisole (Hugounenq, A., 1890, 240) with hydrobromic acid yields 2 : 4-*dichloro*-6-*nitrophenol*, m. p. 124°, whilst by reduction with tin and hydrochloric acid is obtained the oily 2 : 4-*dichloro*-o-*anisidine* (*acetyl* derivative, m. p. 72°). This acetyl derivative is nitrated by a mixture of concentrated sulphuric acid and fuming nitric acid to 2 : 4-*dichloro*-3 : 5-*dinitro*-o-*acetanisidide*, m. p. 219°, which is hydrolysed to 2 : 4-*dichloro*-3 : 5-*dinitro*-o-*anisidine*, m. p. 135°. Bromination of 2 : 4-dichloro-*o*-anisidine with bromine in acetic acid yields a *substance*, m. p. 169°, from which by heating with water 2 : 4-*dichloro*-3 : 5-*dibromo*-o-*anisidine*, m. p. 83°, is obtained. J. W. Baker.

Bromophenols. XXXI. 3 : 4 : 5-Trichlorophenol. M. Kohn and R. Kramer (Monatsh., 1928, 49, 161—168).—When chloro-*o*-anisidine is treated in acetic acid solution with 4 mols. of dry chlorine diluted with carbon dioxide, a reddish-black, tarry product is obtained. This contains 3 : 4 : 5-*trichloroanisidine*, for when it is treated with alcohol and sulphuric acid, followed by sodium nitrite, the mixture yields on steam distillation and fractionation of the ethereal extract of the distillate 3 : 4 : 5-*trichloroanisole*, m. p. 63°, b. p. 256—261°, identified by hydrolysis by hydrobromic and acetic acids to 3 : 4 : 5-trichlorophenol, m. p. 91°, b. p. 271—277°/746 mm. (benzoyl derivative, m. p. 120°; cf. Holleman, A., 1921, i, 102). This when treated with bromine yields 3 : 4 : 5-*trichloro*-2 : 6-*dibromophenol*, m. p. 180°, *d* 2·554; the crystallographic constants, $a : b : c = 2{\cdot}0625 : 1 : 3{\cdot}6962$, $\beta = 96° 13' 20''$, closely resemble those of *m*-chlorotetrabromo- and 3 : 5-dichlorotribromo-phenol [K. Hlawatsch]. The trichlorodibromophenol is oxidised by nitric acid to 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, stable at 240°.

3 : 4 : 5-Trichloroanisole is nitrated by nitric and sulphuric acids to 3 : 4 : 5-*trichloro*-2 : 6-*dinitroanisole*, m. p. 95—96°. E. W. Wignall.

Bromophenols. XXXIII. Chloro- and bromo-pyrogallol ethers. M. Kohn and (Frl.) E. Gurewitsch (Monatsh., 1928, 49, 173—186).—4-Bromopyrogallol trimethyl ether (cf. Kohn and Grün, A., 1926, 284) is now obtained by the action of phosphorus pentabromide. 4 : 6-Dibromo-5-nitropyrogallol trimethyl ether, m. p. 114° (cf. Kohn and Grün, *loc. cit.*), is also obtained by the action of bromine on 5-nitropyrogallol trimethyl ether (Will, A., 1888, 457). By the action of phosphorus pentachloride, pyrogallol trimethyl ether yields the 4-chloro-derivative, b. p. 252—256°/748·5 mm. (cf. Grabe and Suter, A., 1905, i, 703); this is nitrated in acetic acid by fuming nitric acid to 4-*chloro*-5 : 6-*dinitropyrogallol trimethyl ether*, m. p. 116—118°. The last is also prepared, m. p. 118—119°, from the 4-*chloro*-5-*nitro*-derivative, m. p. 77—78°, obtained by passing chlorine into the molten 5-nitro-derivative, which is further chlorinated, in presence of iron, to 4 : 6-*dichloro*-5-*nitropyrogallol trimethyl ether*, m. p. 103—104°. The 4-chloro-derivative is converted by bromine into 4-*chloro*-5 : 6-*dibromopyrogallol trimethyl ether*, m. p. 57—58°.

Pyrogallol dimethyl ether is chlorinated by sulphuryl chloride to 4-*chloropyrogallol* 1 : 3-*dimethyl ether*, b. p. 270—275°/754 mm., 175°/18 mm.; this is identified by methylation and by nitration of the resultant trimethyl ether. This shows that the *p*-directive effect of the free hydroxyl group (cf. Peratoner and Genco, A., 1895, i, 342) is counteracted by the stronger influence of the methoxyl groups. Chlorination in carbon tetrachloride solution by rather more than 3 mols. of chlorine, diluted with carbon dioxide, yields *trichloropyrogallol* 1 : 3-*dimethyl ether*, m. p. 121—122° (*benzoyl* derivative, m. p. 102°); 4 : 5-dibromopyrogallol 1 : 3-dimethyl ether (Kohn and Grün, *loc. cit.*) is similarly converted into 4-*chloro*-5 : 6-*dibromopyrogallol* 1 : 3-*dimethyl ether* (*benzoyl* derivative, m. p. 119—120°). If only 2 mols. of chlorine are employed, 4 : 5-*dichloropyrogallol* 1 : 3-*dimethyl ether*, m. p. 103—104° (*benzoyl* derivative, m. p. 122—123°), can be obtained; the product is brominated to the 6-*bromo*-derivative, m. p. 117—118°.

Tribromopyrogallol dimethyl ether (Kohn and Grün) is oxidised by chromic acid to 2 : 6-dibromo-3 : 5-dimethoxybenzoquinone (cf. Will, *loc. cit.*); the trichloro-compound gives similarly the 2 : 6-dichloro-analogue (cf. Gräbe and Hess, A., 1905, i, 698). The yields are poor. E. W. Wignall.

Condensation of chloral with substituted phenols. F. D. Chattaway and F. Calvet (J.C.S., 1928, 1088—1094).—A republication of work already abstracted (this vol., 632). The following is new: anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (6-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin) on bromination in acetic acid yielded the 4-*bromo*-compound (7-*bromo*-dioxin derivative), m. p. 171—173° (*acetyl* derivative, m. p. 231—232·5°). R. K. Callow.

Nitration of aromatic thiocyanates and selenocyanates. F. Challenger and A. T. Peters (J.C.S., 1928, 1364—1375).—Nitration of *o*-tolyl thiocyanate at 3—8° with nitric and sulphuric acids yields mainly 5-*nitro*-o-*tolyl thiocyanate*, m. p. 117·5—118·5°, together with 4-*nitro*-o-*tolyl thiocyanate*, m. p. 70—71°, both of which have been prepared by the action of cuprous and potassium thiocyanate on the requisite nitrotoluenediazonium sulphate. Nitration of *phenyl selenocyanate*, b. p. 134°/10 mm., with nitric acid (*d* 1·5) gives chiefly *p*-nitrophenyl selenocyanate, m. p. 141° (cf. Bauer, A., 1913, i, 263), together with a small amount of the *o*-nitro-derivative, m. p. 143°. When *p*-tolyl selenocyanate is treated with nitric and sulphuric acids, 2-*nitro*-p-*tolueneseleninic acid* (I),

m. p. 151°, and *di-2-nitro-p-tolyl diselenide* (II), m. p. 69°, are obtained, but nitric acid (*d* 1·5) at −10° gives 2-*nitro*- (III), m. p. 69—70°, and 3-*nitro-p-tolyl selenocyanate*, m. p. 150°. Reduction of (I) with zinc and hydrochloric acid furnishes (II), also obtained by the action of potassium hydroxide on (III). Similarly, *p*-chlorophenyl selenocyanate yields either a mixture of di-*p*-chlorophenyl diselenide and *p*-chlorobenzeneseleninic acid (IV), or a mixture of 4-*chloro-2-nitrophenyl selenocyanate*, m. p. 127°, and (IV). *p*-Bromophenyl selenocyanate gives *p*-bromobenzeneseleninic acid. p-*Dithiocyanobenzene*, m. p. 106°, prepared by the Sandmeyer reaction from *p*-aminophenyl thiocyanate, is nitrated to a *nitrodithiocyanobenzene*, m. p. 143—144°, which is obtained together with 4-*bromo*-, m. p. 83°, and 4-*chloro-3-nitrophenyl thiocyanate*, m. p. 63°, by the action of cuprous and potassium thiocyanates on diazotised 4-bromo- and chloro-3-nitroaniline. Treatment of p-*thiocyanoselenocyanobenzene*, m. p. 109—110°, with nitric and sulphuric acids affords p-*thiocyanobenzeneseleninic acid*, m. p. 154°. *p*-Thiocyanoacetanilide on nitration furnishes 2-*nitro-4-thiocyanoacetanilide*, m. p. 138—139°, together with 2-*nitro-4-thiocyanoaniline*, m. p. 113°. When treated with alcoholic alkali, this last substance gives di-3-nitro-4-aminophenyl disulphide (?), m. p. 169°. 2-*Nitro-4-thiocyanophenyl selenocyanate* has m. p. 147°.

Selenocyanates containing an *o*-nitro-group give strong purple colorations with alcoholic potassium hydroxide (cf. Bauer, *loc. cit.*). H. BURTON.

Varying valency of platinum with respect to mercaptanic radicals. VII. (SIR) P. C. RAY, K. C. BOSE-RAY, and S. RAY-CHAUDHURY (J. Indian Chem. Soc., 1928, 5, 139—147).—Benzyl sulphide and platinic chloride react in alcohol solution, forming the compound $PtCl_2,2(CH_2Ph)_2S$ (I), m. p. 159°, together with the *substance* $PtCl_3,2(CH_2Ph)_2S$ (II), m. p. 183° (decomp.). If an excess of platinic chloride is used, a *complex*, $Pt_2Cl_5,4(CH_2Ph)_2S$, m. p. 158°, is first obtained which is separable into (I) and (II) by crystallisation from alcohol. The action of several bases on (II) has been examined. Ammonia, benzylamine, and ethylenediamine give tetrammineplatinous dichloride, tetrabenzylammineplatinous dichloride, and the compound $PtCl_2,2C_2H_4(NH_2)_2$, respectively (cf. this vol., 44). Aniline yields $PtCl_2,2NH_2Ph$, whilst dimethylaniline gives (I). Piperidine affords the *substances* $PtCl_3,2C_5H_{11}N,(CH_2Ph)_2S$, m. p. 172°, and $PtCl_2,3C_5H_{11}N$, whilst pyridine gives the compounds $PtCl_2,4C_5H_5N$ (III) and $Pt_2Cl_7,4C_5H_5N$ (*loc. cit.*). The action of pyridine on (I) is to form (III) together with the compound $PtCl_2,2C_5H_5N$ (IV). The effect of heat on (III) is to furnish (IV). It is concluded that (II) is best represented by the formula $[2(CH_2Ph)_2S,PtCl_2]Cl$. H. BURTON.

Detection of β-naphthol. K. REBER (Schweiz. Apoth.-Ztg., 1927, 65, 589; Chem. Zentr., 1928, i, 384).—1 C.c. of a mixture of 25% hydrochloric acid (1 part) and 25% nitric acid (3 parts) is heated at 55—60° with 5 c.c. of aqueous β-naphthol; a carmine-red coloration, extractable with amyl alcohol, soon appears. 1 Part in 6000 parts can be detected. The red coloration produced when aqueous β-naphthol (5 c.c.), 0·03% aqueous sodium nitrite (2 c.c.), and dilute sulphuric acid (1 drop) are warmed together is not extractable with amyl alcohol.

A. A. ELDRIDGE.

Action of chlorosulphonic acid on phenols. V. [Naphthols.] J. POLLAK, E. GEBAUER-FULNEGG, and E. BLUMENSTOCK-HALWARD (Monatsh., 1928, 49, 187—202).—[With E. PETERTIL.] Chlorosulphonic acid acts on α-naphthol at the ordinary temperature (cf. B.P. 186,515; B., 1922, 933), and from the reaction mixture crystalline α-naphthol-2-sulphonic acid separates. With excess of chlorosulphonic acid, crystals of *α-naphthol-2 : 4-disulphonyl chloride*, m. p. 149°, separate (*disulphonanilide*, m. p. 228°). By the prolonged action of chlorosulphonic acid, a new *α-naphthol-*[2 : 4 : 7(?)]-*trisulphonyl chloride*, m. p. 172°, [$+0{\cdot}5C_6H_6$, 160°], is obtained (cf. Claus and Mielcke, A., 1886, 716); this on alkaline hydrolysis loses one and on acid hydrolysis two chlorosulphonyl groups, yielding probably α-naphthol-7-sulphonic acid. The corresponding *α-naphtholtrisulphonanilide* has m. p. 240° (decomp.).

α-Naphthol with chlorosulphonic acid yields at 100° α-naphthol-4-sulphonic acid; at 160°, a black product, or, with excess of the reagent, a resinous product from which a yellow *trichloronaphthalenesulphonyl chloride*, m. p. 214°, is isolated.

[With K. WINTER.] The action of chlorosulphonic acid on β-naphthol at the ordinary temperature does not yield a monosulphonyl chloride, but only β-naphthol-1-sulphonic acid; on keeping, a mixture of disulphonyl chlorides (see below) is obtained. With 1 mol. of chlorosulphonic acid in tetrachloroethane at 130°, β-naphthol yields β-naphthol-6-sulphonic acid. Excess of chlorosulphonic acid yields a mixture of two *β-naphtholdisulphonyl chlorides*, m. p. 111° (I) and 177° (II), respectively (see following abstract). These are almost insoluble in water; on treatment with phosphorus pentachloride in a sealed tube only octachloronaphthalene is obtained. With aniline the corresponding *disulphonanilides*, m. p., from (I) 191°, from (II) 231°, are obtained.

When β-naphthol is heated with excess of chlorosulphonic acid at 130—140°, a product is obtained from a carbon disulphide solution of which *β-naphthol-3 : 6 : 8-trisulphonyl chloride*, m. p. 196°, crystallises. The formulation is based on the preparation of the substance by the action of chlorosulphonic acid on β-naphthol-3 : 6-disulphonic acid, or -3 : 6 : 8-trisulphonic acid; the above-mentioned disulphonyl chlorides also yield the trisulphonyl chloride. The last gives the -3 : 6 : 8-*trisulphonanilide*, m. p. 140—145°, which can also be prepared, m. p. 152—155°, from O-*carbethoxy-β-naphthol-3 : 6 : 8-trisulphonyl chloride*.

β-Naphthol with great excess of chlorosulphonic acid at 150—160° yields a resinous product from which a substance, m. p. 120—122°, containing chlorine but not sulphur (? a dichloronaphthalene), and a product, m. p. 135—140°, containing sulphur, probably a naphthaquinone derivative, were isolated.

E. W. WIGNALL.

Constitution of the β-naphtholdisulphonyl chlorides. J. POLLAK and E. BLUMENSTOCK-

HALWARD [with A. SCHLESINGER, V. WEINMAYR, and K. WINTER] (Monatsh., 1928, **49**, 202—212).—The two β-naphtholdisulphonyl chlorides, m. p. 111° (I) and 177° (II) (see preceding abstract) are investigated. The former is obtained by the action of chlorosulphonic acid on β-naphthol-6-sulphonic acid, and also from the 1-acid in the cold; it is therefore β-*naphthol*-1 : 6-*disulphonyl chloride*. It was thought that (II) might be obtainable from β-naphthol-8-sulphonic acid; the latter, however, yields the 6 : 8-*disulphonyl chloride* (III), m. p. 161—162°, from which the 6 : 8-*disulphonanilide*, m. p. 195°, is obtained. The constitution of the latter is established by preparing, from β-naphthol-6 : 8-disulphonic acid, the *potassium* salt of the *O*-carbethoxy-derivative, and thence, by the action of phosphorus pentachloride, O - *carbethoxy* - β - *naphthol*-6 : 8-*disulphonyl chloride*, m. p. 131°; this yielded the corresponding 6 : 8-*disulphonanilide*, m. p. 178°, and, by hydrolysis, the same disulphonanilide (m. p. 196°) as obtained from (III).

Similarly, from β-naphthol-3 : 6-disulphonic acid, the O-*carbethoxy*-β-*naphthol*-3 : 6-*disulphonyl chloride*, m. p. 125°, and the corresponding *disulphonanilide*, m. p., crude, 153—163°, have been prepared, and, from the latter, β-*naphthol*-3 : 6-*disulphonanilide*, m. p. 202°. This is not identical with the anilide prepared from (II), as might be expected from the conversion of (II) into β-naphthol-3 : 6 : 8-trisulphonyl chloride: it is, however, noteworthy that the latter is also obtained from (I), a process involving migration of the chlorosulphonyl group from the 1-position. It is therefore suggested that (II) may be β-*naphthol*-1 : 8-*disulphonyl chloride*. This formula is excluded by the rule of Armstrong and Wynne (Proc. C.S., 1890, 130), to which there are, however, exceptions (cf. Dressel and Kothe, A., 1894, i, 378).

The " β-naphthol-1-sulphonyl chloride " described by Anschutz and Maxim (A., 1918, i, 426), prepared by way of the acetyl derivative, does not form a sulphonylide. It was therefore thought that the substance described might actually have the chlorosulphonyl group in a different position. Accordingly, the *acetyl* derivatives of β-naphthol-6- and -8-sulphonic acids were prepared and converted by phosphorus pentachloride in chloroform into O-*acetyl*-β-*naphthol*-6- and -8-*sulphonyl chlorides*, m. p. 103° and 129°, respectively. Since these differ in m. p. from the compound described by Anschutz, and since in their case it is impossible to hydrolyse the acetyl group without affecting the chlorosulphonyl group, there is no reason to question the Anschutz formula. It is suggested, however, that the conditions for the formation of a sulphonylide cause a migration of the chlorosulphonyl group before condensation can occur.

O-*Acetyl*-β-*naphthol*-6-*sulphonanilide*, m. p. 95°, is hydrolysed to β-naphthol-6-sulphonanilide, m. p. 161° (cf., G.P. 278,091). Since the m. p. did not agree with that given by Zincke and Dereser (A., 1918, i, 220), viz., 100—105°, the substance was prepared by their method; it was found to contain 2 mols. of water, and after heating, or recrystallisation from benzene, to melt at 160—161°; but since recrystallisation of the anhydrous substance from an aqueous solvent failed to yield the low-melting variety, the latter must be regarded as a labile form.

O-*Acetyl*-β-*naphthol*-8-*sulphonanilide* yields β-*naphthol*-8-*sulphonanilide*, m. p. 195°, also obtained by the hydrolysis of the *anilide* derived from O-*carbethoxy*-β-*naphthol*-8-*sulphonyl chloride*, m. p. 118°.

E. W. WIGNALL.

Dehydrogenation of sitosterol. L. SCHMID and M. ZENTNER (Monatsh., 1928, **49**, 92—97).—A *hydrocarbon*, m. p. 245—247·5°, has been isolated from the mother-liquor of the product, m. p. 325°, obtained by the dehydrogenation of sitosterol with palladised charcoal (A., 1927, 661). A mixed-m. p. determination with the hydrocarbon chrysene, m. p. 246—248°, obtained in a similar manner from cholesterol (Diels and Gadke, *ibid.*, 241) gives no conclusive evidence, but on complete nitration it yields a *tetranitro*-derivative, decomp. 200°, which, although it contains the correct percentage of nitrogen, is not identical with tetranitrochrysene, m. p. above 300°. Crystallographic investigation (by MARCHET) of the hydrocarbon and of chrysene confirms the non-identity of the two substances. J. W. BAKER.

Plant sterols. L. SCHMID and G. BILOWITSKI (Monatsh., 1928, **49**, 98—106).—Phytosterols isolated from various sources have been separated into stigmasterol and sitosterol by the action of bromine on their acetates. Thus the phytosterol, m. p. 132°, isolated from *Radix bardanæ* is acetylated with acetic anhydride, and addition of bromine in ether and acetic acid solution to the acetyl derivative precipitates the sparingly soluble tetrabromostigmasterol acetate identical with the corresponding derivative prepared from stigmasterol isolated from the calabar bean. The filtrate, after reduction with sodium amalgam, debromination by heating with zinc dust, and repetition of the process to remove all the stigmasterol, yields the sitosteryl acetate (*benzoate*, m. p. 144°) identical with a genuine specimen and yielding identical derivatives. By similar methods the sterols isolated from *Ficus carica* and *Ulmis campestris* are separated into stigmasterol and sitosterol. From the latter plant was also isolated a *substance*, m. p. 240°, which was not investigated. J. W. BAKER.

Transformation of benzoylmethylcarbinol into acetylphenylcarbinol by sulphuric acid and under the conditions of alcoholic fermentation. (MLLE.) E. M. KOTCHERGINE (Bull. Soc. chim., 1928, [iv], **43**, 573—575).—Benzoylmethylcarbinol (obtained in 81% yield by the action of alcoholic potassium acetate on *phenyl α-bromoethyl ketone*, b. p. 134—135°/18 mm., 1·454) when heated with alcoholic sulphuric acid at 120—125° for 8 hrs. is converted into acetylphenylcarbinol; the same transformation takes place when the ketone is added to an aqueous solution of raffinose fermenting with brewer's yeast, some *s*-phenylmethylethylene glycol being also produced in the latter case. Accordingly the acetylphenylcarbinol obtained by Neuberg (A., 1921, i, 480) is regarded as a transformation product of the primarily formed benzoylmethylcarbinol. R. BRIGHTMAN.

Syntheses with diazomethane. III. *o*-Nitrophenylethylene oxide and the compounds derived

therefrom. F. ARNDT, B. EISTERT, and W. PARTALE (Ber., 1928, 61, [*B*], 1107—1118).—The nitroso-compound obtained by the action of formic acid on "nitraldin" (A., 1927, 360) yields small amounts of *N*-hydroxyisatin, m. p. 201° (decomp.), under the influence of alkali hydroxide. It is identified as o-*nitrosobenzoylcarbinol*, since it is smoothly reduced by hydrazine carbonate to o-*aminobenzoylcarbinol*, m. p. 98° (N-*acetyl* derivative, m. p. 141°; *diacetyl* compound; *dibenzoyl* derivative, m. p. 167—168°; *phenylhydrazone*, m. p. 198°), which can be diazotised and is readily transformed by warm alkali hydroxide into indoxyl. Since nitraldin itself does not give reactions characteristic of the hydroxyl or carbonyl groups it must have the constitution

$$NO_2\cdot C_6H_4\cdot CH{<}\begin{array}{l}O\\ |\\ CH_2\end{array} \quad\text{or}\quad C_6H_4{<}\begin{array}{l}NO{-}O\\ \;{>}O\;\;|\\ CH{-}CH_2\end{array}$$

; the latter structure involves an apparent, constitutive co-operation of the nitro-group which, however, is illusory, since other aldehydes are converted by diazomethane into ethylene oxides instead of the expected methyl ketones. "Nitraldin" is therefore regarded as o-*nitrophenylethylene oxide*. It is unaffected by phenylcarbimide at 130—140°, whilst profound decomposition ensues at higher temperatures. Reduction with tin and glacial acetic acid gives anthranil in small amount. Traces of indole are obtained by the action of hydrazine hydrate in boiling alcoholic solution. The action of hydrogen chloride on *o*-nitrophenylethylene oxide in pyridine affords o-*nitrophenylethylene chlorohydrin*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2Cl$, m. p. 60—61°, b. p. 170°/17 mm. (decomp.), re-converted by sodium hydroxide into the parent substance and transformed by benzoyl chloride and alkali hydroxide into the *benzoyl* derivative, m. p. 87—88°. The corresponding *acetyl* compound, b. p. 186—188°/15 mm., m. p. 69—70°, is obtained by addition of *o*-nitrophenylethylene oxide to a solution of acetyl chloride in pyridine. ω-Chloro-*o*-nitroacetophenone, m. p. 66—67°, is obtained by oxidising *o*-nitrophenylethylene chlorohydrin with potassium dichromate and sulphuric acid. o-*Aminophenylethylene chlorohydrin*, m. p. 86—87°, prepared by reduction of the nitro-compound by stannous chloride and concentrated hydrochloric acid, appears to be converted by successive treatment with cold dilute acid and sodium hydroxide into a polymeric *o*-aminophenylethylene oxide, whereas if the treatment is followed by steam distillation it gives indole and, probably, polymerised indoles. *o*-Nitrophenylethylene oxide is converted by acetic anhydride containing anhydrous ferric chloride into o-*nitroso*-ω-*acetoxyacetophenone*, m. p. 104°.

o-*Nitrophenylacetone*, m. p. 26—27° [*semicarbazone*, m. p. 213—214° (decomp.)], and *o*-nitroacetophenone are identified among the by-products of the action of diazomethane on *o*-nitrobenzaldehyde. The former compound is prepared by the action of diazomethane on *o*-nitrophenylacetaldehyde in ether or by that of boiling dilute sulphuric acid on *ethyl* α-o-*nitrophenylacetoacetate*, m. p. 76—77°. o-*Nitrophenylacetylacetone*, m. p. 62—63°, is converted by hydrazine hydrate into 5-o-*nitrophenyl*-3-*methylpyrazole*, m. p. 120—121°. H. WREN.

Glycol from α-methyl-*n*-butaldehyde and benzaldehyde. A. FRANKE and R. STERN (Monatsh., 1928, 49, 21—26).—α-Methyl-*n*-butaldehyde condenses with benzaldehyde (2 mols.) in the presence of alcoholic potassium hydroxide, and the resulting aldol is reduced by the excess of benzaldehyde to yield γ-*phenyl*-β-*methyl*-β-*ethylpropane*-αγ-*diol*, b. p. 188—190°/17 mm. (*diacetate*, b. p. 189—191°/20 mm.). In two cases the cyclic *benzylidene ether*, $\begin{array}{l}CHPh\cdot CMeEt\cdot CH_2\\ O{-}{-}CHPh{-}{-}O\end{array}$ b. p. 214—215°/13 mm., m. p. 80—81°, was also obtained. The same compound is synthesised by the action of benzaldehyde on the glycol in the presence of concentrated hydrochloric acid. By oxidation the glycol is converted into phenyl *sec*.-butyl ketone, and when it is distilled in steam with 14% sulphuric acid it yields ωω-*methylethylstyrene*, b. p. 205—206° (*dibromide*, m. p. 57°), together with the *methylene ether*, b. p. 150°/13 mm., which is formed in accordance with the scheme: $CHPh(OH)\cdot CMeEt\cdot CH_2\cdot OH$ (I) $\longrightarrow$ $CHPh(OH)\cdot CHMeEt + CH_2O$; (I) $+ CH_2O \longrightarrow$ $\begin{array}{l}CHPh\cdot CMeEt\cdot CH_2 + H_2O\\ O{-}{-}{-}CH_2{-}{-}{-}O\end{array}$ (cf. Reik, A, 1898, i, 245). The same ether is synthesised by the action of a 40% formaldehyde solution on the glycol in the presence of an equal quantity of hydrochloric acid, *d* 1·19. J. W. BAKER.

Reaction between magnesium compounds and ethylene oxides. I. I. RIBAS (Anal. Fís. Quím., 1928, 26, 122—132).—α-*Methoxypropylene* βγ-*oxide*, b. p. 110°/751 mm., is prepared by treatment of α-chloro-γ-methoxy*iso*propyl alcohol (Fourneau and Ribas, A., 1927, 131) with sodium hydroxide solution. With magnesium phenyl bromide the oxide yielded α-*bromo*-γ-*methoxy*iso*propyl alcohol*, b. p. 90°/15 mm., and 25% of the theoretical yield of γ-*methoxy*-α-*phenyl*iso*propyl alcohol*, b. p. 135—140°/15 mm. (*phenylurethane*, m. p. 56°; *allophanate*, m. p. 150—151°). The same compound was obtained by the action of magnesium phenyl bromide (2 mols.) on α-chloro-γ-methoxy*iso*propyl alcohol, and the constitution assigned to it was proved by its formation by the condensation of α-phenylpropylene βγ-oxide with methyl alcohol in the presence of sulphuric acid (cf. Fourneau and Ribas, *loc. cit.*).

R. K. CALLOW.

Constitution of *iso*campholic acid. J. VON BRAUN and A. HEYMONS (Ber., 1928, 61, [*B*], 1089—1092).—*iso*Campholic acid is isolated with some difficulty from the campholic acid obtained with it by fusion of camphor with potassium hydroxide as the *ethylamide*, m. p. 41—42°. *Campholethylamide*, b. p. 160°/20 mm., m. p. 88°, is converted by an excess of phosphorus pentachloride into the corresponding imido-chloride, from which the original material is smoothly regenerated. *iso*Campholethylamide under similar conditions yields *dichloro*iso*campholethylamide*. $C_{12}H_{21}ONCl_2$, m. p. 73—77°, b. p. 125—127°/0·2 mm. (intermediate *imidochloride*, $C_{12}H_{20}NCl_3$, b. p. 145—150°/15 mm.). Hydrolysis of the ethylamide affords the unsaturated monochloro-*acid*, $C_{10}H_{15}O_2Cl$, b. p. 125°/0·5 mm. *iso*Campholic acid behaves therefore

as a compound containing two hydrogen atoms attached to the α-carbon atom and hence has the constitution

H. WREN.

cycloPentylalkylacetic acids and β-cyclopentylethylalkylacetic acids, and their action towards *B. lepræ*. XI. G. R. YOHE and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 1503—1508; cf. following abstract).—As in the series previously examined, the toxicity of these acids towards *B. lepræ* reaches a maximum with the members containing 16—18 carbon atoms. It is shown that with *cyclo*alkyl-alkylacetic acids of equal mol. wt. or having equally long side-chains, there is no marked difference in bactericidal power between *cyclo*hexyl, *cyclo*pentyl, and *cyclo*pentenyl derivatives. The following were successively prepared from *cyclo*pentyl bromide by standard methods: β-cyclo*pentylethyl alcohol*, b. p. 96·5—97°/24 mm., n_D^{20} 1·4577, d_4^{20} 0·9180, after purification through β-cyclo*pentylethyl bromide*, b. p. 75—77°/19 mm., n_D^{20} 1·4863, d_4^{20} 1·2860, and *acetate*; δ-cyclo*pentylbutyl alcohol*, b. p. 88—92°/2 mm., n_D^{20} 1·4613, d_4^{20} 0·9033; δ-cyclo*pentylbutyl bromide*, b. p. 110—111°/17 mm., n_D^{20} 1·4820, d_4^{20} 1·1872, from which δ-cyclo*pentylvaleronitrile*, b. p. 124—126·5°/17 mm., 1·4542, d_4^{20} 0·8887, and δ-cyclo*pentylvaleric acid*, b. p. 124—128°/2 mm., n_D^{20} 1·4594, d_4^{20} 0·9752, are obtained; *ethyl* δ-cyclo*pentylbutylmalonate*, b. p. 154—160°/2·2 mm., n_D^{20} 1·4493, d_4^{20} 0·9934; δ-cyclo*pentylbutylmalonic acid*, m. p. 121—124°; and ε-cyclo*pentylhexoic acid*, b. p. 133—138°/1·8 mm., m. p. 33—33·5°, n_D^{35} 1·4549, d_4^{35} 0·9518. The following *ethyl* cyclo*pentyl-alkylmalonates* (b. p., n_D^{20}, and d_4^{20} being given in this order) were obtained in 50—60% of the theoretical yields from ethyl *cyclo*pentylmalonate: -n-*heptyl*-, 143—146°/1 mm., 1·4548, 0·9749; -n-*octyl*-, 160—165°/1 mm., 1·4553, 0·9659; -n-*nonyl*-, 152—155°/0·6 mm., 1·4567, 0·9617; -n-*decyl*-, 169—171°/1 mm., 1·4571, 0·9560; -n-*undecyl*-, 186—189°/1 mm., 1·4580, 0·9522; the following *ethyl* β-cyclo*pentylethyl-alkyl-malonates* from *ethyl* β-cyclo*pentylethylmalonate*, b. p. 125°/2 mm., n_D^{0} 1·4478, d_4^{20} 1·0082: -*ethyl*-, 126—129°/1·9 mm., 1·4511, 0·9924; -n-*propyl*-, 134—135°/1·7 mm., 1·4510, 0·9873; -n-*butyl*-, 136—140°/1·8 mm., 1·4523, 0·9783; -n-*amyl*-, 148—150°/1·1 mm., 1·4526, 0·9688; -n-*hexyl*- 157—162°/1 mm., 1·4531, 0·9624; -n-*heptyl*-, 172—174°/2 mm., 1·4541, 0·9563, and -n-*octyl*-, 182—184°/1·2 mm., 1·4548, 0·9524. From these are prepared the following *alkyl* derivatives of β-cyclo*pentylethylmalonic acid*, m. p. 126·5°: *ethyl*, m. p. 141—143°; n-*propyl*, m. p. 137—138°; n-*butyl*, m. p. 139—140·5°; n-*amyl*, m. p. 124—127°, and n-*hexyl*, m. p. 129·5—130°; the following cyclo*pentyl-alkyl-acetic acids*: -n-*heptyl*-, 155—160°/1·4 mm., 1·4594, 0·9312; -n-*octyl*-, 166—169°/2 mm., 1·4609, 0·9279; -n-*nonyl*-, b. p. 177—178·5°/1·4 mm., m. p. 37—37·5°; -n-*decyl*-, b. p. 189—190·5°/1·7 mm., m. p. 34·5—36°; -n-*undecyl*-, b. p. 193—197°/1·3 mm., m. p. 43·5—45·5°; and the following *alkyl* derivatives of β-cyclo*pentylethylacetic acid*, b. p. 115—118°/2·4 mm., n_D^{20} 1·4575, d_4^{20} 0·9849: *ethyl*, 122—124·5°/1·3 mm., 1·4590, 0·9602; n-*propyl*, 130—132°/1·9 mm., 1·4595, 0·9533; n-*butyl*, 136—137°/1 mm., 1·4608, 0·9435; n-*amyl*, 150—154°/1·9 mm., 1·4610, 0·9360; n-*hexyl*, 157—161°/1·9 mm., 1·4616, 0·9303; n-*heptyl*, 167—169°/2 mm., 1·4621, 0·9252, and n-*octyl*, 173—176°/1·5 mm., 1·4629, 0·9210.

H. E. F. NOTTON.

cycloHexyl- and cyclohexylmethyl-alkylacetic acids and their action towards *B. lepræ*. X. R. ADAMS, W. M. STANLEY, and H. A. STEARNS (J. Amer. Chem. Soc., 1928, 50, 1475—1481).—These have been prepared by methods previously described. As in other series, the acids containing 16—18 carbon atoms show a maximum toxicity towards *B. lepræ*. Comparison with the isomeric *cyclo*hexylalkyl-alkylacetic acids previously obtained (A., 1926, 1136, 1137; this vol., 62) indicates that the bactericidal power is almost independent of the position of the carboxyl group in the hydrocarbon chain. The b. p., n^{25}, and d_4^{25}, respectively, are recorded for the following: (*a*) *ethyl* cyclo*hexyl-alkyl-malonates*: -n-*amyl*-, 121—125°/2 mm., 1·4553, 0·9850; -n-*hexyl*-, 126—130°/2 mm., 1·4559, 0·9755; -n-*heptyl*-, 135—139°/2 mm., 1·4562, 0·9685; -n-*octyl*-, 144—148°/2 mm., 1·4564, 0·9638; -n-*nonyl*-, 149—154°/2 mm., 1·4567, 0·9574; -n-*decyl*-, 157—161°/2 mm., 1·4570, 0·9540; -n-*undecyl*-, 170—175°/2 mm., 1·4574, 0·9532, and -n-*dodecyl*-, 185—189°/2 mm., 1·4589, 0·9466; (*b*) cyclo*hexyl-alkyl-acetic acids*: -n-*amyl*-, 136—139°/3 mm., 1·4640, 0·9544; -n-*hexyl*-, 145—149°/3 mm., 1·4641, 0·9449; -n-*heptyl*-, 148—152°/2 mm., 1·4641, 0·9350; -n-*octyl*-, 158—161°/2 mm., 1·4642, 0·9298; -n-*nonyl*-, 167—171°/3 mm., 1·4645, 0·9245; -n-*decyl*-, 165—169°/2 mm., 1·4649, 0·9224; -n-*undecyl*-, 173—177°/2 mm., 1·4650, 0·9166; -n-*dodecyl*-, 187—191°/2 mm., 1·4653, 0·9129; (*c*) cyclo*hexylmethyl-alkyl-acetic acids*: -*ethyl*-, 131—132°/2 mm., 1·4623, 0·9814; -n-*propyl*- 141—143°/4·5 mm., 1·4628, 0·9720; -n-*butyl*-, 133—136°/3 mm., 1·4620, 0·9564; -n-*amyl*-, 139—142°/2 mm., 1·4630, 0·9516; -n-*hexyl*-, 174—175°/3 mm., 1·4627, 0·9448; -n-*heptyl*-, 202—204°/3 mm., 1·4632, 0·9393, and -n-*octyl*-, 186—190°/4 mm., 1·4640, 0·9331. The b. p., n_D^{20}, and d_4^{20} of the following *ethyl* cyclo*hexylmethyl-alkyl-malonates* are: -*ethyl*-, 143—145°/4·5 mm., 1·4542, 1·0104; -n-*propyl*-, 154—155°/3 mm., 1·4529, 1·0062; -n-*butyl*-, 157—159°/4·5 mm., 1·4548, 0·9910; -n-*amyl*-, 159—160°/4 mm., 1·4558, 0·9853; -n-*hexyl*-, 160—163°/2·5 mm., 1·4544, 0·9721; -n-*heptyl*-, 183—185°/5 mm., 1·4560, 0·9679; -n-*octyl*-, 178—181°/3 mm., 1·4570, 0·9612. The m. p. of the following cyclo*hexylmethyl-alkyl-malonic acids* are: -*ethyl*-, 127·5—130°; -n-*propyl*-, 145—147°; -n-*butyl*-, 132—134°, and -n-*amyl*-, 132—135°.

H. E. F. NOTTON.

β-Oxidation. I. Conjugation of benzoic and phenylacetic acids formed as end-products from the oxidation of phenyl-substituted fatty acids. A. J. QUICK (J. Biol. Chem., 1928, 77, 581—593).—Previous workers on the subject of β-oxidation have confined themselves to determining hippuric and phenaceturic acids in the urine as indications of the benzoic and phenylacetic acids excreted. Quantitative results cannot be so obtained, since, in the dog, about 70% of the benzoic and 30% of the phenylacetic acid excreted is in conjugation with glycuronic acid. By determining the sum of the hippuric and benzoylglycuronic acids, or of the phenaceturic and phenylacetylglycuronic acids excreted, it is shown

that cinnamic and phenylpropionic acids give rise exclusively to benzoic acid, whilst phenyl*iso*crotonic and phenylbutyric acids give exclusively phenylacetic acid, so that, in these cases at least, oxidation must occur entirely in the β-position.

C. R. Harington.

Oxidation of nitrophenylcyanoacetates. II. A. Fairbourne and H. R. Fawson (J.C.S., 1928, 1077—1080).—The compounds described previously (A., 1927, 244) as ethyl chloro- and bromo-2 : 4-dinitrophenylcyanoacetates are now shown to be *ethyl* 2 : 4-*dinitrophenylchlorocyanoacetate* (I), and *ethyl* 2 : 4-*dinitrophenylbromocyanoacetate* (II) since the action of warm 0·5*N*-sodium hydroxide solution is to yield a product which, when subsequently oxidised with chromic anhydride in acetic acid and treated with phenylhydrazine, gives ethyl 2 : 4-dinitrobenzoylformate phenylhydrazone, m. p. 170°. The action of chromic anhydride in acetic acid or of concentrated sulphuric acid at 80° on (I) and (II) is to form *ethyl* 2 : 4-*dinitrophenylchloro-*, m. p. 121°, and *ethyl* 2 : 4-*dinitrophenylbromo-malonamates*, m. p. 157°, and not intermediate hydroxycyanoacetates (cf. *loc. cit.*), whilst concentrated sulphuric acid at 120—130° furnishes 2 : 4-*dinitrophenylchloro-*, m. p. 134°, and 2 : 4-*dinitrophenylbromo-acetamides*, m. p. 160°, respectively. When the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate is boiled either alone, or with iodine or (I) in presence of alcohol, there is produced in each case *ethyl* αβ-*bis*-2 : 4-*dinitrophenyl*-αβ-*dicyanosuccinate*, m. p. 156°. *Ethyl* 2 : 4 : 6-*trinitrophenylchlorocyanoacetate*, m. p. 118°, is formed by the action of chlorine on the corresponding cyanoacetate in sodium hydroxide solution.

Oxidation of ethyl *p*-nitrophenylcyanoacetate with hydrogen peroxide or 20% nitric acid affords ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate (cf. *loc. cit.*), whilst concentrated nitric acid oxidises ethyl 2 : 4-dinitrophenylcyanoacetate to ethyl 2 : 4-dinitrobenzoylformate.

H. Burton.

Condensation of α-cyanocinnamic acid and potassium cyanide. M. Henze (J. pr. Chem., 1928, [ii], **119**, 157—172).—To elucidate the course of the reaction between chloroacetic acid, potassium cyanide, and benzaldehyde (Henze, A., 1926, i, 961; cf. Lapworth, J.C.S., 1922, **121**, 1699), the interaction of α-cyanocinnamic acid, which is regarded as an intermediate product in the above reaction, and potassium cyanide in the presence of 1 mol. of sodium hydroxide has been studied. It is assumed that (I) is first formed and this adds on α-cyanocinnamic acid

$$\underset{\text{(I.)}}{\mathrm{CHPh(CN){\cdot}CK(CN){\cdot}CO_2H}} \qquad \text{(II.)}\ \begin{array}{l}\mathrm{CHPh(CN){\cdot}\overset{*}{C}H(CN){\cdot}CO_2H}\\ \mathrm{PhCH{:}\overset{\dagger}{C}(CN){\cdot}CO_2H}\end{array}$$

(Michael reaction) with the production of (II); carbon dioxide is then eliminated from either the carbon atoms marked * or † with the formation of the compound $C_{20}H_{17}O_2N_3$ (previously assumed to be $C_{20}H_{15}O_2N_3$) existing in two forms and now shown to be *αγδ-tricyano-βδ-diphenylvaleric acid*. Elimination of carbon dioxide from each of these acids by heating at 170° or preferably with zinc acetate and acetic acid led to a mixture of the two *αγδ-tricyano-βδ-diphenyl*-n-*butanes*, m. p. 228° and 183°, respectively. Hydrolysis of the mixture of nitriles with aqueous baryta gave *γ-carboxy-βδ-diphenyladipic acid*, m. p. 220° (decomp.) (*methyl* ester, m. p. 61°), and a small quantity of an *isomeride*, m. p. 195—196° (decomp.). Heating the acid m. p. 220° at 220—230° led to 3-*keto*-2 : 5-*diphenyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 158° (*oxime*, m. p. 183°; *methyl* ester, m. p. 99°), which gave 2 : 5-*diphenyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 119—120°, on reduction with amalgamated zinc and hydrochloric acid. The constitution of the latter was established by oxidation with alkaline permanganate, when γ-benzoyl-β-phenylbutyric acid, m. p. 152°, was obtained. A compound, $C_{19}H_{15}N_3$, the exact constitution of which was not elucidated, was separated from the initial condensation product between α-cyanocinnamic acid and potassium cyanide.

I. Vogel.

Asymmetric hydrolysis of esters by enzymes. I. R. Willstätter, R. Kuhn, and E. Bamann (Ber., 1928, **61**, [*B*], 886—895; cf. Rona and Ammon, A., 1927, 377).—Partial hydrolysis of ethyl *r*-mandelate by liver esterase leads to a mixture of (+)-mandelic acid and ethyl (—)-mandelate. The immediate hypothesis that the (+)-ester is more rapidly hydrolysed than the (—)-ester by the asymmetric enzyme is directly contradicted by experiments with the individual esters. The ratio of the rates with which the (+)- and (—)-ester in the racemic mixture are hydrolysed is considered to depend on (1) the ratio of the affinities of the esterase to the (+)- and (—)-esters and (2) the relative rates of decomposition of the compounds of the enzyme with the respective esters. Separate measurements of these factors show that, whereas the (—)-ester by itself is more rapidly hydrolysed than the (+)-ester, the latter substance is favoured during hydrolysis of the mixed esters, since its affinity towards esterase is 32 times that of its antipode, whereas the ratio of rates of hydrolysis is only 1·6 : 1 in favour of the compound of esterase and (—)-ester. Within the limits of the experiments (p_H 6·0—8·0) the optical activation of ethyl *r*-mandelate is independent of the hydrogen-ion concentration and of the quantity of enzyme used (1 : 3); the optical activity of the mandelic acid depends only on the extent to which hydrolysis has proceeded. From the linear relationship of the reaction it is to be expected that $[\alpha]_D$ for mandelic acid would remain constant for a considerable period in the early stages of the change and sink only when the greater part of the (+)-ester has been hydrolysed. An immediate rise in the $[\alpha]_D$ graph is not immediately explicable. The highest recorded value is $[\alpha]_D$ +70°, corresponding with the hydrolysis of 2·6 mols. of (+)-ester per mol. of (—)-ester in the initial stages.

H. Wren.

Condensation of formaldehyde with arylides of 2 : 3-hydroxynaphthoic acid. K. Brass and P. Sommer (Ber., 1928, **61**, [*B*], 993—1002).—Stabilisation of "Naphthol AS" baths by formaldehyde is shown to be due to the production of methylenedinaphthols. 2-Hydroxynaphthalene-3-carboxylic acid is converted by formaldehyde in alkaline solution into *methylenebis*-2-*hydroxynaphthalene*-3-*carboxylic*

acid, decomp. above 280° (*diacetyl* derivative. unchanged below 295—300°). The constitution of the acid is established by reductive fission to 2-*hydroxy-1-methylnaphthalene*-3-*carboxylic acid*, m. p. 231° [*acetyl* derivative, m. p. 184—184·5° (cf. Fries and Hübner, A., 1906, i, 190)]. Methylenebis-2-hydroxynaphthalene-3-carboxylic acid is also produced when condensation is effected in glacial acetic acid, but the product is not completely identical with that formed in an alkaline medium. 2-Hydroxynaphthalene-3-carboxyanilide, formaldehyde, and sodium hydroxide afford *methylenebis-2-hydroxynaphthalene-3-carboxyanilide*, m. p. 263·5°; the anilide is obtained in small yield when condensation occurs in glacial acetic acid in the presence of concentrated sulphuric acid, but is then accompanied by a preponderating amount of a *product*, $C_{35}H_{26}O_4N_2$, m. p. about 284° after softening and darkening at 240°, which is insoluble in alkali hydroxide and cannot be acetylated. The *mono-* and *di-sodium* derivatives of the anilide are described. Coupling with benzenediazonium chloride is accompanied by loss of the methylene group and formation of benzeneazo-2-hydroxynaphthalene-3-carboxyanilide identical with that derived from "Naphthol AS." *Methylenebis-2-acetoxynaphthalene-3-carboxyanilide*, m. p. 252°, and 2-*acetoxynaphthalene*-3-*carboxyanilide*, m. p. 160°, are described. Condensation of the necessary naphthalide with formaldehyde in alkaline solution affords *methylenebis-2-hydroxynaphthalenecarboxy-α-naphthalide*, m. p. 268—269°, and the corresponding -β-*naphthalide*, m. p. 287—288°.

H. WREN.

Lichen substances. V. Synthesis of orsellinic acid. A. SONN (Ber., 1928, **61**, [*B*], 926—927).—Ethyl methylhydroresorcylate, prepared by the condensation of ethyl crotonate with ethyl acetoacetate in the presence of sodium ethoxide, is converted by bromine in glacial acetic acid into *ethyl dibromo-orsellinate*, m. p. 143—144°, which is transformed by hydrogen in the presence of palladium and calcium carbonate into ethyl orsellinate, m. p. 132°; hydrolysis of the ester by cold sodium hydroxide affords orsellinic acid identical with the natural product.

H. WREN.

Gallodeoxycholic acid. S. YONEMURA (J. Biochem. Japan, 1927, **8**, 79—84).—Gallodeoxycholic acid (from chicken bile) is identical with chenodeoxycholic acid (goose) and anthropodeoxycholic acid (man). The acid has $[\alpha]_D^{18}$ −33·04° in alcohol; oxidation yields gallodeoxybiliobanic acid, $[\alpha]_D^{18}$ −45·83° in alcohol, whilst reduction affords gallocholanic acid $[\alpha]_D^{18}$ −39·26° in alcohol.

CHEMICAL ABSTRACTS.

5-Bromo-2 : 4-dimethoxybenzoylacrylic acid and its esters. G. P. RICE (J. Amer. Chem. Soc., 1928, **50**, 1481—1491).—Bromination of methyl 5-bromo-2 : 4-dimethoxybenzoylacrylate (this vol., 290) in chloroform affords a mixture (I), m. p. 127°, of the racemic *forms*, m. p. 150·5° (70—80% of crude product), and, m. p. 149—150°, of methyl αβ-5-*tribromo*-2 : 4-*dimethoxybenzoylpropionate*. These are converted by methyl-alcoholic potassium acetate into yellow *methyl* α(or β)-5-*dibromo*-2 : 4-*dimethoxybenzoylacrylate* (II), m. p. 139°, and a colourless *stereoisomeride*, m. p. 164°, which is formed from the yellow derivative in sunlight. The mixture (I) and sodium methoxide probably yield first methyl 5-bromo-2 : 4-dimethoxybenzoylpropiolate, from which, according to the conditions, (*a*) *methyl* 5-*bromo*-α-2 : 4-*trimethoxybenzoylacrylate* (III), m. p. 157° (colourless *stereoisomeride*, m. p. 113°), the *dibromide*, m. p. 97°, of which is converted by methyl alcohol into β-5-*dibromo*-α-2 : 4-*trimethoxybenzoylacrylate* (IV), m. p. 123°; (*b*) *methyl* 5-*bromo*-αα-2 : 4-*tetramethoxybenzoylpropionate*, m. p. 128°, which is brominated to the ester (IV) and hydrolysed by cold hydrochloric acid to yellow *methyl* 5-*bromo*-α-*hydroxy*-2 : 4-*dimethoxybenzoylacrylate*, m. p. 168° (*copper* derivative), or (*c*) 5-*bromo*-αα-2 : 4-*tetramethoxybenzoylpropionic acid*, m. p. 152°, is formed together with a little 5-*bromo*-α-*hydroxy*-2 : 4-*dimethoxybenzoylacrylic acid* (V), m. p. 179° (*dibromide*, m. p. 170°), by addition and hydrolysis. Bromine titrations with the acid (V) and its methyl ester indicate that the enolic formulæ attributed to them are correct. The product (I) is converted by aqueous-alcoholic potassium hydroxide into a mixture containing the ester (III), the acid (V), and 5-*bromo*-α-2 : 4-*trimethoxybenzoylacrylic acid* (VI), m. p. 202°, whilst (II) or (III) give a mixture of the tetramethoxy-acid and (V). This indicates that (II) is an intermediate in the formation of the benzoylpropiolic ester from (I).

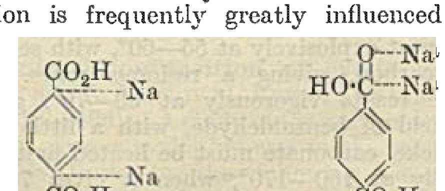
A similar series of products has been prepared from ethyl 5-bromo-2 : 4-dimethoxybenzoylacrylate. Bromination gives a mixture of the racemic *forms*, m. p. 141° (80% of crude product) and m. p. 160—161°, and *ethyl* αβ-5-*tribromo*-2 : 4-*dimethoxybenzoylpropionate*, which give with potassium acetate mixtures of yellow *ethyl* α(or β)-5-*dibromo*-2 : 4-*dimethoxybenzoylacrylate*, m. p. 144°, and a colourless *isomeride*, m. p. 114°; and with sodium ethoxide, the acid (V), *ethyl* 5-*bromo*-2 : 4-*dimethoxy*-α-*ethoxybenzoylacrylate*, m. p. 162°, and *ethyl* 5-*bromo*-2 : 4-*dimethoxy*-αα-*diethoxybenzoylpropionate*, m. p. 132°, but not, as with the methyl ester, the acid corresponding with the last. The ethoxy-esters are hydrolysed with difficulty by cold hydrochloric acid to *ethyl* 5-*bromo*-α-*hydroxy*-2 : 4-*dimethoxybenzoylacrylate*, m. p. 143° (*copper* derivative). αβ-5-*Tribromo*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 184·5° (also $+CHCl_3$, m. p. 177·5°), is less reactive than its esters, being converted by sodium acetate or methoxide into yellow, m. p. 200°, and colourless, m. p. 178—180°, *isomerides* of α(or β)-5-*dibromo*-2 : 4-*dimethoxybenzoylacrylic acid*, and by potassium hydroxide in methyl alcohol into the acid (VI) and in ethyl alcohol into 5-*bromo*-2 : 4-*dimethoxy*-α-*ethoxybenzoylacrylic acid*, m. p. 197°, a little of the acid (V) being formed in each case.

H. E. F. NOTTON.

Hydrogenation by sodium amalgam. R. WILLSTATTER, F. SEITZ, and E. BUMM (Ber., 1928, **61**, [*B*], 871—886).—Comparison of the effects produced by the reduction of organic compounds by sodium amalgam and water and by hydrogen activated by catalysts shows that the action of the amalgam cannot be ascribed to the evolution of nascent hydrogen which is subsequently added to the organic molecule. It is more probable that sodium is primarily added at the double linking yielding a product which is decomposed by water. Pure sodium amalgam is

conveniently prepared in quantity by heating mercury which has been twice distilled in a vacuum at 120° in a porcelain dish covered by a glass plate bored with two holes; through one orifice a rapid current of nitrogen is passed, whereas the other serves for the introduction of the sodium which is freed from the film of oxide and cut into suitable pieces under ether in a glass mortar with a glass knife. Such amalgam becomes oxidised superficially to only a very slight extent and the slight skin of oxide may be removed by passage through filter-paper in which a few holes have been pierced by a platinum needle. This amalgam differs widely in properties from that prepared in an iron vessel or a Hessian crucible. It does not react at a measurable rate with conductivity water prepared according to the directions of Baker and Parker (J.C.S., 1913, **103**, 2060). The action between the amalgam and water is accelerated by impurities present in either. Among readily amalgamated metals, copper, silver, magnesium, zinc, aluminium, tin, and lead act in order of increasing readiness; a negative catalyst could not be found. The "utilisation coefficient" for the hydrogen is determined by allowing reduction of the organic substance by sodium amalgam to occur in an atmosphere of nitrogen; the total hydrogen produced is determined by titration of the sodium hydroxide produced, whilst the evolved hydrogen is swept forward by the nitrogen through phosphoric oxide tubes and over red-hot copper oxide; the water formed is absorbed by phosphoric oxide and weighed. Oxygen must be completely excluded, since if present in sufficient amount it entirely prevents evolution of hydrogen. An indirect method of determination is based on the perhydration of the product with hydrogen and spongy platinum or on the more rapid measurement of bromine absorption.

Pure sodium amalgam reacts very rapidly and with very high utilisation of hydrogen on many aromatic and olefinic compounds. Whereas, according to von Baeyer, terephthalic acid is reduced exclusively to $\Delta^{2:5}$-dihydroterephthalic acid which cannot be hydrogenated further, the pure amalgam under otherwise similar conditions transforms terephthalic acid in cold solution into Δ^2-tetrahydrophthalic acid. Contrary to the views of von Baeyer and the postulates of Thiele's theory, the Δ^2-tetrahydro-acid is very much more readily hydrogenated than the corresponding Δ^1-acid; in cold solution at p_H 9—10·5 it gives the hexahydro-acid in 60—70% yield with 90% utilisation of hydrogen. The observed differences are possibly explained by the differing rates of reduction and consequent variation in the periods during which the acids are subjected to the isomerising influence of the alkali hydroxide. The course of the reduction is frequently greatly influenced by the

(I.)  (II.)

alkalinity of the medium. Thus at p_H 12—15 and above, terephthalic acid suffers hydrogenation in the nucleus. If, however, the solution is buffered with phosphate or, preferably, sodium aminoacetate to p_H 9—9·8, *p*-toluic acid is obtained in 50% yield. It is suggested that primary addition of the sodium takes place according to (I) or (II) and that the partial affinities of the terephthalic acid molecule exercise their effects in various parts of the molecule in differing degree, according to the conditions of experiment and the reaction of the solution.

H. WREN.

Separation of phthalic and homophthalic acids. H. G. POOLE (J.C.S., 1928, 1378—1379).—When a mixture of sodium phthalate and homophthalate is treated in dilute solution with copper sulphate, *copper homophthalate* (solubility in water 1 in 5000 at 25°) is precipitated. The reaction must be performed in the cold, otherwise a basic copper phthalate is also formed. Decomposition of the copper salt with boiling hydrochloric acid gives pure homophthalic acid, m. p. 181°.

H. BURTON.

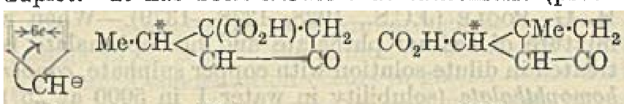
Photobromination of ethyl *m*-nitrobenzylidenemalonate. II. J. C. GHOSH, K. P. BASU, and S. C. BHATTACHARYYA (J. Indian Chem. Soc., 1928, **5**, 183—190; cf. this vol., 176).—The addition of bromine to ethyl *m*-nitrobenzylidenemalonate under the influence of light in carbon disulphide solution is analogous to the reaction in carbon tetrachloride (*loc. cit.*). The equilibrium constant is approximately proportional to the square root of the intensity of incident light. The velocity in the initial stage is proportional to the concentration of bromine and increases considerably with increase in concentration of the ester. The values for the equilibrium constant and velocity are about seven times as great in carbon tetrachloride as in carbon disulphide.

H. BURTON.

Monoacyl derivatives of quinic acid. II. K. JOSEPHSON (Ber., 1928, **61**, [*B*], 911—917; cf. this vol., 63; Karrer and Link, *ibid.*, 63).—Opening of the lactone ring of 4-benzoylquinide without simultaneous removal of the benzoyl group cannot readily be effected by alkali hydroxide. If, however, 4-benzoyl*iso*propylidenequinide dissolved in aqueous acetone at 55° is treated with hydrochloric acid, 4-*benzoylquinic acid*, m. p. 188° (corr.), $[\alpha]^{20}$ −3·9° in alcohol (also *monohydrate*), is easily prepared. Acyl migration does not occur during the change, since the product is re-converted by acetone containing a little hydrogen chloride into 4-benzoyl*iso*propylidenequinide. 4-Cinnamoyl*iso*propylidenequinide is similarly converted by hydrogen chloride in aqueous acetone into 4-*cinnamoylquinide*, m. p. 165° (corr.), $[\alpha]^{20}_D$ −18·3° in acetone, and 4-*cinnamoylquinic acid*, m. p. 188° (corr.), +5·9° in 95% alcohol. Hydrolysis of 4-cinnamoylquinide is also effected by sodium hydroxide in aqueous acetone, but the process is less advantageous. *iso*Propylidenequinide is transformed by acetic anhydride in the presence of pyridine at the ordinary temperature into 4-*acetyl*iso*propylidenequinide*, m. p. 109°, $[\alpha]^{?}_{\text{Hg yellow}}$ −4·4° in chloroform, and by ethyl chloroformate in pyridine at 0° into 4-*carbethoxy*iso*propylidenequinide*, m. p. 108°, $[\alpha]^{20}_{\text{Hg yellow}}$ −4·7° in chloroform.

H. WREN.

Tautomerism of *cyclo*pentadienes. I. Derivatives of methyl*cyclo*pentadiene. F. R. Goss and C. K. Ingold (J.C.S., 1928, 1268—1278).—The formation of a sextuple valency group (cf. Bamberger, A., 1891, 1090) in the *cyclo*pentadiene series must be accompanied by appropriation of the electrons of one hydrogen atom, thus explaining why stable metallic derivatives of *cyclo*pentadiene, indene, and fluorene can be formed, and also the stability of the anion (I). In (I) each arrow denotes a contributing duplet. It has been shown that tautomeric (proto-



(I.) (II.) (III.)

tropic) mobility exists in the indene series (Ingold and Piggott, J.C.S., 1923, **123**, 1469), and it is now demonstrated that the acids represented as (II) and (III) are identical, thus indicating that the nuclear hydrogen atom * is mobile in either or both compounds. Methyl malonate and methyl αα'-dibromo-β-methylglutarate condense in presence of sodium methoxide to form *methyl sodio-5-methyl*-dicyclo*penten*(or cyclo*pentadien*)-3-*ol*-1 : 2 : 4 - *tricarboxylate* (IV), m. p. 270° (decomp.) (*hydroxy*-ester, b. p. 180°/1 mm.; *ethyl* ester), which on long treatment with 30% methyl-alcoholic potassium hydroxide gives *dimethyl potassium potassio-5-methyl*dicyclo*pentenoltricarboxylate*. Decomposition of this salt with acid affords *methyl hydrogen 5-methyl*dicyclo*penten*(or cyclo*pentadien*)-3-*ol*-1 : 2(or 1 : 4)-*dicarboxylate*, which when boiled with hydrochloric acid yields 5-*methyl*dicyclo*pentan*(or cyclo*penten*)-3-*one*-1-*carboxylic acid* (II), m. p. 60° [*oxime*, m. p. 216° (decomp.)]. *Methyl 5-methyl*-2(or 4)-*ethyl*dicyclo*pentan*(or cyclo*penten*)-3-*one*-1 : 2 : 4-*tricarboxylate*, b. p. 210°/6 mm., is obtained by the action of ethyl iodide on (IV).

Methyl 3-methyl- Δ^2-*cyclo*propene-1 : 2-dicarboxylate and methyl sodiocyanoacetate condense to form *methyl* 3-*methyl*-1 : 2-*dicarbomethoxy*cyclo*propane*-3-*cyanoacetate*, b. p. 200°/20 mm., which when treated with sodium methoxide forms *methyl 3-amino*-1-*methyl*dicyclo*pentene*(or cyclo*pentadiene*)-2 : 4 : 5-*tricarboxylate*, isolated in two forms, *A*, stable, m. p. 130° (decomp.), and *B*, m. p. 186° (decomp.). On keeping, *B* is converted into *A*. When *A* is hydrolysed with cold 3*N*-methyl-alcoholic potassium hydroxide a yellow *potassium potassio*-salt is produced which on acidification yields *dimethyl hydrogen 3-amino*-1-*methyl*dicyclo*pentene*(or cyclo*pentadiene*)-2 : 4 : 5-*tricarboxylate*, m. p. 226° (decomp.). Hydrolysis of *A* with boiling hydrochloric acid yields 1-*methyl*dicyclo*pentan*(or cyclo*penten*)-3-*one*-5-*carboxylic acid* (III), m. p. 60°. Oxidation of *A* with potassium persulphate and a small amount of silver oxide in 2*N*-sulphuric acid gives oxalic and fumaric acids, whilst hydrogen peroxide and a small amount of ferrous sulphate yields α- and β-methylglutaconic, and β-acetylacrylic acids.

Ethyl 3-*amino*-1-*methyl*dicyclo*pentene* (or cyclo*pentadiene*)-2 : 4 : 5-*tricarboxylate* (V), m. p. 107° [*sodio*-derivative (VI); *diethyl hydrogen* ester, m. p. 199° (decomp.)], is described also. Treatment of (VI) with methyl and ethyl iodides yields the corresponding *methyl*, m. p. 113°, and *ethyl*, m. p. 118°, derivatives of (V). Hydrolysis of (V) with boiling hydrochloric acid gives (III). H. Burton.

Polycyclic structures in relation to their homocyclic unsaturated isomerides. IX. Effect of the *spirocyclo*pentane grouping on the five-carbon intra-annular tautomeric nucleus. F. R. Goss (J.C.S., 1928, 1306—1310).—Oxidation of 5-*cyclo*pentane*spirodicyclo*pentan(or *spirocyclo*penten)-3-one-1-carboxylic acid (I) with alkaline potassium ferricyanide solution yields after esterification of the acids produced with methyl alcohol and sulphuric acid, 3-*methoxy*-5-cyclo*pentane*spirocyclo*pentene*-1 : 4-*dione*, m. p. 65°, hydrolysed by boiling hydrochloric acid to 5-cyclo*pentane*spirocyclo*penten-3-ol*-1 : 4-*dione* (II), m. p. 154°, and *methyl* 5-cyclo*pentane*spirodicyclo*pentan*(or spirocyclo*penten*)-4-*ol*-3-*one*-1-*carboxylate*, m. p. 145° [free *acid*, m. p. 110° (decomp.)]. Oxidation of 5-*cyclo*pentane*spirodicyclo*penten (or *spirocyclo*pentadien)-3-ol-1 : 2-dicarboxylic acid (III) with alkaline potassium ferricyanide gives (II). Oxidation of (I) with alkaline potassium permanganate yields αα-*dihydroxy*cyclo*pentane*-1 : 1-*diacetic acid* (IV), m. p. 98°, which when heated at 90° affords α-keto*cyclo*pentane-1 : 1-diacetic acid (V). Similar oxidation of (III) gives a mixture of (IV) and (V). The ready production of (II), and the non-formation of substituted aconitic acids from this series of compounds, indicates that the bridged-ring phase predominates (cf. Ingold, Seeley, and Thorpe, J.C.S., 1923, **123**, 853). H. Burton.

Colorimetric test for tannic acid. J. Rae (Pharm. J., 1928, **120**, 539).—Permanent reddish-brown colorations are given by solutions of tannic acid with 10% aqueous ammonium molybdate solution. Gallic acid and pyrogallol give the coloration also. H. Burton.

Manufacture of carboxylic acids of acenaphthene. I. G. Farbenind. A.-G.—See B., 1928, 362.

Manufacture of 3 : 4-diaminobenzoyl-*o*-benzoic acid. R. Adams, J. M. Davidson, and J. Gubelmann, Assrs. to Newport Co.—See B., 1928, 440.

Manufacture of bromo-derivatives of 1 : 1'-dinaphthyl-8 : 8'-dicarboxylic acid. I. G. Farbenind. A.-G.—See B., 1928, 441.

Action of iron, cobalt, and nickel carbonates on benzylidene chloride. J. J. Vanin and A. A. Tschernojarova (J. Russ. Phys. Chem. Soc., 1927, **59**, 891—894).—The products of the action on warming of the carbonates of the metals of the iron group on benzylidene chloride in a stream of carbon dioxide were investigated. The activity of the metals decreases in their periodic order. Iron carbonate reacts almost explosively at 55—60°, with separation of free carbon, giving a resinous mass. Cobalt carbonate reacts vigorously at 60—70°, giving a 76·1% yield of benzaldehyde, with a little benzoic acid. Nickel carbonate must be heated first at 120° and finally at 160—170°, when it gives 70·6% of benzaldehyde and some benzoic acid.

The mechanism of the reactions is discussed.

M. Zvegintzov.

Photolysis of benzaldehyde. M. DE HEMPTINNE.—See this vol., 720.

Tautomerism of *o*-nitrobenzaldehyde. F. ARNDT (Ber., 1928, 61, [*B*], 1125—1126).—The assumption that *o*-nitrobenzaldehyde exists in tautomeric forms, $C_6H_4{<}{}^{CHO}_{NO_2} \rightleftharpoons C_6H_4{<}{}^{C(OH)}_{NO—}{>}O$ (cf. Tanasescu (A., 1926, 1247) is not in harmony with the following observations. (1) *o*-Nitrotriphenylmethane, for which a tautomeric form is impossible, resembles *o*-nitrobenzaldehyde in exhibiting a mobile hydrogen atom (for the detection of which the Zerevitinov method is inapplicable). (2) *o*-Nitrotriphenylmethane is isomerised to *o*-nitrosotriphenylcarbinol by light. (3) Solubility in alkali hydroxide is not peculiar to *o*-nitrobenzaldehyde, but is exhibited to a smaller extent by *p*-nitrobenzaldehyde. (4) *o*-Nitroacetophenone, which cannot yield a tautomeric form, is reduced to *C*-methylanthranil as readily as *o*-nitrobenzaldehyde is converted into anthranil. H. WREN.

Benzylidene derivatives of glycols. A. FRANKE and E. GIGERL (Monatsh., 1928, 49, 8—20).—A series of cyclic benzylidene derivatives of the type $R''{<}{}^{O}_{O}{>}CHPh$ has been prepared by the condensation of benzaldehyde with various glycols. When anhydrous hydrogen chloride is passed into a mixture of benzaldehyde and the glycol at 0°, condensation occurs only in the case of the $\alpha\gamma$-diols ($\alpha\beta$-diols not reacting under these conditions), and thus are obtained the cyclic *benzylidene* derivatives of $\beta\beta$-dimethylpropane-$\alpha\gamma$-diol, b. p. 123—124°/10 mm., m. p. 35° (yield, 68%); α-phenyl-$\beta\beta$-dimethylpropane-$\alpha\gamma$-diol, m. p. 98° (50%); β-methylpentane-$\beta\delta$-diol, b. p. 124°/9 mm.; and $\beta\delta$-dimethylpentane-$\beta\delta$-diol, b. p. 127—128°/10 mm., m. p. 42° (20%). The yield is greatest with the diprimary glycol and decreases through the series primary-secondary, secondary-tertiary, and ditertiary glycols. The cyclic *benzylidene* derivative, b. p. 126°/12 mm., m. p. 35°, of $\beta\beta$-dimethylpropane-$\alpha\gamma$-diol is obtained (yield, 65%) only by heating the glycol and benzaldehyde with a 1% alcoholic solution of hydrogen chloride for 1 hr. Pentane-$\alpha\delta$-diol by treatment with benzaldehyde and anhydrous hydrogen chloride at 0° yields only the $\alpha\delta$-oxide together with resinous products, and no derivative could be obtained from "camphor glycol" or decane-$\alpha\kappa$-diol. In the absence of moisture the benzylidene derivatives develop intense colours in the presence of anhydrous hydrogen chloride (these colours also being observed during the preparation of the derivatives) which, it is suggested, are due to the formation of oxonium complexes with hydrogen chloride. J. W. BAKER.

Pyrogenic decomposition of cyclic ketones. V. IPATIEV and A. PETROV (J. Russ. Phys. Chem. Soc., 1928, 60, 491—496).—A study of the pyrogenic decomposition of various cyclic ketones in the presence of ferric oxide leads to the following conclusions. Phenols are yielded only by compounds possessing an ethylenic linking, whether in the nucleus or in the side-chain, such as homo*iso*phorone and pulegone; the former substance loses more than one of its ethyl groups, whilst the latter compound yields a mixture of phenols, unsaturated hydrocarbons, and cymol, as well as a number of aliphatic hydrocarbons produced by the breaking up of the ring, and liberation of carbon monoxide. Thymol, which is also produced, is further decomposed under the conditions of the experiment. 1-Methyl*cyclo*hexan-2-one, on the other hand, yields no phenolic products but a mixture of hydrocarbons, of which about 40% are unsaturated. These are probably of the amylene series, whilst the remainder are mainly saturated cyclic hydrocarbons, with a small admixture of toluene. R. TRUSZKOWSKI.

Pyrogenic decomposition of ketones at high pressures. V. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1927, 59, 903—913).—The products of heating under pressure acetophenone and benzophenone between 270° and 430° and acetone above 500°, in an iron tube with alumina as a catalyst, were investigated. Acetophenone at 270—300° gives 30% of *s*-triphenylbenzene and diphenylfuran. At 380—420°, a 15% yield of benzene, toluene, ethylbenzene, and *o*-xylene is obtained, together with increasing quantities of tar containing a little benzoic acid. If hydrogen is added, the yield increases to 40%, showing that the ethylbenzene and *o*-xylene are formed by the direct reduction of acetophenone.

Benzophenone and hydrogen at 400—430° yield 80% of diphenylmethane, with a little benzene and tar. When heated alone, benzophenone is unchanged even at 430°, but decomposes completely into carbon and gas above 500°.

Acetone at 500—530° gives large quantities of paraffin hydrocarbons, including propane, phenols (1—2%, chiefly 1 : 3 : 5-xylenol), *iso*phorone, xylitone, mesitylene, cymene, and ψ-cumene. The possible mechanism of the reactions is discussed, and its bearing on the composition of coal and low-temperature tars is emphasised. M. ZVEGINTZOV.

Interaction of benzoyl chloride and diazomethane. Discussion of the reactions of diazenes. W. BRADLEY and R. ROBINSON (J.C.S., 1928, 1310—1318).—The reaction between benzoyl chloride and diazomethane in cold, dry ethereal solution takes place thus, $Ph{\cdot}COCl+2CH_2N_2 \rightarrow Ph{\cdot}CO{\cdot}CHN_2+CH_3Cl+N_2$, diazoacetophenone, m. p. 48—48·5° (cf. Wolff, A., 1903, i, 203), being obtained in 91% yield. ω-Chloroacetophenone is not produced (cf. Clibbens and Nierenstein, A., 1915, i, 1602). Benzoyl bromide and diazomethane give diazoacetophenone also (cf. Lewis, Nierenstein, and Rich, A., 1925, i, 935). The mechanisms of the reactions of diazomethane are discussed on an electronic basis. H. BURTON.

Syntheses with diazomethane. V. Action of acid chlorides with diazomethane. F. ARNDT and J. AMENDE (Ber., 1928, 61, [*B*], 1122—1124; cf. Nierenstein, A., 1925, i, 34; Staudinger and Machling, A., 1916, i, 855).—The nature of the product of the reaction of acid chlorides and diazomethane depends greatly on the conditions of the reaction. If the acid chloride is added to the diazomethane so that the latter is always present in excess, the liberated hydrogen chloride is absorbed by the diazomethane and the diazo-ketone remains mainly intact. If the

reactants are mixed in the reverse order, the primary diazo-ketone is decomposed by the liberated hydrogen chloride with formation of the chloro-ketone which then constitutes the main product. The nature and stability of the diazo-ketone cannot, however, be entirely neglected. Benzoyl chloride and an excess of diazomethane afford ω-diazoacetophenone, m. p. 49°, converted by warm, dilute sulphuric acid into benzoylcarbinol. The preparation of diazoacetone, b. p. 49°/13 mm., and *chlorodiazoacetone*, b. p. 75°/13 mm., m. p. +3°, is described. Benzoyl chloride and 1·5 mols. of diazomethane afford chiefly ω-chloroacetophenone. H. Wren.

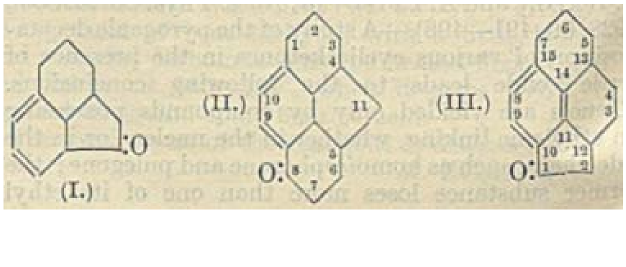
Conversion of hydroaromatic into aromatic compounds. II. Action of bromine on 5-chloro- and 5-bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one. L. E. Hinkel and D. H. Hey (J.C.S., 1928, 1200—1204).—Phenyldihydroresorcinol is converted by phosphorus tribromide in presence of chloroform into *5-bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one*, m. p. 81·5°, which with bromine affords *4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one*, m. p. 82° (decomp.). This compound exists in stable (from alcohol) and unstable (ether) forms which are probably *cis–trans* modifications. When the tribromoketone is heated on the water-bath there are formed as decomposition products *4 : 5-dibromo-3-hydroxydiphenyl*, m. p. 81° (*benzoyl* derivative, m. p. 104°), and *5-bromo-3-hydroxydiphenyl*, b. p. 208—210°/11 mm. (*benzoyl* derivative, m. p. 108°), and a small amount of phenyldihydroresorcinol. When decomposed with alcoholic potassium hydroxide the tribromoketone furnishes in addition to the above hydroxy-compounds some *5-bromo-3-ethoxydiphenyl*, m. p. 70—71°. *5-Chloro-4 : 5-dibromo-1-phenyl*cyclo*hexan-3-one*, stable, m. p. 98·5° (alcohol), unstable, m. p. 88·5° (ether), is decomposed by alcoholic potassium hydroxide yielding an equimolecular *mixture*, m. p. 68—69°, of 5-chloro- and 5-bromo-3-ethoxydiphenyl, together with halogenohydroxydiphenyl derivatives. H. Burton.

Reactions of strongly electropositive elements with organic substances in liquid ammonia solution. VI. Reduction of benzophenone; hydrolysis of metal ketyls. C. B. Wooster (J. Amer. Chem. Soc., 1928, 50, 1388—1394; cf. Kraus and White, A., 1923, i, 456).—In liquid ammonia benzophenone readily forms mono- and di-sodio-derivatives (cf. Beckmann and Paul, A., 1892, 169) the colour of the latter being deep purple. The disodio-compound is quantitatively converted by excess of water or ammonia into benzhydrol. With ethyl bromide only one sodium atom is replaced by alkyl, giving diphenylethylcarbinol, whilst with iodobenzene, benzene, sodium iodide, and the sodio-derivative of α-aminobenzhydrol are formed. Dipotassiobenzophenone is formed analogously to the disodio-derivative, or from benzhydrol and potassamide in liquid ammonia. Monosodiobenzophenone gives with ammonium chloride a mixture of benzhydrol and benzophenone and with ethyl bromide a mixture of diphenylethylcarbinol and benzophenone. The disodio-derivative is converted by 1 mol. of ammonium chloride into a blue *ammoniosodio*-derivative, $CPh_2NH_4(ONa)$, which decomposes completely in liquid ammonia in some 7—8 hrs. The same compound is formed from 1 mol. of ammonium chloride and 2 mols. of the monosodio-derivative, and appears as a transient green coloration in the decomposition of the sodio-derivatives by water. The primary reaction with the monosodio-derivative is, therefore, addition to the free valency and not replacement of the sodium atom (cf. Schlenk, A., 1911, i, 545). H. E. F. Notton.

Comparative stability of isomerides and their absorption spectra. (Mme.) Ramart-Lucas (Compt. rend., 1928, 186, 1301—1303).—Of two mutually interconvertible substances the absorption curve of the stable form is nearer to the visible than that of the labile form. Moreover, in a transformation involving separation of water, acid, or salt, with possible formation of two isomerides through a common unstable intermediate stage, it is, in general, possible to obtain either of the two forms at will if the conditions are known for the formation of the isomeride having its absorption curve further from the visible than the other. For example, the absorption curve of deoxybenzoin is nearer the visible than that of diphenylacetaldehyde, the usual dehydration product of hydrobenzoin; and by passing hydrobenzoin over kieselguhr at 300—400°/20 mm. an almost quantitative yield of deoxybenzoïn may be obtained. B. W. Anderson.

Benzopolymethylene compounds. XIV. Syntheses of tetracyclic compounds and of pyrene. J. von Braun and E. Rath (Ber., 1928, 61, [B], 956—963; cf. A., 1927, 666).—Further experiments on ring closure support the accuracy of the theory of Sachse and Mohr.

Tetraphthen ketone (I) is readily converted by zinc and ethyl bromoacetate into the *ester*, $C_{16}H_{18}O_2$, b. p. 214—215°/14 mm., of the unsaturated acid, which is smoothly hydrogenated in the presence of nickel to *ethyl tetraphthylacetate*, b. p. 196°/14 mm. *Tetraphthylacetic acid*, m. p. 108°, is described; as expected, its chloride is unaffected by aluminium chloride. Reduction of ethyl tetraphthylacetate by sodium and alcohol affords *β-tetraphthylethyl alcohol*, b. p. 188°/15 mm., m. p. 53°, converted successively into *β-tetraphthylethyl bromide*, b. p. 182—185°/15 mm., *tetraphthylpropionitrile*, b. p. about 205°/16 mm., m. p. 38°, and *tetraphthylpropionic acid*, m. p. 97°. The corresponding *chloride*, b. p. 215—220°/14 mm. (slight decomp.), is transformed by aluminium chloride in the presence of carbon disulphide into *α-keto-octahydromethylenephenanthrene* (II), b. p. 168—170°/0·5 mm., m. p. 104° (*oxime*, m. p. 213°; *semicarbazone*, m. p. 266°), reduced by Clemmensen's method to *1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-4 : 5-methylenephenanthrene*, b. p. 130—132°/15 mm., m. p. 47°. This substance could not be dehydrogenated by lead oxide, zinc dust, palladium, nickel, or sulphur.



α-Ketohexahydrobenznaphthen, zinc, and ethyl bromoacetate afford the unsaturated *ester*, $C_{17}H_{20}O_2$, b. p. 218—219°/14 mm., smoothly hydrogenated to *ethyl hexahydrobenznaphthylacetate*, b. p. 196°/14 mm. The corresponding *acid*, b. p. 220—222°/13 mm., m. p. 93°, is converted through its *chloride* into the *ketone* (III), b. p. 170—172°/0·5 mm., m. p. 98° (*oxime*, m. p. 199°; *semicarbazone*, m. p. 256°), which is reduced to 3 : 4 : 5 : 6 : 12 : 13-*hexahydro*peri*benzo-acenaphthen*, b. p. 130—132°/12 mm., m. p. 29°. Dehydrogenation of the last substance could not be effected. Reduction of ethyl hexahydrobenznaphthylacetate yields β-*hexahydrobenznaphthylethyl alcohol*, b. p. 192—194°/12 mm., m. p. 23—24°, converted successively into the corresponding *bromide*, b. p. 192—194°/12 mm., and *hexahydrobenznaphthyl-propionitrile*, b. p. 212—214°/12 mm., which is hydrolysed to *hexahydrobenznaphthylpropionic acid*, b. p. 238—240°/12 mm., m. p. 118°. The *chloride* of the acid is very easily transformed by aluminium chloride into α-*ketodecahydropyrene*, b. p. 182—183°/0·4 mm., m. p. 63° (*oxime*, m. p. 158°; *semicarbazone*, m. p. 242°). *Decahydropyrene*, prepared by reduction of the ketone by Clemmensen's method, has b. p. 151—152°/12 mm., m. p. 34°, d_4^{20} 1·0612, n_D^{20} 1·5806; it is very readily dehydrogenated by passage over lead oxide–pumice to pyrene. H. WREN.

Isomerism of styryl alkyl ketones. IV. 4-Hydroxy- and some derivatives of 2-hydroxy-styryl alkyl ketones. A. McGOOKIN and D. J. SINCLAIR (J.C.S., 1928, 1170—1177).—Treatment of 5-bromo-2-hydroxystyryl methyl ketone with sodium hydroxide solution and subsequent acidification of the green sodium salt produced gives 5 : 5′-dibromo-2 : 2′-dihydroxydistyryl ketone, yellow, m. p. 188°, also obtained by interaction of the styryl methyl ketone or acetone and 5-bromosalicylaldehyde in presence of alkali. When the method of preparation using acetone is employed a colourless *modification*, m. p. 174·5°, of the distyryl ketone was isolated in addition to the yellow form. The following styryl ketones have been prepared by condensing substituted benzaldehydes with the appropriate ketone in presence of alkali hydroxide solution, and found to exist in yellow and colourless modifications with the same m. p.: 2-*hydroxy-4-methoxystyryl ethyl*, m. p. 123°, and *propyl ketones*, m. p. 111—112°; 4-*hydroxystyryl methyl*, m. p. 111—112°, *ethyl*, m. p. 115°, and *propyl ketones*, m. p. 90°; 2-*hydroxystyryl* iso*propyl ketone*, m. p. 107°; 2-*hydroxystyryl* tert.-*butyl ketone*, m. p. 128°, from salicylaldehyde and pinacolin, and 2-*hydroxystyryl* iso*butenyl ketone*, m. p. 141°, obtained in small yield together with 2-hydroxystyryl methyl ketone and 2 : 2′-dihydroxydistyryl ketone from salicylaldehyde and mesityl oxide. 2-*Hydroxy*-3-*methoxystyryl ethyl*, m. p. 86·5° (*hydrate*, m. p. 77—79°), and *propyl ketones*, m. p. 82·5°, and 3-hydroxystyryl methyl ketone, m. p. 97—98° (cf. Murai, A., 1925, i, 1157), are described. 4 : 4′-Dihydroxydistyryl ketone, m. p. 237—238°, can be prepared only from 4-hydroxybenzaldehyde and acetone or 4-hydroxystyryl methyl ketone by means of condensation in alcoholic hydrogen chloride. The condensation of salicylaldehyde or *p*-dimethylaminobenzaldehyde with 2-hydroxystyryl ethyl ketone could not be effected in alkaline media.

Styryl alkyl ketones of the types >CH:CH·COMe and >CH:CH·CO·CH_2Alk give red solutions with boiling concentrated hydrochloric acid and undergo fission when treated with alkali. In the first type the fission products recombine, forming distyryl ketones, but in the second, high-melting, unsaturated substances of undetermined nature are obtained. 2-Hydroxystyryl *tert.*-butyl, *iso*butenyl, and phenyl ketones are unaffected by either acid or alkali. Examples of other cases of isomerism amongst styryl ketones recorded in the literature are given.

H. BURTON.

Mononitrobenzils and heteronuclear dinitrobenzils. F. D. CHATTAWAY and E. A. COULSON (J.C.S., 1928, 1080—1088; cf. A., 1926, 728).—When a solution of benzoin in acetic anhydride and sulphuric acid is treated with powdered potassium nitrate at −10° to 0° and the resulting product oxidised with boiling nitric acid (*d* 1·5), there are obtained 4-nitrobenzil (I, 42%; *monophenylhydrazones*, m. p. 200° and 162°; *osazone*, m. p. 216°; *quinoxaline* derivative, m. p. 161°), and small amounts of 2-nitrobenzil (II), m. p. 102° (cf. List, A., 1894, i, 39), and 3-*nitrobenzil* (III), m. p. 120°. Nitration of (II) and (III) furnishes 2 : 2′- and 3 : 2′-dinitrobenzils and 3 : 2′- and 3 : 3′-dinitrobenzils, respectively, whilst from (I) there are obtained 3 : 4′-*dinitrobenzil*, labile, m. p. 127°; stable, m. p. 137° [*monophenylhydrazone*, m. p. 182°; *osazone*, m. p. 287° (decomp.); *quinoxaline* derivative, m. p. 221°], and 2 : 4′-*dinitrobenzil*, m. p. 135° (*monophenylhydrazones*, m. p. 224° and 201°; *quinoxaline* derivative, m. p. 186°). When benzoin or acetylbenzoin is nitrated at 25—30° with an excess of nitric acid and the resulting product oxidised, a mixture of 2 : 4′-, 3 : 4′-, and 4 : 4′-dinitrobenzils is produced. 2 : 2′- and 2 : 3′-*Dinitrobenzilmonophenylhydrazones*, m. p. 199° and 193° (decomp.), respectively, and 2-m-*nitrophenyl*-3-o-*nitrophenylquinoxaline*, m. p. 168°, are described. The constitutions of the above mono- and di-nitrobenzils are established by oxidation with chromic anhydride in acetic acid and subsequent identification of the benzoic or nitrobenzoic acids formed. H. BURTON.

4 : 4′-Dinitrobenzil. F. D. CHATTAWAY and E. A. COULSON (J.C.S., 1928, 1361—1364).—Nitration of hydrobenzoin with nitric acid (*d* 1·5), and oxidation of the product with nitric acid of *d* 1·4, gives 4 : 4′-dinitrobenzil, m. p. 213° [*monophenylhydrazone*, m. p. 257°; *osazone*, m. p. 293° (decomp.); *quinoxaline* derivative, m. p. 201°], oxidised by chromic anhydride in acetic acid to *p*-nitrobenzoic acid. The group HO·CH·CH·OH exerts a strong *p*-directing influence as in benzoin (cf. this vol., 761). 4 : 5-Diphenylglyoxalone (Biltz, A., 1909, i, 740) is converted by fuming nitric acid into 3 : 3′-dinitrobenzil, but in presence of sulphuric acid gives a mixture of 3 : 3′- and 4 : 4′-dinitrobenzils.

H. BURTON.

Some hydrochalkones and hydrochalkols. P. PFEIFFER, E. KALCKBRENNER, W. KUNZE, and K. LEVIN (J. pr. Chem., 1928, [ii], 119, 109—130).—Chalkone on reduction with hydrogen and platinum-

black gives phenyl β-phenylethyl ketone, m. p. 72°, whilst with sodium amalgam hydrochalkol (αγ-diphenylpropan-γ-ol) (phenylurethane, m. p. 82—83°; p-*nitrobenzoate*, m. p. 89—90°, d^{21} 1·0614, n_D^{21} 1·5724, $[R_L]_D$ 65·8, calc. 66·1) is formed. Treatment of hydrochalkol with zinc chloride led to diphenylpropene: no phenylhydrindene was isolated. The undermentioned hydrochalkones were prepared by the reduction of the appropriate chalkones with hydrogen and platinum-black: *phenyl* β-3 : 4-*dimethoxyphenylethyl ketone*, m. p. 67·5—68·5° (*oxime*, m. p. 109°; *tertiary alcohol* with magnesium phenyl bromide, m. p. 102—103°); phenyl β-3 : 4-methylenedioxyphenyl ketone, m. p. 57—58° (Bargellini and Bini, A., 1912, i, 118, give m. p. 39—41°) (*tertiary alcohol* with magnesium methyl bromide, m. p. 50—52°); p-*anisyl* β-3 : 4-*dimethoxyphenylethyl ketone*, m. p. 57°; *phenyl* β-2-*chlorophenylethyl ketone* (from *phenyl* 2-*chlorostyryl ketone*, m. p. 51·5°), m. p. 46·5° (*oxime*, m. p. 113°); p-*anisyl* β-2-*chlorophenylethyl ketone* (from p-*anisyl* 2-*chlorostyryl ketone* from *o*-chlorobenzaldehyde and *p*-methoxyacetophenone, m. p. 91·5—92°), m. p. 48·5° (*oxime*, m. p. 90—91°); p-*anisyl* β-2-*bromophenylethyl ketone* (from p-*anisyl* 2-*bromostyryl ketone*, m. p. 79·5°), m. p. 65° (*oxime*, m. p. 99·5—100°); 1-*hydroxy*-2-*naphthyl* β-*phenylethyl ketone*, m. p. 98° (*acetyl* derivative, m. p. 89—90°); 1-*hydroxy*-2-*naphthyl* β-p-*anisylethyl ketone*, m. p. 108°; 1-*hydroxy*-2-*naphthyl* β-3 : 4-*methylenedioxyphenylethyl ketone*, m. p. 103—104°. 3-o-*Chlorobenzylidene*-7-*methoxychromanone*, m. p. 132°, is reduced to the corresponding o-*chlorobenzyl* derivative, m. p. 75° (*oxime*, m. p. 162—163°). Reduction of phenyl 2-chlorostyryl ketone with sodium amalgam gave α-*phenyl*-γ-o-*chlorophenylpropan*-α-*ol*, d^{21} 1·1636, $n^{18·0}$ 1·5831, $[R_L]_D$ 70·83, calc. 71·06 (p-*nitrobenzoate*, m. p. 115°; *phenylurethane*, m. p. 100·5°); the latter yielded α-*chloro*-α-*phenyl*-γ-o-*chlorophenylpropane*, b. p. 151—154°/2 mm., on treatment with hydrogen chloride. The following compounds are described: 3-o-*bromobenzylidene*-7-*methoxychromanone*, m. p. 164°; *benzylidenenaphthachromanone*, from naphthachromanone and benzaldehyde, m. p. 131—132°; *piperonylidenenaphthachromanone*, m. p. 170—171°, from naphthachromanone and piperonal; *furfurylidenenaphthachromanone*, m. p. 145°, from naphthachromanone and furfuraldehyde.

I. Vogel.

Active constituents of true coto-bark. Constitution of cotoin. E. Späth and F. Wessely (Monatsh., 1928, 49, 229—240).—Cotoin, regarded by Späth and Fuchs (A., 1922, i, 558) as 2 : 6-dihydroxy-4-methoxybenzophenone (I), might alternatively be 2 : 4-dihydroxy-6-methoxybenzophenone (II) (cf. Karrer, A., 1927, 564); the constitution (I) is, however, now established as follows. The monoalkylation of (I) can yield only one product, whereas (II) would be expected to yield two. Actually only one cotoin methyl ether (cf. Späth and Fuchs, *loc. cit.*) can be isolated from the product of the action of diazomethane in ether. This must be 2-hydroxy-4 : 6-dimethoxybenzophenone, since it yields 3 : 5-dimethoxy-2-phenylcoumarone (Motylewski, A., 1909, i, 822). Similarly, diazoethane in ether yields only one product, 2-*hydroxy*-4-*methoxy*-6-*ethoxybenzophenone*, m. p. 91—92°, which when treated with sodium and ethyl bromoacetate in absolute alcohol yields a product hydrolysed by alcoholic potassium hydroxide to a mixture from which 5-*methoxy*-3-*ethoxy*-2-*phenylcoumarone*, m. p. 108—109·5°, is obtained by distillation.

Secondly, when cotoin methyl ether is ethylated, or the ethyl ether is methylated, the same product is obtained, viz., 2 : 4-*dimethoxy*-6-*ethoxybenzophenone*, m. p. 103—104°; this makes it probable that the two hydroxyl groups of cotoin are equivalent, *i.e.*, in the *o*-position to the keto-group; the methoxyl group is then in the *p*-position.

Lastly, the *cotoin diethyl ether*, m. p. 82—83°, b. p. 160—170°/0·001 mm., obtained by the action of excess of diazoethane, is shown to be 4-*methoxy*-2 : 6-*diethoxybenzophenone*, for it is reduced in alcoholic potassium hydroxide solution by zinc to 4-*methoxy*-2 : 6-*diethoxybenzhydrol*, m. p. 104—105°, of which the constitution is established by oxidation by chromic acid to 2 : 6-diethoxybenzoquinone, new m. p. 127—128°, identical with that obtained by oxidation of phloroglucinol diethyl ether, new m. p. 75—76°. The dimethoxyethoxybenzophenone is reduced by zinc and potassium hydroxide to 2 : 4-*dimethoxy*-6-*ethoxybenzhydrol*, m. p. 80—81°, which is oxidised by chromic acid to 2-*methoxy*-6-*ethoxybenzoquinone*, m. p. 135—136°, identical with that obtained by oxidation of *phloroglucinol methyl ethyl ether*, m. p. 50—51°, obtained by partial ethylation of phloroglucinol methyl ether with diazoethane.

E. W. Wignall.

Dark-coloured dimeric keten. W. Langenbeck and H. Langenbeck (Ber., 1928, 61, [*B*], 938—942).—Benzilic acid which has been mixed with a small proportion of anhydrous sodium carbonate yields, when very energetically heated, a mixture of benzilide, m. p. 194°, and 3 : 3 : 4 : 4-*tetraphenylcyclobutane*-1 : 2-*dione*, m. p. 168°. The new compound is coloured red, the colour intensity being that of a true dye. It shows general absorption in the blue and violet. Proof of the constitution of the latter rests mainly on its oxidation by chromic acid to benzophenone (yield 49%). With alcoholic potassium hydroxide or potassium cyanide, phosphorus pentachloride, thionyl chloride, alcoholic bromine, zinc dust and glacial acetic acid, magnesium ethyl bromide, or phenylhydrazine it yields resinous, apparently highly polymerised products.

H. Wren.

Preparation of phenolic ketones by the Hoesch method. A. Korczynski and A. Novakovski (Rocz. Chem., 1928, 8, 254—262).—See this vol., 523.

Synthesis of benzoquinone. J. F. Durand (Compt. rend., 1928, 186, 1221).—The statement that benzoquinone was obtained from acetylene and carbon monoxide (A., 1927, 566) is withdrawn.

J. D. Fulton.

Bromophenols. XXXII. Preparation of 2 : 6-dibromo-*m*-xyloquinone from *s*-xylenol. M. Kohn and M. K. Feldmann (Monatsh., 1928, 49, 169—172).—*s*-Xylenol is brominated in acetic acid to tribromo-*s*-xylenol (methyl ether, m. p. 116°; cf. Blanksma, A., 1903, i, 164), which when oxidised

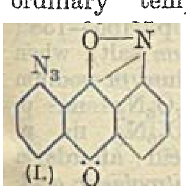
by fuming nitric acid yields 2 : 6-*dibromo*-m-*xyloquinone*, m. p. 176°, rhombic prisms of angle 68° 4′, doubly refracting, α=1·4804 [HLAWATSCH]. This is reduced by sulphurous acid to 2 : 6-*dibromo*-m-*xyloquinol*, charring at 180° (*benzoyl* derivative, m. p. 253°; *methyl ether*, m. p. 116°, b. p. 309—311°/741 mm.).

E. W. WIGNALL.

Manufacture of a 2 : 3-dichloronitro-1 : 4-naphthaquinone. I. G. FARBENIND. A.-G.—See B., 1928, 441.

Diazides of anthraquinone. K. BRASS and F. ALBRECHT (Ber., 1928, **61**, [*B*], 983—993).—The stability of diazides of anthraquinone depends on the position of the azido-groups in the anthraquinone nucleus and the manner in which they are distributed. Proximity to the carbonyl group causes instability in the α-derivatives which decreases from the 1 : 4- to the 1 : 5- and to the 1 : 8-compound. If, however, the residual affinity of the carbonyl group is engaged by the residue formed from the decomposition of one azido-radical, the second azido-group becomes stabilised. Anthraquinone-2 : 6-diazide, on the other hand, is completely stable.

1 : 4-Diaminoanthraquinone is converted by diazotisation in concentrated sulphuric acid followed by treatment of the diazonium sulphate with bromine into the very unstable *perbromide* which, with ammonia, yields the corresponding *diazide*; this last compound, even when strongly cooled, steadily evolves nitrogen and passes into anthraquinone-1 : 4-dianthranil. Decomposition of the dianthranil by concentrated sulphuric acid at 200° gives about equal quantities of 1-amino-4-hydroxyanthraquinone, m. p. 208°, and 1 : 4-diaminoanthraquinone, m. p. 268°, contaminated by products of high mol. wt. The formation of the latter substance is explained by intermediate radical production, whereas that of the former remains unexplained, since it is not due to hydrolysis of the 1 : 4-diamino-compound. 1 : 5-Diaminoanthraquinone is converted similarly into *anthraquinone*-1 : 5-*diazide*, which gradually passes at the atmospheric temperature into anthraquino-1 : 5-dianthranil. The freshly-prepared diazide is decomposed by 90% sulphuric acid into 4 : 8-diaminoanthrarufin; 1 : 5-diaminoanthraquinone does not appear to be regenerated. When rapidly prepared at a low temperature, nearly homogeneous *anthraquinone*-1 : 8-*diazide* can be obtained from 1 : 8-diaminoanthraquinone; it gives a *compound* with triphenylphosphine. When preserved at the ordinary temperature, it gradually loses one third of its nitrogen, giving 1-*anthraniloanthraquinone*-8-*azide* (I), more rapidly prepared by crystallisation of the diazide on treatment of it with boiling water; with triphenylphosphine it affords *anthraniloanthraquinonetriphenylphosphineimine*.

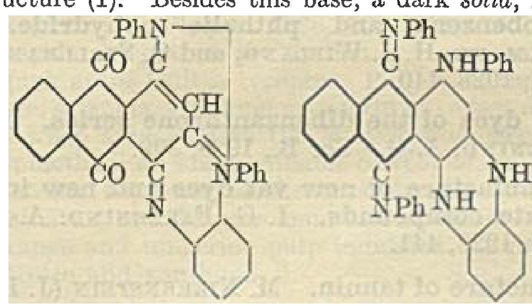


4 : 5-Diaminochrysazine comprises 90% of the products of the decomposition of the anthraniloazide by sulphuric acid, the remainder consisting of insoluble compounds of high mol. wt.; regeneration of 1 : 8-diaminoanthraquinone is not observed. *Anthraquinone*-2 : 6-*diazide*, decomp. 202°, forms pale brown crystals, sensitive to light; *anthraquinone*-2 : 6-*ditriphenylphosphineimine*, $C_{50}H_{36}O_2N_2P_2$, m. p. above 280°, is described. Decomposition of the diazide by sulphuric acid follows an ill-defined course, the sole isolable product being 2 : 6-diaminoanthrarufin.

H. WREN.

Anthraquinonedichlorodi-imine [1 : 4-dichloroiminodihydroanthraquinone] and its compounds with amines. A. A. SANIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 867—875).—1 : 4-*Dichloroiminodihydroanthraquinone* was prepared by treating 1 : 4-diaminoanthraquinone with bleaching powder in aqueous suspension, and recrystallising the precipitate from carbon tetrachloride, when a reddish-brown *solid* was obtained, m. p. 155—156°, soluble in nitrobenzene and pyridine, less soluble in the other usual organic solvents. When warmed in alcohol or acetic acid solution, it was reduced to the amine. On reduction with hyposulphite, it showed the properties of a vat dye. Other diamines of the anthraquinone series, such as 1 : 4 : 5 : 8-tetra-aminoanthraquinone, 1 : 5-diamino-4 : 8-dihydroxyanthraquinone, 1-amino-4-hydroxyanthraquinone, as well as the *O*-substituted compounds, gave similar products.

On condensing the *dichloroimino*-compound with aniline in the presence of anhydrous sodium acetate or copper acetate, a *chloride* was obtained, of which the free base was a black *compound*, m. p. 204—206°, dissolving in concentrated sulphuric acid with a blue colour, and possessing, probably, the azonium structure (I). Besides this base, a dark *solid*, m. p.

(I.)  (II.)

234—235°, easily soluble in aniline, pyridine, and nitrobenzene, was obtained, probably having the structure (II).

M. ZVEGINTZOV.

Rubiadin. I. Synthesis of 2 : 4-dihydroxy-1-methylanthraquinone. P. C. MITTAR, M. SEN, and P. K. PAUL (J. Indian Chem. Soc., 1927, 4, 535—540).—2 : 4 - Dihydroxy-*o*-toluic acid (cresorsellenic acid), prepared by a slight modification of the method of Jacobsen and Wierss (A., 1883, 1121), when heated with benzoic and sulphuric acids at 125—130° for 12—15 hrs. yields 2 : 4-*dihydroxy*-1-*methylanthraquinone*, m. p. 265—266° (*diacetate*, m. p. 181—182°), which is not identical with rubiadin to which Schunck and Marchlewski (J.C.S., 1894, **65**, 183) ascribed this constitution. Cresorsellenic acid by methylation yields 2 : 4-*dimethoxy*-*o*-toluic *acid*, m. p. 160°, the *methyl* ester, b. p. 289—291°, of which condenses with chloral hydrate in the presence of cold 90% sulphuric acid to yield 3 : 5-*dimethoxy* - 6 - *methyl* - 2 - *trichloromethylphthalide*, m. p. 176°, which is converted by heating with 20% sodium hydroxide solution on a water-bath for 5 hrs. into

3 : 5 - *dimethoxy* - 6-*methyl-2-phthalidecarboxylic acid*, $C_6HMe(OMe)_2<\begin{matrix}CO\text{------}\\CH(CO_2H)\end{matrix}>O,H_2O$, m. p. 218—219° (*ethyl* ester, m. p. 134°), which is decarboxylated by heating with sulphuric acid at 225—235°, yielding 3 : 5-*dimethoxy*-6-*methylphthalide*, m. p. 249°. The latter could not be oxidised to 3 : 5-dimethoxy-6-methylphthalic acid. J. W. Baker.

Rubiadin. II. Synthesis of 1 : 3-dihydroxy-2-methylanthraquinone. P. C. Mitter and P. Gupta (J. Indian Chem. Soc., 1928, **5**, 25—28; cf. preceding abstract).—Repetition of the preparation of 1 : 3-dihydroxy-2-methylanthraquinone (Schunck and Marchlewski, J.C.S., 1893, **63**, 969) shows that the product obtained by those authors by the condensation of benzoic and 2 : 6-dihydroxy-*p*-toluic acids probably contained traces of 1 : 3 : 5 : 7-tetrahydroxy-2 : 6-dimethylanthraquinone. When an excess of benzoic acid is used, pure 1 : 3-dihydroxy-2-methylanthraquinone, m. p. 290° (*acetyl* derivative, m. p. 225°), identical with rubiadin, is obtained. In the preparation of 2 : 6-dihydroxy-*p*-toluic acid by fusion of the corresponding sulphonic acid with potassium hydroxide, small amounts of 2-hydroxyterephthalic acid are obtained. G. A. C. Gough.

o-Aminocarboxylic acids of the anthraquinone series and substitution products thereof. I. G. Farbenind. A.-G.—See B., 1928, 361.

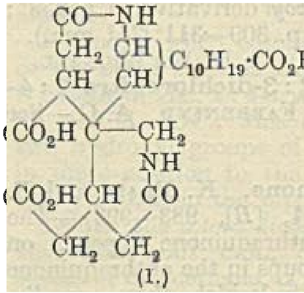
Manufacture of 2 : 4-dichloro-1-aminoanthraquinone and intermediate products from *m*-dichlorobenzene and phthalic anhydride. I. Gubelmann, H. J. Wieland, and O. Stallmann.—See B., 1928, 440.

Vat dyes of the dibenzanthrone series. I. G. Farbenind. A.-G.—See B., 1928, 399.

Manufacture of new vat dyes and new intermediate compounds. I. G. Farbenind. A.-G.—See B., 1928, 441.

Structure of tannin. M. Nierenstein (J. Russ. Phys. Chem. Soc., 1927, **59**, 951—952).—A criticism of Fischer's formula for tannin, in the light of the author's researches. On exhaustive methylation with diazomethane of Chinese tannin, followed by acid hydrolysis, 2 : 3 : 5 : 6-tetramethylglucose, and not dextrose as is demanded by Fischer's formula, is obtained. Under the same conditions, synthetic pentagalloyl-β-glucose also yields dextrose. Further, brewer's yeast ferments tannin, giving an optically active compound, free from sugar, possessing well-defined tanning properties, without the formation of either metadigallic or gallic acids. M. Zvegintzov.

Bile acids. XIX. M. Schenck and H. Kirchhof (Z. physiol. Chem., 1928, **175**, 135—144).—The dioxime of bilianic acid on treatment with sulphuric acid yields an isomeride for which formula (I) is suggested (cf. A., 1927, 665), although the position of the nitrogen atoms is hypothetical. By the action of nitric acid on this di*iso*oxime two crystalline products have been obtained, only one of which has been examined carefully. This *compound*, $C_{24}H_{34}O_8N_2$, m. p. 230—232° with frothing and charring, is blue and is formed by the action of nitric acid at the ordinary temperature. Analytical data and the absence of heat production or gas evolution suggest that no marked decomposition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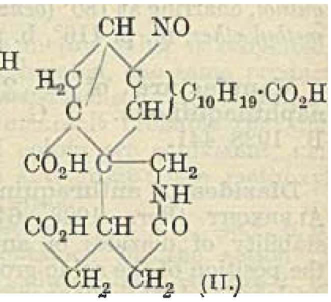
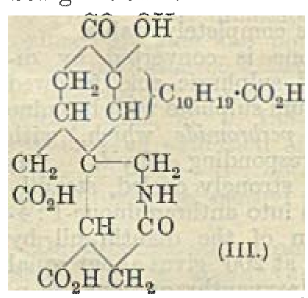

(II.)

occurs, and it is considered probable that a change occurs in the lactam grouping of the upper ring in (I) with the production of a bridged ring; formula (II) is tentatively suggested for this compound; the latter decolorises alkaline potassium permanganate only slowly, and is soluble in alkalis, the blue colour being stable unless excess of alkali is present. If the treatment with nitric acid is more prolonged, the blue colour disappears and a colourless crystalline *product*, which has not been investigated further, is obtained. The di*iso*-oxime of *iso*bilianic acid (cf. this vol., 639), heated with 25% hydrochloric acid, yields a crystalline *substance*, $C_{24}H_{35}O_9N,HCl$, m. p. about 248° after sintering, and it is concluded that the nitrogen atom is probably removed from the upper ring; formula (III) is suggested for the corresponding free base, but the latter has not yet been isolated.


(III.)

A. Wormall.

Nitration products of abietic acid. J. Dubourg (Bull. Inst. Pin, 1927, 241—246; Chem. Zentr., 1928, i, 341—342).—Johansson's results (Ark. Kemi, Min. Geol., 1917, No. 19) could not be repeated. Addition of nitric acid (120 c.c.) to abietic acid (300 g.) in boiling alcohol (600 c.c.) yields *dinitrodecahydroretenecarboxylic acid*, $C_{19}H_{26}O_2(NO_2)_2$, m. p. 162—165°, $[\alpha]_{yellow}$ —115·2°, $[\alpha]_{g}$ —135·9° (in alcohol) (*sodium*, *potassium*, *ammonium*, *zinc*, and *magnesium* salts; *methyl* ester, m. p. 135—138°). *Aminodecahydroretenecarboxylic acid*, $C_{19}H_{27}O_2NH_2$, has m. p. 226—228°. *Trinitro-octahydromethylphenanthrenecarboxylic acid*, $C_{16}H_{16}(NO_2)_3\cdot CO_2H$, m. p. 156—158°, $[\alpha]_{yellow}$ —136·4°, $[\alpha]_{g}$ —157·2° (*sodium* salt), when treated in alcoholic solution with sodium or sodium ethoxide, yields an *acetal*, $C_{16}H_{17}O_6N_2$, m. p. 212—215°, and a *product*, $C_{20}H_{27}O_{10}N_2$, m. p. 120°; the latter with sulphuric acid affords a *product*, $C_{16}H_{13}O_8N_2$, m. p. 97°. *Trinitroabietic acid*, $C_{20}H_{27}O_2(NO_2)_3$, m. p. 177—178°, $[\alpha]_{yellow}$ —95°, $[\alpha]_{green}$ —125°, is obtained by nitration of abietic acid (20 g.) in carbon tetrachloride (200 c.c.) with ordinary nitric acid (100 c.c.). An explosive *polynitro*-compound is precipitated by water from a solution of abietic acid in fuming nitric acid. A. A. Eldridge.

Carotin. R. PUMMERER and L. REBMANN (Ber., 1928, 61, [*B*], 1099—1102).—The absorption spectrum of carotin in *cyclo*hexane is compatible only with the presence of a large number of conjugated double linkings. When treated with perbenzoic acid in chloroform, carotin absorbs eight atoms of oxygen per mol., indicating the presence of eight double linkings if the normal course of the action be assumed. With iodine chloride, 11—11·5 mols. of reagent are absorbed per mol. of carotin. This value corresponds closely with the results expected from hydrogenation. The reaction does not, however, proceed normally, since it is accompanied by loss of about 3 mols. of halogen acid. The presence of eight double linkings appears definitely established, to which three "inert" double linkings may possibly be added. When similarly investigated, xanthophyll is found to have eight double linkings. H. WREN.

Rotenone, the active principle of the derris root. S. TAKEI (Ber., 1928, 61, [*B*], 1003—1007; cf. A., 1925, i, 761).—Determinations of the mol. wt. of rotenone in benzene and camphor, combined with the isolation of a phenylhydrazone, m. p. 243—244°, and an *oxime*, m. p. 239°, lead to an alteration of the formula from $C_{19}H_{18}O_5$ to $C_{23}H_{22}O_6$. This change is applicable also to *iso*rotenone produced from rotenone by boiling 50% sulphuric acid or from *rotenone hydrochloride*, m. p. 188°, by the action of zinc dust and glacial acetic acid. Rotenic acid, $C_{12}H_{12}O_4$ (formerly $C_9H_{10}O_3$), is characterised by its *thallium* salt, m. p. 203°, and *acetyl* derivative, m. p. 155°. It is converted by ethereal diazomethane into the non-crystalline *methyl* ester of the methylated acid, from which the *methylated acid*, $C_{12}H_{11}O_3{\cdot}OMe$, m. p. 115°, is obtained by hydrolysis; the latter substance yields a (?) *hydroxamic acid*, $C_{13}H_{14}O_3{:}N{\cdot}OH$, m. p. 120°. Nitration of rotenic acid gives ill-defined products from which *methyl nitromethylrotenate*, $NO_2{\cdot}C_{11}H_9O(OMe){\cdot}CO_2Me$, m. p. 120°, is obtained by aid of diazomethane. Distillation of rotenic acid causes loss of carbon dioxide and formation of a *phenol*, $C_{11}H_{12}O_2$, b. p. 271°/760 mm., m. p. 42°, and a *substance*, (?) $C_{22}H_{20}O_4$, m. p. 136°; the p-*toluenesulphonyl* derivative, m. p. 105—106°, and the *methyl ether*, b. p. 137°/13 mm., of the phenol are described. An oxime could not be prepared from the phenol or its methyl ether. Oxidation of rotenic acid by aqueous permanganate affords *iso*butyric acid, whereas acetic acid is derived similarly from the phenol methyl ether. Rotenic acid is therefore regarded as a hydroxy*iso*propylcoumaronecarboxylic acid in which the position of the substituents remains undecided.
H. WREN.

Constituents of *Myoporum lætum*, Forst. ("Ngaio"). III. Oxide rings of ngaione. F. H. MCDOWALL (J.C.S., 1928, 1324—1331).—Ngaiol (A., 1927, 566), when treated with hydrogen and platinum-black in glacial acetic acid solution, gives an *oxido-glycol*, $C_{15}H_{28}O(OH)_2$, d^{20} 0·966, 1·4664, differing in its colour reaction and in its physical constants from that obtained using Skita's colloidal palladium (*loc. cit.*). The oxide rings of the hydrogenated derivatives of ngaione can be opened by the action of hydrogen halides in glacial acetic acid solution. Tetrahydrongaiene dioxide gives opening of only one oxide ring with formation of an oily *chloro-oxido-acetate*, $C_{15}H_{28}OCl{\cdot}OAc$. Tetrahydrongaiol with hydrogen iodide in glacial acetic acid suffers fission of both oxide rings with formation of an oily *polyiodide acetate*, probably $C_{15}H_{28}I_3(OAc)_3$, which cannot be reduced without the formation of an ethylenic linking. Hydrogenation of the product of reduction gives, after hydrolysis, a mixture of alcohols from which, by fractional distillation under reduced pressure, a paraffin *alcohol*, $C_{15}H_{31}OH$, b. p. 168—172°/29 mm., d_{20}^{20} 0·841, n_D^{20} 1·4474, was isolated. In one experiment, a paraffin *glycol*, $C_{15}H_{30}(OH)_2$, b. p. 200—215°/13 mm., n_D^{20} 1·4655, was obtained. The isolation of these last two compounds proves definitely the absence of carbocyclic rings from the molecule of ngaione. From the stability of ngaiol to water under pressure and of ngaiol and tetrahydrongaiol to acetic anhydride, it is concluded that an ethylene oxide ring is not present in ngaione. An *isomeride* of ngaiol, b. p. 188—190°/29 mm., d_{20}^{20} 1·013, n_D^{0} 1·4794, and a *sesquiterpene monoxide*, $C_{15}H_{24}O$, b. p. 160—170°, n^{20} 1·4894, d_{20}^{20} 0·9485, have been isolated from crude ngaiol.

The colour reaction given by furan derivatives with vanillin and concentrated hydrochloric acid (Asahina, A., 1924. i, 977) is also given by the majority of the oxides now described, as well as by ethyl ether, acetal, *iso*amyl ether, phenetole, anisole, diphenyl ether, and dimethylpyrone. M. CLARK.

Colouring matter of citrus juices. M. B. MATLACK (Amer. J. Pharm., 1928, 100, 243—246).—The principal pigment of the Indian red pummelo and the pink grape fruit is lycopin. Pulp from the sweet orange, satsuma, and king mandarin gave less definite tests when subjected to the Molisch microcrystallisation method, an unsaponifiable *compound*, m. p. 75°, influencing the form of the crystals. Spectroscopic examination of light petroleum and alcoholic extracts of orange and tangerine pulp indicated the presence of carotin and xanthophyll. S. COFFEY.

Ultra-violet absorption curves of pulegone and *iso*pulegone. J. SAVARD (Compt. rend., 1928, 186, 1436—1438, and Bull. Soc. chim., 1928, [iv], 43, 524—529).—Whilst β-pulegone (A., 1926, 408) possesses the two absorption bands in the ultra-violet corresponding with those often observed in unsaturated and ketonic compounds, the bands of *iso*pulegone merge into each other. Pulegone obtained by distillation has a greater absorption in the band due to the double linking. Since this absorption is unchanged by treatment of the substance with potassium hydroxide, it is probably caused by the presence of the more unsaturated enolic tautomeride.
G. A. C. GOUGH.

Optical activity and polarity of substituent groups. VIII. Growing-chain effects and *ortho*-effect in benzoic esters. H. G. RULE, W. HAY, and J. PAUL (J.C.S., 1928, 1347—1361).—The rotatory powers of a series of menthyl *n*-alkoxyacetates and menthyl hydrogen dicarboxylates have been measured for different wave-lengths both in solution and in the homogeneous state. The values for the alkoxyacetates fall steeply to a minimum at propoxy-, rise

rapidly to a maximum at butoxy- and amyloxy-, and then fall to a minimum at heptyl- and octyl-oxy-acetates. The menthyl hydrogen dicarboxylates give a maximum for glutarate, a minimum for suberate, and another maximum for azelate. When these values are plotted against the length of the chain, which is measured from and includes the asymmetric atom, it is found that the maxima for one series almost coincide with the minima for the other. It is concluded from these results that the influence of *o*-substituents in optically active benzoates (this vol., 221) is propagated through space. A pronounced alternation in the rotatory powers of the menthyl hydrogen dicarboxylates is found, which disappears in the sodium salts. It is suggested that the alternation is a superimposed secondary effect due to association of the hydrogen esters through the carboxyl groups.

The following compounds are described: l-*menthyl propoxyacetate*, b. p. 161°/14 mm.; n-*butoxyacetic acid*, b. p. 115—116°/10 mm. (l-*menthyl* ester, b. p. 172·5°/14 mm.), from sodium butoxide and sodium chloroacetate; n-*amyloxyacetic acid*, b. p. 134°/12 mm. (*acid chloride*, b. p. 103°/64 mm.; l-*menthyl* ester, b. p. 148°/14 mm.); n-*hexyloxyacetic acid*, b. p. 143—144°/10 mm. (*acid chloride*, b. p. 106—108°/22 mm.; l-*menthyl* ester, b. p. 187°/10 mm.); n-*heptyloxyacetic acid*, b. p. 156°/10 mm., m. p. 7·5—8·5° (*acid chloride*, b. p. 116°/16 mm.; l-*menthyl* ester, b. p. 200°/11 mm.), and n-*octyloxyacetic acid*, b. p. 166°/10 mm., m. p. 12·5—13·5° (*acid chloride*, b. p. 125—126°/12 mm.; l-*menthyl* ester, b. p. 183°/2 mm.). l-*Menthyl hydrogen glutarate, adipate, pimelate, suberate, azelate,* and *sebacate* were obtained by partial hydrolysis of the corresponding dimenthyl esters. H. BURTON.

Carene. M. LAGACHE (Bull. Inst. Pin, 1927, 233—239; Chem. Zentr., 1928, i, 339).—The oil from *Pinus longifolia* has d^{20} 0·875, n_Y (Hg yellow) 1·4797, n_G^{20} (Hg green) 1·4803, α_Y −1·51°, α_G −1·18°, and yields *l*-pinene 24·8%, nopinene 9·7%, a terpene and carene 37·6%, an *l*-terpene 1·7%, oxidation products and longifolene 20·2%, and residue 6·8%. The carene has b. p. 70°/10 mm., d^{25} 0·8635, n^{25} 1·4678, 1·4682, 1·4700, $[\alpha]_Y$ +17·13°, $[\alpha]_C^{25}$ +19·88° (nitrosochloride, m. p. 101—102°, $[\alpha]_Y$ +254·80°, $[\alpha]_G$ +288·62°); nitrosocarene has m. p. 89—90°, $[\alpha]_Y$ +160°, $[\alpha]_G$ +185°; carenenitrolmethylamine, m. p. 180°, $[\alpha]_Y$ +153·90, $[\alpha]_G$ +188·9°; carenenitrolethylamine, m. p. 155°, $[\alpha]_Y$ +135·6°, $[\alpha]_G$ +176°; carenenitrolpropylamine, m. p. 95°, $[\alpha]_Y$ +123·4°, $[\alpha]_G$ +181·4°. A. A. ELDRIDGE.

Preparation of bromocamphor. F. CHEMNITIUS (Pharm. Zentr., 1928, 69, 307—309).—The slow addition of bromine (1 mol.) to camphor at 40—45° yields dibromocamphor, which loses hydrogen bromide when heated at 70° and finally at 120° for 3 hrs. The crude product is then poured into 10% potassium carbonate solution. By recrystallisation from alcohol and recovery from mother-liquors, a total yield of 80% of theory of bromocamphor, m. p. 76°, is obtained. R. K. CALLOW.

Dynamic isomerism. XXVII. Absorption spectra of prototropic compounds. Physical properties of the stable and labile forms of benzoylcamphor. T. M. LOWRY, C. A. H. MACCONKEY, and H. BURGESS (J.C.S., 1928, 1333—1347).—Measurements have been made of the m. p., optical rotation, rotatory dispersion, solubility, and ultraviolet absorption of the enolic and ketonic forms of benzoylcamphor. Contrary to the statement of Morton and Rosney (A., 1926, 454) "that the two isomeric forms of benzoylcamphor give bands at the same wave-length but of unequal intensity," the absorption bands of the enol and ketone are shown to be of almost equal intensity, whilst differing widely in wave-length. The absorption of the equilibrium mixture in very dilute alcoholic solutions corresponds closely with that of a mixture of two parts of enol and one part of ketone. Van 't Hoff's relation between the solubilities of the two forms and their equilibrium concentrations has been tested for solutions in alcohol, acetone, and benzene and found to hold good within ±8%. The ratio of the initial and final solubilities of the enolic form indicates that the equilibrium mixture in a saturated alcoholic solution contains about 58% of enol, in close agreement with the proportion, 59%, deduced from the optical rotations of the solutions.

Improved methods of preparation of the enolic and ketonic forms of benzoylcamphor are described. M. CLARK.

β-2-Furylethylamine. T. YABUTA and K. KAMBE (Proc. Imp. Acad. Tokyo, 1928, 4, 120—121).—β-2-Furylethylamine (*picrolonate*) (Windaus and Dalmer, A., 1921, i, 117) is conveniently prepared by reducing β-nitro-2-furylethylene with aluminium amalgam to 2-furylacetaldoxime (Asahina and Fujita, A., 1923, i, 239) and then the latter with sodium amalgam. The nitrofurylethylene is obtained by the action of nitrous fumes on β-2-furylacrylic acid in benzene solution. J. STEWART.

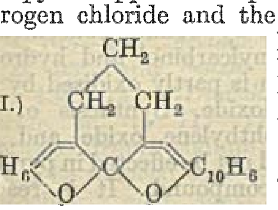
Condensation products of furfuraldehyde with acid amides. K. BEAUCOURT (Monatsh., 1928, 49, 1—7).—Condensation of furfuraldehyde (1 mol.) with acid amides (2 mols.) by heating the components together for 3½—4 hrs. on a water-bath in a current of carbon dioxide, occurs thus: $C_4H_3O{\cdot}CHO + 2NH_2{\cdot}COR = C_4H_3O{\cdot}CH(NH{\cdot}COR)_2 + H_2O$. In this way from the appropriate acid amide are prepared *furfurylidene-diacetamide* (yield 40%), m. p. 197° (decomp.); *-dipropionamide* (yield 35%), m. p. 195° (decomp.); *-di*-n-*butyramide* (yield 35—40%), m. p. 181° (decomp.); *-dibenzamide* (30—35% yield), decomp. 185°. With formamide only resinous products, from which no crystalline compound could be isolated, were obtained. The use of condensing agents (hydrochloric acid or pyridine) reduces the yields to nearly one half. J. W. BAKER.

Esters of furoylacetic acid. J. E. ZANETTI and C. O. BECKMANN (J. Amer. Chem. Soc., 1928, 50, 1438—1442).—The *methyl* ester, b. p. 144—145°/20 mm. [*sodium*, *potassium*, and *copper* salts; *oxime*, m. p. 124—125°; *semicarbazone*, m. p. 141—142° (decomp.)]; n-*propyl* ester, b. p. 110—112°/1 mm. (*sodium* and *copper* salts; *oxime*, m. p. 120—121°; *semicarbazone*, m. p. 137—138°), and n-*butyl* ester, m. p. 25·2°, b. p. 136—138°/3 mm. (*copper* salt; *oxime*, m. p. 102°; *semicarbazone*, m. p. 127—128°),

of furoylacetic acid have been prepared. The m. p. of the above oximes are determined at a standard rate of heating (4°/min.), and are actually the temperatures of conversion into 3-furyloxazolone (A., 1910, i, 892). The stability of these oximes is not in accordance with the order of attraction of the furyl group for hydroxyl given by Hantzsch, whilst their relative stability is not in accordance with Abegg's theory (A., 1899, i, 327). H. E. F. NOTTON.

Action of ethyl formate on dibenzyl ketone. E. BENARY and G. A. BITTER (Ber., 1928, **61**, [*B*], 1057—1060).—Dibenzyl ketone is converted by an excess of sodium ethoxide and ethyl formate in anhydrous ether into the disodium salt of di(hydroxymethylenebenzyl) ketone, recognised by its conversion by water and aniline hydrochloride into the *dianilide*, $CO(CPh{:}CH{\cdot}NHPh)_2$, m. p. 165—166°. If, however, the sodium salt is treated with dilute sulphuric acid, 3 : 5-*diphenyl* : 4-*pyrone*, m. p. 186—187°, is obtained. The latter substance is transformed by ammonium acetate into 4-*hydroxy*-3 : 5-*diphenylpyridine*, m. p. 376° after darkening, reduced by sodium and alcohol to 4-*hydroxy*-3 : 5-*diphenylpiperidine*, m. p. about 310° after darkening at 290°, and converted by distillation with zinc dust into 3 : 5-*diphenylpyridine*, m. p. 193—194° (*picrate*, m. p. 276°). If excess of sodium ethoxide and ethyl formate is avoided in the action on dibenzyl ketone, the main product is *hydroxymethylenedibenzyl ketone*, converted by phenylhydrazine into 1 : 4-*diphenyl*-5(3)-*benzylpyrazole*, m. p. 128°. Diethyl ketone gives only the monohydroxymethylene derivative when an excess of ethyl formate and sodium ethoxide is employed.
H. WREN.

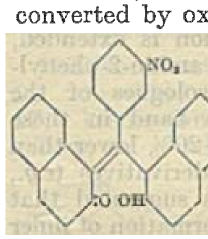
Heteropolar carbon compounds. VI. *spiro*-Pyrans. W. DILTHEY and H. WUBKEN (Ber., 1928, **61**, [*B*], 963—968).—The development of colour in hot solutions of *spiro*dinaphthapyran, $\left(\begin{matrix}CH{=}CR\\C_{10}H_6{\cdot}O\end{matrix}>\right)_2C$ (cf. Lowenbein and Katz, A., 1926, 956; Dilthey and others, A., 1926, 1254; Dickinson and Heilbron, A., 1927, 251) has been ascribed by Dilthey to ionic dissociation, and this view has been shared by Dickinson and Heilbron (A., 1927, 884), who, however, find that coloration is not developed by 3 : 3′-dialkyl*spiro*naphthapyrans. Confirmation of the authors' theories is found in the observation that the ability of *spiro*pyrans to yield coloured solutions is paralleled by their tendency towards salt formation and that the phenomenon is not principal in nature. Thus 3 : 3′-diethyl*spiro*benzopyran appears incapable of forming a salt with hydrogen chloride and the diminished basicity goes hand in hand with a hypsochromic effect. Also the *spiro*dinaphthopyran from *cyclo*hexanone (I) (cf. Dickinson and Heilbron, *loc. cit.*) gives only violet salts which are not readily isolated; in alcohol, pyridine, xylene, or chlorobenzene it does not develop colour when heated, but this is due only to insufficiently high temperature, since in diphenyl ether (b. p. 250°) it is violet and

(I.)


becomes colourless again when cooled. The inhibitive effect of 3 : 3′-disubstitution is therefore not absolute. Further, the development of colour by 3-amyl*spiro*dinaphthopyran in pyridine is greatly facilitated by the addition of a little water; the observation is more readily explained by an ionic dissociation than by a quinonoid transformation.

3-*Amyl*spiro*dinaphthopyran*, m. p. 182° [*perchlorate*, m. p. 256°; *perchlorate* of *acetylated base*, m. p. 204° (decomp.)], is prepared by saturating an alcoholic solution of 2-hydroxynaphthaldehyde and methyl hexyl ketone with hydrogen chloride. 3 : 3′-Trimethylene*spiro*dinaphthopyran forms colourless crystals, m. p. 238°; the normal *hydrochloride* and the *perchlorate*, complete decomp. 190°, are described. 3 : 3′-Dimethyl*spiro*dinaphthopyran, m. p. 237—238°, is obtained with certainty by the action of 2-hydroxynaphthaldehyde on diethyl ketone in glacial acetic acid saturated with hydrogen chloride; the unstable *picrate* is described. 3 : 3′-*Diphenyl*spiro*dinaphthopyran*, $C_{37}H_{24}O_2$, m. p. 247—248°, is prepared from dibenzyl ketone and a large excess of 2-hydroxynaphthaldehyde. In glacial acetic acid saturated with hydrogen chloride, the reactants give, after addition of perchloric acid, 3-*phenyl*-2-*benzylnaphthopyrylium perchlorate*, m. p. indef. 212—214°, which in boiling alcohol passes into 3-*phenyl*-2-*benzylidene*-5 : 6-*benzo*-2-*chroman*, m. p. 146°. H. WREN.

***m*-Nitrobenzylidenedi-β-naphthol [*m*-nitrophenyldi-2-hydroxy-α-naphthylmethane].** O. DISCHENDORFER (Monatsh., 1928, **49**, 133—145).—The formation of a yellow *compound*, m. p. 61·5°, of 1 mol. of β-naphthol with 1 mol. of *m*-nitrobenzaldehyde when the two substances are melted together at 70°, or heated in petroleum solution on a water-bath, is confirmed by thermal analysis. The eutectic mixture has m. p. 47·5° and contains 17·5% of β-naphthol. Since solutions of this compound are colourless it is assumed that it is completely dissociated in solution. *m*-Nitrophenyldi-2-hydroxy-α-naphthylmethane (I) (Zenoni, A., 1894, i, 136) yields a *monosodium* salt when it is dissolved in 6% sodium hydroxide solution, a *dibenzoate*, m. p. 193—194°, and a *dimethyl ether*, m. p. 216°. It is converted by oxidation with sodium hypobromite in alcohol solution into *dehydro*-m-*nitrobenzylidenedi*-β-*naphthol* (annexed formula), m. p. 221—222° [*oxime*, m. p. 216—217° (decomp.)]. Dehydration of (I) with concentrated sulphuric acid yields 9-m-*nitrophenyl*-1 : 2 : 7 : 8-*dibenzoxanthen* (II) (Zenoni, *loc. cit.*), which is also obtained by heating *m*-nitrobenzaldehyde and β-naphthol in a mixture of acetic and concentrated sulphuric acids at 50°. It is oxidised by heating with concentrated sulphuric acid on a water-bath to the hydrogen sulphate of 9-*nitrophenyl*-1 : 2 : 7 : 8-*dibenzoxanthhydrol* (III), m. p. 286—287° (decomp.) (*ethyl ether*, m. p. 266—267°; *methyl ether*, m. p. 256—257°), which is best obtained by decomposition with aqueous acetone of the *ferric chloride double* salt, m. p. 264° (decomp.), of the pyrylium chloride (below), which is obtained by



(I.)

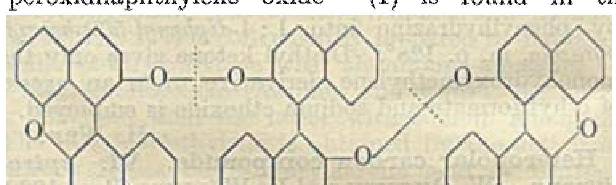
oxidation of the pyran (II) with manganese dioxide in a boiling mixture of acetic and hydrochloric acids and treatment of the resulting solution with ferric chloride. When a chloroform solution of (III) is treated with acetyl chloride and anhydrous hydrogen chloride passed into the solution at the ordinary temperature, it is converted into 9-*nitrophenyldi naphthopyrylium chloride hydrochloride*, m. p. 281° (decomp.) [*mercurichloride*, m. p. 286° (decomp.); *perbromide*, m. p. 225° (decomp.); *perchlorate*, m. p. 307° (decomp.)]. When (II) is reduced with zinc dust and acetic acid it yields 9-m-*acetamidophenyl*-1 : 2 : 7 : 8-*dibenzoxanthen*, m. p. 246—247°, which, on hydrolysis, is converted into the corresponding 9-m-*aminophenyl* derivative, m. p. 242—243°.

J. W. Baker.

Colour and chemical constitution. XXIII. The pigments of flowers. J. Moir (Trans. Roy. Soc. S. Africa, 1928, **16**, 121—130; cf. this vol., 184).—The variation in colour of natural anthocyanidins and similarly constituted synthetic substances with the number and position of hydroxyl groups in the molecule has been investigated spectroscopically and the results are tabulated and discussed. A regular gradation of shade is found as the anthocyanidin is simplified down to the parent substance by the successive removal of hydroxyl groups. The presence of these groups in positions 4′ and 7 has the greatest effect in heightening the colour. When hydroxyl groups are present in these positions the presence of a hydroxyl group in positions 3 or 5 only broadens the absorption band without changing its position, but when they are absent the introduction of a hydroxyl group in position 3 has a marked effect. In acid solution, in which the compounds are supposed to exist as double oxonium chlorides, there is a gradual shift of colour from the yellow (flavylium chloride, λ 392) to the violet end of the spectrum (delphinidin, λ 545) as the number of hydroxyl groups is increased, this effect being due, probably, to loading by inactive (non-ionised) hydroxyl groups. In acid solution the methoxyl group has only a very slightly greater effect than the hydroxyl. A similar colour shift towards the violet occurs when the solution approaches neutrality, and the absorption spectra of nine derivatives in a medium of p_H 5—6 are recorded. The investigation is extended, in a medium of p_H 5, to a series of amino-2-phenylquinoline derivatives which are isologues of the anthocyanidins; the centre of the band in these derivatives occurs at a position 10—20% lower than that of the corresponding oxygen derivatives (*e.g.*, 2-phenylquinoline, λ 358), and it is suggested that this is due to the possibility of the formation of inner oxonium salts in the oxygen but not in the nitrogen derivatives. In alkaline solution the colour of the anthocyanidin is shifted towards the violet end of the spectrum (delphinidin, λ 690 and 590), this being due to the hydroxyl groups acting as positive centres and not as loading groups, the oxonium structure disappearing and the substances having the carbinol configuration. A displacement of the band towards the violet also occurs when the distance between the auxochrome group and the other active centre (oxonium atom) is increased by lengthening the side-chain, and the positions of the bands of numerous flavylium, benzopyrylium, and carbocyanine derivatives are tabulated. The observation of Buck and Heilbron (J.C.S., 1922, **121**, 1204) that the absorption spectra of their styrylbenzopyrylium salts does not change when the colour changes from red to bluish-green is incorrect, the green phase possessing a strong band in the far red (λ 675 for the 4′-hydroxy-, and λ 700 for the 3′ : 4′-dihydroxy-compounds respectively) which was overlooked. The effect of replacing the quinoline ring by benzthiazole, benzoxazole, and benziminazole rings is also considered. The following new compounds have been prepared in the course of the investigation (no experimental details are given): 7-*amino*- (λ 426), 4′-*amino*- (λ 407), 7 : 4′-*diamino*- (λ 430), 5 : 7 : 4′-*triamino*- (λ 440) -2-*phenylquinolines*, which are obtained by condensation of the appropriate nitrobenzaldehyde with *p*-nitroacetophenone in the presence of potassium hydroxide, reduction of the resulting nitrophenyl styryl ketone with sodium hyposulphite, and closure of the quinoline ring by the action of acids.

J. W. Baker.

Oxidation of phenols. X. Addition of triphenylmethyl to radicals with univalent oxygen and to aromatic peroxides. R. Pummerer and F. Luther (Ber., 1928, **61**, [*B*], 1102—1107).—Confirmation of the views of Pummerer and Rieche (A., 1926, 1135) on the constitution of "dinaphthyldiperoxidnaphthylene oxide" (I) is found in the



(I.)

observation that it suffers fission at the dotted lines when treated with a solution of triphenylmethyl in benzene in complete absence of oxygen, the yield of the *ditriphenyl ether* of *dinaphthol*, m. p. 289° (from the middle portion), amounting to 60% if the triphenylmethyl is added to the compound. The ether, obtained also from β-dinaphthol and triphenylmethyl chloride in pyridine solution, is an unusually stable substance which is unaffected by permanganate, and hence undoubtedly contains the triphenylmethyl group attached to oxygen. The *triphenylmethyl ether* of *hydroxydinaphthylene oxide*, m. p. 237°, is more difficult to isolate. It is stable towards permanganate and therefore cannot be a derivative of the corresponding keto-methyl. It is unusually stable towards alcoholic potassium hydroxide or hydrogen chloride, but is converted by boiling concentrated sulphuric acid into triphenylcarbinol and hydroxydinaphthylene oxide, which is partly oxidised by the acid to dinaphthylene dioxide. Synthesis of the ether from hydroxydinaphthylene oxide and triphenylmethyl chloride could not be effected in pyridine or through the sodium compound. It is readily obtained from hydroxydehydrodinaphthylene oxide and triphenylmethyl in benzene.

H. Wren.

2 : 7-Dimethylsulphonefluoran, 2′-hydroxy-5′-toluoylbenzene-2-sulphonic acid, and some of

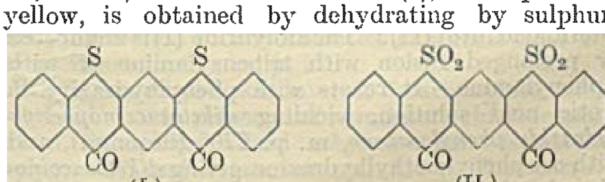
their derivatives. W. R. ORNDORFF and I. T. BEACH (J. Amer. Chem. Soc., 1928, **50**, 1416—1421).—*o*-Chlorosulphonylbenzoyl chloride and sodium *p*-tolyloxide give at 30—35° p-*tolyl* o-*chlorosulphonylbenzoate*, m. p. 138°, and at 100°, *di*-p-*tolyl* o-*sulphobenzoate** (* crystallographic data), m. p. 95·5°. When this is fused with zinc chloride and the product extracted with aqueous sodium carbonate, it affords the *sodium* salt* (+1·5EtOH) of 9-*hydroxy*-9-*phenyl*-2 : 7-*dimethylxanthen*-o-*sulphonic acid* [*barium* salt (+$4H_2O$); *methyl* ester; yellow *perchlorate*], which is converted by acid into orange 2 : 7-*dimethylsulphonefluoran**, decomp. 250°. This is probably similar in constitution to 3 : 6-dimethylsulphonefluoran (A., 1926, 1036); it is formed in poor yield from *o*-sulphobenzoic anhydride, *p*-cresol, and zinc chloride at 123°. With sodium hydroxide at 200—220° it gives 2 : 7-dimethylxanthone, and at 280—290°, 2-hydroxy-5-toluic acid, with hydrogen chloride, an unstable *monohydrochloride*, with bromine, products of indefinite composition, with zinc dust and boiling water, the *zinc* salt of 2 : 7-*dimethylhydrosulphofluoranic acid* (9-*phenyl*-2 : 7-*dimethylxanthene*-o-*sulphonic acid*), and with sulphuric acid at 200°, reddish-brown 2 : 7-*dimethylsulphonecœroxonol*, $C_{21}H_{16}O_4S$ (cf. Decker and Ferrario, A., 1906, i, 687). 2′-*Hydroxy*-5′-*toluoylbenzene*-2-*sulphonic acid*, m. p. 90° (*ammonium* salt*), is obtained from *o*-sulphobenzoic anhydride and *p*-cresol in presence of tetrachloroethane and aluminium chloride at 100—110°. When heated with *p*-cresol it gives 2 : 7-dimethylsulphonefluoran. H. E. F. NOTTON.

Cyclic disulphides derived from diphenyl. H. J. BARBER and S. SMILES (J.C.S., 1928, 1141—1149).—An improved method of preparing sodium 2-iodobenzenesulphonate is described. From this by treatment with copper powder (merely in boiling aqueous suspension) and then with phosphorus pentachloride are obtained successively diphenyl-2 : 2′-disulphonic acid and diphenyl-2 : 2′-disulphonyl chloride. Reduction of this disulphonyl chloride with zinc dust and hydrochloric acid yields 2 : 2′-*dithioldiphenyl*, m. p. 78—79°; oxidation of the dimercaptan with ferric chloride gives *diphenylene* 2 : 2′-*disulphide*, m. p. 113° (*disulphoxide*, m. p. 128°), converted by copper powder at 250° into dibenzthiophen. 2 : 2′-Dithioldiphenyl gives, with sodium chloroacetate, 2 : 2′-*dicarboxymethylthioldiphenyl*, m. p. 201—202°, with carbonyl chloride it gives *diphenylene*-2 : 2′-*dithiolcarbonate*, m. p. 101·5°, whilst it condenses with aldehydes and ketones, yielding, for example, *benzaldehyde diphenylene*-2 : 2′-*mercaptol*, m. p. 105—106°, *acetone diphenylene*-2 : 2′-*mercaptol*, m. p. 95°, and *benzil diphenylene*-2 : 2′-*mercaptol*, m. p. 198°. 4 : 4′-*Dimethyldiphenyl*-2 : 2′-*disulphonyl chloride*, m. p. 117—118°, prepared by general reactions from sodium-4-iodotoluene-3-sulphonate, cannot be reduced to a cyclic disulphide by zinc and hydrochloric acid, since *m*-tolylmercaptan (p-*nitrobenzoyl* derivative, m. p. 96°) is the main product. Diphenyl-3 : 3′-disulphonyl chloride gives the corresponding *dithiol* (*dimethyl* derivative, m. p. 50°) when reduced with zinc dust and acid, and this compound is converted into amorphous, insoluble products when it is oxidised. 4 : 4′-*Dichlorodiphenyl*-3 : 3′-*disulphonyl chloride*, m. p. 179°, obtained from benzidine-3 : 3′-disulphonic acid, yields on reduction the corresponding *dithiol* (*dimethyl* derivative, m. p. 130°), which is converted by oxidation into amorphous, insoluble material.

Diphenyl-4 : 4′-*disulphinic acid*, m. p. 143°, prepared by reduction of the corresponding disulphonyl chloride with boiling alkaline sulphite solution, is converted by mineral acid into an amorphous material, probably a disulphoxide of high mol. wt. 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonic acid* (*potassium* salt) is formed by the action of copper powder on potassium 1-iodonaphthalene-2-sulphonate in the presence of a little copper sulphate. Reduction of 1 : 1′-*dinaphthyl*-2 : 2′-*disulphonyl chloride*, m. p. 202—203°, with zinc dust and hydrochloric acid yields 2-naphthyl mercaptan. With alkaline sulphite followed by acidification, the cyclic *disulphoxide* is produced, and this on reduction with hydriodic acid gives 1 : 1′-*dinaphthylene* 2 : 2′-*disulphide*, m. p. 214°. When this substance is kept at 250° with copper powder, 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*, m. p. 202°, is obtained. It is pointed out that the fact that no cyclic disulphides are obtained from the 4 : 4′- and 3 : 3′-dithioldiphenyl derivatives, whereas 2 : 2′-dithioldiphenyl readily affords a cyclic disulphide, is in harmony with recent views on the stereochemistry of the diphenyl nucleus. The following compounds are described: *di*-2-*iodophenyl disulphide*, m. p. 133°; 2-*iodophenylsulphinic acid*, m. p. 108°; 2-*iodophenylmethylsulphone*, m. p. 109°; 2-*iodotoluene*-o-*sulphonic acid* [*barium* salt (+$1\frac{1}{2}H_2O$); *sulphonyl chloride*, m. p. 61—62°; *amide*, m. p. 135°]; 4-*iodotoluene*-3-*sulphonic acid* [*potassium* salt (+H_2O); *sulphonyl chloride*, m. p. 68°; *amide*, m. p. 161—162°]; *di*-4-*iodo*-m-*tolyl disulphide*, m. p. 104—105°; 1-*iodonaphthalene*-2-*sulphonic acid* (*barium* salt; *sulphonyl chloride*, m. p. 94°); 1-*iodonaphthalenesulphinic acid*, m. p. 143°; and *di*-1-*iodo*-2-*naphthyl disulphide*, m. p. 154°. Thianthren derivatives are formed when *o*-iodo-disulphides are heated with copper powder.

From di-*o*-iodophenyl disulphide, di-4-iodotolyl 3-disulphide, and di-1-iodonaphthyl 2-disulphide are thus obtained thianthren, 2 : 6-dimethylthianthren, and dinaphthathianthren, respectively. M. CLARK.

***lin*Dithioxanthone.** C. FINZI (Gazzetta, 1928, **58**, 269—278; cf. Davis and Smiles, J.C.S., 1910, **97**, 1290).—lin*Dithioxanthone* (I), m. p. 316°, yellow, is obtained by dehydrating by sulphuric



(I.) (II.)

acid at 100° the m-*phenylenedithio*-2 : 2′-*dibenzoic acid* [1 : 3-*bis*(o-*carboxyphenylthiol*)*benzene*], $C_6H_4(S{\cdot}C_6H_4{\cdot}CO_2H)_2$, m. p. 270°, which is obtained by the condensation of thioresorcinol with diazotised anthranilic acid. (When the latter condensation is effected in an acid medium, m-*phenylenebis*[*thio*-o-*diazobenzoic acid*], $C_6H_4(S{\cdot}N_2{\cdot}C_6H_4{\cdot}CO_2H)_2$, is obtained, unstable towards alkali.) The acid is

oxidised by peracetic acid to m-*phenylene bis*-o-*carboxyphenylsulphone*, m. p. 201°, with probably some sulphonic acid, and the dithioxanthone, stable to mild oxidising agents, by persulphuric acid to the corresponding *dibenzophenonedisulphone* (II), m. p. 305° (decomp.). When the dithioxanthone is dissolved in alcohol containing potassium ethoxide, and is treated with zinc, the colour of the solution changes through purple to green; on acidification, the *dithioxanthhydrol*, m. p. 224° (decomp.), is obtained.

In either an acid or an alkaline medium, the sodium salt of dithioresorcinol reacts with diazotised *o*-aminobenzyl alcohol to give the stable m-*phenylenebis*(*thio*-o-*diazobenzyl alcohol*); in acid solution, diazotised 3-amino-β-naphthoic acid similarly reacts to give m-*phenylenebis*(*thio*-3-*diazo*-β-*naphthoic acid*).

E. W. Wignall.

Imide ring closure in derivatives of diketosuccinic acid phenylosazone. F. D. Chattaway and W. G. Humphrey (J.C.S., 1928, 1094—1098).—The formation of derivatives containing the imide ring by the action of ammonia, primary amines, and α-hydrazines on diketosuccinic anhydride phenylosazone (I) (A., 1927, 776) is described.

Fusion of the anhydride (I) with carbamide yields *diketosuccinimide phenylosazone*, m. p. 189°, which dissolves in boiling sodium hydroxide solution with evolution of ammonia, giving sodium diketosuccinate phenylosazone (II). The last-named compound is immediately converted by acids into 4 : 5-diketo-1-phenylpyrazoline-3-carboxylic acid 4-phenylhydrazone (III). Benzylamine combines with the anhydride (I), yielding the *benzylamine* salt of *diketosuccinobenzylamic acid phenylosazone*, m. p. 165° (decomp.), from which the base is readily removed with regeneration of the anhydride by heating with acetic anhydride. Acidification of the benzylamine salt yields *diketosuccinobenzylimide phenylosazone*, m. p. 179°. Dibenzylamine reacts similarly, giving the *dibenzylamine* salt of *diketosuccinodibenzylamic acid phenylosazone*, m. p. 161—162° (decomp.), converted on acidification into *diketosuccinodibenzylamic acid phenylosazone*, m. p. 180°. Aniline reacts with the anhydride (I) giving a mixture of *diketosuccinanilic acid phenylosazone* (IV), m. p. 201° (decomp.) (+AcOH, m. p. 135—200°, dependent on rate of heating), and *diketosuccinanil phenylosazone* (V), m. p. 252° (decomp.). The compound (IV) is converted by prolonged boiling with aniline into (V) and by prolonged boiling with aqueous-alcoholic hydrochloric acid into (III). The anhydride (I) is unaffected by prolonged fusion with tribenzylamine or with diphenylamine. It reacts with phenylhydrazine in acetic acid solution, yielding *diketosuccinophenylhydrazide phenylosazone*, m. p. 270° (decomp.), and with *as*.-phenylmethylhydrazine, giving *diketosuccinophenylmethylhydrazide phenylosazone*, m. p. 243·5° (decomp.). Analogous derivatives of certain substituted phenylhydrazones and osazones of diketosuccinic anhydride have also been prepared. The tolylhydrazones yield with aniline the corresponding anils, the ketonic group remaining unchanged. Phenylhydrazine acts on the ketonic group as well as forming the hydrazide. The 2 : 4-dichloro- and 2 : 4-dibromo-anhydrides react with aniline less readily, the products consisting entirely of the corresponding anils. The following are described: *diketosuccinanil* p-*tolylhydrazone*, m. p. 199° (decomp.); *diketosuccinophenylhydrazide* o-*tolylphenylosazone*, m. p. 250° (decomp.); *diketosuccinanil* 2 : 4-*dichlorophenylosazone*, m. p. 308° (decomp.); *diketosuccinanil* 2 : 4-*dibromophenylosazone*, m. p. 309° (decomp.); *diketosuccinophenylhydrazide* 2 : 4-*dichlorophenylosazone*, m. p. 280° (decomp.); *diketosuccinophenylhydrazide* 2 : 4-*dibromophenylosazone*, m. p. 295° (decomp.). All the compounds described containing the succinimide ring are, like the parent substance, very stable towards acids, but are converted by boiling 10% sodium hydroxide solution into sodium diketosuccinate phenylosazones.

M. Clark.

Action of aniline on *d*-glutamic acid. W. H. Gray (J.C.S., 1928, 1264—1267; cf. Hugounenq and others, A., 1924, i, 17).—Abderhalden and Schwab (A., 1926, 734) state that 2-hydroxypyrroline-5-carboxylic acid, the enolic form of 2-pyrrolidone-5-carboxylic acid, is obtained when *d*-glutamic acid is heated with aniline or diphenylamine. The product obtained in the first case is shown to be l-2-*pyrrolidone*-5-*carboxyanilide*, m. p. 191°, $[\alpha]_D$ +17·9° in 80% alcohol (p-*bromo*-derivative, m. p. 212°; 1-*acetyl* derivative, m. p. 166°; 1-*dibenzyl* derivative, m. p. 158°). In the second case, only *l*- and *dl*-2-pyrrolidone-5-carboxylic acids could be isolated, and neither these nor the anilide could be reduced by catalytic hydrogenation. dl-2-*Pyrrolidone*-5-*carboxyanilide* has m. p. 204°.

M. Clark.

Pirylene. J. von Braun and W. Teuffert (Ber., 1928, 61, [*B*], 1092—1099).—The constitutions $CH_2{:}C{<}^{CH=}_{CH_2}{>}CH$ or $CH{\ll}^{CMe}_{C{:}CH_2}$, are rendered probable for pirylene, the ultimate product of the Hofmann degradation of piperidine.

2-*Methylene*-N-*dimethylpyrrolidinium chloride*, m. p. 217° (corresponding chloroaurate, m. p. 265°), is converted by hydrogen in the presence of colloidal palladium or nickel into 2-*methyl*-N-*dimethylpyrrolidinium chloride*, m. p. not below 280°. The methylene compound is smoothly transformed by distillation with potassium hydroxide into *N*-dimethylpiperideine, $CH_2{:}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, b. p. 136—138°, d^{19} 0·7979, n_D^{19} 1·4635 (*chloroaurate*; *methochloride* and the corresponding *chloroplatinate* and *chloroaurate*), the constitution of which is established by catalytic hydrogenation to α-dimethylamino-*n*-pentane. Treatment of dimethylpiperideine methiodide with potassium hydroxide affords pirylene, b. p. 60°, d_4^{19} 0·7443, n_D^{1} 1·4505. The hydrocarbon contains two double linkings, since it readily yields an oily tetrabromide and absorbs 2 mols. of hydrogen. It is oxidised by permanganate to a mixture of acetic and oxalic acids.

The initial stages of the transformation of tetrahydro*iso*quinoline resemble closely those of piperidine. Thus, *o*-vinylbenzyldimethylamine is converted by bromine in chloroform into 2-*bromomethyl*-N-*dimethyldihydroisoindolium bromide*, $C_6H_4{<}^{CH(CH_2Br)}_{CH_2}{>}NMe_2Br$, m. p. 181—182° (decomp.) (corresponding *chloride* and *chloroplatinate*, decomp. 198°). It is converted by the successive action

of silver oxide and hydrochloric acid into 2-*methylene*-N-*dimethyldihydro*iso*indolium chloride*,
$C_6H_4<\begin{smallmatrix}C(:CH_2)\\ -CH_2-\end{smallmatrix}>NMe_2Cl$, m. p. 159° (*chloroaurate*, m. p. 184°, decomp. 190°; *chloroplatinate*, m. p. 218—219°), which is catalytically hydrogenated to 2-*methyl*-N-*dimethyldihydro*iso*indolium chloride*, m. p. 229° (*chloroaurate*, m. p. 166°; *chloroplatinate*, m. p. 201°). Treatment of the unsaturated chloride with potassium hydroxide yields a highly unstable liquid (possibly a basic alcohol) and, mainly, the *ether*, $[CH_2:C(NMe_2)\cdot C_6H_4\cdot CH_2]_2O$, b. p. 180—190°/3 mm. (*methiodide*, m. p. 211°), which is indifferent to phenylhydrazine, semicarbazide, Fehling's and ammoniacal silver solutions. It is reduced to the corresponding *tetrahydro*-derivative, b. p. about 190—200°/3 mm. (*methiodide*, m. p. 188°).

H. WREN.

Isomerisation phenomena in heterocyclic nitrogen compounds. N. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1928, **59**, 761—817).—A detailed *résume* is given of former work on isomerisation reactions in heterocyclic nitrogen compounds, and an investigation of the effect of condensations with alkyl halides and formaldehyde on such reactions. It is suggested that condensation first occurs on the nitrogen atom, followed by a migration to a carbon atom of the nucleus, with or without a change in the size of the ring. Such reactions proceed the more easily the more active are the atoms taking part and the more readily are unstable intermediate ring systems formed.

The magnesium iodide derivatives of indole, 2-methylindole, and pyrrole were allowed to react in the cold with ethyl formate and ethyl acetate. With methyl formate, indole yielded 1-formylindole, $d_4^{18\cdot5}$ 1·175, $n_D^{18\cdot5}$ 1·62. On raising the temperature of the reaction to 70—75°, indole-3-aldehyde, m. p. 194°, is obtained. With 2-methylindole the reaction is analogous—1-formyl-2-methylindole, d_4^{16} 1·1353, n^{16} 1·617, and 2-methylindole-3-aldehyde resulting.

Under similar conditions, pyrrole does not give 1-formylpyrrole, but only pyrrolealdehyde, n_D^{16} 1·5939 (oxime, m. p. 163°). If with indole instead of ethyl formate, ethyl acetate is used, the corresponding 1-acetylindole, b. p. 144—145°/10 mm., is obtained in the cold, which when heated passes into 3-acetylindole, m. p. 189°.

On heating 1-formylindole in a sealed tube at 300—350° some crystalline *substance* is formed, which does not melt even at 300°.

Under similar conditions 1-acetylindole yielded a small quantity of quinoline.

Pyrrolidine condenses with formaldehyde at 140—150° in a sealed tube, giving 1-*methoxypyrrolidine*, 1 : 1′-dipyrrolidylmethane and 2-methoxypyrrolidine. Under similar conditions, piperidine yields small quantities of 1- and 2-methylpiperidines, and 1 : 1′-*dipiperidylmethane*, b. p. 120—125°/3·5 mm., d^{15} 0·9335, n_D 1·4883.

Trimethyleneimine, if prepared by Howard and Marckwald's method by reducing *p*-tolyltrimethylenesulphonimide with sodium in amyl alcohol, gives as a by-product a dihydric *amino-alcohol*, $C_6H_{15}O_2N$. On condensation with formaldehyde in a sealed tube at 120°, trimethyleneimine forms hexamethylenedi-imine, b. p. 185°, d_4^{10} 0·911, n^{10} 1·4685.

M. ZVEGINTZOV.

Organic catalysts. II. Reinforcement of the catalytic activity of isatin by nuclear substitution. W. LANGENBECK (Ber., 1928, **61**, [*B*], 942—947; cf. A., 1927, 546).—Comparison of the effect of isatin, isatin-1-acetic acid, 5-bromo-, 5 : 7-dibromo-, 5-chloro-isatin, and potassium isatinsulphonate on the decolorisation of methylene-blue by alanine shows that substitution of the imino-hydrogen atom has little influence, whereas the introduction of a halogen atom or a sulphonic group into the benzene nucleus causes enhanced catalytic activity. *Isatin*-1-*acetic acid*, m. p. 206—207°, is prepared in 72% yield by the action of chloroacetic acid and sodium carbonate on a boiling solution of isatin in 10% sodium hydroxide. *Isatin*-1-*acetyl chloride*, *isatin*-1-*acetamide*, m. p. about 260° (decomp.), l-*menthyl isatin*-1-*acetate*, m. p. 122°, and 5-*nitroisatin*-1-*acetic acid*, m. p. 207°, are incidentally described.

α-Amino*iso*butyric acid can be dehydrogenated to acetone, carbon dioxide, and ammonia by *p*-benzoquinone, but not by alloxan or isatin. Since the process cannot take place through the intermediate formation of an α-imino-acid, there must be a method of dehydrogenation of amino-acids differing from that previously assumed and probably depending on the formation of a radical with tervalent nitrogen.

H. WREN.

Reaction of disulphoisatides. A. WAHL and LOBECK (Compt. rend., 1928, **186**, 1303—1305).—Disulphoisatide, when gently heated with dry cuprous chloride in acetic acid suspension, forms a black precipitate and an orange solution, yielding 50—60% of *iso*indigotin with some free sulphur and isatin: $C_{16}H_{12}O_2N_2S_2+2CuCl=C_{16}H_{10}O_2N_2+2CuS\ \ 2HCl$. The reaction may be applied to dimethyl- and dichloro-disulphoisatides (this vol., 428) and to the two *naphthodisulphoisatides* (insoluble substances, contaminated with excess of sulphur) prepared from the corresponding naphthoisatins. α-*Naphthodisulphoisatide* forms α-*dinaphtho*iso*indigotin* when thus treated.

B. W. ANDERSON.

Pyrrole and complex salts. H. FISCHER and B. PÜTZER (Ber., 1928, **61**, [*B*], 1068—1074).—2 : 4-Dimethylpyrrole is converted by bromine in glacial acetic acid into 3 : 5-dibromo-4-methylpyrryl-3-bromo-2 : 4-dimethylpyrrolenylmethane, oxidised by chromic acid in presence of concentrated sulphuric acid to bromocitraconimide, m. p. 170°.

Ethyl 4-methyl-2-ethylpyrrole-5-carboxylate and acetyl chloride in presence of aluminium chloride and carbon disulphide afford *ethyl* 3-*acetyl*-4-*methyl*-2-*ethylpyrrole*-5-*carboxylate*, m. p. 134°. The corresponding *acid*, m. p. 204° (decomp.), loses carbon dioxide when heated and yields 3-*acetyl*-4-*methyl*-2-*ethylpyrrole*, m. p. 122°. The ester is converted by sodium ethoxide and hydrazine hydrate in alcohol at 175° into 4-*methyl*-2 : 3-*diethylpyrrole*, b. p. 95—97°/20 mm. (*picrate*, m. p. 104·5°; additive *compound* with mercuric chloride; diazobenzenesulphonic acid *derivative*). 3 : 4-*Dimethyl*-2-*ethylpyrrole picrate*, m. p. 122·5° (corr.), is obtained from ethyl 3-aldehydo-

4-methyl-2-ethylpyrrole-5-carboxylate by the Wolff–Kishner method. Ethyl 2-methyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate is converted by bromine in glacial acetic acid at 18° into *ethyl 2-bromoethyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 96·5° (corresponding *anilide*, m. p. 95°).

Treatment of ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate with bromine yields *ethyl 2-bromo-4-methylpyrrole-3 : 5-dicarboxylate*, m. p. 147° (corr.). With hydrazine, the aldehyde gives the corresponding *hydrazone*, m. p. 100° (corr.), converted by a further portion of the aldehyde into the *aldazine*, $C_{24}H_{30}O_8N_4$, m. p. 196° (corr.), obtained directly from the aldehyde and hydrazine in acetic acid. The ester yields the complex *copper* derivative, $C_{24}H_{28}O_8N_4Cu$, m. p. 203° (corr.); it can be hydrolysed to the *tetracarboxylic acid*. The *aldazine* of 2 : 4-dimethylpyrrole-5-aldehyde has m. p. 251° (corr.). Treatment of ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate with magnesium methyl iodide affords *ethyl 4-methyl-2-α-hydroxyethylpyrrole-3 : 5-dicarboxylate*, m. p. 95° (corr.).

Attempts to decarboxylate mesoporphyrin by means of piperidine lead to the isolation of a *substance*, $C_{44}H_{60}O_4N_6$, possibly a molecular compound of the reactants (1 : 2), which yields a crystalline *copper* salt, $C_{44}H_{54}O_2N_6Cu$, apparently derived from the dipiperidide of mesoporphyrin; the corresponding *zinc* salt, m. p. 286° (corr.), is described. Mesoporphyrin dimethyl ester is converted by stannous chloride and sodium acetate in glacial acetic acid into the *compound* $C_{36}H_{42}O_4N_4,SnCl_2$, and in a mixture of glacial acetic acid and pyridine into the halogen-free *substance*, $C_{40}H_{52}O_{10}N_4Sn$. H. Wren.

Reactions of ethyl 2-methylpyrrole-3-carboxylate, 2-methyl- and 2 : 3-dimethyl-pyrrole. H. Fischer, H. Beller, and A. Stern (Ber., 1928, **61**, [*B*], 1074—1083).—Ethyl 2-methylpyrrole-3-carboxylate is converted by 2 mols. of bromine in glacial acetic acid at 15—16° into *ethyl 4 : 5-dibromo-2-methylpyrrole-3-carboxylate*, m. p. 138—139°, whereas with 1 mol. of the halogen it affords a *substance*, $C_{16}H_{18}O_4N_2$, m. p. 255—256°. With ethyl cyanoformate, ethyl 2-methylpyrrole-3-carboxylate gives the *iminochloride*, $C_{12}H_{17}O_4N_2Cl$, m. p. 180—181° (decomp.), converted by water into the *glyoxylic ester*, $C_{12}H_{15}O·N$, m. p. 128°. 2-Methylpyrrole, b. p. 148°, obtained in 70% yield by decarboxylation of ethyl 2-methylpyrrole-3-carboxylate by potassium hydroxide at 170—200°, is converted through the Grignard compound with ethyl chloroformate into *ethyl 2-methylpyrrole-5-carboxylate*, m. p. 100°. 2-Methylpyrrole is also readily obtained by Wolff and Kishner's method from pyrrole-2-aldehyde, prepared by the action of chloroform and potassium hydroxide on pyrrole and isolated through the hydrogen sulphite compound. Bromination of ethyl 2-methylpyrrole-5-carboxylate in acetic acid at 40° affords a *dibromo*-compound, $C_8H_9O_2NBr_2$, m. p. 176° (decomp.); the ester condenses with formaldehyde, acetone, and ethyl methoxymethylmalonate, yielding, respectively, *di-5-carbethoxy-2-methylpyrryl-4-methane*, m. p. 195—196°, the corresponding *dimethylmethane*, m. p. 217°, and *ethyl 2-methyl-3-ββ-dicarbethoxyethylpyrrole-5-carboxylate*, m. p. 75°; bromination of the latter compound affords a *substance*, $C_{16}H_{22}O_6NBr$, m. p. 105°. The successive action of water and chloroacetonitrile on ethyl 2-methylpyrrole-5-carboxylate yields the *compound* $C_{10}H_{12}O_2NCl$, m. p. 190°. *Ethyl 3-aldehydo-2-methylpyrrole-5-carboxylate*, m. p. 119° (corresponding *aldimide*, m. p. 215—216°; *semicarbazone*, m. p. 258°; *phenylhydrazone*, m. p. 216°), is readily prepared from ethyl 2-methylpyrrole-5-carboxylate and anhydrous hydrocyanic acid, it is converted by hydrazine hydrate and sodium ethoxide into 2 : 3-dimethylpyrrole, b. p. 63°/12 mm. (picrate, m. p. 144°). Similarly, ethyl 2-ethylpyrrole-5-carboxylate is converted into *ethyl 3-aldehydo-2-ethylpyrrole-5-carboxylate*, m. p. 89—90° (corr.) [*phenylhydrazone*, m. p. 188° (corr. decomp.); *oxime*, m. p. 194° (corr.)], reduced Wolff and Kishner's method to 3-methyl-2-ethylpyrrole. Ethyl 2-ethylpyrrole-5-carboxylate is converted by formaldehyde and concentrated hydrochloric acid into the *methane* derivative, $C_{19}H_{26}O_4N_2$, m. p. 197° (corr.).

5-Aldehydo-2-methylpyrrole-3-carboxylic acid is transformed in a vacuum at 220° into *2-methylpyrrole-5-aldehyde*, m. p. 68° (corr.). *3-Nitro-2 : 4-dimethylpyrrole*, m. p. 138° (corr.), obtained by heating 3-nitro-2 : 4-dimethylpyrrolecarboxylic acid in a vacuum at 200°, is converted by hydrocyanic acid and hydrogen chloride in ether into *3-nitro-2 : 4-dimethylpyrrole-5-aldehyde*. Ethyl 2 : 3-dimethylpyrrole-5-carboxylate is converted by bromine in carbon tetrachloride at 70° into the *compound* $C_9H_{12}O_2NBr$, m. p. 157° (corr.). 2 : 3-Dimethylpyrrole and propionyl chloride give the *substance* $C_9H_{13}ON$, m. p. 128° (corr.). H. Wren.

Fission of pyridine nucleus by oxidation with alkaline potassium permanganate. B. D. Shaw and A. L. Wilkie (J.C.S., 1928, 1377—1378).—When pyridine is oxidised with aqueous potassium permanganate there are formed ammonium carbonate, potassium carbonate, oxalate, nitrate, and nitrite.

H. Burton.

Crystallisation and absorption of moisture by quaternary pyridine bases. G. D. Sytschev (J. Russ. Phys. Chem. Soc., **60**, 1928, 325—330).—Deals with the formation of the quaternary salts from pyridine and benzyl chloride, bromide, and iodide.

A. Ratcliffe.

Iodination of 2-aminopyridine. O. Magidson and G. Menschikov (Trans. Sci. Chem.-Pharm. Inst., 1926, [**16**], 23—30; Chem. Zentr., 1928, i, 63—64).—5-Iodo-2-aminopyridine (cf. A., 1926, 844), m. p. 129° (*picrate*, m. p. 240°), is produced by the action of hydrogen peroxide and hydrogen iodide, or of potassium iodide and iodate, on 2-aminopyridine in acid solution, or of iodine in aqueous potassium iodide; the periodide is converted into the base by means of hot alkali hydroxide solution. Pyrid-2-one is iodinated with difficulty. The following compounds were prepared: *5-iodopyridyl-2-nitroamine* (from 5-iodo-2-aminopyridine, 2 g., sulphuric acid, 15 c.c., water, 4 c.c., and nitric acid, *d* 1·4, 1 g., and cooling), m. p. 189° (decomp.); *5-iodopyrid-2-one* from 5-iodo-2-aminopyridine and nitrous acid, yellow, m. p. 183—189°; *5-iodo-2-chloropyridine*, m. p. 99°; *5-iodo-2-methoxypyridine*, b. p. 231° (*picrate*, m. p. 147°);

5-nitro-2-methoxypyridine, m. p. 110°; 5-amino-2-methoxypyridine. A. A. ELDRIDGE.

1-Dimethylaminopyridine and its derivatives. A. E. TSCHITSCHIBABIN and I. L. KNUNIANZ (J. Russ. Phys. Chem. Soc., 1928, **60**, 673—682).—See this vol., 427.

Nitro-2-acetamidopyridines. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 651—653).—See this vol., 301.

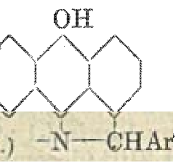
Nitration of 3-ethoxypyridine. E. KOENIGS, H. C. GERDES, and A. SIROT (Ber., 1928, **61**, [*B*], 1023—1030).—3-Bromopyridine is converted by methyl-alcoholic sodium methoxide into *3-methoxypyridine*, b. p. 179° (*chloroplatinate*, m. p. 269°). Nitration of 3-ethoxypyridine by nitric acid (*d* 1·54) and concentrated sulphuric acid affords *6-nitro-3-ethoxypyridine*, m. p. 31—32°, b. p. 175°/50 mm., which has no basic properties but is very sensitive towards alkalis. It is reduced by stannous chloride and concentrated hydrochloric acid to *6-amino-3-ethoxypyridine*, m. p. 86° (*picrate*, m. p. 235°), hydrolysed by hydrogen bromide in glacial acetic acid at 130° to *6-amino-3-hydroxypyridine* (*hydrobromide*, m. p. 173°; *hydrochloride*, m. p. 185°); attempts to diazotise the sulphate of the base were unsuccessful. Unexpectedly, 6-nitro-3-ethoxypyridine is converted by hydrogen bromide in glacial acetic acid at 130° into *6-bromo-3-ethoxypyridine*, b. p. 257—259° [*hydrobromide*, m. p. 185° (decomp.)], and by concentrated hydrochloric acid at 130° into *6-chloro-3-hydroxypyridine hydrochloride*, m. p. 208° (decomp.). 6-Bromo-3-ethoxypyridine is transformed by sodium ethoxide in alcohol into *3 : 6-diethoxypyridine*, b. p. 215—217°/760 mm., hydrolysed by concentrated hydrochloric acid to 3 : 6-dihydroxypyridine, m. p. 248° (*hydrochloride*, m. p. 154°), thus establishing the position of the nitro-group in the nitro-3-ethoxypyridine. 3-Methoxypyridine is converted by energetic nitration into *dinitro-3-methoxypyridine*, m. p. 69°; a homogeneous mononitro-derivative could not be isolated.

Cautious nitration of 3 : 5-diethoxypyridine affords 2 : *6-dinitro-3 : 5-diethoxypyridine*, m. p. 120°, reduced to 2 : *6-diamino-3 : 5-diethoxypyridine*, m. p. 60° (decomp.). 2 : *6-Dibromo-3 : 5-diethoxypyridine*, m. p. 165°, prepared from the dinitro-compound and hydrogen bromide in glacial acetic acid at 100°, appears to be converted by sodium ethoxide into unstable tetraethoxypyridine, b. p. 285—290° (partial decomp.). H. WREN.

Condensation products of homophthalimide [2 : 4-dihydroxy*iso*quinoline] and aromatic aldehydes. H. MEYER (Compt. rend., 1928, **186**, 1214—1216).—In order to compare the properties of derivatives of homophthalimide and 2 : 4-dihydroxyquinoline with those of oxindole, especially with regard to colour and constitution, condensation of these substances with aromatic aldehydes has been studied. Whilst homophthalimide is found to react readily, molecule for molecule, in alcohol or acetic acid solution in presence of diethylamine or hydrochloric acid with the aldehyde, 2 : 4-dihydroxyquinoline condenses only with difficulty, suggesting an enolic formula for the substance. The condensation products of homophthalimide vary in colour from yellow to red, like the *iso*indogenides. The influence of the aromatic nucleus on the colour is pointed out. The following condensation products with 2 : 4-dihydroxy*iso*quinoline and aldehydes were prepared : p-*toluylidene*-, m. p. 199°; *cinnamylidene*-, m. p. 223°; o-*nitrobenzylidene*-, m. p. 236°; m-*nitrobenzylidene*-, m. p. 273°; p-*nitrobenzylidene*-, m. p. 263°; *furfurylidene*-, m. p. 210°; iso*phthalylidene*-, m. p. 292°; *terephthalylidene*-, m. p. 297—298°; *salicylidene*-, m. p. 215°; o-*methoxybenzylidene*-, m. p. 176°; m-*methoxybenzylidene*-, m. p. 176°; p-*hydroxybenzylidene*, m. p. 238°; *anisylidene*-, m. p. 195°; o-*vanillylidene*, m. p. 211°; *vanillylidene*-, in two forms, m. p. 178—180° and 165°; *piperonylidene*-, m. p. 218—219°, p-*dimethylaminobenzylidene*-, m. p. 195°.

J. D. FULTON.

Free organic radicals. VII. Aryl*peri*pyrrolinoanthranolazyls. R. SCHOLL [with E. STIX, J. DONAT, and W. LEONHARDT] (Ber., 1928, **61**, [*B*], 968—972; cf. A., 1927, 675, 885).—Further investigation of aryl*peri*pyrrolinoanthranolazyls (I) shows that the electrolytic conductivity of pure alcohol and pyridine is not increased by the radical, so that disproportionation or electron displacement does not occur as with triarylmethyls in certain solvents.

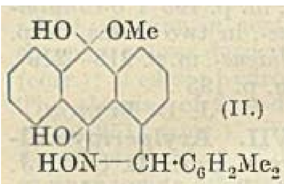


(I.)

Alkaline solutions which have changed in colour from blue to red under the influence of the quartz mercury lamp in an atmosphere of nitrogen or from blue to yellow in the presence of air do not again become blue when placed in the dark or treated with cold phenylhydrazine and therefore probably do not contain aryl*peri*pyrrolinoanthrone; when heated with alcoholic, alkaline hyposulphite or phenylhydrazine they become impure blue, probably owing to re-formation of the radical from some unknown dehydrogenation or oxidation product. The stability of aryl*peri*pyrrolinoanthranolazyls, when crystalline, towards air and light, the ease with which they are re-formed from their closely related, non-radical oxidation and reduction products, and their ability to pass under ordinary conditions of reactions and without loss of radical nature into azylium salts, acyl derivatives, and *O*-ethers cause them to resemble very closely the dye molecules with normal valency fulfilment and ally them more closely to the normal, non-radical compounds than any other type of organic radicals.

Phenyl 1-anthraquinonyl ketoxime, m. p. 225° after darkening at 215—220°, prepared from 1-benzoylanthraquinone, is converted by the action of zinc dust and ammonia or its alcoholic solution into py-1-*phenyl-1 : 9-pyrrolinoanthranolazyl* (I. Ar=Ph), m. p. 266°. Anthraquinone-1-carboxylic acid is converted by the successive action of phosphorus pentachloride and a little sublimed ferric chloride in presence of toluene into *p*-tolyl 1-anthraquinonyl ketone, m. p. 207—208°, which is transformed into the corresponding *ketoxime*, m. p. 230—231°, when rapidly heated and thence into py-p-*tolyl-1 : 9-pyrrolinoanthran-10-olazyl* (I. Ar=p-C_6H_4Me), decomp. above 310°. Treatment of *m*-xylyl*peri*pyrrolinoanthranolazyl (*loc. cit.*) with

methyl sulphate and sodium hydroxide affords py-1-m-*xylyl*-1 : 9-*pyrrolinoanthranolazyl methyl ether*, m. p. 181° (*perchlorate*); the ether is much more closely related to the parent compound than is the benzoyl derivative (*loc. cit.*). It has a marked tendency towards solvate formation, yielding variously coloured solutions in ether, dioxan, xylene, pyridine, alcohol, and glacial acetic acid; the solutions become rapidly decolorised when exposed to light. The absorption curves of the ether and parent compound in alcohol or pyridine are closely similar. When titrated in nitrobenzene or acetic acid with permanganate and sulphuric acid until colourless, the methyl ether requires five equivalents of oxygen in place of the expected three. The compound (II) becomes decomposed into hydrogen peroxide, methyl alcohol, and *py-m*-xylyl*peri*pyrroleninoanthone and the liberated hydrogen peroxide utilises the additional two equivalents of oxygen. The preparation of p-*chlorophenyl* 1-*anthraquinonyl ketoxime*, m. p. 251—252° (decomp.) when rapidly heated, py-1-p-*chlorophenyl*-1 : 9-*pyrrolinoanthran*-10-*olazyl*, m. p. about 330° (decomp.) after softening at 310°, *anisyl* 1-*anthraquinonyl ketoxime*, m. p. 235—236°, and py-1-*anisyl*-1 : 9-*pyrrolinoanthran*-10-*olazyl*, m. p. about 310° (decomp.) after softening at 300°, is described.



(II.)

[With L. Wanka.]—1-Amino-2-methylanthraquinone is converted by diazotisation in concentrated sulphuric acid and subsequent treatment of the *diazonium sulphate* with potassium cuprocyanide into 1-*cyano*-2-*methylanthraquinone*, m. p. 268°, hydrolysed by sulphuric acid to 2-*methylanthraquinone*-1-*carboxylic acid*, m. p. 263—264°; the acid *chloride* decomposes at about 192°.

[With H. Dehnert.]—2-Methylanthraquinone-1-carboxyl chloride is converted with some difficulty by benzene in presence of ferric chloride but not of aluminium chloride into *phenyl* 2-*methylanthraquinonyl ketone*, m. p. 207—208°, from which *phenyl* 2-*methylanthraquinonyl ketoxime*, m. p. 239—240° after softening at 234°, and py-1-*phenyl*-1 : 9-*pyrrolino*-2-*methylanthran*-10-*olazyl*, m. p. 232—233°, decomp. about 285°, are successively derived. p-*Xylyl* 2-*methylanthraquinonyl ketone*, m. p. 192—193°, its *oxime*, m. p. 226—227·5° after softening, and py-1-p-*xylyl*-1 : 9-*pyrrolino*-2-*methylanthran*-10-*olazyl* have been prepared.

[With E. Weber.]—m-*Xylyl* 2-*methylanthraquinonyl ketone*, m. p. 175°, its *oxime*, m. p. 232—233° after softening, and *py*-1-*m*-xylyl-1 : 9-pyrrolino-2-methylanthran-10-olazyl are described. H. Wren.

Red compounds of barbituric acid, picric acid, and sodium or lead hydroxide. I. Greenwald (J. Amer. Chem. Soc., 1928, **50**, 1469—1474).—The red coloration obtained by adding excess of alkali to a solution of the two acids is not due to the formation of picramic acid (cf. Dox, A., 1926, 180), since the picric acid may be recovered almost quantitatively, but to an additive *compound* of approximate composition, $3C_4H_4O_3N_2.2C_6H_3O_7N_3,9NaOH,1$ or $2H_2O$, which is precipitated from the solution by alcohol. It dissociates in solution, since the colour-intensity is increased by adding excess of any of the components. It is converted by lead hydroxyacetate into a brick-red insoluble *substance*, $3C_4H_4O_3N_2.2C_6H_3O_7N_3,11Pb(OH)_2$. H. E. F. Notton.

Reactions of carbohydrazide. II. A. M. Munro and F. J. Wilson (J.C.S., 1928, 1257—1261).—The view previously expressed (A., 1927, 232) that in the thermal decomposition which carbohydrazones (or δ-aminosemicarbazones) undergo at their m. p. the hydrazidicarbohydrazone (or hydrazidicarbohydrazide itself) is the intermediate product has now been confirmed by investigation of the thermal decomposition of dibenzaldehydehydrazidicarbohydrazone, *diacetonehydrazidicarbohydrazone* (I), m. p. 256°, and hydrazidicarbohydrazide. In each case, the end-products were those anticipated. The decomposition of diacetonecarbohydrazone (II) and *dipinacolincarbohydrazone* (III), m. p. 188°, both in boiling alcoholic solution and at the m. p., is also found to conform to the general scheme. The compound (II) yields (I) and thence dimethylketazine and 4-aminourazole. The compound (III) yields *dipinacolinhydrazidicarbohydrazone*, m. p. 230°, and thence pinacolinazine and 4-aminourazole. Equimolecular proportions of ethyl acetoacetate and carbohydrazide react in boiling alcohol, giving *ethyl acetoacetate* δ-*aminosemicarbazone* (IV), m. p. 219°. When 2 mols. of the ester react with 1 mol. of carbohydrazide, *di*(*ethyl acetoacetate*) *carbohydrazone* (V), m. p. 196°, and 3-*methyl*-5-*pyrazolone*-1-*carboxy*-α-*carbethoxy*iso-*propylidenehydrazide*, m. p. 230° (decomp.), are obtained. In one instance only, the compound (V) and 3 : 3′-*dimethyl*-5 : 5′-*dipyrazolonyl* 1 : 1′-*ketone*, m. p. 183°, were obtained. In boiling alcoholic solution, the compound (IV) yields hydrazine and *di*(*ethyl acetoacetate*) *hydrazidicarbohydrazone* (VI), m. p. 213°. When heated at its m. p. it gives hydrazine, 4-aminourazole, and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (VII). After prolonged boiling in alcoholic solution, the compound (V) yields (VI) and (VII). When heated at its m. p. it gives 4-aminourazole and (VII). M. Clark.

Reduction of saturated by unsaturated amino-acids. M. Bergmann and H. Ensslin (Z. physiol. Chem., 1928, **174**, 76—93).—The ethyl ester of glycylaspartic acid anhydride (ethyl 2 : 5-diketopiperazine-3-acetate) condenses with benzaldehyde by Sasaki's method to give the *ethyl* ester of *benzylideneglycylaspartic anhydride* (*ethyl* 2 : 5-*diketo*-6-*benzylidenepiperazine*-3-*acetate*) converted by hydrochloric acid into 2 : 5-*diketo*-6-*benzylidenepiperazine*-3-*acetic acid* (*methyl* ester, m. p. 204°; position of double linking established by hydrolysis with hydrochloric acid, when no phenylalanine or pyruvic acid is produced). If the ester is saponified with sodium hydroxide, however, an *anhydride* isomeric with the above is obtained, but the double linking is now in the αβ-position to the carboxyl group (*methyl* ester, m. p. 147°; position of double linking established by ozonisation), *i.e.*, a derivative of aminofumaric or aminomaleic acid is produced. This may be regarded as a carboxyl derivative of aminoacrylic acid, and it is

suggested that derivatives of acrylic acid play an important part in the metabolism of amino-acids. The above example of the reduction of a saturated amino-acid (aspartic acid portion of molecule) by an unsaturated amino-acid (aminocinnamic portion of the molecule) is typical of a labile equilibrium which probably exists in the animal body between saturated and unsaturated amino-acids. H. D. KAY.

Transformations of peptide substances. XXIII. Histidine. Peptide formation by acyl wandering. XXIV. Synthesis of a *dl*-histidylglycine. M. BERGMANN and L. ZERVAS (Z. physiol. Chem., 1928, **175**, 145—153, 154—157).—XXIII. *Methyl hippurylbenzoyl*-1-*histidine* (I : R—$\cdot CO\cdot CH_2\cdot NHBz$), m. p. 157° (corr.), dissolved in chloroform and treated with 1 mol. of glycine in *N*-sodium hydroxide (1 mol.) at the ordinary temperature and shaken for 12 hrs. yields benzoylglycylglycine (35% of theoretical) and methylbenzoylhistidine (I : R=H).

$$CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot C\Big<\begin{matrix}N=CH\\ CH\cdot \;\; R\end{matrix} \quad (I.)$$

Methyl acetylbenzoyl-1-*histidine* (I : R=Bz), m. p. 168° (corr.), under similar conditions also loses its ring acyl group and with *d*-arginine yields acetyl-*d*-arginine (55% yield) and with glycine, acetylglycine (65% yield). 1-Benzoyltheobromine similarly gives up its acyl group to glycine yielding hippuric acid (75% yield). The acyl groups may be transferred to compounds other than amino-acids and an acetylhistidine derivative and tetra-acetylglucosamine yield penta-acetylglucosamine.

XXIV. Acetyl-*dl*-histidine warmed with acetic anhydride and treated with glycine ethyl ester yields *ethyl acetyl*-dl-*histidylglycine* (II), m. p. 180°,

$$CO_2Et\cdot CH_2\cdot NH\cdot CO\cdot CH(NHAc)\cdot CH_2\cdot C\Big<\begin{matrix}N-CH\\ CH\cdot NH\end{matrix} \quad (II.)$$

which when heated with *N*-hydrochloric acid yields dl-*histidylglycine*, m. p. 235° (corr.) with frothing and charring. A. WORMALL.

2 : 2′-Dipyridylamine and its nitration products. A. E. TSCHITSCHIBABIN and V. A. PREOBRASHENSKY (J. Russ. Phys. Chem. Soc., 1928, **60**, 641—650).—See this vol., 307.

3 : 4 : 5 : 6 - Tetrahydro - 4 - carboline. J. N. ASHLEY and R. ROBINSON (J.C.S., 1928, 1376).—Reduction of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (I), m. p. 185—186°, with sodium and *n*-butyl alcohol yields 3 : 4 : 5 : 6-tetrahydro-4-carboline (Asahina, Irie, and Ohta, J. Pharm. Soc. Japan, 1927, No. 545). β-3-Indolylpropionhydrazide (II) has m. p. 140—141°. Erroneous m. p. were previously recorded for compounds (I) and (II) (Manske and Robinson, A., 1927, 256). M. CLARK.

Quinazolines. I. Mechanism of the reaction between formaldehyde and *p*-substituted aromatic amines in presence of acids. G. MAFFEI (Gazzetta, 1928, **58**, 261—269).—Mainly theoretical. The reaction between a *p*-substituted amine and formaldehyde is considered to give a methylenedi-*p*-amine (I), which undergoes an inversion to an *o*-aminobenzylphenylamine (II). The latter reacts with formic acid (produced, with methyl alcohol, from the formaldehyde) to give a 2-hydroxy-3-aryltetrahydroquinazoline (III); loss of water now yields the dihydroquinazoline (IV) and methyl alcohol [which also yields the *N*-methyl derivative (V) of the original amine] converts the latter into the methohydroxide (VI). Products of types (I) to (VI) have been isolated (cf. Lepetit, Maffei, and Maimeri, this vol., 284).

From *p*-nitroaniline the product 3-nitro-6-aminobenzyl-*p*-nitroaniline (VII) of type (II) has been isolated by Meyer and Stillich (A., 1902, i, 319), who also obtain an alternative product (VIII) of m. p. 207—208°, which they regard as 3-nitro-6-amino-5-methylolbenzylidene-*p*-nitroaniline. The author regards this as of type (III), since he obtains it by heating (VII) with formic acid in a sealed tube at 140°; it is renamed 6-*nitro*-2-*hydroxy*-3-p-*nitrophenyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*quinazoline* (*acetyl* derivative, m. p. 223—235°). The product of the elimination of water, held by Meyer and Stillich to be 3-nitro-5 : 6-methyleneiminobenzylidene-*p*-nitroaniline, obtained by the action of glacial acetic acid on (VIII), is correspondingly renamed 6-*nitro*-3-p-*nitrophenyl*-3 : 4-*dihydro*-1 : 3-*quinazoline* (m. p. 243—246°).

From *p*-toluidine the base of m. p. 158° (Lepetit, Maffei, and Maimeri, *loc. cit.*) is regarded as 3-p-*tolyl*-6-*methyl*-3 : 4-*dihydro*-1 : 3-*quinazoline*, and that of m. p. 97—98° as the corresponding *methohydroxide*. From *p*-phenetidine the base of m. p. 140° is 6-*ethoxy*-3-p-*ethoxyphenyl*-3 : 4-*dihydro*-1 : 3-*quinazoline*, which has been synthesised; the compound of m. p. 210° (*loc. cit.*) is regarded as the corresponding 4-ketone, also obtained (cf. Busch, A., 1895, i, 306) by oxidising the compound $C_{18}H_{18}O_2N_2S$, m. p. 192—193° (Lepetit, A., 1917, i, 198), which is thus the thio-analogue of the ketone. E. W. WIGNALL.

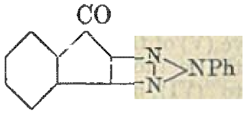
Manufacture of acid dyes of the phenonaphthasafranine series. J. R. GEIGY A.-G.—See B., 1928, 441.

Manufacture of alkylpyrazolanthrones. I. G. FARBENIND. A.-G.—See B., 1928, 441.

Sulphoxytriazines [ketothiontriazines]. J. BOUGAULT and L. DANIEL (Compt. rend.. 1928, **186**, 1216—1218).—5 - *Keto* - 3 - *thiol*- 6 - *methyl* - 1 : 2 : 4 - *triazine*, m. p. 220°, is readily prepared by dehydrating pyruvic acid thiosemicarbazone in faintly alkaline solution. When treated with sodium hypobromite followed by removal of excess of the latter with sodium hydrogen sulphite and subsequent acidification, 5-keto-3-thion-6-benzyl-1 : 2 : 6-triazine gives the corresponding dihydroxytriazine. The formation of an intermediate compound, *e.g.*, the 3-sulphonic acid, is suggested, as the dihydroxytriazine is itself decomposed by hypobromite (cf. A., 1916, i, 609). In a similar manner, 3 : 5-diketo-6-methyltriazine is obtainable (cf. A., 1914, i, 1004) from the corresponding hydroxythiol compound. J. D. FULTON.

Phenylene 2-aryltriazolylene ketones and phenylene-2-phenyltriazolylenemethane. (1:2:3-Triazole analogues of fluorene and fluorenone.) G. CHARRIER [with C. SALA] (Gazzetta, 1928, **58**, 254—260).—The action of chromic acid on sodium

phenylene-2-phenyltriazolyleneglycollate (Charrier and Gallotti, A., 1925, i, 306) yields *phenylene 2-phenyl-1 : 2 : 3-triazolylene ketone* (annexed formula), m. p. 158° (*oxime*, m. p. 223°; *phenylhydrazone*, m. p. 214°; p-*chlorophenylhydrazone*, m. p. 226°; *semicarbazone*, m. p. 309°), which is reduced by hydriodic acid and phosphorus to *phenylene-2-phenyl-1 : 2 : 3-triazolylenemethane*, m. p. 128°.

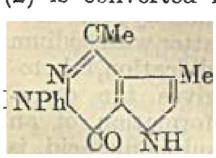


When 2-N-p-*tolylnaphthotriazolequinone*, m. p. 216—217°, is treated with boiling aqueous sodium hydroxide, *phenylene-2-p-tolyl-1 : 2 : 3-triazolyleneglycollic acid*, m. p. 194°, is obtained; the *sodium* salt, m. p. 205° (decomp.), of the latter is oxidised by chromic acid to *phenylene 2-p-tolyl-1 : 2 : 3-triazolylene ketone*, m. p. 196° (*phenylhydrazone*, m. p. 207°; *semicarbazone*, m. p. 228°). E. W. WIGNALL.

Manufacture of new pharmaceutical compounds [alkyloxymethyltheobromines]. I. G. FARBENIND, etc.—See B., 1928, 427.

[Porphyrins and their syntheses.] O. SCHUMM (Ber., 1928, **61**, [*B*], 784—787).—In his general account of this subject, Fischer (*ibid.*, 1927, **60**, [*B*], 2611) has made little or no reference to the results obtained by Schumm and his co-workers. H. WREN.

Porphyrin syntheses. XV. Synthesis of 2 : 2′-disubstituted pyrroles and porphyrin syntheses from simple pyrroles. H. FISCHER, E. STURM, and H. FRIEDRICH (Annalen, 1928, **461**, 244—277).—An improved method is described for the preparation of aminoacetone hydrochloride by the reduction of *iso*nitrosoacetone. This method is more convenient for laboratory purposes than that of Gabriel starting with chloroacetone and potassium phthalimide, which is suitable for production on a larger scale. The condensation in alkaline solution, described by Piloty (Ber., 1912, **45**, 3749), of aminoacetone with ethyl acetopyruvate has been re-investigated. Three products result: (1) 3-acetyl-4-methylpyrrole-2-carboxylic acid, (2) 2 : 4-dimethyl-3-glyoxylic acid, and (3) the *ethyl* ester, m. p. 124°, of (2). The yields depend greatly on the purity of the aminoacetone and increase in the amount of alkali used increases the amount of (2). The potassium salt of (2) is converted into (3) by ethyl sulphate, whilst diazomethane converts (1) into the *methyl* ester, m. p. 100°. The acid (1) or its esters reacts with phenylhydrazine in 50% acetic acid at 100° to give the *pyridazinopyrrole* (annexed formula), m. p. 297° (corr.), whilst the acid is converted by hydrazine hydrate in presence of sodium ethoxide into opsopyrrole.



3-*Acetyl-4-methylpyrrole*, m. p. 117°, results when acid (1) is distilled at 50 mm. pressure or (2) is heated with 10% sodium hydroxide solution at 140°. The acetylmethylpyrrole, when heated at 170° with alcoholic sodium ethoxide and hydrazine hydrate, is converted into 3-methyl-4-ethylpyrrole (opsopyrrole). Decarboxylation of (2) gives a *dimethylpyrrolealdehyde* (?), m. p. 88—89°, reduced by the sodium ethoxide–hydrazine method to a *base*, $C_7H_{11}N$, b. p. 74—75°/11 mm., named iso*opsopyrrole*. This with diazotised sulphanilic acid affords a yellow *azo-dye* containing one azo-grouping.

When the above methylethylpyrrole is heated with formic acid or with similar compounds at 160° it is transformed into ætioporphyrin, whilst when excess of formic acid is used and the condensation is stopped when the product becomes red, opsopyrrolemethene, isolated as the *perchlorate*, results. The hydrobromide of the methene is converted by bromine in acetic acid at 30—40° into a " dibromide," the free base derived from which is identical with the methene, m. p. 175—176°, from hæmocarbethoxypyrrole.

Sulphuryl chloride (5 mols.) converts ethyl 2 : 5-dimethylpyrrole-3-carboxylate in ethereal solution into a product which, when decomposed with steam, affords *ethyl 4-chloro-2 : 5-dialdehydopyrrole-3-carboxylate*, m. p. 131°. 2 : 5-Dimethylpyrrole-3-carboxylic acid similarly affords *4-chloro-2 : 5-dialdehydopyrrole-3-carboxylic acid*, decomp. above 237°, and ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate affords (6 mols. of sulphuryl chloride) *ethyl 2 : 4-di(trichloromethyl)pyrrole-3 : 5-dicarboxylate*, m. p. 72° (crystallographic data by STEINMETZ; monoclinic prismatic; $a : b : c = 1{\cdot}4041 : 1 : 1{\cdot}6005$; $\beta = 111° 20'$), converted (1) by concentrated potassium hydroxide at 60—70° into a *compound*, m. p. 187°, (2) by chromic anhydride in acetic acid into a *pentachloro-hydroxy*-compound, $C_{12}H_{12}O_5NCl_5$, m. p. 110° (also formed by oxidising the hexachloro-compound with concentrated nitric acid or by treating it with concentrated sulphuric acid), and (3) by zinc dust in acetic acid into *ethyl 4-methyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 116°. Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is converted by sulphuryl chloride etc. into a *compound*, m. p. 142°. Treatment of ethyl 2 : 4-dimethyl-3-carboxylate with sulphuryl chloride in ether, without subsequent decomposition with steam, gives *(3-carbethoxy-2 : 4-dimethylpyrryl)-(5-chloro-3-carbethoxy-4-methylpyrryl)methene hydrochloride*, m. p. 143°.

Phenylsulphur chloride converts ethyl 2 : 4-dimethylpyrrole-3-carboxylate into *ethyl 5-phenylthiol-2 : 4-dimethylpyrrole-3-carboxylate*, m. p. 111°, ethyl 2 : 4-dimethylpyrrole-5-carboxylate into *ethyl 3-phenylthiol-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 157°, and ethyl 2 : 5-dimethylpyrrole-3-carboxylate into *ethyl 4-phenylthiol-2 : 5-dimethylpyrrole-3-carboxylate*, m. p. 143°.

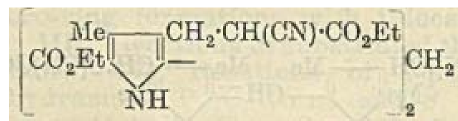
When ethyl 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate is treated with 2 mols. of sulphuryl chloride (ether; 0°) there is formed *ethyl 4-methyl-3-ethyl-2-chloromethylpyrrole-5-carboxylate*, m. p. 130° (corr.), converted by boiling water into the known bis(5-carbethoxy-4-methyl-3-ethylpyrryl)methene. Using 3 mols. of sulphuryl chloride and boiling the initial product with aqueous alcohol, *5-carbethoxy-4-methyl-3-ethylpyrrole-2-carboxylic acid*, m. p. 211°, results, together with some ethyl 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylate, m. p. 90° (corr.). The last-named acid is readily hydrolysed to *4-methyl-3-ethyl-2 : 5-dicarboxylic acid*, m. p. 232°, is converted by boiling acetic anhydride in presence of anhydrous sodium acetate into a *pyrocoll*, $C_{22}H_{26}O_6N_2$, m. p. 150°,

whilst when it is heated at 215—220° it affords *opsocarbethoxypyrrole* (*ethyl* 3-*methyl*-4-*ethylpyrrole*-2-*carboxylate*), m. p. 25°. The last-named is converted by hydrogen cyanide and hydrogen chloride into a product which affords 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid when hydrolysed with dilute alkali. Bromination of opsocarbethoxypyrrole in acetic acid gives *ethyl* 2-*bromo*-4-*methyl*-3-*ethylpyrrole*-5-*carboxylate*, m. p. 103° (corr.), also formed when the carbethoxy-acid, m. p. 211°, is brominated in acetic acid solution. Opsopyrrole is conveniently prepared either by heating the carbethoxy-acid, m. p. 211°, with hydriodic acid or by heating it with 10% sodium hydroxide at 160°.

The oxime of ethyl 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylate is converted by boiling acetic anhydride in presence of sodium acetate into *ethyl* 2-*cyano*-4-*methyl*-3-*ethylpyrrole*-5-*carboxylate*, m.p. 131° (corr.), hydrolysed by boiling 10% sodium hydroxide to the corresponding dicarboxylic acid. Ethyl 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylate is readily hydrolysed by dilute alkali to the expected aldehydo-acid (above), and condenses in alcoholic hydrobromic acid with cryptopyrrole, with methyl hæmopyrrolecarboxylate, and with cryptopyrrolecarboxylic acid to give *methenes* melting respectively at 160°, 168°, and 197°.

When cryptopyrrole is heated either alone or in presence of its carboxylic acid with hydrogen bromide in acetic acid, no porphyrin formation occurs, but when cryptopyrrole is heated under pressure at 100° with formic acid and perchloric acid, a quantitative yield of cryptopyrrolemethene perchlorate is obtained. On the other hand, porphyrin formation does occur when ethyl cryptopyrroleglyoxylate (ethyl 2 : 4-dimethyl-3-ethylpyrrole-5-glyoxylate) is heated with hydrogen bromide in acetic acid, and the same reagent converts ethyl 5-bromo-2 : 4-dimethyl-3-ethyl-2-carboxylate into ætioporphyrin, and converts 5-carbethoxy-4-methyl-2-bromomethylpyrrole-3-propionic acid into a mixture of coproporphyrin ("III") and (the tetramethyl ester of) *iso*coproporphyrin, separable only with difficulty and then melting, respectively, at 250° (corr.) and 139°. The carbethoxy-propionic acid also affords a mixture of porphyrins when heated with succinic acid. Porphyrin formation occurs when 5-carbethoxy-2 : 4-dimethylpyrrole-3-propionic acid is heated with hydrogen bromide in acetic acid, but not when carbethoxyxanthopyrrolecarboxylic acid is so treated. E. E. Turner.

Porphyrin syntheses. XVI. Syntheses of porphyrins with nitrile function. H. Fischer and H. Wasenegger (Annalen, 1928, **461**, 277—295).—Ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate condenses with ethyl cyanoacetate in presence of boiling alcoholic aniline to give ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylate (A., 1924, i, 543) (yield 90—95%), which is reduced by sodium in alcoholic solution containing some acetic acid to ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)ethylpyrrole-5-carboxylate. The latter is converted by alcoholic hydrogen chloride into ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-5-carboxylate and by hydrobromic and acetic acids into ethyl acetate and the substance previously obtained (A., 1925, i, 834) from alkali and ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-5-carboxylate, and on bromination affords *ethyl* 4-*methyl*-2-*bromomethyl*-3-(β-*cyano*-β-*carbethoxy*)*ethylpyrrole*-5-*carboxylate*, m. p. 129°, which is converted by methyl alcohol, ethyl alcohol, and aniline into the -2-*methoxymethyl*- (m. p. 113°), the -2-*ethoxymethyl*- (m. p. 123°), and the -2-*anilinomethyl*- (m. p. 138°) compounds, respectively, and transformed by boiling water into formaldehyde and *bis*-[2-*carbethoxy*-3-*methyl*-4-(β-*cyano*-β-*carbethoxy*)-*ethylpyrryl*]-5-*methane* (I). The latter is brominated in



(I.)

acetic acid solution to give a *dibromo*-derivative, m. p. 131°, and is converted by warm dilute aqueous alcoholic alkali into *bis*-[2-*carbethoxy*-3-*methyl*-4-(β-*cyano*-β-*carboxy*)*ethylpyrryl*]-5-*methane*. The latter, when melted in a vacuum, affords *bis*-(2-*carbethoxy*-3-*methyl*-4-β-*cyanoethylpyrryl*)*methane*, m. p. 194°, also obtained by boiling with water for 8 hrs. (with air bubbling through) *ethyl* 4-*methyl*-2-*bromomethyl*-3-β-*cyanoethylpyrrole*-5-*carboxylate*, m. p. 185°, which is the product of brominating ethyl 2 : 4-dimethyl-3-β-cyanoethylpyrrole-5-carboxylate, and reacts with methyl alcohol, ethyl alcohol, and aniline to give the -2-*methoxymethyl*, -2-*ethoxymethyl*, and -2-*anilinomethyl* compounds, these melting, respectively, at 140°, 113°, and 188°. Ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)ethylpyrrole-5-carboxylate is converted by acetic and hydriodic acids into cryptopyrrolecarboxylic acid, m. p. 138°.

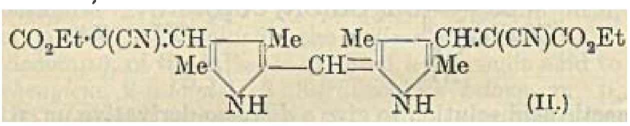
When (I) is treated in alcoholic solution with hydrogen chloride, bis-(2-carbethoxy-3-methyl-4-ββ-dicarbethoxyethylpyrryl)-5-methane, m. p. 126°, separates, and this substance, when boiled in aqueous alcoholic alkali solution, affords a mixture of bis-(2-carbethoxy-3-methyl-4-β-carboxyethylpyrryl)-5-methane and bis-(2-carboxy-3-methyl-4-β-carboxyethylpyrryl)-5-methane.

Bromination of ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylate gives a bromo-compound which is not crystalline but clearly contains bromomethyl groups, since methyl and ethyl alcohols convert it respectively into a *methoxy*- (m. p. 101°) and an *ethoxy*- (m. p. 120°) compound. The desired *ethyl* 4-*methyl*-2-*bromomethyl*-3-(β-*cyano*-β-*carbethoxy*)*vinylpyrrole*-5-*carboxylate*, m. p. 135°, is, however, obtained by treating the last-named ethoxy-compound with hydrogen bromide in acetic acid. The bromo-compound is not convertible into a methane by the general methods.

Condensation of 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylic acid with ethyl cyanoacetate in boiling alcoholic aniline solution gives 2 : 4-*dimethyl*-3-(β-*cyano*-β-*carbethoxy*)*vinylpyrrole*-5-*carboxylic acid*, m. p. 242°, which is converted by boiling acetic anhydride into a *pyrocoll*, m. p. 276°, hydrolysed by hot concentrated alkali to give 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylic acid.

Hydrolysis of 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole with alcoholic alkali produces the

corresponding β-*carboxylic acid*, m. p. 210°. 2 : 4-Dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylic acid passes, when heated in a vacuum, into 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole, converted by hydrogen cyanide and chloride in chloroform solution into 2 : 4-*dimethyl*-3-(β-*cyano*-β-*carbethoxy*)*vinylpyrrole*-5-*aldehyde* (*oxime*, m. p. 185°; *semicarbazone*, m. p. 253°; *azlactone*, m. p. 185°), which, when heated in alcoholic hydrochloric acid with the pyrrole from which it is prepared, affords the *bis*-[2 : 4-*dimethyl*-3-(β-*cyano*-β-*carbethoxy*)*vinylpyrryl*]-*methene* (II), sintering at 250° (obtained from the *hydrochloride*).



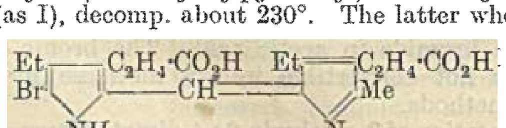
(II.)

In cold alcoholic hydrochloric acid solution, cryptopyrrolealdehyde condenses with 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole to give the *hydrochloride*, m. p. 220°, of the expected *methene*, m. p. 132°. The last-named vinylpyrrole reacts with aqueous formaldehyde (boiling solution) to give green and colourless forms of *bis*-[2 : 4-*dimethyl*-3-(β-*cyano*-β-*carbethoxy*)*vinylpyrryl*]-5-*methane*, m. p. 217° (corresponding β-*carboxylic acid*, m. p. 268°).

The condensation product of 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole and cryptopyrrolealdehyde condenses with bis-(2-bromo-3-methyl-4-ethylpyrryl)-5-methene when heated with succinic acid, to give ætioporphyrin.

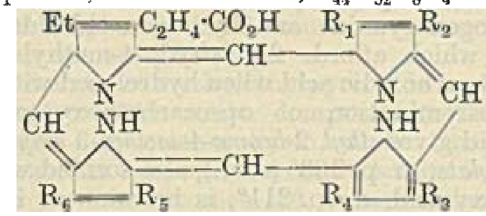
2 : 4-Dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-aldehyde when heated with a little alkali affords the corresponding β-*carboxylic acid*, m. p. 240°, and when heated with concentrated (1 : 1) potassium hydroxide is converted into 2 : 5-*dimethylpyrrole*-3 : ɑ-*dialdehyde*, m. p. 166°. E. E. Turner.

Porphyrin syntheses. XVIII. Synthesis of three tetraethylporphintetrapropionic acids (homologous coproporphyrins). Xanthoporphinogen from ætioporphyrin III and one of the homologous opsopyrrolecarboxylic acids. H. Fischer and G. Stangler (Annalen, 1928, 462, 251—267).—2-*Methyl*-4-*ethylpyrrole*-3-*propionic acid*, m. p. 78° (*picrate*, m. p. 140°), is obtained by heating its 5-carbethoxy-derivative with hydrogen iodide in acetic acid at 100°, and is converted by bromine into (2-*bromo*-3-*ethyl*-4-β-*carboxyethylpyrryl*)(2′-*methyl*-4′-*ethyl*-3′-β-*carboxyethylpyrrolenyl*)*methene hydrobromide* (as I), decomp. about 230°. The latter when heated



(I.)

with succinic acid (cf. this vol., 651) affords a product which with methyl-alcoholic hydrogen chloride gives the *methyl* ester, m. p. 193°, of a *tetraethylporphintetrapropionic acid* (II; $R_1=R_3=R_5=Et$; $R_2=R_4=R_6=\cdot[CH_2]_2\cdot CO_2H$), also obtained but with m. p. 180° (isomeride ?) by heating 4-ethyl-2-bromomethyl-5-carbethoxypyrrole-3-propionic acid with succinic acid and subsequently esterifying. The methyl ester, m. p. 193°, depresses the m. p. of the isomeride (below) of m. p. 182°, and forms a *copper* salt, $C_{44}H_{52}O_8N_4Cu$, m. p. 265°, and an *iron* salt, $C_{44}H_{52}O_8N_4ClFe$, m. p.



(II.)

170°. Hydrolysis of the ester, followed by heating in a high vacuum at 300° gives a sublimate consisting of ætioporphyrin and acid porphyrins, the main product, however, being a black material from which *octa-ethylporphin*, m. p. 292—293° [mixed with synthetic compound of m. p. 312—314° (Fischer and Baumler; details to appear shortly), m. p. was 302—303°], is isolable.

5-Carbethoxy-2-methyl-4-ethylpyrrole-3-propionic acid undergoes bromination in ethereal solution to give 5-*carbethoxy*-4-*ethyl*-2-*bromomethylpyrrole*-3-*propionic acid*, m. p. 174°, converted by boiling water into formaldehyde and *ethyl bis*-(4-*ethyl*-3-β-*carboxyethylpyrryl*)*methane*-2 : 2′-*dicarboxylate*, m. p. 161°, which on hydrolysis affords the not very stable free tetracarboxylic *acid*, decomp. 180°. The latter is converted by formic acid into a poor yield of the corresponding homologous iso*coproporphyrin* (II; $R_2=R_3=R_6=Et$; $R_1=R_4=R_5=\cdot[CH_2]_2\cdot CO_2H$), the *methyl* ester of which has m. p. 170°. Bromine converts the last-named tetracarboxylic acid in acetic acid into *bis*-(2-*bromo*-3-*ethyl*-4-β-*carboxyethylpyrryl*)-*methene hydrobromide*, decomp. indef. above 200°. *Bis*-(2-*methyl*-4-*ethyl*-3-β-*carboxyethylpyrryl*)*methene hydrobromide* is formed when 2-methyl-4-ethylpyrrole-2-propionic acid is heated in formic acid with bromine, and when heated with bromine in acetic acid is converted into *bis*-(4-*ethyl*-2-*bromomethyl*-3-β-*carboxyethylpyrryl*)*methene hydrobromide*, whilst when it is heated with bis-(2-bromo-3-ethyl-4-β-carboxyethylpyrryl)methene hydrobromide it affords an acid (II; $R_2=R_4=R_5=Et$; $R_1=R_3=R_6=\cdot[CH_2]_2\cdot CO_2H$) which on esterification gives the *methyl* ester, m. p. 182°.

The three new methyl ester porphyrins (methyl esters of tetraethyl-tetrapropionic acid porphins) are spectroscopically similar to their lower homologues, the coproporphyrins (methyl esters of tetramethyl-tetrapropionic acid porphins), three of which have been synthesised by Fischer, the fourth to be described shortly.

5-Carbethoxy-4-ethyl-2-bromomethylpyrrole-3-propionic acid is converted by sulphuryl chloride in ethereal solution into a *chloro-compound*, m. p. 118°, which when boiled with water gives 5-*carbethoxy*-4-*ethyl*-3-β-*carboxyethylpyrrole*-2-*carboxylic acid*, m. p. 248° (decomp.), the latter affording 3-*ethylpyrrole*-4-*propionic acid*, m. p. 133°, when heated with aqueous sodium hydroxide at 165—170°, under pressure.

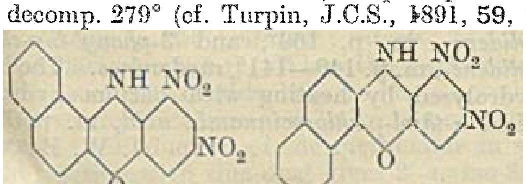
A second synthesis of the ætioporphyrin ("III"), m. p. 360°, described previously (A., 1927, 1206), has been effected by heating the methene from opsopyrrole with (3-methyl-4-ethyl-2-bromomethyl)(4′-methyl-3′-ethyl-2′-bromomethylpyrrolenyl)methene

(hydrobromides) in presence of succinic acid. The ætioporphyrin, which is the basis of the blood colouring matter, is converted by lead dioxide in chloroform-acetic acid into the corresponding xanthoporphinogen, decomp. 298°. The latter is converted back into the ætioporphyrin by reduction in methyl-alcoholic solution with sodium amalgam.

Mesoporphyrin, m. p. 206°, is obtained (cf. this vol., 76) when a mixture of (3-methyl-4-ethyl-2-bromomethylpyrryl)(4′-methyl-3′-ethyl-2′-bromomethylpyrrolenyl)methene hydrobromide is added to concentrated sulphuric acid. Isolation is effected through the sodium salt. E. E. TURNER.

Isomerisation of an *iso*oxazole to a triazole derivative. G. WITTIG, F. BANGERT, and H. KLEINER (Ber., 1928, **61**, [*B*], 1140—1143).—4 : 5-Diphenyl-3-methyl*iso*oxazole cannot be prepared by the action of hydroxylamine on *acetyldeoxybenzoin*, m. p. 99—99·5°, prepared by the action of acetyl chloride and sodamide on deoxybenzoin in ether, since the diketone is either not attacked or suffers extensive decomposition. A possible source of the desired compound appeared to be 4-benzeneazo-5-phenyl-3-methyl*iso*oxazole, which, however, when distilled in the presence of copper powder or sand, becomes isomerised to 5-*benzoyl*-2-*phenyl*-4-*methyl*-1 : 2 : 3-*triazole*, m. p. 74° (p-*nitrophenylhydrazone*, m. p. 231—231·5°). Isomerisation also occurs vigorously at 180—240°, but is not observed in solvents of lower b. p., whereas with media of high b. p. (phenol, dimethylaniline, nitrobenzene) smeary products are obtained. The identity of the triazole is established by its production from acetic anhydride and any of the stereoisomeric forms of the *phenylmethylhydrazone* of *oximinobenzoylacetone*. The a-*form*, m. p. 126°, of the latter compound is prepared from oximinobenzoylacetone and *as*-phenylmethylhydrazine in cold ether, the b-*variety*, m. p. 150—151°, being isolated from the mother-liquors or obtained directly from the components in boiling methyl alcohol. The stable c-*form*, m. p. 164—165°, is prepared by more extended action under the latter conditions. The *b*- and *c*-isomerides with acetic anhydride afford an *acetate*, m. p. 119°, hydrolysed to the *c*-variety by cold methyl-alcoholic sodium methoxide. The *phenylhydrazone* of *oximinobenzoylacetone*, m. p. 170—171° (decomp.), is converted when heated into 4-nitroso-1 : 5-diphenyl-3-methylpyrazole. H. WREN.

Azoxines. V. Application of the Turpin reaction to aminonaphthols. H. GOLDSTEIN and A. WARNERY (Helv. Chim. Acta, 1928, **11**, 489—495).—When a mixture of 1-amino-β-naphthol and picryl chloride is treated with alcoholic potassium hydroxide there is formed 9 : 11-*dinitro*-βα-*naphthaphenoxazine* (I), decomp. 279° (cf. Turpin, J.C.S., 1891, **59**, 714),

(I.)  (II.)

which when reduced and subsequently oxidised with ferric chloride yields 11-*amino*-βα-*naphthaphenoxazine*-9-*imine* [*perchlorate*; *hydrochloride*; *acetyl* derivative (*perchlorate*)]. Similarly, 2-amino-α-naphthol furnishes 8 : 10-*dinitro*-αβ-*naphthaphenoxazine* (II), which yields 10-*amino*-αβ-*naphthaphenoxazine*-8-*imine* (*perchlorate*). 3-Amino-β-naphthol affords 1 : 3-*dinitro*-*naphthaphenoxazine*, m. p. 313° (decomp.), from which 1-*amino*-ββ-*naphthaphenoxazine*-3-*imine* [*perchlorate*; *acetyl* derivative (*perchlorate*)] is obtained.

3-(2 : 4 : 6-*Trinitrophenyl*)*amino*-β-*naphthol* and 3-(2 : 4-*dinitronaphthyl*)*amino*-β-*naphthol* have m. p. 205° (decomp.) and 205°, respectively. H. BURTON.

Hetero-ring formations with thiocarbohydrazide. III. Reactions of substituted thiocarbohydrazides. IV. Reactions of 1-phenylthiocarbohydrazide. P. C. GUHA and S. K. ROY-CHOUDHURY (J. Indian Chem. Soc., 1928, **5**, 149—161, 163—174).—III. Substituted thiocarbohydrazides have been prepared by the action of hydrazine on dithiocarbazinates, $NH_2·NH_2 + NRR'·NH·CS_2Me(Et) \longrightarrow NRR'·NH·CS·NH·NH_2(I) + SHMe(Et)$. Thus, methyl phenyldithiocarbazinate and hydrazine hydrate yield *phenylthiocarbohydrazide* (I, R=Ph, R′=H), m. p. 149—150° (*hydrochloride*, m. p. 181°); *ethyl* m-*tolyldithiocarbazinate*, m. p. 99°, prepared by successive treatment of *m*-tolylhydrazine with carbon disulphide and potassium hydroxide solution, and ethyl bromide, gives m-*tolylthiocarbohydrazide*, m. p. 163—164° (decomp.), and *ethyl* 1-*phenyl*-1-*methyldithiocarbazinate* affords 1-*phenyl*-1-*methylthiocarbohydrazide* (I, R=Ph, R′=Me), m. p. 228—229° (decomp.). The following *phenylthiocarbohydrazones* are described: *benzaldehyde*-, m. p. 185°; p-*nitrobenzaldehyde*-, m. p. 192°; *cinnamaldehyde*-, m. p. 167—198° (168?); *salicylaldehyde*-, m. p. 206° (decomp.), and *acetone*-, m. p. 162°. p-*Nitrobenzaldehyde*-m-*tolylthiocarbohydrazone* has m. p. 165—166°. When benzaldehydephenylthiocarbohydrazone is heated with ferric chloride solution there is formed 2-*phenyl*-5-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 172°. The formation of this compound is explained by an initial isomerisation of the thiocarbohydrazone and subsequent loss of two atoms of hydrogen, viz.,

$$NHPh·NH·C(SH){:}N·N{:}CHR \longrightarrow N{\Large<}\begin{matrix}N{-}C·NH·NHPh\\ \quad\; CR·S\end{matrix}.$$

2-*Cinnamyl*- and 2-p-*nitrophenyl*-5-*phenylhydrazino*-1 : 3 : 4-*thiodiazoles* have m. p. 173° and 263—264°, respectively. Phenylthiocarbohydrazide and *o*-chlorobenzaldehyde react yielding 2-*phenylhydrazino*-6 : 7-*benzo*-1 : 3 : 4-*heptathiodiazine*,

$$C_6H_4{\Large<}\begin{matrix}CH{:}N \\ S{-}C·NH·NHPh\end{matrix}{>}N$$, m. p. 195°, formed by elimination of hydrogen chloride from the intermediate thiocarbohydrazone. The action of phenyl- and *m*-tolyl-thiocarbohydrazides on phenanthraquinone is to form the *phenylhydrazone*, m. p. above 300°, and m-*tolylhydrazone*, m. p. above 295°, of 2-*keto*-5 : 6-*phenanthra*-1:3:4-*oxadiazine*, $\left(\begin{matrix}·C·N{:}N \\ ·C·O·C.N·NHR\end{matrix}\right)$, respectively, thus differing from the action of thiocarbohydrazide on benzil (A., 1926, 417). Acenaphthaquinone, phenanthraquinone monoxime, and isatin react with phenylthiocarbohydrazide yielding 2-*keto*-

5 : 6-*acenaphtha*-1 : 3 : 4-*oxadiazine phenylhydrazone*, m. p. above 300°, 2-*keto*-5 : 6-*phenanthra*-1 : 3 : 4 : 7-*heptaoxatriazine phenylhydrazone*, m. p. above 300°, and 2-*keto*-5 : 6-*isatino*-1 : 3 : 4-*thiodiazine*, darkens at 260°, respectively.

Ethyl acetoacetate and phenylthiocarbohydrazide form the corresponding *phenylthiocarbohydrazone*, m. p. 115—116°, which with sodium methoxide eliminates 1 mol. of alcohol giving 1-*thiocarbophenylhydrazido*-3-*methyl*-5-*pyrazolone*, m. p. 142° (decomp.). Similarly, acetonylacetone furnishes 5 : 8-*dimethyl*-2-*phenylhydrazino*-1 : 3 : 4-*octathiodiazine*, m. p. 230° (decomp.); ω-bromoacetophenone yields 5-*phenyl*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 199°, and ethyl chloroacetate gives the *hydrazone*, m. p. 152—153° (*benzylidene* derivative, m. p. 158°), of 2 : 5-*diketo*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine*. Salicylaldehydephenylthiocarbohydrazone and ethyl chloroacetate give the *salicylidene* derivative, m. p. 220° [*benzylidene* derivative, m. p. 189° (decomp.)], of 2 : 5-*diketo*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine* 2-*hydrazone* [(*hydrochloride* ?), m. p. 247—248° (decomp.)], whilst from ω-bromoacetophenone there is formed the *salicylidene* derivative, m. p. 221°, of 2-*keto*-4 : 5-*diphenyldihydro*-1 : 3 : 4-*thiodiazine* 2-*hydrazone*.

IV. Phenylthiocarbohydrazide is converted by 100% formic acid into 2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 220°, and by acetic anhydride into its 5-*acetyl* derivative, m. p. 172—173° (decomp.). With potassium ethyl xanthate there is formed 5-*thion*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 127° (decomp.), oxidised by ferric chloride to a *disulphide* (?), $C_{16}H_{14}N_8S_4$, m. p. 237° (decomp.). Carbonyl, acetyl, and benzoyl chlorides convert phenylthiocarbohydrazide into its hydrochloride, but phthalyl, malonyl, and thionyl chlorides yield 5-*hydroxy*-8-*keto*-2-*phenylhydrazino*-6 : 7-*benzo*-1 : 3 : 4-*octathiodiazine*, m. p. 206° (decomp.), 5-*hydroxy*-7-*keto*-2-*phenylhydrazino*-6 : 7-*dihydro*-1 : 3 : 4-*heptathiodiazine*, m. p. 201—202° (decomp.), and 2-*phenylhydrazino*-1 : 5 : 4 : 3-*dithiodiazole* 5-*oxide*, m. p. 220° (decomp.), respectively. Benzylidene- and *p*-nitrobenzylidene-phenylthiocarbohydrazones react with carbonyl chloride, yielding the *benzylidene*-, m. p. 204—205°, and p-*nitrobenzylidene*-, m. p. 258°, derivatives of 2 : 5-*diketo*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazole* 2-*hydrazone*, respectively.

Phenylthiocarbohydrazide reacts with phenylcarbimide and phenylthiocarbimide to form the *phenylcarbamide* (II), NHPh·NH·CS·NH·NH·CO·NHPh, m. p. 209° (decomp.), and the corresponding *phenylthiocarbamide* (III), m. p. 173—174°. The *phenylthiocarbamides* from 1-phenyl-1-methyl- and *m*-tolylthiocarbohydrazides have m. p. 219—220° (decomp.) and 160° (decomp.), respectively. Treatment of (II) with hot 20% potassium hydroxide solution furnishes 5-*keto*-1-*phenyl*-2-*phenylhydrazino*-4 : 5-*dihydro*-1 : 3 : 4-*triazole*, m. p. 244—245°, whilst similar treatment of (III) yields a mixture of 5-*anilino*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole* (IV), m. p. 199°, and 5-*thiol*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 258—259° (*triacetyl* derivative, m. p. 206—207°). Oxidation of this last compound with ferric chloride gives the corresponding *disulphide*, m. p. 205° (decomp.). Treatment of (III) with hot concentrated hydrochloric acid furnishes 2 : 5-*diketotetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 222°. Oxidation of (II) with ferric chloride affords a *compound*, $C_{28}H_{28}O_2N_{10}S_2$, m. p. 198—199° (decomp.), whilst (III) yields 2-*anilino*-5-*phenylazo*-1 : 3 : 4-*thiodiazole*, $\begin{array}{l}N{:}C{\cdot}NHPh \\ \mid \quad >S \\ N{:}C{\cdot}N{:}NPh\end{array}$, m. p. 256—257°, also obtained by oxidation of (IV) with hydrogen peroxide.

When methyl phenyldithiocarbazinate is treated with ethylenediamine and *o*-phenylenediamine, there are formed 2-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3-*thiazole phenylhydrazone*, m. p. 223°, and 5-*thiol*-1-*phenyl*-2 : 3-*benzodihydro*-1 : 4 : 6-*triazine*, m. p. 292—293° (*acetyl* derivative, m. p. 203—204°), respectively. This last compound is oxidised by ferric chloride to the *disulphide*, $C_{26}H_{20}N_6S_2$, m. p. above 300°.

H. BURTON.

Rhodanine and related compounds. R. ANDREASCH (Monatsh., 1928, **49**, 122—132).—Reduction of 5-benzylidene-3-phenylrhodanine with zinc dust and alcoholic hydrogen chloride yields 4-*keto*-3-*phenyl*-5-*benzylidenetetrahydrothiazine*, $\begin{array}{l}NPh{\cdot}CH_2{\cdot}S \\ CO\text{———}C{:}CHPh\end{array}$ m. p. 206°. 3-Phenylrhodanine similarly yields 4-*keto*-3-*phenyltetrahydrothiazine*, m. p. 115°, whilst 3-*p*-tolylrhodanine by reduction with amalgamated zinc yields 4-*keto*-3-p-*tolyltetrahydrothiazine*, m. p. 243°. When the reduction of rhodanine itself was attempted only the products of hydrolytic fission (thioglycollic acid and ammonia) could be isolated. *Benzylidenediphenylthiohydantoin*, m. p. 206°, is obtained in 86% yield when diphenylthiohydantoin and benzaldehyde are heated together in acetic acid. Sodium β-bromo-β-phenylpropionate reacts with ammonium phenyldithiocarbamate to yield 2-*thioketo*-3 : 6-*diphenyltetrahydro*-1 : 3-*azthine*, $\begin{array}{l}NPh{\cdot}CS{\cdot}S \\ CO{\cdot}CH_2{\cdot}CHPh\end{array}$, 122°, which by heating with alkali is converted into β-phenyl-β-thiolpropionic acid. Similarly, sodium α-bromo-β-phenylpropionate and ammonium phenyldithiocarbamate yield 5-*benzyl*-3-*phenylrhodanine*, m. p. 118—119°. The anilide of thioglycollic acid when heated with benzaldehyde in acetic acid is converted into the *dianilide* of benzylidenedithioglycollic acid, $CHPh(S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, m. p. 178°. By the action of sodium hydroxide on a mixture of rhodanine and the hydrogen sulphite compound of *iso*butaldehyde is obtained 5-*isopropylidenerhodanine*, m. p. 128°. α-Bromo*iso*valeric acid or its ester reacts with thiocarbamide in alcohol solution to yield iso-*propylthiohydantoin*, m. p. 229°. By heating rhodanine or 3-phenylrhodanine with *o*-chlorobenzaldehyde in acetic acid are obtained, respectively, 5-o-*chlorobenzylidene*-, m. p. 169°, and 3-*phenyl*-5-o-*chlorobenzylidene*-, m. p. 140—141°, *rhodanines*. The latter is hydrolysed by heating with barium hydroxide to yield α-*thiol*-p-*chlorocinnamic acid*, m. p. 119—120°.

J. W. BAKER.

1 : 3 : 4-Oxdiazines. I. J. VAN ALPHEN (Rec. trav. chim., 1928, **47**, 673—682).—Derivatives of 1 : 3 : 4-oxdiazine are produced by the action of

oxalyl chloride on β-acylphenylhydrazines in benzene solution in accordance with the scheme :

$$\begin{array}{l} CO{\cdot}Cl \\ | \\ CO{\cdot}Cl \end{array} \quad \begin{array}{r} HO{\cdot}CR \\ HNR'{\cdot}N \end{array} = \begin{array}{l} CO{-}O{-}CR \\ | \\ CO{\cdot}NR'{\cdot}N \end{array} + 2HCl$$

and evidence in favour of the structure assigned is adduced. Thus from the appropriate acylphenylhydrazine the following are obtained : Δ^2-4-*phenyl-2-methyl*-5 : 6-*diketo*-1 : 3 : 4-*oxdiazine*, m. p. 141°. This is hydrolysed by water in two stages, rupture of the 1 : 6-linking occurring first, followed by the 4 : 5-linking with the regeneration of oxalic acid and β-acetylphenylhydrazine. Decomposition with substances of the type NH_2R or $NHR{\cdot}NH_2$ yields the corresponding substituted amide or hydrazide of oxalic acid, whilst the action of alcohol produces *α-ethoxalyl-β-acetylphenylhydrazine*, $CO_2Et{\cdot}CO{\cdot}NPh{\cdot}NHAc$, m. p. 95°, which is synthesised by the action of ethoxalyl chloride on β-acetylphenylhydrazine. Δ^2-2 : 4-*Diphenyl*-5 : 6-*diketo*-1 : 3 : 4-*oxdiazine*, m. p. 175°, which by treatment with alcohol yields *α-ethoxalyl-β-benzoylphenylhydrazine*, m. p. 157° (synthesised from β-benzoylphenylhydrazine) ; Δ^2-4 - *phenyl* - 2 - *benzhydryl* - 5 : 6 - *diketo*-1 : 3 : 4-*oxdiazine*, m. p. 167—168°, which is converted by boiling alcohol into *α-ethoxalyl-β-diphenylacetylphenylhydrazine*, m. p. 189° (also synthesised). J. W. BAKER.

Alkaloids of *Ceanothus Americanus*. II. A. H. CLARK (Amer. J. Pharm., 1928, **100**, 240—242; cf. A., 1926, 548).—Various methods have been used for extracting the alkaloids without materially increasing the yield. Fractional extraction with acetone and recrystallisation from butyl alcohol afforded a *compound*, m. p. 260—263°. The *phosphate*, *oxalate*, *sulphate*, *tartrate*, and *chloride* (m. p. 255—260°) have been prepared.

A light petroleum extract furnished a fat, saponification value 136—155, and a non-alkaloidal *substance*, m. p. 175°. A sample of very pure "gallotannic" acid was also obtained. S. COFFEY.

Simplest homologues of codeine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 691—694).—See this vol., 188.

Syntheses in the aporphine group. II. Synthesis of bulbocapnine methyl ether. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 1132—1137).—Condensation of β-piperonylethylamine with 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (Kay and Pictet, J.C.S., 1913, **103**, 952) yields 2′-*nitro*-3′ : 4′ - *dimethoxyphenylaceto* - β - 3 : 4 - *methylenedioxyphenylethylamide*, m. p. 158°. Treatment of a cold chloroform solution of this substance with phosphorus pentachloride gives a good yield of 2′-*nitro*-3′ : 4′-*dimethoxy*-6 : 7-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 164° [*sulphate* ; *nitrate* ; *hydrochloride*, m. p. 230° (decomp.)]. When the *methiodide*, m. p. 215° (decomp.), of this base is heated with dilute alkali, oxyhydrastinine and 2-nitrohomoveratrole are obtained. Reduction of the methiodide in strongly acid solution with zinc dust gives 2′-*amino*-3′ : 4′-*dimethoxy*-6 : 7 - *methylenedioxy* - 1 - *benzyl* - 2 - *methyltetrahydro*iso*quinoline* (I), isolated as the *dihydrochloride*, m. p. 231° (decomp.). Phenanthrene ring-closure is effected by diazotisation of the base (I) in a mixture of methyl alcohol and 2*N*-sulphuric acid. *dl*-Bulbocapnine methyl ether (*methiodide*, m. p. 243°), isolated as the *hydriodide*, m. p. 250° (decomp.), is thus obtained (cf. Gadamer, A., 1911, i, 1011). M. CLARK.

Alkaloids of some Indian aconites (*A. Balfourii*, *A. deinorrhizum*, and "Chumbi aconite"). T. A. HENRY and T. M. SHARP (J.C.S., 1928, 1105—1121).—ψ-Aconitine, the alkaloid present in *Aconitum Balfourii*, was extracted in quantity from *A. deinorrhizum*, Stapf. The pure substance has m. p. 214° (decomp.), $[\alpha]_D^{20}$ +17·06° in alcohol, +22·75° in chloroform. It forms a *hydrochloride*, m. p. 179—182° (decomp.), $[\alpha]_D^{20}$ −18·1° in water ($+4H_2O$, $+3H_2O$), *oxalate*, m. p. 216° (decomp.), *perchlorate*, m. p. 239° (decomp.), and *picrate*, m. p. 196° (decomp.). From their analytical results, the authors incline to the provisional formula $C_{36}H_{51}O_{12}N$ suggested by Dunstan and Andrews (*ibid.*, 1905, **87**, 1636). ψ-Aconitine, which contains six methoxyl groups, yields on hydrolysis 1 mol. proportion each of acetic and veratric acids and, in addition, ψ-aconine, $C_{25}H_{41}O_8N$, m. p. 93—94°, $[\alpha]_D^{20}$ +38·7° in water ($+1Me_2CO$), which gives a *tetra-acetyl* derivative, m. p. 228°, $[\alpha]^{20}$ −8·1° in alcohol. The two oxygen atoms unaccounted for must therefore be present as hydroxyl groups. The nitrogen is present as a methylimino-group. On oxidation with cold nitric acid, ψ-aconitine yields a pale yellow *substance*, (A), $C_{33}H_{40}O_{16}N_4$, blackening at 260°, decomp. 270°, and a bright yellow *substance* (B), $C_{34}H_{43}O_{17}N_3$, decomp. 195 . Product (A) still contains the acetyl group, but the veratroyl residue has been nitrated in position 6. Five methoxyl groups remain, two belonging to the nitroveratroyl radical. The methylimino-group has been converted into a :N·NO group, since the compound gives Liebermann's nitrosoamine reaction. The remaining nitrogen atom is probably present as a nitro-group, indicating the presence of a benzene ring in the nucleus. When (A) is treated with acetyl chloride at 100° under pressure, nitrosyl chloride, obtained by the conversion of the :N·NO group into a *N*-acetyl group, is formed together with a *substance*, m. p. 227—230°, which furnishes on hydrolysis 3 mol. proportions of acetic acid. Two of these are obtained by alkaline hydrolysis, arising (1) from the acetyl group originally present in ψ-aconitine and persisting in (A) and (2) from an acetyl group formed in the reaction by acetylation of a hydroxyl group in A. The third mol. of acetic acid, obtained by subsequent acid hydrolysis, comes from the acetyl group attached to nitrogen by replacement of the nitroso-group in the reaction. Alkaline hydrolysis of (A) gives, in addition, 6-nitroveratric acid and a *substance* (C), $C_{22}H_{31}O_{10}N_3$, m. p. 215°, $[\alpha]_D^{20}$ +30·9° in alcohol. The function of the unaccounted-for oxygen atom in (A) is demonstrated by the behaviour of (C) on being dissolved in methyl alcohol containing sodium methoxide, when a *sodium* salt, $C_{22}H_{32}O_{11}N_3Na$, is produced by addition of the elements of sodium hydroxide, showing the presence of a lactim group in the hydrolytic product and also in A. ψ-Aconitine, therefore, probably contains a group such as NMe·CH·OH, oxidised by nitric acid to ·N(NO)·CO.

Acetylation of (C) gives a *substance*, ($C_{26}H_{35}O_{12}N_3$?), m. p. 257° (decomp.), and a small amount of a *substance*, decomp. 322°. The nitric acid oxidation product, (B), gives on hydrolysis acetic and 6-nitroveratric acids and an amorphous nitrogenous product. It contains 5 methoxyl groups, of which 2 are in the nitroveratroyl residue, and a nitroso-group eliminated on treatment with acetyl chloride as in the case of (A). On oxidation with permanganate, ψ-aconitine yields acetaldehyde and a complex mixture of solid products (cf. Carr, J.C.S., 1912, **101**, 2243). Oxidation with chromic acid yields a neutral *substance*, $C_{34}H_{45}O_{11}N$, decomp. 255°, $[\alpha]_D^{20}$ −67·95° (*hydrochloride*, decomp. 180°, $[\alpha]_D^{20}$ +39·5° in alcohol; *picrate*, m. p. 229—230°; *chloroaurate*, $4C_{34}H_{45}O_{11}N,3HAuCl_4$, sintering 175°, decomp. 185°), containing 5 methoxyl groups and retaining intact the methylimino-group. On hydrolysis by alkalis, this substance gives acetic and veratric acids and a *compound*, ($C_{23}H_{35}O_7N$?), m. p. 175—177°.

The alkaloid from the "Chumbi aconite," collected on the pass between Sikkim and the Chumbi valley in Tibet, resembles aconitine rather than japaconitine (Dunstan and Read, J.C.S., 1900, **77**, 45). It has m. p. 203° (decomp.), $[\alpha]^{20}$ +16·3° in chloroform. It yielded a hydrobromide, m. p. 175°, $[\alpha]_D^{20}$ −34·8° in water (contaminated with a minute quantity of a *substance*, m. p. 199°), *hydrochloride*, m. p. 174°, $[\alpha]^{20}$ −35·9° in water, *hydriodide*, m. p. 225°, and *chloroaurate*, m. p. 152°. Hydrolysis and subsequent acetylation of the alkaloid residues after extraction of the crystalline material, gave a *substance*, m. p. 241°, $[\alpha]^{20}$ −32·5° in chloroform. M. CLARK.

Grignard's reaction. Preparation of tetraphenylphosphonium salts. J. DODONOV and H. MEDOX (Ber., 1928, **61**, [*B*], 907—911).—The production of tetraphenylphosphonium bromide, m. p. 287° (also *dihydrate*), during the action of an ethereal solution of magnesium phenyl bromide on triphenylphosphine is due to atmospheric oxidation; the yield of the compound attains 72% if a brisk current of oxygen is passed through the reaction mixture. Triphenylphosphine oxide does not appear to react under any conditions with an ethereal solution of magnesium phenyl bromide. An explanation of the course of the reaction is afforded, based on the views of Meisenheimer and Casper (A., 1921, i, 654). When treated in aqueous solution with precipitated silver oxide at the ordinary temperature, the bromide gives a strongly alkaline solution of tetraphenylphosphonium hydroxide, which readily loses benzene when concentrated even in a vacuum and yields a residue of triphenylphosphine oxide, m. p. 154·5—155°, and tetraphenylphosphonium carbonate. Treatment of the dilute aqueous solution of tetraphenylphosphonium hydroxide with the requisite acid yields the following salts: *chloride*, m. p. 265°, and its *pentahydrate*; normal *sulphate*, m. p. indef. (also $+18H_2O$). The *nitrate*, m. p. 284° (decomp.), and *iodide*, m. p. 333°, are described. A modification of Pfeiffer's method (A., 1905, i, 164) for the preparation of triphenylphosphine from phosphorus trichloride and magnesium phenyl bromide gives the compound in 76% yield. H. WREN.

Nature of the alternating effect in carbon chains. XXVII. Nitration of aromatic phosphonium, arsonium, and stibonium salts. C. K. INGOLD, F. R. SHAW, I. S. WILSON, and J. W. BAKER (J.C.S., 1928, 1280—1286).—Investigation of the nitration of phenyltrimethyl-phosphonium, -arsonium, and -stibonium picrates and of benzyltrimethyl-phosphonium and -arsonium picrates shows that the proportion of *m*-substitution of quaternary salts of the same general type diminishes with the increasing atomic number of the central positively-charged atom. The possible causes of this effect are discussed. The following are described: *Phenyltrimethylphosphonium picrate*, m. p. 132—133° (m-*nitro*-derivative, m. p. 166—167°); *benzyltrimethylphosphonium picrate*, m. p. 173° (o-*nitro*-derivative, m. p. 152—153°; m-*nitro*-derivative, m. p. 171—172°; p-*nitro*-derivative, m. p. 188—189°); *benzyltrimethylarsonium picrate*, m. p. 175—176° (p-*nitro*-derivative, m. p. 166—168°); *phenyltrimethylstibonium picrate*, m. p. 153° (m-*nitro*-derivative, m. p. 203°); m-*nitrophenyltrimethylarsonium picrate*. M. CLARK.

Aliphatic-aromatic arseno-compounds. II. β-Hydroxyethylarsinic acid and some aryl β-arsenoethyl alcohols. R. H. EDEE (J. Amer. Chem. Soc., 1928, **50**, 1394—1399; cf. A., 1927, 579).—Orange-yellow, amorphous arylarsenoethyl alcohols, $C_6H_4R\cdot[As]_n\cdot CH_2\cdot CH_2\cdot OH$, are formed by reducing a solution of β-hydroxyethylarsinic acid, m. p. 157—159° (also $+H_2O$; cf. Quick and Adams, A., 1922, i, 600), and the appropriate arylarsinic acid in hydrochloric acid with hypophosphorous acid at a low temperature. In this way p-*hydroxyphenylarsenoethyl alcohol*, p-*aminophenylarsenoethyl alcohol* (*hydrochloride*), 3-*amino*-4-*hydroxyphenyltetra-arsenoethyl alcohol*, and p-*carboxymethylaminophenyltetra-arsenoethyl alcohol* are prepared. A mixture of *p*-acetoxyphenylarsinic acid and β-hydroxyethylarsinic acid is reduced at the ordinary temperature to p-*acetoxyphenylarsenoethyl alcohol* and at 60° to (?) p-*acetoxyphenyltriarsenoethyl alcohol*, $C_{10}H_{12}O_4As_3$. H. E. F. NOTTON.

Conversion of diaminodiphenylarsinic acid into diphenylarsinic acid. V. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 877—880).—The possibility of obtaining diphenylarsinic acid by the diazotisation and subsequent reduction of diaminodiphenylarsinic acid, which is a waste by-product of arsanilic acid manufacture, was studied. Since the reduction by means of alcohol or alkaline stannite was impossible, excess of hypophosphite was used; the yields of diphenylarsinic acid, however, were low (38·5%) even with five times the theoretical quantity of the salt. Addition of a small amount of copper sulphate raised the yield to 60%, and increased the rate of reduction. M. ZVEGINTZOV.

Diphenylamine-*p*-arsinic acid. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 1286—1288).—A corrected m. p., 295—297° (decomp.) after darkening at 287°, is recorded for diphenylamine-*p*-arsinic acid [*hydrochloride*, m. p. 153—155° (decomp.)] (cf. Burton and Gibson, A., 1926, 419; Lieb and Wintersteiner, this vol., 312). -Acetyl-*p*-aminodiphenylamine has m. p. 127—128°. M. CLARK.

Diphenylamine- and triphenylamine-arsinic acids. II. O. WINTERSTEINER and H. LIEB [with M. BASILIOUS, F. SEELICH, and H. MAYER (Ber., 1928, **61**, [*B*], 1126—1135).—Direct arsenication of diphenylamine gives diphenylamine-*p*-arsinic acid in only very modest yield (cf. this vol., 312) and the reaction is less successful when applied to the nitro- and amino-diphenylamines. *p*-Arsanilic acid does not react with bromobenzene according to Ullmann's method in boiling nitrobenzene or amyl alcohol, whereas reaction occurs readily with *o*-arsanilic and bromobenzene or its derivatives; amyl alcohol is generally a suitable solvent, since decomposition frequently takes place at the temperature of boiling nitrobenzene. Thus *o*-arsanilic acid, bromobenzene, potassium carbonate, copper powder, and cuprous iodide at 130—140° afford *diphenylamine*-o-*arsinic acid*, m. p. 162° (*disodium* salt ($+6H_2O$)]. If the temperature of the reacting mixture is raised to 160—170°, the main product is o-*diphenylaminophenylarsinic acid*, $NPh_2{\cdot}C_6H_4{\cdot}AsO_3N_2$, decomp. 150°. Similarly, o-*acetamidophenylarsinic acid*, m. p. 215°, is readily converted into o-*acetanilidophenylarsinic acid*, $NPhAc{\cdot}C_6H_4{\cdot}AsO_3H_2$, decomp. 158°. *o*-Arsanilic acid and *p*-dibromobenzene at 130—140° yield op'-*bromophenylaminophenylarsinic acid*, m. p. 80°, and at 150—160° afford *o*-di-*p*'-bromophenylaminophenylarsinic acid, $(C_6H_4Br)_2N{\cdot}C_6H_4{\cdot}AsO_3H_2$, m. p. 215°. The three isomeric bromobenzoic acids condense analogously with *o*-arsanilic acid yielding, respectively, *oo*'-carboxyphenylaminophenylarsinic acid, decomp. 237° (hydrated *monosodium* salt), *om*'-carboxyphenylaminophenylarsinic acid, decomp. 238° (cf. Burton and Gibson, A., 1927, 1098), and op'-*carboxyphenylaminophenylarsinic acid*, decomp. 210°; in the last case the action appears to follow a different course if cuprous iodide is used in place of potassium iodide in the condensation. The yield is quantitative with the *o*-bromobenzoic acid, good and mediocre, respectively, with the corresponding *m*- and *p*-compounds. The isomeric bromonitrobenzenes yield oo'-*nitrophenylaminophenylarsinic acid*, decomp. 245° (temperature of condensation 110°), om'-*nitrophenylaminophenylarsinic acid*, decomp. 205—210°, and op'-*nitrophenylaminophenylarsinic acid*, decomp. 245—250°. Formation of triphenylamine-arsinic acids is not observed with the bromonitrobenzenes or bromobenzoic acids.

Direct action of arsenic acid on *m*-nitrodiphenylamine at 140—150° gives pm'-*nitrophenylaminophenylarsinic acid*, decomp. above 330° (*trihydrated disodium* salt), in 10% yield. Analogously, po'-*nitrophenylaminophenylarsinic acid*, decomp. 342° (*hexahydrated disodium* salt), and pp'-*nitrophenylaminophenylarsinic acid*, decomp. above 320°, are obtained in very poor yield. The three acids are reduced by hypophosphorous acid to the corresponding arsenobenzenes. H. WREN.

Preparation of organo-mercury compounds of phenols, phenol ethers, and aromatic amines. P. NEOGI and M. P. CHATTERJI (J. Indian Chem. Soc., 1928, **5**, 221—229).—Mercury derivatives of aromatic compounds can be prepared by the action of mercuric chloride and sodium hydrogen carbonate solution in presence of glycerol (cf. A., 1927, 214). In this way phenol gives *o*- and *p*-hydroxyphenylmercuric chlorides, but pyrocatechol, resorcinol, orcinol, guaiacol, phloroglucinol, and quinol yield derivatives in which each ·OH group is replaced by ·OHgCl. These mercurated derivatives are insoluble in, and are decomposed by sodium hydroxide solution. When alcoholic solutions of primary and secondary amines are treated with sodium hydrogen carbonate and mercuric chloride, the amino-hydrogen atoms are replaced by the ·HgCl grouping. Under similar conditions dimethylaniline gives *p*-mercurodiphenylenetetramethylmercurodiammonium chloride (cf. Pesci, A., 1894, i, 248). H. BURTON.

Position occupied by acetatomercuri (Hg·OAc')-groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. III. L. VECCHIOTTI (Gazzetta, 1928, **58**, 231—239; cf. this vol., 655).—*p*-Bromoaniline reacts with 1 mol. of mercuric acetate in alcoholic solution to give 4-*bromo*-2-*acetatomercurianiline*, m. p. 194° (*acetyl* derivative, m. p. 204°), from which the corresponding 2-*hydroxymercuri*-, m. p. 180°, and 2-*bromidomercuri*-, decomp. 194°, derivatives are prepared, and 2 : 2'-*mercury bis*-(4-*bromoaniline*), m. p. 220°. The position of the acetatomercuri-group is shown by the action of bromine in acetic acid, which yields 2 : 4-dibromoacetanilide.

It is observed that anilides *p*-substituted by halogen or a hydrocarbon residue do not (except *p*-nitroaniline) take up more than one acetatomercuri-group, which enters in the *o*-position to the amino-group. E. W. WIGNALL.

Action of mercuric acetate on *o*-bromoaniline. L. VECCHIOTTI (Gazzetta, 1928, **58**, 239—244).—The action of mercuric acetate in aqueous solution, slightly acidified with acetic acid, on an equimolecular proportion of *o*-bromoaniline yields 2-*bromo*-4-*acetatomercurianiline*, (I), m. p. 152—153°, (*acetyl* derivative, m. p. 220—221°), of which the corresponding 4-*hydroxymercuri*-, m. p. 253—254°, and 4-*bromidomercuri*-, m. p. 213—214°, derivatives are prepared. The action of sodium thiosulphate solution on (I) yields 4 : 4'-*mercury bis*-o-*bromoaniline*, m. p. 125°.

The structure of (I) is shown by the action of bromine, sodium bromide, and acetic acid on the acetyl derivative, which yields 2 : 4-dibromoacetanilide, with an unidentified substance, m. p. 183—184°. E. W. WIGNALL.

Mol. wt. of hæmocyanin. T. SVEDBERG and E. CHIRNOAGA (J. Amer. Chem. Soc., 1928, **50**, 1399—1411).—The partial specific vol. of hæmocyanin from *Helix pomatia* is approx. 0·734 at p_H 3·8—7·0 and 0·754 at p_H 8·0. Its ultra-violet and visible absorption spectrum is unchanged from p_H 8·0 to p_H 4·7, but at p_H 3·8 the maximum is displaced towards the red on account of partial molecular disintegration. The diffusion coefficient, unlike that of other proteins, approaches a constant value only in 0·1% or more dilute solutions, decreasing rapidly at higher concentrations, probably as a result of intermolecular frictional forces. Using low concentrations near the isoelectric point, the mol. wt. determined from the sedimentation velocity (cf. A., 1927, 716; this vol., 191) is $4{\cdot}93\times10^6$, and

from the sedimentation equilibrium, which is attained only with small centrifugal forces, $5{\cdot}08\times10^6$. The good agreement indicates that the particles are approximately spherical ($r=12{\cdot}2\times10^{-7}$ cm.), and the results of both experiments together with the sharp differentiation between solvent and solution produced by high-speed centrifuging show that they are of uniform size. H. E. F. NOTTON.

Action of alkalis, acids, and enzymes on proteins and allied substances. III. E. ABDERHALDEN and H. MAHN (Z. physiol. Chem., 1928, **174**, 47—75).—The effect of the following reagents on gelatin, dispersed in 12·5% lithium bromide solution, has been investigated: (1) *N*-hydrochloric acid at 18°, 38°, 50—55°, 70—75°; (2) 0·5*N*-sodium hydroxide at 18°; (3) *N*-sodium hydroxide at 18°, 38°, 50—55°; (4) a borate buffer of p_H 8·3 at 38°; (5) pepsin–hydrochloric acid at 38°; (6) trypsin at p_H 7·6—8 and 38°. Measured by the rate of increase in amino-nitrogen the order of increasing activity of the acid or alkali is as follows: *N*-hydrochloric acid at 38°, *N*-sodium hydroxide at 18°, *N*-hydrochloric acid at 50—55°, *N*-sodium hydroxide at 38°, *N*-hydrochloric acid at 70—75°, *N*-sodium hydroxide at 50—55°. There is no constant relationship between the alteration in the optical rotation of these reaction mixtures with time and the increase in amino-nitrogen. At p_H 8·3 in absence of enzyme there is a slow change in the rotation of a gelatin solution, but no increase in the amino-nitrogen. If gelatin or elastin is digested for 3 days with trypsin, subsequent treatment with *N*-sodium hydroxide brings about a further slow hydrolysis, but treatment with pepsin–hydrochloric acid or with 0·1*N*-hydrochloric acid has little if any further effect. The relationship of the experimental findings to the possible structure of proteins is discussed at some length. H. D. KAY.

Apparatus for the determination of carbon by the baryta method. P. DICKENS (Chem. Fabr., 1928, 293—294).—The barium hydroxide is contained in an absorption tube with a glass filter plate at the bottom above the gas inlet. The restriction on the passage of the gas causes the combustion tube to be under pressure during operation, whilst the apparatus is previously swept out with pure oxygen. Above the tube is a filter and flask so arranged that after combustion the apparatus may be inverted and the barium carbonate filtered and washed with water free from carbon dioxide. The excess of barium hydroxide is titrated and the precipitated barium carbonate weighed as sulphate. The method gives results accurate to ±0·001%. C. IRWIN.

Analysis of mixtures of ethyl alcohol, ethyl acetate, acetic acid, and water. S. POZNANSKI (J. Amer. Chem. Soc., 1928, **50**, 981—988, and Rocz. Chem., 1928, **8**, 152—164, 229—241).—Alcohol in the absence of esters may be accurately determined by a modification of the Bourcart–Kuriloff method (A., 1897, ii, 352); in the presence of esters, the alcohol is boiled with a known excess of acetic anhydride, excess of water is added, and the acetic acid produced determined by titration. Ethyl acetate is determined by hydrolysing at 60—65° with excess of barium hydroxide solution. The micro-titration of acetic acid in a modified Pilch apparatus is described. The methods are applied successfully to the analysis of a mixture of the four substances. S. K. TWEEDY.

Furfuraldehyde–sulphuric acid reaction. O. COQUELET (Compt. rend. Soc. Biol., 1927, **97**, 747—748; Chem. Zentr., 1928, i, 386—387).—The optimal conditions for the detection and determination of bile acids and cholesterol are described. A. A. ELDRIDGE.

Colorimetric determination of histidine. K. SUZUKI and Y. KAISHIO (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 33—34).—The yellow colour developed when excess of a 2% solution of sulphanilic acid in 10% sulphuric acid, and concentrated acid to produce a 11—15% solution, are added to an aqueous solution of histidine, the mixture shaken and rendered alkaline with sodium hydroxide, is compared with that of 0·01*N*-potassium dichromate solution. CHEMICAL ABSTRACTS.

Measurement of quantities of chloroplast pigments. H. B. SPRAGUE (Science, 1928, **67**, 167—169).—The chlorophylls *a* and *b* are obtained as aqueous solutions of the chlorophyllins, which are green by transmitted light. The comparison solution for the chlorophyllins from maize was prepared by diluting 0·3 c.c. of 0·5% aqueous malachite-green and 11·2 c.c. of 0·5% aqueous naphthol-yellow to 5500 c.c. with distilled water. The colour is equivalent to that of 10·708 mg. of chlorophyll hydrolysed to chlorophyllins and diluted to 1 litre. The carotin standard (equivalent to 1·890 mg. of carotin per litre of light petroleum) is made by adding 3·5 c.c. of 0·5% aqueous naphthol-yellow and 0·5 c.c. of 0·5% aqueous orange-G to 1 litre of distilled water. The xanthophyll standard (equivalent to 1·537 mg. of xanthophyll per litre of light petroleum) is made by adding 2·8 c.c. of 0·5% aqueous naphthol-yellow to 1 litre of distilled water. A Duboscq colorimeter is employed. A. A. ELDRIDGE.

Biochemistry.

Oxygen-carrying ability of the blood. K. YABUKI (Acta Schol. Med. Univ. Imp. Kyoto, 1927, **10**, 25—32).—Replacement of blood-serum by isotonic salt solution decreases the oxygen-carrying capacity of the red blood-corpuscles, but the effect of Locke's solution is less marked. Gum-arabic is without influence, but the presence of sodium hydrogen carbonate tends to increase the oxygen-carrying capacity. W. O. KERMACK.

Combination of hæmoglobin with oxygen. I. Aggregation of hæmoglobin molecules in the blood studied from the oxygen dissociation curve. K. YABUKI (J. Biochem. Japan, 1927, **8**,

107—133).—The value of n in Hill's formula $y/100=Kx^n/(1+Kx^n)$ is variable. Log K is a linear function of p_H, but the angle of inclination is 60°.

CHEMICAL ABSTRACTS.

Influence of reduced atmospheric pressure on the hæmoglobin concentration of the blood-corpuscles and on the action of the spleen on blood regeneration. L. DRASTICH (Biochem. Z., 1928, **195**, 189—205).—An apparatus provided with an animal container and suitable for continuous use with pressures reduced to 300 mm. mercury, is described. The hæmoglobin concentration (g. of hæmoglobin/100 c.c. of corpuscles by hæmatocrit) of the corpuscles of an animal after living under reduced pressure for some time is below normal but later increases. In splenectomised animals the blood regenerates under reduced pressure more slowly than in non-operated animals. Under reduced pressure, as in pernicious anæmia, the erythrocytes increase in size. Injection of spleen pulp favours the formation of corpuscles.

P. W. CLUTTERBUCK.

Respiratory proteins of the blood. III. Acid-combining capacity and dibasic amino-acid content of hæmocyanin of *Limulus polyphemus*. A. C. REDFIELD and E. D. MASON (J. Biol. Chem., 1928, **77**, 451—457).—The hæmocyanin of *Limulus polyphemus* reacts as a univalent base with pK 3·3; it is able to bind 160×10^{-5} mol. of acid per g. as determined by titration, whilst calculation from the content of dibasic amino-acids leads to a combining capacity for acid of $155{\cdot}5\times10^{-5}$ mol. per g.

C. R. HARINGTON.

Vapour pressure of dog's blood at body temperature. A. GROLLMAN (J. Gen. Physiol., 1928, **11**, 495—506).—The vapour pressures of dog's plasma and whole blood measured by the dynamic method at 37·5° are both equal to 48·10 mm. of mercury, corresponding with an osmotic pressure of about 8·2 atm. The vapour pressure of the ultrafiltrate of the plasma is but slightly lower than that of the plasma itself by an amount corresponding with an osmotic pressure of 0·06 atm. for the plasma-colloids.

W. O. KERMACK.

Molecules and ions in plasma. R. KELLER (Biochem. Z., 1928, **195**, 14—19).—A theoretical discussion of the effect of recent work on conceptions of the mobility of ions in plant and animal tissues and fluids.

P. W. CLUTTERBUCK.

Electrodialysis of serum. G. ETTISCH and W. EWIG (Biochem. Z., 1928, **195**, 175—188).—The conditions are outlined for fractionation of serum-globulin by electrodialysis and compared with those of other authors. The best results are obtained with quick fractionation of undiluted serum, care being taken to avoid any considerable change of p_H and the temperature being maintained within physiological limits. An albumin–collodion membrane is described and used as anodic membrane together with a parchment membrane. This membrane cannot be replaced by a pure collodion membrane. Under the conditions described, the globulin of about 40 c.c. of serum is completely precipitated in about 1 hr.

P. W. CLUTTERBUCK.

Phosphates in blood and the urinary excretion of phosphates. R. T. BRAIN, H. D. KAY, and P. G. MARSHALL (Biochem. J., 1928, **22**, 628—648).—The acid-soluble phosphorus in the plasma consists of inorganic phosphate, of which at least 80% is ultra-filtrable and dialysable, and of organically combined (ester) phosphoric acid. The latter is about 10% of the former. The amount of inorganic phosphate is less than the amount expected from the Donnan equilibrium between corpuscles and plasma. The very low concentration of ester phosphorus in the plasma cannot be raised by taking phosphoric esters by mouth, but can be raised temporarily by intravenous injection of these compounds. Doubling the plasma concentration of inorganic phosphate in the rabbit by intravenous injection results in about tenfold increase of excretion of the compound in the urine. When sodium glycerophosphate or fermentation sodium hexosediphosphate is injected there is a rapid rise of organic phosphorus in the plasma, which is followed by a fairly rapid fall. At the same time the inorganic phosphate in the plasma increases. This is reflected by an immediate increased excretion of inorganic phosphate in the urine, which reaches its maximum in the second hour after the injection, when the phosphoric ester content of the plasma has almost returned to its normal value. Similar results were obtained by injecting intravenously sodium glycerophosphate in human subjects. There appears to be a renal threshold for phosphate excretion. Within wide limits there is no relationship between the amount of urinary phosphate and the urinary volume. The various theories of the origin of urinary phosphate are critically discussed.

S. S. ZILVA.

Colorimetric determination of iron and hæmoglobin in blood. II. S. Y. WONG (J. Biol. Chem., 1928, **77**, 409—412).—The blood is treated with concentrated sulphuric acid and potassium persulphate in the cold, the mixture is diluted and treated with sodium tungstate; iron is determined in an aliquot portion of the filtrate by the author's colorimetric method (A., 1923, ii, 435).

C. R. HARINGTON.

Effects of congestion and heat on the composition of venous blood samples. Indirect determination of iron and chlorine in blood-corpuscles. F. H. SMIRK (Biochem. J., 1928, **22**, 739—744).—The errors in the determinations of corpuscular blood-chloride are due to incomplete separation of plasma from the corpuscles and not to the chemical analysis. Congestion of the arm causes a concentration of iron and increased venosity in samples from the median basilic vein. This is associated with a reduced percentage of chlorine in the plasma and an increased percentage in the corpuscles. Heating the arm renders the venous sample more arterial in appearance and this is associated with a transference of chlorine ions from corpuscles to plasma. The iron content of the blood may be raised. Venous samples should be taken with a minimum of congestion and should be thoroughly shaken with atmospheric or alveolar air if they are to form a trustworthy index of changes in the plasma-chlorides of the general circulation.

S. S. ZILVA.

Determination of chloride in blood-serum. D. RAQUET (J. Pharm. Chim., 1928, [viii], 7, 487—489).—A protein-free filtrate is prepared by precipitating the proteins with zinc ferrocyanide and chloride is then determined by Volhard's method.
W. O. KERMACK.

Uric acid. I. Comparison of the direct and isolation methods for determining uric acid in blood filtrate, and a modification of Folin's method. R. E. WIENER and H. J. WIENER (J. Lab. Clin. Med., 1926, **11**, 1035—1045).—Preliminary isolation of the uric acid is recommended in the determination of uric acid in the filtrate obtained by Folin's method. Silver lactate (5% in 5% lactic acid, 5 c.c.) is added to the filtrate (10—20 c.c.), the mixture being centrifuged for 5—7 min., after keeping in the dark for 5 min. The supernatant liquid is stirred with 10% lithium chloride solution (3 c.c.) and with water (8—10 c.c.), immediately centrifuged for 8—10 min., 15% sodium cyanide solution (2 c.c.) added, then 1 c.c. of reagent, and the colour allowed to develop for 20—30 min. The method is also applicable to the determination of uric acid in urine, details for which are given. Phenol, resorcinol, and tyrosine intensify the blue colour developed by uric acid and Benedict's reagent; phenol and resorcinol react less markedly, and tyrosine only slightly, with Folin's reagent. CHEMICAL ABSTRACTS.

Determination of urea in serum and whole blood. L. BALLIF, A. RESNIC, and I. LUNEVSKY (Compt. rend. Soc. Biol., 1927, **97**, 1026—1027; Chem. Zentr., 1928, i, 386).—The statement of Pagel (A., 1924, ii, 575) and of Pechon (A., 1926, 763) that the first quantities of blood removed are richest in urea is not confirmed. A. A. ELDRIDGE.

Micro-method for the colorimetric determination of urea in blood. (MISS) F. BEATTIE (Biochem. J., 1928, **22**, 711—719).—The method is based on the precipitation of urea as dixanthylcarbamide from deproteinised serum by the addition of an alcoholic solution of xanthhydrol. The results are in good agreement with those obtained by the urease method. S. S. ZILVA.

Lipochromes. III. Determination of carotin in blood and tissues. C. L. CONNOR (J. Biol. Chem., 1928, **77**, 619—626).—Blood-plasma is treated with an equal volume of 95% alcohol, the excess of the latter poured off, and the residue shaken with light petroleum; tissues are hydrolysed with aqueous-alcoholic potassium hydroxide, water is removed from the hydrolysate with calcium sulphate, and the whole is then extracted with light petroleum; further extraction with 85% alcohol removes xanthophyll; the carotin in the light petroleum extracts is determined colorimetrically by comparison with a solution of potassium dichromate. Figures are given for the carotin content of human blood and of various animal tissues. C. R. HARINGTON.

Colorimetric determination of lipoid phosphorus in blood. A. R. HARNES (J. Biol. Chem., 1928, **77**, 405—407).—Dried blood is extracted with chloroform and the phosphorus in the extract determined by the method of Briggs (A., 1922, ii, 718).
C. R. HARINGTON.

Determination of blood-sugar. O. FOLIN (J. Biol. Chem., 1928, **77**, 421—430).—Blood is freed from protein by treatment with a dilute solution of tungstic acid; an aliquot portion of the filtrate is heated with potassium ferricyanide in presence of sodium cyanide and sodium carbonate; ferric sulphate is then added and the resulting blue colour compared with that resulting from similar treatment of a known solution of dextrose. The method requires only 0·1 c.c. of blood. C. R. HARINGTON.

Mercurial deproteinisation of blood in the determination of dextrose. G. FONTES and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, **10**, 581—589).—The copper amalgam, produced in the previously described method of deproteinisation (A., 1927, 690), is found to absorb small amounts of dextrose. The amount of this amalgam produced may be reduced to a minimum by the use of potassium hydroxide and tartaric acid in place of sodium hydroxide and acetic acid, respectively.
G. A. C. GOUGH.

Condition of the ("free") sugar in serum. L. F. LOEB and D. KRUGER (Z. klin. Med., 1927, **106**, 354—359; Chem. Zentr., 1928, i, 372).—"Free" blood-sugar consists of the reducing substances, chiefly dextrose, present after the deproteinisation of whole blood, plasma, or serum; "bound" blood-sugar consists of the substances which exhibit reducing properties only after hydrolysis. The latter substance has not yet been identified. The free sugar in normal and diabetic individuals is molecularly disperse. A. A. ELDRIDGE.

Reducing substances in the blood of the dogfish and certain other fishes. F. D. WHITE (J. Biol. Chem., 1928, **77**, 655—669).—Figures are given for the sugar content of the blood of various fishes; that of the dogfish is very low immediately after capture, but on keeping the fish for 4 days, under normal or fasting conditions, it rises to a constant level of 55—60 mg. %; in this fish the blood-sugar is almost entirely fermentable by yeast, but in various teleostean fishes there is present 10—12 mg. % of non-fermentable reducing substance. Asphyxiation does not produce hyperglycæmia in the dogfish.
C. R. HARINGTON.

Course of glycolysis in the blood of normal and diabetic subjects. S. A. HOLBOLL (Acta med. scand. Suppl.-Bd., 1926, **16**, 509—514; Chem. Zentr., 1928, i, 84).—A discussion; lack of "neoglucose" is indicated. A. A. ELDRIDGE.

Role of calcium in the action of the glycolytic enzyme and the phosphatase of blood. A. ROCHE and J. ROCHE (Compt. rend. Soc. Biol., 1927, **97**, 804—806; Chem. Zentr., 1928, i, 371).

Determination of succinic acid in blood. P. W. CLUTTERBUCK (Biochem. J., 1928, **22**, 745—748).—The amount of succinic acid recovered from tissues by Moyle's method (A., 1924, i, 791) was 86—2% and not as high as that obtained by Moyle in determinations in muscle (95±5%). The method has been modified and adapted to the determination of succinic acid in blood, the amount of acid recorded being 87±3%. S. S. ZILVA.

Serum lipase. Influence of chemical and physical treatment. E. Adler (Deut. med. Woch., 1927, **53**, 1987—1988; Chem. Zentr., 1928, i, 364).—A study of changes caused by injection of protein, disturbance of mineral metabolism, and so-called specific stimulation. A. A. Eldridge.

Acid fixation and swelling of fibrin. I. E. Voit. **II.** F. Schuldenzucker. **III.** F. Lochmuller.—See this vol., 706.

Physico-chemical properties of the cell membrane. IV. Change in the permeability of red blood-corpuscles [caused] by hæmolytic agents. V. Observations on the hæmolytic process with the ultramicroscope. M. Suzue (J. Biophys., 1927, **2**, 49—65, 67—80).—IV. Experiments on the conductivity of red blood-cells, subjected to the action of saponin, ethyl alcohol, and high temperature, show that the permeability of the cell membrane increases with increasing application of the agent until hæmolysis takes place, whilst in the cases of hydrochloric acid and ammonia no alteration in permeability is observed until the cell membrane disrupts and hæmolysis occurs.

V. Three types of hæmolysis are distinguished. The first is brought about by acids and bile, the second by bases, high temperature, or hypotonic solutions, and the third by saponin, alcohols, and hypertonic solutions. W. O. Kermack.

The erythrocyte as a colloidal chemical system. II. Isoelectric zone of erythrocytes. A. P. Konikov (Zhur. exp. Biol. Med., 1927, **6**, 406—418).—The acid agglutination of erythrocytes in an 8% sucrose solution occurs within a definite p_H range in each series, and the degree of agglutination varies in each species. The acid hæmolysis and agglutination reactions are reciprocally related.

Chemical Abstracts.

Poison of the water snake (*Tropidonotus natrix*). I. Action of the water snake blood on the isolated cold-blooded heart. O. Gessner (Arch. exp. Path. Pharm., 1928, **130**, 375—383).—The substance present in blood-serum or -plasma of the water snake acting on the isolated heart of the frog or toad is probably not related to digitonin but from its pharmacological action appears to be of a saponin nature. W. O. Kermack.

Inorganic composition of human and animal tissues. L. Lematte, G. Boinot, and E. Kahane (Bull. Soc. Chim. biol., 1928, **10**, 553—567).—Detailed determinations of the inorganic components of various organs of man and animals are given and special precautions are taken to avoid analytical errors. Although human brain contains more phosphorus than the liver or the spleen, in animals the testes and the thymus gland often possess higher phosphorus contents. In all cases examined the spleen has the highest iron value and nearly all the iodine of the body is concentrated in the thyroid gland. The sulphur and nitrogen values for the same organs in different animals show wide variations.

G. A. C. Gough.

Animal nutrition. VI. Distribution of the mineral elements in the animal body as influenced by age and condition. A. G. Hogan and J. L. Nierman (Mo. Agric. Exp. Sta. Res. Bull., 1927, [107], 1—45).—Determinations of the composition of the ash of cattle indicate that the mineral content of the lean and fat, or of the hide and hair is unaffected by age or condition, but the total mineral content of the internal organs decreases with age. The blood-sodium tends to decrease with age. The skeletal calcium, phosphorus, and magnesium contents increase with age. Chemical Abstracts.

Iodine as a biogenic element. XV. Animal organs and products and their iodine content. XVI. Occurrence of iodine in fodders and manures. K. Scharrer and J. Schwaibold (Biochem. Z., 1928, **195**, 228—232, 233—237; cf. A., 1926, 638; 1927, 372, 798, 903).—XV. The iodine content of pig's heart, liver, lung, kidney, and spleen is subject to considerable variation, but is always low (5·5—40 γ-%) and after continued peroral administration of iodide only the liver, kidney, and spleen show any increase, the kidney reaching 66 γ-%. The iodine content of the milk of cows fed on marshy pasture or on hay obtained therefrom, is only 50% higher than normal, whereas milk of cows fed on pastures after flooding with sea-water contained 300—800% more iodine than that of Swiss cows.

XVI. Tables indicate the iodine contents of different types of fodder, artificial manures, and of a variety of samples of Chile saltpetre. The last-named contains almost all its iodine as iodate.

P. W. Clutterbuck.

Determination of iodine in the thyroid gland. K. Winterfeld and H. Roederer (Apoth. Ztg., 1928, **43**, 132).—The dry material (0·5 g.) is fused with borax (1·5 g.) and sodium potassium carbonate (1 g.), the cool mass extracted with warm dilute sulphuric acid (7 c.c.) and water, filtered, and the filtrate shaken in a glass-stoppered flask with bromine water. After 10 min., 2—5 drops of liquefied phenol are added, and after mixing and keeping for several minutes, 0·1 g. of potassium iodide and 5 c.c. of 25% phosphoric acid are added, the liberated iodine being titrated with thiosulphate solution.

Chemical Abstracts.

Embryonic metabolism. I. Isolation of four pentose nucleotides from chicken embryos. II. Isolation of a hexose nucleic acid. H. O. Calvery (J. Biol. Chem., 1928, **77**, 489—495, 497—503).—I. There was isolated from chicken embryos a β-nucleoprotein, similar in properties to that of Hammarsten (A., 1894, i, 310), which yielded, on hydrolysis, the same four pentose nucleotides as are obtained by hydrolysis of yeast nucleic acid. It is proposed to substitute the terms hexose nucleic acid and pentose nucleic acid for the thymus nucleic acid and yeast nucleic acid at present employed.

II. In addition to the above-described β-nucleoprotein, chicken embryos contain a hexose nucleic acid which is apparently identical with the nucleic acid obtainable from other animal tissues.

C. R. Harington.

Rapid formation of adipocere during cadaveric putrefaction. E. Barral (J. Pharm. Chim., 1928, [viii], 7, 486—487).—More than twice the normal

amount of fat has been found in a cadaver three months after death. W. O. Kermack.

Hydrolysis of keratin for tryptic digestion. III. Z. Stary (Z. physiol. Chem., 1928, **175**, 178—236; cf. A., 1924, i, 1007; 1925, i, 847).—Keratin is converted by the action of bromine, chlorine, or by weak oxidising agents into products which are almost as complex as and physically similar to the original substance, but are readily hydrolysed by trypsin, and it is considered that long-chain polypeptides are formed by the bromination or oxidation. Hydrolysis of keratin by acids or alkalis gives products, however, which are resistant to trypsin. Thus by the action of bromine and acetic acid on human hair, fractions containing bromine are obtained which have the properties of peptones or even higher proteins; these fractions differ in composition, precipitation reactions, and solubilities, but they are all digested by trypsin. It is concluded that keratin consists of substances which, on oxidation by this method, yield polypeptides and that this change cannot be produced, except perhaps to a slight extent, by the partial hydrolysis of hair. Fractionation, purification, or drying of these fractions results in a loss of digestibility by trypsin and a decrease in solubility. Possible explanations of the resistance of keratin to tryptic digestion are discussed. Examination of the values given by other workers for the amounts of the different amino-acids present in various proteins leads to the conclusion that a relatively large amount of the original protein (never less than 20%) is unaccounted for as carbon, nitrogen, oxygen, hydrogen, and sulphur of these amino-acids and the term protein " residue " is applied to this remainder. This " residue " contains a much higher percentage of oxygen than the original protein and this excess of oxygen cannot be attributed to imperfect determinations of the hydroxy-amino-acids. The protein " residues " from various animal proteins are of fairly constant composition, but the " residues " from the alcohol-soluble vegetable proteins (zein, gliadin, hordein, and rye-prolamin) contain rather less oxygen. Scleroproteins (fibroin, koilin, ovokeratin, and elastin) give figures which are in general agreement with those for the other proteins, although greater individual variations occur here. The possible nature of the substances or groups containing oxygen is discussed. A. Wormall.

Determination of carbamide and amino-acid nitrogen in animal tissues. V. C. Kiech and J. M. Luck (J Biol. Chem., 1928, **77**, 723—731).—The tissue is minced, frozen with liquid air, and pulverised; a weighed sample is suspended in ice-water and treated with tungstic acid; aliquot portions of the filtrate are employed for the determination of carbamide by the xanthhydrol method and of amino-acid nitrogen by the Van Slyke method; in the latter case ammonia is removed by boiling with sodium hydroxide. C. R. Harington.

Thiol titrations with iodine-starch and sodium nitroprusside. R. Bierich and K. Kalle (Z. physiol. Chem., 1928, **175**, 115—134).—These two methods for the determination of the thiol content of tissues have various sources of error and different dilution factors. If corrections are applied to the nitroprusside drop method, the values obtained are nearer the theoretical value than are those given by the iodine-starch method. Both methods give results which are too high for tissue extracts and with more dilute solutions the error is still greater. The dilution factors are specific for each of the methods, but the factors are not affected appreciably by acids (concentrations of 0·5—8·0% hydrochloric acid) or by the presence of trichloroacetic acid. If the titration is carried out at a higher temperature, the iodine requirement of a tissue extract increases, whilst the effect of dilution on the titration value is less pronounced at low temperatures. The iodine value for a trichloroacetic acid extract of tissues (liver, muscle, or yeast) decreases if the extract is exposed to the air. This decrease is attributed to the oxidation of the thiol group, and in an atmosphere of oxygen the decrease is five times as large as that in air. Determinations on tissues which have been exposed to the air for some hours and then extracted show that the iodine requirement rises with increased exposure. The total sulphur in the extracts is approximately constant and the increase in the thiol value is attributed to the cleavage of cysteine from complexes containing the thiol group. Yeast does not show this increase in iodine requirement on keeping. To reduce the errors obtained by both methods it is suggested that the tissues should be " fixed " as quickly as possible by means of trichloroacetic acid, or if necessary kept on ice, and that the filtrates should be as concentrated as possible and be titrated at a low temperature (−15°). A. Wormall.

Determination of total chloride and loosely combined chloride in gastric juice. D. Raquet and M. Paget (J. Pharm. Chim., 1928, [viii], 7, 489—492).—Total chlorides in gastric juice are determined by precipitating the organic matter by means of zinc ferrocyanide and determining the chloride in the filtrate by Volhard's method. The loosely combined hydrochloric acid and the inorganic chlorides are determined in a similar way after expelling the free hydrochloric acid by heat. W. O. Kermack.

Metabolism of the bile. I. Determination of bile acids in blood. M. Aldrich and M. S. Bledsoe (J. Biol. Chem., 1928, **77**, 519—537).—Blood is treated with alcohol and filtered; the filtrate is decolorised with charcoal and an aliquot portion is treated with barium hydroxide and evaporated to dryness; the residue is extracted with ether and the insoluble portion, containing the bile acids as barium salts, is treated with sucrose and sulphuric acid; the resulting solution, after removal of barium sulphate, is compared colorimetrically with one obtained by subjecting a known solution of sodium glycocholate to the Pettenkofer reaction under similar conditions. The method is applicable to 5 c.c. of blood; when applied to mixtures of bile salts it gives results in agreement with those obtained by the method of Schmidt and Dart (A., 1921, ii, 284). C. R. Harington.

Origin of bile acids. I. Determination of bile acid, cholesterol, and the other unsaponifiable

constituents in dog's bile. M. Jenke. **II. Cholesterol-bile-acid balance in a dog with complete bile fistula. III. Steric configuration of sterols and their influence on the formation of bile acids.** E. Enderlen, S. J. Thannhauser, and M. Jenke (Arch. exp. Path. Pharm., 1928, **130**, 280—291, 292—307, 308—318).—I. The bile is freed from mucin by addition of alcohol and the bile acids and cholesterol are liberated by hydrolysis with potassium hydroxide solution. The cholesterol is separated by extracting the alkaline solution with ether. From this extract the cholesterol is precipitated by means of digitonin and the unsaponifiable materials left after separation of the cholesterol are determined gravimetrically. The bile acids and fatty acids are extracted with a mixture of ether and light petroleum, and the bile acids are then determined from polarimetric observations. In dogs with bile fistula free cholic acid is eliminated in the bile as well as conjugated acids, and bile acids administered by the mouth are quantitatively excreted in the bile. A titration method for the determination of bile acids is given.

II. Evidence is adduced that the bile acids are not formed from cholesterol in the animal body.

III. When administered intravenously, coprosterol and *allo*cholesterol, which are stereochemically closely related to cholic acid, increase the output of bile acids. It is not certain whether coprosterol and *allo*cholesterol are converted into bile acid or whether they exert some specific action on the synthesis or excretion. W. O. Kermack.

Determination of pancreatic secretion. S. Okada, E. Sakurai, T. Imazu, and K. Kuramochi (Proc. Imp. Acad. Tokyo, 1928, **4**, 131—133).—The contents of the duodenum are collected, by means of a duodenal tube, for a period of 3 hrs. and the trypsin, amylase, and lipase contents are then determined. The total enzymic efficiency is not markedly affected by the addition of stimulants, is somewhat less for subjects above 40 years of age, and is low in females. J. Stewart.

Diffusion of carbamide in various body fluids. C. T. Rietti (Compt. rend. Soc. Biol., 1927, **97**, 1038—1039; Chem. Zentr., 1928, i, 373).—In a dog the kidneys of which had been excluded from the circulation, carbamide injected into the blood was found first in the saliva, in the cerebrospinal fluid, fairly soon in the pancreatic juice, in the bile, and very soon in the lymph. A. A. Eldridge.

Determination of carbamide in urine. M. Hopf (Biochem. Z., 1928, **195**, 206—209).—Laubender's method (A., 1927, 896) for the micro-determination of carbamide is very trustworthy provided the directions are rigidly followed. The urease method is equally good provided that the action of the urease is carried out by Pincussen's or Laubender's method, that distillation of ammonia proceeds for 50 min., and that the temperature never rises above 45°. P. W. Clutterbuck.

Determination of hippuric acid and free benzoic acid in the urine of cattle. F. J. Warth and N. C. D. Gupta (Biochem. J., 1928, **22**, 621—627).—After alkaline hydrolysis the liquid is acidified and shaken with a definite volume of petroleum. The liberated benzoic acid is determined with the aid of a partition coefficient. The method when applied to unhydrolysed urine gives some indication that titratable impurities are likely to be determined with the free benzoic acid. The partition coefficient of benzoic acid between water and different solvents has been determined. S. S. Zilva.

Indican in urine analysis. E. Schlecht (Pharm. Ztg., 1928, **73**, 567).—Polemical, maintaining that urine containing indican reduces Nylander's solution. S. Coffey.

Indican in urine analysis. C. Otto (Pharm. Ztg., 1928, **73**, 567; cf. preceding abstract).—A sample of horse urine containing indican no longer reduced Fehling's or Nylander's solutions when freed from protein. Potassium indoxylsulphonate has no reducing action on the above reagents either alone or when mixed with urine containing comparatively small or large amounts of indican, provided the latter has been freed completely from other reducing substances (cf. Jolles, this vol., 662). S. Coffey.

Detection of albumin in urine. A. Jolles (Deut. med. Woch., 1927, **53**, 1906—1907; Chem. Zentr., 1928, i, 99).—The usual methods are critically discussed; the Spiegler–Jolles reagent is modified. A. A. Eldridge.

Determination of urobilin in urine and fæces. E. Greppi (Folia clin. chim. micros., 1926, **1**, 61—67; Chem. Zentr., 1928, i, 99).—In Terwen's method, a second reduction after neutralisation is recommended. A. A. Eldridge.

Determination of silicic acid in urine and fæces. B. Kindt (Z. physiol. Chem., 1928, **174**, 28—39).—The urine (300—500 c.c.) or fæces (40—50 g.) is carefully oxidised with 100 c.c. of concentrated nitric acid, the mixture evaporated almost to dryness, the residue mixed with a little water and incinerated, the ash warmed with hydrochloric acid for 15 min., and the mixture evaporated to dryness and heated at 140° for 1 hr. Dilute hydrochloric acid is again added and the process repeated twice. The residue is finally boiled with hydrochloric acid and filtered through a special paper. Some silicic acid remains unprecipitated in the first filtrate, and may be recovered by evaporating to dryness and treating three times with dilute hydrochloric acid followed by evaporation and heating at 140°, as before. The second precipitate is collected on a second paper. Both precipitates are dried in a platinum dish, ashed, and weighed. Hydrofluoric acid and a few drops of sulphuric acid are added, and the dish is again heated to constant weight. The difference in weight represents the weight of silica. For the latter stages of the analysis an alternative precipitation method in which mercury ammonium carbonate is used is also described, but the first method is recommended for most purposes. H. D. Kay.

Silicic acid excretion in man after ingestion of sodium silicate. O. Riesser and B. Kindt (Z. physiol. Chem., 1928, **174**, 40—46).—After a diet relatively rich in silicic acid (bread containing 1·28 g. per day of SiO_2 added as sodium silicate) there is an

increase of silicic acid both in the urine and in the fæces. In two subjects, at least 34% of the ingested silicic acid is absorbed from the intestine, and both the urinary and fæcal excretion of this substance increase. A portion (22—34%) is not excreted during the 24 hrs. following the ingestion.

H. D. KAY.

Nature of material in liver effective in pernicious anæmia. II. E. J. COHN, G. R. MINOT, G. A. ALLES, and W. T. SALTER (J. Biol. Chem., 1928, 77, 325—358; cf. *ibid.*, 1927, 74, lxix).—Fresh minced liver was brought to p_H 5·0 by addition of sulphuric acid and the water-soluble substances were thoroughly extracted; coagulable protein was removed from the extract by heating at 70°, and the filtrate concentrated under diminished pressure. The solution was treated with alcohol to make a 70% concentration of the latter, the precipitate was rejected, the filtrate was again concentrated, and poured into enough alcohol to make a final concentration of 95%; the aqueous solution of the resulting precipitate was cleared with basic lead acetate, and, after removal of excess of lead, was treated with phosphotungstic acid. The solution obtained on recovery from the phosphotungstates was rich in the active substance; of the best preparations doses of 0·6 g. per day (calculated as ash-free organic matter) exercised a definite physiological effect. These preparations contained, on an ash-free basis, about 19% of nitrogen; they were free from carbohydrate and from iron. The active substance is precipitated by mercuric acetate in neutral solution; the possibility of its identity with vitamin-*L* is excluded. The physiological assay of the active substance is discussed.

C. R. HARINGTON.

Iron in nutrition. V. Availability of rat for studies in anæmia. J. WADDELL, H. STEENBOCK, C. A. ELVEHJEM, and E. B. HART. **VI. Iron salts and iron-containing ash extracts in correction of anæmia.** J. WADDELL, C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART. **VII. Copper as supplement to iron for hæmoglobin formation in the rat.** E. B. HART, H. STEENBOCK, J. WADDELL, and C. A. ELVEHJEM (J. Biol. Chem., 1928, 77, 769—775, 777—795, 797—812).—V. Young rats weaned at 3—4 weeks and placed on a diet of cow's milk form suitable subjects for the investigation of nutritional anæmia.

VI. Inorganic iron salts (0·5 g. Fe per day) are not effective in curing nutritional anæmia in young rats, whilst the ash of liver, lettuce, and maize containing 0·5 g. of iron, or an acid extract of such ash, is highly effective.

VII. An extract of liver as used for the treatment of pernicious anæmia in man, as also the ash of this preparation, formed, in combination with inorganic iron, a cure for nutritional anæmia in rats. The active portion of the above ash could be concentrated by treatment of a dilute hydrochloric acid extract of the ash with hydrogen sulphide, and the effect of the ash could indeed be imitated by that of small amounts of copper.

C. R. HARINGTON.

Detection of homogentisic acid in serum in alkaptonuria. G. KATSCH and E. METZ (Deut. Arch. klin. Med., 1927, 157, 143—157; Chem. Zentr., 1928, i, 386).—In a case of alkaptonuria the serum contained 1 mg.-%.

A. A. ELDRIDGE.

Amino-acids of flesh. II. Diamino-acid content of some normal and pathological tissues. J. L. ROSEDALE (Biochem. J., 1928, 22, 826—829).—The diamino-acid contents of the tissues of different animals and of different parts of a normal animal are similar. There is a low content of lysine in carcinoma and in chickens which have derived the whole of their food protein from maize. No marked differences were observed between the results obtained by Van Slyke's and by the modified Kossel's method for the determination of diamino-acid.

S. S. ZILVA.

Cholesterol content of the blood of infants and children. A. GOLDBLOOM and R. GOTTLIEB (Can. Med. Assoc. J., 1927, 17, 1333—1336).—The cholesterol content of whole blood is the greater, the younger is the individual. The effect of various pathological conditions was investigated.

CHEMICAL ABSTRACTS.

Pancreatic activity in diabetes mellitus. S. OKADA, T. IMAZU, K. KURAMOCHI, K. HORIUCHI, and T. TSUKAHARA (Proc. Imp. Acad. Tokyo, 1928, 4, 134—135).—The disturbance of pancreatic function manifests itself in the diminution of enzymic activity, or of the amount of juice, or of both, the greatest alteration in enzymic efficiency and activity being in the proteolytic and lipolytic enzymes. There may be disturbance either of the internal or of the external secretion of the pancreas, or of both, the severity of the diabetes not necessarily running parallel to the degree of disturbance in the external secretion.

J. STEWART.

Significance of the non-fermentable reducing substances of the blood in diabetes. I. M. RABINOWITCH (Biochem. J., 1928, 22, 751—757).—The non-fermentable reducing substances of the blood vary between 16 and 31 mg. per 100 c.c. (as dextrose) and are fairly constant for the individual. There are no significant differences between normal and diabetic bloods. Blood-sugar curves after the administration of dextrose show no significant differences in the amounts of these substances between normal and diabetic subjects. Arterial and venous blood-sugar-time curves obtained simultaneously are identical in normal and diabetic subjects as far as variations of non-fermentable reducing substances are concerned. The amounts of non-fermentable reducing substances are not influenced in the blood of the diabetic by insulin administration. The metabolism of non-fermentable substances is therefore not disturbed in diabetes.

S. S. ZILVA.

Plasma lipoids. I. Fatty acids of blood-plasma in diabetes and nephrosis. S. M. LING and S. H. LIU (Chinese J. Physiol., 1928, 2, 157—161).—The fatty acids of normal plasma are highly unsaturated, with an average iodine value of 156·6. In diabetes mellitus and in nephrosis they are much less unsaturated, and their iodine value is lower, being 45—98 in the former and 59—87 in the latter disease.

H. D. KAY.

Iodine and exophthalmic goitre. W. H. JANSEN and F. ROBERT (Deut. Arch. klin. Med., 1927, 157, 224—246; Chem. Zentr., 1928, i, 539).—The

iodine content of the normal human thyroid gland is 2·2—4·58 (average 3·3) mg. Values in exophthalmic goitre are recorded. A. A. ELDRIDGE.

Lactic acid content of the blood in hepatic disease. A. ADLER and H. LANGE (Deut. Arch. klin. Med., 1927, **157**, 129—142; Chem. Zentr., 1928, i, 371).—The normal blood-lactic acid value is 7—13 mg.-%. In hepatic disease the value is raised. A. A. ELDRIDGE.

Esterification of serum-cholesterol in hepatic disease. M. BURGER and H. HABS (Klin. Woch., 1927, **6**, 2221—2223; Chem. Zentr., 1928, i, 376).—A study of the relation of free and esterified serum-cholesterol values to various pathological conditions of the liver. A. A. ELDRIDGE.

Protein metabolism and phosphorus content in experimental hæmolytic and stasis icterus. T. HATAKEYAMA (J. Biochem. Japan, 1927, **8**, 261—273). CHEMICAL ABSTRACTS.

Composition of blood in lipæmia after hæmorrhage. E. H. FISHBERG and A. M. FISHBERG (Biochem. Z., 1928, **195**, 20—27).—In rabbits, from which 35 c.c. of blood were removed daily, lipæmia developed, the increase in blood-fat and -cholesterol being due to loss of serum-proteins, particularly albumin, this loss causing a compensatory mobilisation of fat in order to maintain the colloid osmotic pressure at its normal level. P. W. CLUTTERBUCK.

Acid–base equilibrium in the plasma in malaria. S. H. LIU (Chinese J. Physiol., 1928, **2**, 151—156).—The equilibrium has been studied in 13 cases of malaria. All the values found (for p_H, total base, hydrogen carbonate, chloride, and protein) lie within normal limits. During the feverish stage the p_H remains unchanged, but there is a slight increase of total base and a slight decrease in hydrogen carbonate and chloride. The excess of residual base in fever is bound by organic acids of undetermined nature. The above effects are not a specific result of bacterial infection but are due to the fever. H. D. KAY.

Sugar and chloride content of the cerebrospinal fluid with special reference to neurosyphilis. S. W. BECKER (J. Lab. Clin. Med., 1926, **12**, 43—52).—In neurosyphilis there was a small, variable decrease in the reducing substances of the cerebrospinal fluid. There is a slight normal variation in the sugar content. Alimentary hyperglycæmia produced no increase of sugar in the cerebrospinal fluid. The variation in chloride content is not so great as for blood-chloride; in neurosyphilis the chloride content of the cerebrospinal fluid was normal. CHEMICAL ABSTRACTS.

Avitaminosis. VII. Influence of experimental scurvy on the synthesis of hippuric acid. A. PALLADIN and D. ZUWERKALOW (Biochem. Z., 1928, **195**, 8—13).—In guinea-pigs, the power to synthesise hippuric acid is decreased in proportion to the extent of development of scurvy. P. W. CLUTTERBUCK.

Experimental tetany. C. I. URECHIA and G. POPOVICIU (Compt. rend. Soc. Biol., 1927, **97**, 1012—1015; Chem. Zentr., 1928, i, 373).—Thyro-parathyroidectomised dogs show in the pre-tetanic period an increase in phosphorus content and a reduction in that of calcium. Rigidity and convulsions are accompanied by a reduction of the phosphorus, but scarcely of the calcium, content. The phosphorus content immediately before death is extremely large. A. A. ELDRIDGE.

State of plasma-calcium in parathyroidectomised dogs. C. I. REED (J. Biol. Chem., 1928, **77**, 547—554).—Acute tetany following parathyroidectomy develops when the Ca : P ratio falls to unity or less; in some animals, however, a condition of "latent" tetany occurs in which such low Ca : P ratios are observed without accompanying symptoms. After parathyroidectomy there is a tendency towards both relative and absolute diminution of the diffusible fraction of the plasma-calcium, but this result is not constant. C. R. HARINGTON.

Hydrogen-ion concentration and carbon dioxide content of the blood of dogs after removal of the accessory thyroid. W. F. WENNER and E. MUNTWYLER (Proc. Soc. Exp. Biol. Med., 1927, **24**, 480—482; Chem. Zentr., 1928, i, 84).—Neither in manifest nor in latent tetany was alkalosis observed, even when the carbon dioxide content was reduced. In one case, production of lactic acid caused a change of p_H from 7·29 to 7·09. A. A. ELDRIDGE.

Oxygen consumption by various tissues and by muscle of various animals. K. TSUNEYOSHI (J. Biochem. Japan, 1927, **7**, 227—233).—The oxygen-consuming power of various tissues and muscle is compared. CHEMICAL ABSTRACTS.

Effect of lipin and allied substances on the oxidative activity of tissues. K. TSUNEYOSHI (J. Biochem. Japan, 1927, **7**, 235—258).—Lecithin increases, whilst cholesterol diminishes, the consumption of oxygen by tissue powder and the oxidation of amino-acids on charcoal; kephalin, cuorin, cholesterol esters, hydrogenated or hydrolysed lecithin show no effect. CHEMICAL ABSTRACTS.

Significance of lipins in the oxygen-consuming activity of tissues. I. Oxygen-consuming activity of tissue and the mitochondrial structure. S. KAKINCHI (J. Biochem. Japan, 1927, **7**, 263—265).—The oxygen consumption of dry ox-heart muscle powder was studied in the untreated material and after treatment with alcohol, ether, acetone, and acetic acid. In every case it was found that treatment which destroyed the mitochondrial mechanism (alcohol, acetic acid) also practically abolished the oxidative process. CHEMICAL ABSTRACTS.

Respiration of fat tissue. M. N. SHATERNIKOV, O. P. MOLCHANOVA, and M. T. TONIME (Zhur. exp. Biol. Med., 1927, **7**, 375—382).—Sheep's fat tissue consumes more oxygen than corresponds with the production of carbon dioxide: a conversion of fat into carbohydrate is assumed. CHEMICAL ABSTRACTS.

Sulphur-fixing and -oxidising function of the liver. M. LOEPER, J. DECOURT, and R. GARCIN (Presse med., 1927, **35**, 321—323; Chem. Zentr., 1928, i, 88).—A discussion. A. A. ELDRIDGE.

Acceleration of growth rates by dietary modifications. A. G. HOGAN, J. E. HUNTER, and H. L.

KEMPSTER (J. Biol. Chem., 1928, **77**, 431—436).—A diet is described which yields rates of growth in chicks and turkeys above those hitherto considered to be normal, the results being analogous with those obtained by Osborne and Mendel (A., 1926, 1180) with rats. C. R. HARINGTON.

Growth of rats on vegetarian diets. H. WU and D. V. WU (Chinese J. Physiol., 1928, **2**, 173—194).—Rats do not grow well on exclusively vegetarian diets, although when the "small cabbage" (a Chinese vegetable) is added practically normal growth is obtained. The vitamin-*D* content of spinach is low. H. D. KAY.

Relative utilisation of different calcium compounds in the production of eggs. G. B. BUCKNER, J. H. MARTIN, and A. M. PETER (J. Agric. Res., 1928, **36**, 263—268).—A comparison has been made between the effects of calcium in the form of carbonate, sulphate, chloride, phosphate, and lactate on the rate of egg production of hens fed on a basal diet of wheat, yellow maize, skim milk, and fresh vegetables. Calcium carbonate produced a greater egg yield than either calcium sulphate or lactate; calcium chloride was not consumed by the hens, and calcium phosphate, although consumed, did not affect the rate of egg production. E. A. LUNT.

Sulphur metabolism and partition of sulphur in the urine of fasting dogs. S. MORGULIS (J. Biol. Chem., 1928, **77**, 627—645).—In dogs the N : S ratio in the urine varies from 16·1 to 29·7 and is not generally altered during starvation, so that it appears to be a peculiarity of the individual dog rather than of the metabolic condition. No relationship could be observed between the N : S ratio of the food and that of the urine, nor did the latter indicate the nature of the body-tissues being broken down during starvation. The inorganic sulphate and neutral sulphur show irregular variations during fasting, the proportion of the former being characteristic of the individual dog, and that of the latter being apparently unconnected with diminished oxidative processes. The variations in the excretion of the ethereal sulphates indicate that the latter are largely endogenous in origin. C. R. HARINGTON.

Selective absorption of iodine compounds by the hyperplastic thyroid gland. H. B. VAN DYKE (Arch. Int. Med., 1928, **41**, 615—621).—The rate of iodine absorption by the hyperplastic thyroid gland of the dog diminishes along the sequence of the following substances: potassium iodide, potassium iodate, iodine in sodium chloride solution, and thyroxine. The rate of absorption of the iodine in the last substance is extremely slow. Bilateral ligation of the suprarenal glands 6 hrs. before iodine administration does not affect its absorption. E. A. LUNT.

Increase in the weight, volume, and total nitrogen content of the liver with a diet rich in nitrogen. C. GAUTIER and H. P. THIERS (Bull. Soc. Chim. biol., 1928, **10**, 537—552).—The right lobes of the livers of starved frogs were removed and compared with the remaining portions of the livers of the same animals after feeding for some weeks on a variety of cheese. The remaining portions, although greatly increased in weight, contained actually less nitrogen and water than the removed portions. Control experiments with intact animals were in agreement with these results. G. A. C. GOUGH.

Muscular exercise and nitrogenous metabolism of dogs. W. H. CHAMBERS and A. T. MILHORAT (J. Biol. Chem., 1928, **77**, 603—618).—Muscular work in fasting dogs produced an increase of 50—100% in the nitrogenous metabolism; this increase was entirely prevented by the previous ingestion of carbohydrate, except after very prolonged fasting. It is thought that the extra nitrogen excreted under these conditions originated from a limited store in the body, and did not arise from the breakdown of tissue protein. C. R. HARINGTON.

Biological degradation of uric acid to allantoin. H. BRUNIG, F. EINECKE, F. PETERS, R. RABL, and K. VIEHL (Z. physiol. Chem., 1928, **174**, 94—111).—The 4 : 5-glycol of uric acid, the 4 : 5-dimethyl ether of this glycol, and *spiro*-4 : 5-dihydantoin, all possible intermediate substances in the metabolism of uric acid, are not oxidised to allantoin by the intact dog or by the surviving liver of this animal. Allantoin is found in the urine when any one of the four (1-, 3-, 7-, 9-) monomethyluric acids is administered to a dog. The methyluric acids are precipitable as silver salts, and give a colour similar to that produced by uric acid with Folin's reagent. Methylallantoin may be separated from allantoin by precipitation of the latter with Wiechowski's reagent at p_H 6·2. Carbamide interferes with the precipitation both of allantoin and of methylallantoin with this reagent. H. D. KAY.

Ammonia production on illumination of the retina. H. ROSCH and W. T. KAMP (Z. physiol. Chem., 1928, **175**, 158—177).—The retina of the frog kept for 10 min. in the dark contains varying amounts of ammonia (0·9—3·4 mg. in 12 experiments), but good agreement is obtained when those of the two eyes of one frog are compared; the differences in the latter case are usually less than 10% and the maximum difference obtained is 13%. If one retina is exposed to a strong light for 10 min. there is a marked increase in the ammonia production, the increase being between 74% and 582% of the values for the unexposed retina. Fresh ox retina pulp kept in 2% sodium hydrogen carbonate solution at 40° gives rise to the production of ammonia, thus confirming Warburg, Posener, and Negelein (Biochem. Z., 1924, **152**, 309). This enzymic production of ammonia appears to be rapid and is complete in less than 2 hrs. Addition of guanosinephosphoric acid to the retina pulp in sodium hydrogen carbonate solution does not increase the ammonia production appreciably, although a slight increase is noted on occasions; urea also leads to no marked increase. With adenosinephosphoric acid, however, there is a marked increase in ammonia formation, representing a yield of up to 90% of the amino-group. The precursor of ammonia in the retina is not adenosinephosphoric acid, however, since after treatment of the pulp with 1% hydrochloric acid, treatment which destroys the ammonia-producing enzyme, no ammonia formation can be effected by adding an extract of muscle which has a powerful action on adenosinephosphoric acid. A. WORMALL.

Bile acids. III. Effect of bile acids on the protein metabolism of the rabbit. Antiseptic effect of bile acids in the rabbit intestine. R. KAZIRO (J. Biochem. Japan, 1927, **7**, 293—310).—Rabbits fed on deoxycholates, and particularly cholates, exhibit increased urinary elimination of total nitrogen and inorganic sulphate; larger doses are toxic. Choleinic acid and the conjugated bile acids are less effective. CHEMICAL ABSTRACTS.

Behaviour of pyridine, quinoline, and nicotinic acid in the Eck-fistula dog. T. KAMEL (J. Biochem. Japan, 1927, **7**, 197—210).—Pyridine, quinoline, and nicotinic acid when administered to Eck-fistula dogs appear to a much smaller degree than in normal dogs as methylated derivatives in the urine. The liver is thus regarded as the important seat of the methylation reaction. CHEMICAL ABSTRACTS.

Intracellular oxidation–reduction. I. Reduction potentials of *Amœba dubia* by micro-injection of indicators. B. COHEN, R. CHAMBERS, and P. REZNIKOFF (J. Gen. Physiol., 1928, **11**, 585—612).—*A. proteus* and *A. dubia* have been injected by the micro-technique with 25 different oxidation–reduction indicators, both in the reduced and in the oxidised forms, under definite conditions as regards oxygen tension. The observations made allow conclusions to be reached both as to the toxicity of the indicators and as to the oxidation–reduction potentials of the protoplasms of the organisms. In discussing the results it is pointed out that the reduction intensity, the reducing capacity, and the rate factor must be distinguished from one another.

W. O. KERMACK.

Micrurgical studies in cell physiology. VI. Calcium ions in living protoplasm. H. POLLACK (J. Gen. Physiol., 1928, **11**, 539—545).—The injection by micro-methods into living cells (*Amœba dubia* or *A. proteus*) of the sodium salt of alizarinsulphonic acid, the calcium salt of which is relatively insoluble in water, produces quiescence of the cell and certain other pathological changes. Subsequent injection of small quantities of calcium chloride neutralises these effects. The abnormal behaviour of the amœbæ observed after the reduction of calcium ions, following the injection of sodium alizarinsulphonate, is also seen when the ions are reduced by injection of oxalate, tartrate, citrate, and phosphate or when the sodium- or potassium-ion concentration is increased.

W. O. KERMACK.

Does methylene-blue penetrate living cells ? M. IRWIN (Nature, 1928, **121**, 939).—Polemical.

A. A. ELDRIDGE.

Significance of changes in the composition of the blood and urine after ingestion of dextrose. I. KATAYAMA (J. Lab. Clin. Med., 1926, **11**, 1024—1034).—Ingestion of dextrose causes a slight fall in the inorganic phosphorus of the blood, and increased elimination in the urine; blood-chloride varied inconstantly, but urine-chloride was diminished. Variable changes in the blood non-protein nitrogen and the urine-nitrogen, and increase in blood-lactic acid were observed. CHEMICAL ABSTRACTS.

Disappearance of intravenously injected α-, β-, and αβ-glucose from the blood. E. N. ALLOTT (Biochem. J., 1928, **22**, 773—776).—No definite difference was found between the behaviour of α-, β-, and αβ-glucose when injected intravenously into rabbits. S. S. ZILVA.

Assimilation of lævulose. S. J. STEINBERG (Pflüger's Archiv, 1927, **217**, 686—695; Chem. Zentr., 1928, i, 821).—Lævulose is not consumed by the heart, pancreas, or small intestine. It is consumed as readily as dextrose by the skeletal muscle and kidneys, less readily by the salivary gland, and more readily by the liver and lungs. A. A. ELDRIDGE.

Variations of blood-phosphorus in dextrose tolerance tests. H. C. CHANG (Chinese J. Physiol., 1928, **2**, 195—202).—The inorganic phosphate of the blood diminishes in the normal subject after ingestion of 150 g. of dextrose. There is also a corresponding fall in the inorganic phosphate of the urine. In mild diabetes the fall is still to be observed, but is less marked and longer delayed. In severe diabetes the fall in inorganic phosphate is inappreciable.

H. D. KAY.

Function of the cells of the reticulo-endothelial apparatus. Problem of permeability. N. OKUNEV (Biochem. Z., 1928, **195**, 28—39).—Various colloidal substances, *e.g.* trypan-blue, carmine, cholesterol, Indian ink, colloidal silver and iron, erythrocytes, and bacteria, which are known to be absorbed by the cells of the reticulo-endothelial system, also possess the power of decreasing the surface tension at the limiting surface of water and benzene and of water and olive oil. The results are discussed in relation to absorption and phagocytosis.

P. W. CLUTTERBUCK.

Role of aluminium compounds in animal and plant physiology. E. V. MCCOLLUM, O. R. RASK, and J. E. BECKER (J. Biol. Chem., 1928, **77**, 753—768).—From spectrographic observations it appears that aluminium is not a normal constituent of plant or animal matter. Amounts of aluminium up to 0·6% of the diet exercise no toxic effects on rats, and, indeed, aluminium given by the mouth seems not to be absorbed from the alimentary tract.

C. R. HARINGTON.

Effect of metallic salts on the glycolysis and respiration of tissues. M. JOWETT and J. BROOKS (Biochem. J., 1928, **22**, 720—738).—Measurements made on the glycolysis and respiration of various tissues agree in the main with those of other workers. No aerobic glycolysis of liver was found. The toxicity of metallic salts to glycolysis is in the order HgI_2, $HgCl_2 > Cu^{\cdot\cdot} > Zn^{\cdot\cdot} > Cd^{\cdot\cdot} > Ca^{\cdot\cdot}$. Lead ion at low concentrations accelerates slightly the glycolysis of malignant tissue and at much higher concentrations its respiration. With normal tissues its effects are smaller. The glycolysis of malignant tissue is more sensitive to metallic poisons than that of normal tissues. Glycolysis appears to be more sensitive than respiration to heavy metals in the case of malignant tissue. For normal tissues the converse is the case. A mechanism of the action of mercuric halides on glycolysis and respiration is suggested.

S. S. ZILVA.

Chemical and biological relationships between thallium and lead. A. BUSCHKE and L. BERMAN

(Klin. Woch., 1927, **6**, 2428—2429; Chem. Zentr., 1928, i, 543).—Similarities between the toxic effects of lead and thallium salts on rats and mice were observed. A. A. ELDRIDGE.

Convulsant action of acid and neutral salts of acid fuchsin. J. E. THOMAS (J. Pharm. Exp. Ther., 1928, **33**, 1—19).—Comparative results are given of the time which elapses in the frog between the injection of acid and alkaline solutions of fuchsin either by perfusion of the blood-vessels or by injection into the bloodless aorta and the consequent occurrence of convulsions. Solutions of the acid salts of fuchsin cause convulsions in less time and with greater regularity than solutions of the neutral salts.

E. A. LUNT.

Influence of ingestion of methylxanthines on excretion of uric acid. V. C. MYERS and E. L. WARDELL (J. Biol. Chem., 1928, **77**, 697—722).—Ingestion of caffeine in human subjects is followed by an immediate increase in excretion of uric acid, which increase is not, however, maintained during prolonged administration of caffeine. Theobromine causes no increased excretion of uric acid but theophylline causes a marked increase. Since certain methyl derivatives of uric acid, *e.g.*, 1-methyl- and 1 : 3-dimethyl-uric acids, react with the colorimetric reagent employed in the above determinations, whilst others, *e.g.*, 3 : 7-dimethyluric acid, do not, it is possible that the above methylxanthines appear, partly at least, in the urine as the corresponding methyluric acids and not as uric acid itself. C. R. HARINGTON.

Influence of ultra-violet light on the oxidation quotient of urine. J. SPIRT (Biochem. Z., 1928, **195**, 142—148).—Muller's oxidation quotient (cf. A., 1927, 996), viz., nitrogen content : " oxygen requirement," is obtained and inverted for comparison with the C : N ratio. The quotient is obtained constant for a dog by feeding on a diet containing excess nitrogen and only varies from 0·5 to 0·6 in different dogs, daily variations being very small. The quotient varies with the intensity of irradiation, the variations being caused by alterations of oxygen requirement and not of nitrogen content. Irradiation for ½ hr. at a distance of 80 cm. causes an increased quotient and an inhibition of oxidation, and irradiation for 1 hr. at a distance of 60 cm. a decreased quotient and an increased oxidation. P. W. CLUTTERBUCK.

Action of gallic acid on the sugar and cholesterol content of the blood. C. LANG and H. JUNGMANN (Klin. Woch., 1927, **6**, 2241—2242; Chem. Zentr., 1928, i, 371).—Injection of gallic acid, as of cholic, glycocholic, or taurocholic acid, causes a fall in the blood-sugar of fasting animals.

A. A. ELDRIDGE.

Effect of acetylcholine chloride and pilocarpine on the threshold of sugar elimination. G. EDA (J. Biochem. Japan, 1927, **7**, 319—331).—Diminution of sugar assimilation and rise of the threshold of sugar excretion are caused frequently in mild diabetics by subcutaneous injection of acetylcholine chloride, and invariably in rabbits by injection of pilocarpine.

CHEMICAL ABSTRACTS.

Effect of atropine and scopolamine on the sugar excretion threshold. G. EDA (J. Biochem. Japan, 1927, **7**, 345—360).—In rabbits atropine invariably causes an increase in the sugar-excretion threshold, but the assimilation of sugar is practically unaffected. In patients with Parkinson's disease scopolamine always brought about a rise in the excretion threshold values and an improvement in the power of assimilation. In diabetics the effect of scopolamine varies, causing a rise in some and a lowering in others of the excretory threshold, and the diminution in assimilation corresponding with an increase in threshold is generally not observed. CHEMICAL ABSTRACTS.

Effect of atropine on alimentary hyperglycæmia. S. TERASHIMA (J. Biochem. Japan, 1927, **7**, 489—503).—In diabetics a mild and brief, but not a more marked, hyperglycæmia is inhibited by atropine. The power to increase sugar assimilation attributed to atropine was not observed either in man or in the rabbit. CHEMICAL ABSTRACTS.

Value of iron salts in counteracting toxic effects of gossypol. W. D. GALLUP (J. Biol. Chem., 1928, **77**, 437—449).—Administration of ferric citrate or of ferrous ammonium sulphate, but not of ferric oxide, counteracted the toxic effects of gossypol in rats on a diet containing a large proportion of cotton seed, provided that the ratio of iron to gossypol was not less than 3 : 1. Iron forms an insoluble compound with gossypol of apparently constant composition.

C. R. HARINGTON.

Mechanism of the action of synthalin. G. HETÉNYI (Klin. Woch., 1927, **6**, 2194; Chem. Zentr., 1928, i, 85—86).—Continuous administration of synthalin leads to a progressive reduction of sugar in the organism, no premortal storage of sugar in the liver being observed. A. A. ELDRIDGE.

Similarity of "glukhorment" and synthalin. F. BISCHOFF, N. R. BLATHERWICK, and M. SAHYUN (J. Biol. Chem., 1928, **77**, 467—471).—Glukhorment contains a considerable amount of a guanidine derivative apparently identical with synthalin (cf. Dale and Dudley, Brit. Med. J., 1927, (ii), 1027).

C. R. HARINGTON.

Respiratory exchange, temperature, and blood-sugar of anæsthetised animals. E. T. CONYBEARE, H. B. A. R. DENSHAM, M. MAIZELS, and M. S. PEMBREY (J. Physiol., 1927, **64**, Proc. Physiol. Soc., xix—xx).—Urethane anæsthesia causes a rise in the blood-sugar; in ethylene anæsthesia the values vary. A. A. ELDRIDGE.

Effect of anæsthesia on recovery process in mammalian skeletal muscles. C. N. H. LONG (J. Biol. Chem., 1928, **77**, 563—579).—Stimulation of muscles in animals under general (amytal) anæsthesia was followed by normal breakdown of glycogen to lactic acid, but the recovery phase, as indicated by restoration of the muscle glycogen to its normal level, was almost entirely inhibited; at the same time the lactic acid disappeared from the muscles. This phenomenon may be of practical importance in connexion with the condition of those muscles which are essential to life during anæsthesia.

C. R. HARINGTON.

Hypnotics of barbituric acid series. N. B. EDDY (J. Pharm. Exp. Ther., 1928, **33**, 43—68).—When administered orally to cats in 10% gum-acacia

solution the average fatal dose per kg. body-weight of diethylbarbituric acid is 280 mg., of ethyl*iso*amylbarbituric acid 100 mg., of calcium ethyl*iso*propylbarbiturate 140 mg., of ethyl *n*-butylbarbituric acid 84 mg., and of *cyclo*hexenylethylbarbituric acid 120 mg. As a hypnotic *cyclo*hexenylethylbarbituric acid is the most desirable of this group. E. A. LUNT.

Relation between chemical constitution and ermicidal activity of alcohols and phenols. . M. SCHAEFFER and F. W. TILLEY (J. Bact., 1927, **14**, 259—273).—Isomeric alcohols having the longest straight chains, and isomeric phenols having the longest straight chains in the *para*-position to the hydroxyl group are most efficient germicides. The coefficients of *cyclo*hexanol and the methyl*cyclo*hexanols aro about half as great as those of phenol and the corresponding cresols.

CHEMICAL ABSTRACTS.

Chemical constitution of the respiratory enzyme. O. WARBURG (Naturwiss., 1928, **16**, 345—350).—A close similarity exists between the processes of respiration and fermentation. The principal facts concerning hæmin are: its widespread distribution in nature, the reversible reactions of its iron atom with oxygen and carbon monoxide, the precisely definable distribution of hæmin between the two gases, and also the fact that the carbon monoxide compound dissociates on irradiation. The respiratory enzyme of yeast shows the same properties, but hæmoglobin is not essentially a catalyst and it retains carbon monoxide more strongly than the enzyme. Whilst hæmoglobin, hæmopyridine, and hæmonicotine, like the respiratory enzyme, will react, in the reduced state, with oxygen and carbon monoxide, cytochrome will not do so, at least under 1 atm. pressure. Cytochrome and the respiratory enzyme must therefore be different substances. In the living cell there may be present hæmin belonging to the enzyme and hæmin independent of the respiration process. In order to discriminate between such conditions, the respiration has been hindered by the formation of the carbon monoxide complex. The increased respiration induced by light has been utilised as follows: irradiation by monochromatic light of different wave-lengths but equal intensities results in a measurable increase in respiration; by plotting this effect against wave-length a curve is obtained which indicates the absorption of light by the hæmin belonging to the enzyme. Curves of this type reproduce the absorption spectra of compounds of the type carbon monoxide–hæmonicotine. Using yeast cells it is found that the spectrum of the respiratory enzyme is almost exactly similar in shape to the absorption curve (measured photometrically and bolometrically) of the carbon monoxide compound of reduced hæmin. The maximum of the latter curve is, however, at 408 $\mu\mu$, whereas the respiratory enzyme shows a maximum at 436 $\mu\mu$. This discrepancy is interpreted by assuming that the respiratory enzyme exists in the solid state, adsorbed on the surface of the cells, whilst the absorption spectrum of the hæmin compound is measured in solution. The shift in the entire absorption curve is consistent with this explanation (cf. A., 1926, 1277; 1927, 1221). R. A. MORTON.

Action of neutral salts in enzymic processes. Effect of bromides on salivary amylase. K. C. SEN (J. Indian Chem. Soc., 1928, 5, 245—249).—The optimum p_H for the amyloclastic action of salivary amylase is about 6·7. Addition of sodium chloride accelerates enzyme action but sodium and potassium bromides in small concentration retard it (cf. Thomas, A., 1917, i, 598). H. BURTON.

Digestion of crude starch by saliva. E. POZERSKI (Compt. rend. Soc. Biol., 1927, **97**, 1592—1594; Chem. Zentr., 1928, i, 818).—Pulverised starch is readily attacked, but some, although not all, kinds of potato starch are practically unattacked in the crude state. The grinding produces reducing substances.

A. A. ELDRIDGE.

Polarised light and starch hydrolysis. J. W. M. BUNKER and E. G. E. ANDERSON (J. Biol. Chem., 1928, **77**, 473—488).—No evidence could be obtained of acceleration of the enzymic hydrolysis of starch by illumination with polarised light.

C. R. HARINGTON.

Enzymes and light. L. PINCUSSEN. **X. Diastase. V.** S. KUMANOMIDOH. **XI. Pepsin. I.** K. UEHARA. **XII. Lipase. I.** S. HAYASHI (Biochem. Z., 1928, **195**, 79—86, 87—95, 96—102).—X. The effect of the presence of a series of chlorides on the inactivation of salivary-, malt-, and taka-diastase by heat and by irradiation is investigated. With all three enzymes, potassium has a much greater inactivating effect than calcium. With salivary diastase, magnesium is intermediate, and with malt diastase the effect is in the following order: Mg>K,Na>Li,Rb>Ca. With malt-diastase the effect of these ions on heat inactivation is in the following order: Mg>Ca>Li>Rb>K,Na. Potassium, whilst increasing injury by the action of light, decreases injury by heat, and the reverse is true of calcium (cf. A., 1927, 482).

XI. The greatest injury of the action of pepsin, when reacting with fibrin from the blood of different animals in various buffer solutions, on irradiation with ultra-violet light is obtained at p_H 1·14, and this must therefore be the optimal p_H for the action of this enzyme. The optimum is placed in the literature at from 1·4 to 2·0.

XII. The lipase action of the serum of rabbits is considerably injured by irradiation. Removal of part of the proteins (which have a protective action) causes the injury to be increased. With guinea-pig's serum, the injury by light is greatest in faintly acid solution. P. W. CLUTTERBUCK.

Structure and enzyme reactions. IV. The system glycogen–amylase–lipoids. R. TRUSZKOWSKI (Biochem. J., 1928, **22**, 765—772; cf. Przylecki and others, A., 1927, 1113; this vol., 328).—Amylase is adsorbed on lipoids to about 67% of the quantity present in solution. Adsorbed amylase is quantitatively eluted by narcotics, partly by glycogen, and scarcely at all by water. Glycogen is not adsorbed on lipoids. The addition of lipoids to the system glycogen–amylase causes retardation of hydrolysis and the enzyme is in consequence inactivated. Its activity can, however, be restored by elution.

S. S. ZILVA.

Structure and enzyme reactions. V and VI. The systems dextrose–enzyme and ester–catalyst. S. J. Przylecki, W. Giedroyć, and E. A. Sym (Biochem. J., 1928, **22**, 811—825).—During the first stage (3—7 days) of the reaction in the system dextrose–maltose–maltase the presence of an adsorbent such as charcoal has no appreciable effect on the velocity of the reaction of synthesis. On the other hand, after a lapse of 2—5 months there is a considerable difference between the amounts of disaccharide synthesis in the presence or absence of charcoal. Thus whilst in the latter case 1·4% of biose is found after 2 months and 1·67% after 5 months, in the presence of charcoal there is 2·03 and 2·42% after 2 and 5 months, respectively. This is due to the fact that the product of synthesis (maltose), by being adsorbed to a greater extent than the substrate, is removed from the reacting medium.

The introduction of charcoal into the system glycerol–butyric acid–catalyst increases the equilibrium constant in favour of hydrolysis. In the case of the system ethyl alcohol–acetic acid–catalyst the reaction of hydrolysis does not proceed as far in the presence as in the absence of an adsorbent, the equilibrium constant remaining unaffected in the dispersing medium. There is an increase in the synthesis of ethyl acetate, as a result of the addition of charcoal. The mechanism of reversible reactions in the presence of adsorbents is discussed.

S. S. Zilva.

Glycerophosphatase. H. Kobayashi (J. Biochem. Japan, 1927, **8**, 205—223).—Kaolin adsorbs glycerophosphatase completely at p_H 4·1; alumina shows maximal adsorption at p_H 4·7, and none at p_H 7·0. The adsorbed enzyme can be completely leached out of the kaolin at p_H 5·6; the optimal reaction is p_H 5·45, but a substance *X* which passes through collodion membranes and is precipitable with lead acetate is present. The pure enzyme has optimal activity at p_H 3—4; it can be freed from the substance *X* by adsorption on kaolin and subsequent leaching or by shaking the enzyme with alumina at p_H 7·0.

Chemical Abstracts.

Phosphatases of mammalian tissues. H. D. Kay (Biochem. J., 1928, **22**, 855—866).—The distribution of phosphatases in the tissues of the rabbit, of the cat, and of man has been quantitatively determined. They appear to function at an optimum p_H between 8·8 and 9·3, although the character of the substrate influences this optimum. The distribution is similar to that of ereptase described by Vernon. In the presence of excess of the alcohol concerned, inorganic phosphate can be esterified through the agency of the phosphatases. Thus glycerophosphoric acid, isolated as the barium salt, has been synthesised and several other alcohols have been shown to combine with inorganic phosphate. This reversible reaction catalysed by the enzymes has been studied in the esterification of glycerol.

S. S. Zilva.

Glyoxals. Formation of methylglyoxal from hexosephosphate in presence of living tissues. N. Ariyama (J. Biol. Chem., 1928, **77**, 359—394, 395—404).—Glyoxals may be determined colorimetrically, in presence of sodium cyanide and sodium carbonate, by means of the arsenophosphotungstic acid reagent of Benedict (A., 1922, ii, 405). Glyoxals are stable in neutral aqueous solution; at reactions more alkaline than p_H 8·0 methylglyoxal disappears from the solution, being converted partly into an unknown substance and partly into lactic acid, unless the p_H be greater than 12·0, when conversion into lactic acid is quantitative. Glyoxalase is most active at p_H 7·0; it is not affected by the presence of fluoride or of toluene (cf. Dakin and Dudley, A., 1913, i, 665, 1267); figures are given for the relative concentrations of the enzyme in different tissues. Insulin is without effect on glyoxalase; the antiglyoxalase of pancreas (Dakin and Dudley, *loc. cit.*) apparently acts directly on glyoxalase (cf. Foster, A., 1925, i, 1495) but is only partly destroyed by heating at 120° for 30 min., and may therefore not be enzymic in character. In presence of cyanide, especially at alkaline reactions, methylglyoxal disappears rapidly from solution, but not with production of lactic acid unless the p_H be greater than 12·0 (cf. Meyerhof, A., 1925, i, 1507); at less strongly alkaline reactions a reducing substance is produced which makes possible the above-mentioned colorimetric determination.

Muscle-tissue which has been freed from glyoxalase by incubation for 24 hrs. at 37° is able to convert hexosediphosphate into methylglyoxal to the extent of about 10%; this suggests the presence in the tissue of an enzyme which converts the hexosediphosphate into methylglyoxal as a stage in the formation of lactic acid.

C. R. Harington.

Lactacidogen. Influence of salts on muscle hexosephosphatase. Y. Oda (J. Biochem. Japan, 1927, **8**, 45—55).—Muscle phosphatase causes practically complete hydrolysis of lactacidogen. The reaction is inhibited by sodium fluoride or calcium chloride.

Chemical Abstracts.

Lactic acid formation in muscle extracts. I. Relationship between phosphoric ester accumulation and phosphoric ester breakdown and lactic acid formation from glycogen. II. Effect of sodium hexosediphosphate on the rate of ester accumulation during the incubation of glycogen in certain types of extracts. III. Glycolysis in sterile cell-free extracts of muscle. D. Stiven (Biochem. J., 1928, **22**, 867—873, 874—881, 882—888).—I. Phosphoric ester accumulation is not an essential accompaniment of lactic acid formation from glycogen. When ester accumulation does occur there is no definite constant ratio of the molar amount of lactic acid produced to the molar amount of phosphorus that accumulates as ester. In the second period, when the ester that accumulates in the first period is broken down, the molar ratio of lactic acid produced to phosphorus set free is also very variable. An extract of cat muscle was used in these experiments. It was prepared by extracting in the cold the finely-ground tissue with a solution of sodium hydrogen carbonate and sodium chloride.

II. In a mixture of zymophosphate and glycogen in certain concentrations there is less lactic acid produced than in the corresponding glycogen concentration in the absence of the ester. This is associated, not invariably but very frequently, with an increased

accumulation of phosphoric ester in the mixture as compared with the corresponding glycogen experiment. The "extra ester accumulation" due to the presence of zymophosphate is also associated with a more rapid loss of glycogen in addition to the above-mentioned inhibition of the lactic acid formation.

III. There is glycolysis in sterile extracts of perfused muscle after filtration through Berkefeld filters (cf. Brunton and Rhodes, Proc. Roy. Soc., 1901, 68, 417). S. S. ZILVA.

Rate of reaction between enzyme and substrate. J. BERKSON and L. B. FLEXNER (J. Gen. Physiol., 1928, **11**, 433—457).—Determinations have been made of the rate of hydrolysis of gelatin by commercial pancreatin using the method of Northrop (A., 1923, ii, 271) in which the progress of the reaction is followed by measuring the viscosity of the protein solution at various times. The results are found to fit the equation $v_t-v_w-(v_f-v_w)/\{1-(v_0-v_f)/(v_0-v_w)e^{-rt}\}$, where v_t is the time of flow of the reaction mixture through the viscosimeter, v_w that for water, v_f that of the mixture when proteolysis is complete, v_0 the time of flow at the beginning of the experiment, t the time of observation, and r a constant. An analogous equation fits the data collected from the literature referring to the rate of action of various enzymes on their substrates. The equation may be derived theoretically by assuming a bimolecular reaction between enzyme and substrate following the law of mass action. W. O. KERMACK.

Proteolytic activity of pancreatic juice and the role of enterokinase. V. LOMBROSO (Arch. Int. Physiol., 1927, **29**, 213—226; Chem. Zentr., 1928, i, 364).—A defence of the author's views. Pancreatic juice causes fission of gliadin, fibrin, and zein, which are not attacked by intestinal juice. Calcium chloride has a small inconstant effect. Egg-albumin undergoes fission only in presence of enterokinase, which cannot be substituted by calcium chloride. A. A. ELDRIDGE.

Effect of various substances of the quinine group on the enzymic functions of the organism. VIII. Digestion of edestin by pepsin in presence of quinine hydrochloride. J. A. SMORODINCEV (Biochem. Z., 1928, **195**, 1—7).—0·2% Quinine hydrochloride, under the conditions of the determination of pepsin by the edestin method, has no effect on digestion, but 0·5% often shows inhibition due to the slight shift of p_H to the alkaline side which this amount causes. In more strongly acid medium (p_H 1·7), the inhibition is not obtained (cf. A., 1927, 591). P. W. CLUTTERBUCK.

Fermentation by dried yeast preparations. II. A. HARDEN and M. G. MACFARLANE (Biochem. J., 1928, **22**, 786—789).—The addition of various organic and inorganic salts to zymin in a large volume of sugar solution appreciably reduces the period of induction normally occurring before the onset of rapid fermentation. Sodium arsenate is an exception to this general salt effect in that it prolongs the induction period without toxic effect on the fermentation. S. S. ZILVA.

Potentially unlimited multiplication of yeast with constant environment, and the limiting of growth by changing environment. O. W. RICHARDS (J. Gen. Physiol., 1928, **11**, 525—538).—The decrease in the rate of growth of yeast on culture medium is the result of the presence of toxic products produced by the yeast during its growth and of these, alcohol appears to be the most important. W. O. KERMACK.

***Schizosaccharomyces hominis*, nov. sp.** T. BENEDEK (Zentr. Bakt. Par., 1927, I, **104**, 291—303; Chem. Zentr., 1928, i, 368).—A *Schizosaccharomyces* isolated from eczematous human skin decomposed dextrose, galactose, lævulose, sucrose, maltose, lactose, dextrin, inulin, starch, mannitol, and glycerol, but not dulcitol. A. A. ELDRIDGE.

Lactic acid fermentation. V. A. I. VIRTANEN and H. KARSTROM (Z. physiol. Chem., 1928, **174**, 1—27).—Fermentation of dextrose with dried preparations of *B. casei* ε proceeds quite well in the presence of toluene, and takes place independently of the presence of living cells. The fermentative power of a killed, dried preparation of *B. casei* ε is about 3·7% of that of an equal number of living cells. The dried preparation is most active at p_H 5·6—6·2, with a flat optimum just below 6. It is inactive on the acid side of p_H 4·7, and very slow on the alkaline side of p_H 7·0. With living bacteria the optimum lies a little more toward the alkaline than with the dried preparation, and the rate does not fall so rapidly in either more acid or more alkaline media. For dextrose fermentation there is an optimal phosphate concentration at 0·14*M* with the living cells, at 0·5*M* with the dried preparation.

Half the dextrose that disappears during fermentation with dried *B. casei* ε does not reappear as lactic acid, and so far has not been accounted for. Aeration of a suspension of bacteria containing lactic acid leaves the amount of the latter unchanged. Insulin (several preparations) cannot replace the co-enzyme of *B. casei* ε fermentation. H. D. KAY.

Symbiotic fermentation. A. CASTELLANI (Ann. Inst. Pasteur, 1928, 42, 461—474).—Numerous examples are given of the micro-organisms which do not cause fermentation except in mixed cultures or in mixtures of pure cultures of two organisms. This symbiotic phenomenon may be employed for the identification of certain sugars and bacteria. E. A. LUNT.

Fermentation of substituted carbohydrates by bacteria of the *B. coli* and *B. lactis aërogenes* groups. H. HEES and C. TROPP (Zentr. Bakt. Par., 1926, **100**, 273—284; Chem. Zentr., 1928, i, 367).

Metabolic regulation of bacteria. E. ZIMMERMANN (Zentr. Bakt. Par., 1927, I, **104**, 451—456; Chem. Zentr., 1928, i, 366—367).—The consumption of sugar by *Bacillus coli* and *B. suipestifer* in a synthetic medium depends only on the demand. "Resting" bacteria (*coli*) in aqueous sugar solution do not consume any sugar. A. A. ELDRIDGE.

Properties of the dehydrogenating enzymes of bacteria. J. H. QUASTEL and W. R. WOOLDRIDGE (Biochem. J., 1928, **22**, 689—702).—The enzyme (or active centre) of *B. coli* which activates lactic acid as a hydrogen donator has the property of specifically adsorbing compounds having a particular structure

which seems to be $\cdot CO\cdot C(OH^*)\cdot$ or $\cdot CH(OH)\cdot C(OH^*)\cdot$, where H* is mobile, the compound having acidic properties. The specificity of adsorption is very marked. The enzyme (or active centre) which activates succinic acid has also the property of adsorbing compounds having a particular structure which seems to be $\cdot C\cdot CH\cdot CO_2H$ or $\cdot C\cdot CH_2\cdot CO_2H$. The formic acid enzyme is independent of the lower fatty acids other than formic acid itself and of all the substances so far investigated. The activity of dextrose as a hydrogen donator is not perceptibly inhibited by the presence of oxalic acid or of hydroxymalonic acid. The reduction of methylene-blue by dextrose in presence of bacteria is independent, therefore, of the intermediate production of lactic acid. The action of toluene on *B. coli* is to eliminate the activity of the organism to many substances which can still be shown to be adsorbed at an active centre. Toluene appears also to affect the adsorption coefficient of the active centre towards substrates.

S. S. ZILVA.

Rate of reduction of methylene-blue by *Bacillus coli*. G. S. EADIE (J. Gen. Physiol., 1928, **11**, 459—468).—The rate of reduction of methylene-blue in presence of "resting" *B. coli* with succinic acid as hydrogen donator conforms to the equation $v=a+b \log c$ (v=rate of reduction, c=concentration of succinic acid, a and b are constants) as found by Quastel and Whetham (A., 1925, i, 1015). When dextrose is substituted for succinic acid the same equation holds over a wide range of concentration but fails if the concentration of dextrose is too low. The influence of p_H and of temperature on the rates of reduction has been investigated as well as the result of substituting other oxidation-reduction indicators in the place of methylene-blue. The mechanism of reduction is probably dependent on adsorption.

W. O. KERMACK.

Synthesis of acyloins by the enzymes of acetic acid bacteria. T. KITASATO (Biochem. Z., 1928, **195**, 118—127).—After fermentation by acetic acid bacteria of acetaldehyde, ethyl alcohol, and pyruvic acid, in spite of the powerfully oxidising character of these organisms, only acetylmethylcarbinol was obtained, diacetyl and butylene glycol never being detected. P. W. CLUTTERBUCK.

Action of *K*-rays of aluminium on certain micro-organisms. A. LACASSAGNE (Compt. rend., 1928, **186**, 1316—1317).—Agar inoculated with cultures of *B. pyocyaneus*, *B. prodigiosus*, *Staphylococcus*, and *Enterococcus* was exposed at a range of 3 mm. to *K*-rays of aluminium for 1—600 sec. before incubation. The four species differed in their sensitivity to the rays, but in all cases exposure for a few seconds visibly affected the subsequent growth of the bacteria. A longer exposure caused irregular growth in isolated patches, and a surprisingly greater length of exposure (*e.g.*, 40—300 sec.) was necessary to ensure complete sterilisation (cf. following abstract).

B. W. ANDERSON.

Interpretation in terms of energy of the action of *K*-rays of aluminium on micro-organisms. F. HOLWECK (Compt. rend., 1928, **186**, 1318—1319).—An explanation of the long interval between partial and complete extinction of bacteria exposed to *K*-rays of aluminium (cf. preceding abstract). The same mean quantity of energy is capable of producing different effects on different individual bacteria, since the number of quanta each receives and the region in the micro-organism where consequent ionisation takes place may vary considerably. It is calculated in the case of *B. pyocyaneus* that on the average 300 ionised molecules per individual modify growth, 6000 prove fatal to most, but 45,000 are necessary to sterilise them all. B. W. ANDERSON.

Precipitable substances derived from *Bacillus typhosus* and *B. paratyphosus B*. J. FÜRTH and K. LANDSTEINER (J. Exp. Med., 1928, **47**, 171—183).—Specific substances soluble in ether were not obtained from *B. typhosus*; two serologically active protein substances and one non-protein were separated. One of the proteins is soluble in 75% ethyl alcohol. Specific substances similar to this non-protein, and containing much carbohydrate, were prepared from *B. paratyphosus B*, *B. enteritidis*, and *Proteus* HX 19 and OX 19.

CHEMICAL ABSTRACTS.

Oxygen consumption of luminous bacteria. E. N. HARVEY (J. Gen. Physiol., 1928, **11**, 469—475).—At 21·5° the average value of oxygen consumption by *Photobacterium phosphorescens* is $4{\cdot}26\times10^{-11}$ mg. per bacterium or $2{\cdot}5\times10^4$ mg. per kg. (cf. *ibid.*, 1926, **8**, 89). W. O. KERMACK.

Hydrogen-ion concentration of the gastro-intestinal tract and its relation to chemical bacteriology. L. ARNOLD (Chem. Bull. [Chicago], 1928, **15**, 5—6, 30).—A discussion of the p_H in the lumen of the gastro-intestinal tract as influenced by the addition of the various digestive secretions, by the presence of the bacterial flora, and by the character of the food ingested. CHEMICAL ABSTRACTS.

Circulatory hormone. II. H. KRAUT, E. K. FREY, and E. BAUER (Z. physiol. Chem., 1928, **175**, 97—114).—The constituent of the urine (cf. Frey and Kraut, A., 1926, 1168) which has a marked action on the heart, producing an increase in the amplitude and usually an increase in rhythm, has been investigated further. This hormone is also present in blood (dog, human, and horse), but the preparations obtained contain a large amount of impurity. The addition of serum to a preparation of the hormone from urine or blood inactivates the hormone, and this "inactivator" of serum, which does not appear to be of high mol. wt., is destroyed by heat, by the addition of alcohol, or by mild acidification of the serum. This "inactivator" does not destroy the hormone, but an inactive compound is formed from which the active hormone can be regenerated. It is considered that blood contains the hormone as this inactive compound, and by digestion of the proteins of defibrinated blood by papain at p_H 5 with dialysis against running water, a solution with a powerful action on the heart and circulation is obtained. The preparation from blood is not as pure as that from urine, but the two preparations appear to be identical; both are destroyed by heat, and are inactivated by the addition of serum, whilst they differ in several respects from histamine.

The increase in the activity of the heart and the lowering of the blood pressure are due to the same substance in all these preparations. A. WORMALL.

Production of alcohol in the animal body. IV. Influence of adrenaline on the amount of blood-alcohol. M. AOKI (J. Biochem. Japan, 1927, 7, 405—409).—An injection of adrenaline causes an increase in the alcohol content of the blood of animals. CHEMICAL ABSTRACTS.

Changes in the glycogen content of the heart and brain, and the lactic acid and lactacidogen content of the muscle in adrenalectomised rats. B. A. HOUSSAY and P. MAZZOCCO (Compt. rend. Soc. Biol., 1927, 97, 1252—1253; Chem. Zentr., 1928, i, 542).—The glycogen content for normal and adrenalectomised rats was: heart 0·066, 0·069%, brain 0·128, 0·156%; the lactic acid in the muscle was 0·185, 0·169%. A. A. ELDRIDGE.

Causes of the increase of insulin content of venous pancreatic blood after intravenous administration of adrenaline. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1927, 97, 917—919; Chem. Zentr., 1928, i, 370).—Injection of adrenaline into the atropinised blood donor in transfusion experiments causes hyperinsulinæmia, whilst the glycæmia of the other animal falls after transfusion. The injection of adrenaline appears to be the direct cause of the secretion of insulin. A. A. ELDRIDGE.

Effect of insulin on protein metabolism. A. T. MILHORAT and W. H. CHAMBERS (J. Biol. Chem., 1928, 77, 595—602).—After a short period of fasting in the dog injection of insulin causes an increase in the urinary output of nitrogen; no such increase is observed after prolonged fasting unless carbohydrate be administered at intervals, thus producing a nitrogen-sparing effect. C. R. HARINGTON.

Autodigestion. III. Antitrypsin and insulin. H. NECHELES (Chinese J. Physiol., 1928, 2, 229—230).—Insulin in physiological concentrations does not affect the antitryptic titre of dog's blood. H. D. KAY.

Effect of intraperitoneal injections of insulin on the blood-sugar of well-fed rabbits. M. SAHYUN and N. R. BLATHERWICK (J. Biol. Chem., 1928, 77, 459—466).—Whilst the first intraperitoneal injection of insulin into well-fed rabbits may fail to produce hypoglycæmia, subsequent similar injections produce the usual insulin effect, and insulin is more effective when given intraperitoneally than intravenously (cf. Hoskins and Snyder, A., 1927, 1222). C. R. HARINGTON.

Insulin hypoglycæmia, shock, and leucocytosis in man. O. KLEIN and H. HOLZER (Z. Klin. Med., 1927, 106, 360—385; Chem. Zentr., 1928, i, 370).

Antiketogenic influence of insulin in diabetes mellitus. J. A. KILLIAN (J. Lab. Clin. Med., 1926, 11, 1132—1139).—The ketone substances of the blood and urine are immediately decreased, and the alkali reserve of the blood-plasma rises. The rise in carbon dioxide capacity is associated with a proportional rise in the of the blood-plasma. The antiketogenic influence of insulin is apparently due to its stimulation of the oxidation of the carbohydrates. CHEMICAL ABSTRACTS.

Physiological variations of the internal secretion of the pancreas. I. Demonstration of a physiological insulinæmia. II. The pneumogastric, a nerve causing insulin secretion. III. Role of the nervous system in the regulation of physiological insulinæmia. IV. Hyperinsulinæmia following hyperglycæmia provoked by the injection of dextrose. V. Hyperinsulinæmia following the injection of adrenaline. J. LA BARRE (Arch. Int. Physiol., 1927, 29, 227—238).—Normal insulinæmia can be demonstrated in the blood from the superior pancreatic vein. Hyperglycæmia produced by the intravenous injection of dextrose increases the insulin secretion into the pancreatic vein; the hyperinsulinæmia is prevented by atropinisation and vagotomy. Increase of the insulin content of the pancreatic vein caused by intravenous injection of adrenaline is not so prevented. CHEMICAL ABSTRACTS.

Glycæmin and insulin. O. LOEWI (Klin. Woch., 1927, 6, 2169—2176; Chem. Zentr., 1928, i, 83).—The mechanism of the fixation of dextrose by insulin and its conversion into lactic acid is discussed. Diabetic plasma contains an inhibitant, "glycæmin." This antagonistic substance is dialysable, is not decomposed when the dialysate is dried, and is soluble in absolute alcohol. Diabetic hyperglycæmia is ascribed to an increased secretion of glycæmin, and a deficient secretion of insulin. A. A. ELDRIDGE.

Biological standardisation of insulin. R. WERNICKE, F. MODERN, and C. M. SCOTTI (Anal. Asoc. Quím. Argentina, 1927, 15, 324—336).—Details are given of a method, based on that given in Publications of the League of Nations, III, Health, 1926, III, 7, of standardising insulin by a preliminary determination with white mice, followed by exact determination with rabbits. The insulin solution is diluted until a subcutaneous injection of 0·5 c.c. per 20 g. causes the same proportion of mice to show symptoms of hypoglycæmia under standard conditions as controls injected with an equal quantity of standard solution containing 0·025 clinical unit per c.c. The final standardisation is carried out by injecting different groups of rabbits with standard insulin (0·5 clinical unit in 1 c.c. per kg.) and the sample in similar amount. From analysis of samples of blood from each group the initial and mean final blood-sugar levels are determined. The percentage decrease is proportional to the activity of the preparation. Data are given of the variation of sensitivity of rabbits and mice to insulin injections. R. K. CALLOW.

Effect of pituitary extracts on blood-sugar. G. FRITZ (Magyar Orvosi Arch., 1928, 29, 8—15).—Intramuscular injection of pituitary extracts causes a rise in the blood-sugar of normal, but not of adrenalectomised, rabbits, guinea-pigs, and rats. CHEMICAL ABSTRACTS.

Pituitary and urinary excretion of phosphate, sulphate, and chloride. P. C. TUNG, H. C.

CHANG, and S. M. LING (Chinese J. Physiol., 1928, **2**, 231—246).—After extirpation of the pituitary in dogs there is a fall in chloride output. The phosphate excretion usually shows a slight rise, followed by a fall up to the 4th or 5th hr. Later a secondary rise, the recovery phase, occurs. In animals surviving the operation from 1 to 16 weeks, phosphate excretion continued uninterruptedly. The authors therefore disagree with the suggestion of Brull and Eichholtz (A., 1926, 88) that removal of pituitary control abolishes inorganic phosphate excretion.

H. D. KAY.

Adsorbability of the active substances of the posterior lobe of the pituitary on animal charcoal. G. SATO (Arch. exp. Path. Pharm., 1928, **130**, 323—325).—The adsorption on animal charcoal of the pituitary active principles acting on the uterus and on the melanophores of the frog and of the corresponding principles present in the cerebrospinal fluid has been investigated. The conclusion of Houssay and Ungar (Bol. Soc. biol. Argentina, 1924) that the melanophore-expanding substance in the cerebrospinal fluid is different from that of the posterior lobe because of its apparent non-adsorbability on animal charcoal is not considered well founded. W. O. KERMACK.

Fat metabolism and œstrus hormone of the corpus luteum. C. KAUFMANN and W. DUNKEL (Klin. Woch., 1927, **6**, 2228—2229; Chem. Zentr., 1928, i, 369).

Secretin. I—II. Hypoglycæmic action of secretin in animals, man, and in diabetes. L. TAKACS (Z. ges. exp. Med., 1927, **57**, 527—531, 532—536; Chem. Zentr., 1928, i, 83—84).—With rabbits and dogs, secretin from the mucous membrane of the small intestine causes a 50—60% reduction of blood-sugar, the maximum effect occurring in 4—5 hrs. Similar results were obtained in normal and diabetic man. A. A. ELDRIDGE.

Effect of thyroid gland preparation, ovariotomy, and removal of testes on the sugar-excretion threshold. S. KAWASHIMA (J. Biochem. Japan, 1927, **7**, 361—369, 371—377, 379—387).—Administration of "thyroidin" or removal of testes (rabbits) causes a rise in the sugar-excretion threshold; ovariotomy (non-pregnant dogs) had no effect on the assimilation or excretion threshold.

CHEMICAL ABSTRACTS.

Colour tests for sterols and vitamin-*A*. I. Sterol tests. F. WOKES (Biochem. J., 1928, **22**, 830—835).—Pure cholesterol freed from ergosterol gives with concentrated sulphuric acid, arsenic or antimony trichloride red colours persisting for many hours. Similar results are obtained with cholesteryl acetate and chloride, α-cholesterylene, and ψ-cholestene, but with the last two more time may be required for the colour to develop. Cholesterol, cholesteryl acetate or chloride, cholestene, and ψ-cholestene in chloroform solution left in contact with concentrated sulphuric acid for some hours and then diluted with more chloroform give a purple or violet colour. Similar colours can be obtained by removal of the chloroform solution from the acid after less than a minute's contact and addition to the former of a drop of formalin. Irradiation of sterol derivatives generally has the effect of rendering the colours more transient. In the case of cholesterol, however, irradiation under certain conditions may develop the property of producing with the "vitamin" reagents blue colours changing to red on keeping for some hours. Activation with other reagents such as acetic anhydride, benzoyl peroxide, or formaldehyde may lead to blue or purple colours being obtained on addition of the "vitamin" reagents. Cholestenone gives transient red colours with these reagents and negative results with all other tests. The other oxidation products of cholesterol which have been tested give negative results in all cases. Antimony pentachloride gives the colour sequence red ⟶ blue ⟶ red with all cholesterol derivatives examined except the oxidation products. Of these dicholesteryl ether gives both red and blue, cholestenone and hydroxycholesterylene give red only, and β-hydroxycholestenol acetate gives negative results. Introduction of sulphur into the side-chain as in cholesteryl methylxanthate retards the development of the colours but does not necessarily prevent it after the liberation of sulphur compounds has taken place. The "vitamin" reagents give with ordinary concentrations of ergosterol the usual red colour, but if a higher initial concentration be employed the red colour given by arsenic or antimony trichloride changes to purple or blue on diluting with more reagent after a few moments. Sitosterol gives similar results to cholesterol but more slowly.

S. S. ZILVA.

Dual nature of water-soluble vitamin-*B*. II. The effect on young rats of vitamin-B_2 deficiency. Biological assay of vitamin-B_2. H. CHICK and M. H. ROSCOE (Biochem. J., 1928, **22**, 790—799).—The caseinogen in the basal diet is purified by extraction with acid water and acid alcohol, thus removing vitamin-B_2. Rats about 4 weeks old are kept on the diet free from vitamins-B_1 and -B_2 for about 2 weeks, after which time B_1 is administered in the form of Peter's antineuritic concentrate. After 3—4 weeks from the beginning of the experimental period the substance to be tested is administered. The minimum dose which gives an average weekly increase of 10—12 g. is suggested as a standard. A description is given of the effects observed in growing rats when they are fed on diets deficient only in vitamin-B_2. Further evidence in support of the composite nature of vitamin-*B* is also produced. S. S. ZILVA.

Effect of inanition and vitamin-*B* deficiency on the adrenal glands of the pigeon. G. F. MARRIAN (Biochem. J., 1928, **22**, 836—844; cf. Marrian and others, this vol., 91).—The adrenal hypertrophy occurring in the vitamin-*B*-deficient pigeons seems to be mainly due to vitamin-*B* deficiency, but vitamin-B_2 deficiency is also a contributory factor. The adrenal glands of both starving and vitamin-*B*-deficient pigeons are œdematous. This œdema accounts for 19% of the total hypertrophy shown by the vitamin-*B*-deficient birds and 44% in the case of the starving pigeons. A pigeon forcibly fed on a complete diet has developed acute symptoms resembling those due to vitamin-*B* deficiency, but the condition was not

curable by the administration of vitamin-*B*. The relation of adrenal hypertrophy to starvation and to vitamin-*B* deficiency is discussed. S. S. ZILVA.

Bios. V. B. SUZUKI and Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1928, **4**, 158—160).—Treatment of crude bios with sodium hydroxide solution gives in addition to γ-acid (this vol., 177), 2 : 6-dihydroxyquinoline-4-carboxylic, nicotinic, *p*-hydroxybenzoic, and 4-hydroxy-3-methoxycinnamic acids.

H. BURTON.

Antiscorbutic fraction of lemon juice. VII. S. S. ZILVA (Biochem. J., 1928, **22**, 779—785; cf. A., 1927, 702).—When phenolindophenol is added to decitrated lemon juice until the indicator is no longer reduced and the solution is adjusted immediately to p_H 7, the antiscorbutic activity disappears within 24 hrs. Purified antiscorbutic fractions from lemon juice lose their activity much more rapidly than does decitrated lemon juice of similar activity. Decitrated lemon juice dialysed in collodion thimbles of a permeability which leaves the solution inactive after 3 days loses the capacity for reducing phenolindophenol. This reducing capacity is retained to a great extent by the juice when dialysed in thimbles of a permeability which yields an active juice at the end of the dialysis. Acidity retards deterioration on storage of the antiscorbutic activity in anaerobically autoclaved decitrated lemon juice. On storage at p_H 3, however, the deteriorating effect of autoclaving is scarcely perceptible. Lemon juice autoclaved anaerobically, even in a very acid medium, deteriorates much more rapidly at p_H 7 on storage than similar solutions which have not been autoclaved. Comparatively little loss occurs in decitrated lemon juice which has been autoclaved at 40 lb. pressure for 1 hr. under strictly anaerobic conditions. S. S. ZILVA.

Specificity of ergosterol as parent substance of vitamin-*D*. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1928, **22**, 762—766).—Sphingosine, oxycholesterylene, *iso*ergosterol, and digitaligenin cannot be activated by irradiation. The last-named shows only one band with a maximum at 340 $\mu\mu$ extending from 270 to 390 $\mu\mu$. In addition, there is general absorption and possibly secondary bands in the region below 250 $\mu\mu$. The broad absorption band of digitaligenin remains practically unchanged after 2 hrs.' irradiation. The above lends further support to the specificity of ergosterol as the parent substance of vitamin-*D*. The discrepancy between results obtained by Windaus and Holtz (Nachr. Ges. Wiss. Gottingen, 1927, 217) and the authors concerning the antirachitic activity of irradiated digitaligenin is discussed. S. S. ZILVA.

Vitamin-*D* in adults. Its effect on the calcium and inorganic phosphate of the blood. R. E. HAVARD and J. C. HOYLE (Biochem. J., 1928, **22**, 713—716).—Neither addition of 8 mg. per day of irradiated ergosterol to the diet of a healthy adult human subject for 21 days nor irradiation for 16 days during the winter caused any significant change in the blood inorganic phosphate or serum-calcium.

S. S. ZILVA.

Correlation between electromotive series and oxidation potentials and plant and animal nutrition. H. P. COOPER and J. K. WILSON (Science, 1927, **66**, 629—631). CHEMICAL ABSTRACTS.

Vitamin-like substances in plant nutrition. J. F. BREAZEALE (Ariz. Agric. Exp. Sta. Tech. Bull., 1927, **16**, 401—417).—Certain plants, when decomposing, develop compounds which stimulate the growth of other plants. Many plants require for normal growth the presence of small quantities of organic compounds not usually regarded as plant foods. The stimulating property of manure is largely associated with the soluble organic matter.

CHEMICAL ABSTRACTS.

Significance of anthocyanins in plants. T. LIPPMAA (Ber. deut. bot. Ges., 1928, **46**, 267—277).—The occurrence of anthocyanins in the leaves of a large number of plants has been investigated with reference to age of leaf, natural habitat, and climatic factors. From the results obtained the author is unable to support Noack's theory that the function of anthocyanins in the leaves of plants is concerned with the assimilation of carbon dioxide.

E. A. LUNT.

Narcosis of carbon dioxide assimilation and the bubbling method. T. SCHMUCKER (Biochem. Z., 1928, **195**, 149—160).—The bubbling method in assimilation experiments is critically examined with shoots of *Cabomba caroliniana*, modified, and used to investigate the sensitivity of the assimilation of carbon dioxide to various narcotics. Faint stimulation is obtained with ether at 0·1% and ethyl alcohol at 0·3—1%. Reversible inhibition is obtained with chloroform between 0·025 and 0·1 vol.-%, with ether between 0·2 and 2·5%, and with ethyl alcohol between 1 and 3%. The lethal dose with chloroform is only slightly higher than 0·1 vol.-%. Stimulation with acetaldehyde was not obtained.

P. W. CLUTTERBUCK.

Effect of increased atmospheric carbon dioxide on the growth of plants. I. B. D. BOLAS and F. Y. HENDERSON (Ann. Bot., 1928, **42**, 509—523).—An open type apparatus for observing the effect on the growth of plants of air enriched with carbon dioxide is described. In the case of the cucumber, atmospheres containing 0·258—0·424% of carbon dioxide result in a large increase in the dry weight of the plant. E. A. LUNT.

Vegetable assimilation and respiration. XIX. Effect of variations of carbon dioxide supply on the rate of assimilation of submerged water plants. W. O. JAMES (Proc. Roy. Soc., 1928, **B**, **103**, 1—42).—Carbon dioxide and sodium hydrogen carbonate solutions have been used as source of carbon dioxide in the determination of the rate of assimilation of submerged aquatic plants as a function of carbon dioxide concentration and light intensity. For carbon dioxide, the rate of assimilation increases with the rate of flow of solution; for sodium hydrogen carbonate it is constant. For the same rates of flow when no other factor is limiting, sodium hydrogen carbonate gives a higher rate of assimilation than a solution of carbon dioxide of equal partial pressure.

E. A. LUNT.

Physiology of apples. IX. Chemical composition of mature and developing apples and its

relationship to environment and to the rate of chemical change in store. H. K. Archbold (Ann. Bot., 1928, 42, 541—566).—Determinations have been made of the nitrogen, acid, sugar, and starch contents of Bramley's Seedlings as a function of time from the setting of the fruit till maturity. Subsequent losses in the cold store are shown to vary with the initial composition of the mature apple and may in some cases determine the length of storage life.
E. A. Lunt.

Temperature in relation to chemical composition in the apple. J. S. Caldwell (J. Agric. Res., 1928, 36, 367—389).—The theory that every variety of apple has an optimum mean summer temperature at which it attains its best development is confuted. It is concluded that seasonal amount of sunlight is more potent in the determination of the quality of any given crop than the mean summer temperature at which it is grown whatever is the relation that this temperature bears to the optimum mean summer temperature of the variety. E. A. Lunt.

Effect of climatic conditions on the chemical composition of apple juice. J. S. Caldwell (J. Agric. Res., 1928, 36, 289—365).—The annual variations in total astringency, sugar, and free acid contents in the expressed juice of apples of 216 varieties have been determined over a period of 6 years in order to relate such variations with the annual variation in rainfall, sunshine, and temperature. Amount of sunshine is the most potent factor and amount of rainfall the least potent factor in the determination of the acid–astringency–sugar ratio of the juice of any given crop. A high annual average for sunshine and temperature produces increased sugar and acid contents and decreased astringency. E. A. Lunt.

Reduction of picric acid by plants. E. Barral (Compt. rend. Soc. Biol., 1927, 97, 753—755; Chem. Zentr., 1928, i, 365).—The plants were killed by high concentrations of picric acid, but when low concentrations (0·10—0·1%) were employed, the flowers were coloured yellow and contained (chiefly in the ovaries) picramic acid. A. A. Eldridge.

Presence of sodium in plants. G. Bertrand and [Mme.] M. Rosenblatt (Bull. Soc. chim., 1928, [iv], 43, 368—371).—See this vol., 334.

Manganese in the mulberry leaf. S. Bito (Bull. Agric. Chem. Soc. Japan, 1927, 3, 67—68).—More manganese is present in the mesophyll than in the vein and petiole; it increases with growth and varies with species. The flower contains the same amount. Chemical Abstracts.

Search for elements essential in only small amounts for plant growth. A. L. Sommer (Science, 1927, 66, 482—484).—Zinc is necessary for the growth of barley, sunflowers, wheat, buckwheat, broad beans, and red kidney beans; "pyrex" containers in culture experiments do not yield traces of all necessary nutrients. A. A. Eldridge.

Development of calcium oxalate cells with particular reference to medicinal plants. D. Brunzema (Arch. Pharm., 1928, 266, 86—103).—Histological. W. A. Silvester.

Calcium oxalate deposition in grafted plants. L. Daniel (Compt. rend., 1928, 186, 1143—1144).—The deposition of these crystals in certain plants is greatest at those parts of the grafted junction near the callus where the multiplication of the cells is most rapid. G. A. C. Gough.

Pectin. III. Degree of esterification of pectin in juice of the lemon. A. G. Norman (Biochem. J., 1928, 22, 749—752; cf. this vol., 559).—In order to prevent partial de-esterification of the pectin, the juice was pressed out by hand and received in 95% alcohol. The precipitate was redissolved and reprecipitated several times in this way. The apparent methoxyl content of such a preparation corresponded with a trimethylated derivative of pectic acid. If, however, a correction for the calcium pectate yield of the preparation is made, the methoxyl content approaches the theoretical value for tetramethylpectic acid. Some other material, probably pectin degradation products, giving a furfuraldehyde yield similar to that of pectin is associated with pectin in this preparation. S. S. Zilva.

Physiological significance of plant constituents with special reference to lignin. M. Rubner (Sitzungsber. preuss. Akad. Wiss., 1928, 11, 127—145).—The fibrous tissue from various plant sources has been determined quantitatively under the various groups of cellulose, pentosans, lignin, and residual matter and the digestibility of the various fractions has been investigated. E. A. Lunt.

Formation of red anthocyan pigments in the red leaves of *Ampelopsis hederacea*. S. Ionesco (Compt. rend. Soc. Biol., 1927, 97, 975—977; Chem. Zentr., 1928, i, 365).—The chromogen, *leucoanthocyanidin* (the colour reactions and solubilities of which are described), is converted by warming into a true anthoxycyanidin. When treated with nascent hydrogen or a mixture of barium (or manganese) dioxide and sulphuric acid, or when warmed with 20% hydrochloric acid for 5—10 min. a red pigment is obtained. A. A. Eldridge.

Formation and degradation of starch in vegetable cells. A. Maige (Bull. Soc. Chim. biol., 1928, 10, 422—429; see also A., 1927, 388).—The suggestion of Brown and Morris (J.C.S., 1893, 63, 604) that amylase acts both as a hydrolytic and as a synthetic agent is criticised on the following grounds: (*a*) no reversion of the hydrolytic action of amylase is observed *in vitro*; (*b*) the growth of seeds containing large amounts of starch in the presence of dextrose does not inhibit hydrolysis of the starch; (*c*) whilst chloroform or elevation of temperature reduces the formation of starch, the activity of the amylase is unaffected. It is probable that the fall in the amylase content during the production of starch is due to partial cessation of the hydrolysis in the plant-tissues.
G. A. C. Gough.

Physiological significance of pyrocatechol tannins. Michel-Durand (Compt. rend., 1928, 186, 1145—1147).—The acetone-soluble and insoluble components of the pyrocatechol tannins in the leaves, buds, and wood of *Æsculus hippocastanum* and in the tubers of *Rumex hymenosepalus* are determined. The

acetone-soluble tannin is greater only in the leaves of the former plant, and in the tubers the total tannin content falls more rapidly than the carbohydrate content during early growth. Since tannin consumption decreases when the growth becomes slower, it is suggested that it functions as a reserve food.

G. A. C. GOUGH.

Lævulosans of *Iris*. H. COLIN and A. AUGEM (Bull. Soc. Chim. biol., 1928, **10**, 489—494; see also A., 1927, 1116).—Irisin is best isolated from aqueous extracts of *Iris fœtidissima* (*Iris pseudacorus* and *germanica* contain less irisin) through the *barium* derivative followed by treatment with dilute sulphuric acid. The corresponding *calcium* derivative, which is precipitated from aqueous solutions by alcohol, is more soluble. From *Iris fœtidissima* a non-crystalline carbohydrate, $[\alpha]_D$ $-29°$, mol. wt. 287—296, is obtained together with irisin by the barium method. This carbohydrate, which is more soluble in water and in 60% alcohol than irisin, yields an insoluble barium derivative, soluble calcium and strontium derivatives, and, like irisin, is not precipitated by salts of the heavy metals. After hydrolysis the carbohydrate does not reduce Fehling's solution and the rotatory power falls to $-80°$. It is resistant towards the hydrolytic action of emulsin, diastase, and invertase. Whilst the rhizomes of the iris contain only lævulosans and small amounts of sucrose, the leaves contain dextrose and starch in addition. G. A. C. GOUGH.

Seeds of the stone-pine (*Pinus pinea*, L.). A. D. MARANIS (Arch. Pharm., 1928, **262**, 121—122).—The edible seeds of the stone-pine contain water, 4·88%; ash, 1·20%; oil (extracted by carbon disulphide) 51·50%; nitrogenous substances, 37·45%; carbohydrates, 4·80%. The oil has d^{15} 0·92134; setting-point, $-21°$; Zeiss refractometer value at 40°, 61·0; acid value, 4·19; saponification value (Kottstorfer), 192·22; iodine value (Hübl), 119·0; Hehner value, 96·0; Reichert-Meissl value, 0·22; Polenske value, 0·35; ester value, 188·03. Liquid fatty acids (oleic) and solid fatty acids (stearic) are in the proportion 95 : 5.

W. A. SILVESTER.

Mercury compound of allantoic acid by means of which it may be identified in *Phaseolus vulgaris*. R. FOSSE and A. HIEULLE (Bull. Soc. Chim. biol., 1928, **10**, 310—312).—See A., 1927, 1175.

Determination of allantoic acid as xanthylcarbamide. Application to analysis of leaves of *Acer pseudoplatanus*. R. FOSSE and V. BOSSUYT (Bull. Soc. Chim. biol., 1928, **10**, 313—315).—See A., 1927, 891.

Identification of allantoic acid in leaves of *Acer pseudoplatanus*. R. FOSSE and A. HIEULLE (Bull. Soc. Chim. biol., 1928, **10**, 308—309).—See A., 1927, 1116.

Difference in physico-chemical properties of various proteins in plant seeds. II. Four kinds of rice protein. T. TADOKORO, T. TSUJI, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1927, **19**, 93—104).—A comparison of the properties of four rice proteins, soluble, respectively, in water, sodium chloride solution, sodium hydroxide solution, and alcohol. CHEMICAL ABSTRACTS.

Influence of caffeine on the germination of seeds. G. B. ZANDA (Arch. Farm. sperim., 1928, **44**, 278—286).—The germination of seeds of *Zinnia elegans*, Jacq., in Sachs' nutrient solution is favoured by 0·01% of free caffeine, larger plants being obtained. The initial germination is accelerated by 0·02—0·03%, but the effect ceases as soon as the seedling forms. With proportions of the base exceeding 0·1% growth is retarded and 0·2—0·3% solutions exert a definite toxic effect. Seeds thus treated grow normally if transferred to caffeine-free nutrient solution.

T. H. POPE.

Enzymes of *Pythiacystis citrophthora*, Sm. and Sm. L. J. KLOTZ (Hilgardia, 1927, **3**, 27—40).—Definite evidence for the presence of diastase, invertase, maltase, emulsin, phloridzinase, asparaginase, urease, peroxidase, catalase, and some of the lower esterases was obtained.

CHEMICAL ABSTRACTS.

Influence of light and of dextrose on the growth of a soil alga. B. M. B. ROACH (Ann. Bot., 1928, **42**, 317—345).—The growth of the soil alga, *Scenedesmus costulatus*, has been realised in liquid media under purely photosynthetic conditions with a light of comparatively strong intensity; addition of dextrose to the medium under these conditions produces no increase in the growth rate. As the photosynthetic growth rate is diminished by diminishing light intensity, increasing dextrose assimilation takes place. The maximum growth rate due to dextrose assimilation alone is less than the maximum photosynthetic rate. E. A. LUNT.

Co-zymase in respiring organs of plants. H. VON EULER and S. STEFFENBURG (Z. physiol. Chem., 1928, **175**, 38—51).—The co-zymase of washed dry yeast is found in a number of higher fungi (*Armillaria melleus*, *Hygrophorus chlor.*, *Clavaria cristata*, *Polyporus ungulatus*, *Lactarius rufus*) and in the leaves of green plants (*Vicia faba*, *Vaccinium vitis idea*), and is essential for the anaerobic part of respiration. There is also present with the co-zymase in the plant organs a heat-resistant, dialysable inhibiting substance. In the flesh of apples either the co-zymase is present in only minute amount, or its activity is prevented by the inhibitor; the respiration (oxygen consumption) here is probably at the expense of plant acids rather than of sugars. C. HOLLINS.

Protoplasm. IV. Plastin of *Myxomycetes* and its alleged ageing. A. KIESEL (Z. physiol. Chem., 1928, **173**, 169—183).—The usual methods for the preparation of plastin (cf. A., 1927, 382, 799) yield a product which contains, besides other impurities, myxoglucosan and glycogen, whilst there is a possibility that the long treatment with 0·5*N*-sodium hydroxide produces changes in the native plastin. The preparation of plastin from *Lycogala epidendron*, *Fuligo varians*, and *Reticularia lycoperdon* is described and the analytical results are given; differences are found in the nitrogen content (13·58%, 14·93%, and 15·22% respectively), phosphorus, (0·12%, 0·11%, and 0·12%), and sulphur (0·38%, 0·29%, and 0·15%), whilst slight but significant differences are observed in the nitrogen distribution and the amounts of various amino-acids present

after hydrolysis with acid by the method previously described (A., 1927, 799). In general, however, the agreement between the amounts of the various products of hydrolysis is satisfactory but not sufficient to prove that the different plastins are identical. Physical and possibly chemical changes occur in plastin by treatment with the alkali used for the preparation but no marked decomposition occurs. Plastin preparations from young true plasmodium and from two later stages in the development of *Lycogala epidendron* have been compared. Variations in the nitrogen, phosphorus, and sulphur and in the amounts of various amino-acids present are observed, but the results do not establish the identity of the natural plastins of the plasmodium and of the unripe fruiting bodies.
A. WORMALL.

Mechanism of the degradation of fatty acids by mould fungi. I. T. K. WALKER and P. D. COPPOCK (J.C.S., 1928, 803—809).—Fermentation of calcium propionate by *Aspergillus niger*, in the presence of inorganic salts only, affords lactic acid and finally pyruvic and oxalic acids together with some ethyl alcohol and glyoxylic acid. Acetaldehyde and formic acid are also produced in the earlier stages. In a similar way lactic acid yields ethyl alcohol, oxalic and pyruvic acids, and pyruvic acid yields ethyl alcohol. These results (see also A., 1927, 228, 593) indicate that the fermentation of propionic acid follows the course: lactic acid, pyruvic acid, acetaldehyde, ethyl alcohol and acetic acid; the last-named yields oxalic acid through the stages glycollic and glyoxylic acids (cf. Dakin, A., 1926, 428).
G. A. C. GOUGH.

Energy of growth. XII. Comparative energy yield of different sugars in the development of moulds. L. DE CARO (Bull. Soc. Chim. biol., 1928, **10**, 456—460).—Cultures of *Aspergillus niger* grown on similar media containing different sugars show greater energy yield (A., 1922, i, 706; 1925, i, 1117) for the substances in the order, lævulose, inulin, sucrose, dextrose and maltose, lactose.
G. A. C. GOUGH.

Production of fumaric acid from pyruvic acid by *Rhizopus nigricans*. A. GOTTSCHALK (Z. physiol. Chem., 1927, **172**, 314—316).—Ehrlich and Bender's (this vol., 95) inability to repeat the author's results as to the production of fumaric acid from pyruvic acid by this mould may be due to their having used either a morphologically identical strain having different metabolic powers, or possibly a less viable strain.
H. D. KAY.

Production of fumaric acid from pyruvic acid by *Rhizopus nigricans*. F. EHRLICH and I. BENDER (Z. physiol Chem., 1927, **172**, 317—318).—Polemical; a reply to Gottschalk (cf. preceding abstract). The strain of *R. nigricans* used by the authors and by Gottschalk is the same. Fumaric acid is not produced by this mould from pyruvic acid.
H. D. KAY.

Production of gluconic acid by the *Penicillium luteum-purpurogenum* group. II. Optimal conditions for acid formation. H. T. HERRICK and O. E. MAY (J. Biol. Chem., 1928, **77**, 185—195).—Production of gluconic acid from dextrose by the above mould is favoured by a temperature of 25° and a concentration of 20—25% of dextrose; the optimal concentrations of salts have also been determined and the composition of the most suitable medium is given.
C. R. HARINGTON.

Spike disease of Sandal (*Santalum album*, Linn.). I. Diastatic activity of the leaves. R. SREENIVASAYA and B. N. SASTRI (J. Indian Inst. Sci., 1928, **11** *A*, 23—29).—Sap was extracted from leaves and stem by freezing in liquid air, grinding at the ordinary temperature, and pressing. Leaf powders were prepared from materials dried in a vacuum over calcium chloride. 2·0 c.c. or 0·25 g. respectively were allowed to act on 25 c.c. of 2% soluble starch for 20 hrs. at the ordinary temperature in presence of toluene. The sugar formed, after clearing the solution with colloidal ferric hydroxide, was determined as maltose by Bertrand's method. The diseased leaves showed markedly higher diastatic activity than healthy leaves, the figures corresponding to those for growing shoots, which have a similar composition to diseased leaves.
F. E. DAY.

Simultaneous determination of minute amounts of oxygen and carbon dioxide. W. O. FENN (Amer. J. Physiol., 1928, **84**, 110—118).—The apparatus and technique have been devised for the purpose of measuring the respiratory exchange of small amounts of tissues *in vitro*. The apparatus consists essentially of a differential volumeter (A., 1927, 583) in which the absorption of oxygen is measured volumetrically. The carbon dioxide produced is determined by means of the change in conductivity of a solution of barium hydroxide enclosed in the volumeter. The calibration of the instrument is described and a number of typical results are reported demonstrating that the respiratory exchange of 0·1 g. of tissue could be determined every ten minutes with a sensitivity of 0·05 $mm.^3$
R. K. CANNAN.

[Pipette for] micro-determination of sugar and chloride in blood. K. SCHUHECKER (Wien. med. Woch., 1927, **77**, 1519—1520; Chem. Zentr., 1928, i, 98—99).—A rinsing pipette is described, the use of which avoids that of the torsion balance.
A. A. ELDRIDGE.

Simple hydrogen electrode for use in biochemistry. A. D. GARRISON, H. O. NICHOLAS, and J. G. PASTERNACK (J. Lab. Clin. Med., 1926, **11**, 1091—1093).—The p_H can be determined with an accuracy of 0·03 in 1 c.c. of liquid.
CHEMICAL ABSTRACTS.

Distilled water for biological purposes. E. CANALS and M. MOUSSERON (Bull. Soc. Chim. biol., 1928, **10**, 472—477).—Water of low conductivity and p_H 5·5—5·6 may be obtained by the use of a pyrex still; that with similar conductivity and higher p_H often contains traces of alkali from the glass. The water maintains its properties better if kept cold and in the presence of platinum-black.
G. A. C. GOUGH.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1928.

General, Physical, and Inorganic Chemistry.

[Structure of Fraunhofer lines and quantitative spectrum analysis of the atmosphere of the sun.] W. Anderson (Z. Physik, 1928, **48**, 447—448).—The assumption made by Unsold (this vol., 456) that when the partial pressure of free electrons in the chromosphere is 10^{-6} atm. the latter still shows a continuous spectrum is held to be irreconcilable with observation. J. W. Smith.

Ultra-violet spectrum of radium emanation. S. Wolf (Z. Physik, 1928, **48**, 790—794).—About 100 new lines have been measured in the range 3600—2400 Å. A new form of spectrum tube was employed made of "uviol" glass, one end being blown to a thin bulb through which the ultra-violet light passed readily. J. W. Smith.

Relative intensity of spark and arc lines in the spark spectra of various elements. G. Nakamura (Japan. J. Phys., 1928, **4**, 165—169).—The spectrum of radiation emitted from the spark between two electrodes of different metals was analysed by a quartz spectrograph and the intensities were measured by means of a microphotometer. Two spectra of sparks between gold and the metal under test, and between this metal and one from another column of the periodic table, were obtained simultaneously and the relative intensities of the lines of the element under investigation were found. The ratio of the intensities of arc lines to spark lines in the spark spectra is intimately related to the number of the surface electrons of the atom of the material used as the opponent electrode. The ratio usually increases as the number of electrons in the atom increases. A. J. Mee.

Absolute intensity of the mercury line 2537 Å. P. Kunze (Ann. Physik, 1928, [iv], **85**, 1013—1057).—The absolute intensity of the mercury line 2537 Å. was measured by using a photo-electric method of investigating the selective absorption without the widening due to pressure. The apparatus and method are described in detail. A resonance chamber is used the construction of which is explained. The emission from the resonance chamber is discussed and it is shown that the lines may be distorted owing to deviations from the Maxwell distribution. It is possible to reduce the widening of the line due to the Doppler effect and make the line sharper by proper arrangements. The corrections for line structure, scattering due to diffraction and refraction in the resonance chamber, secondary resonance, and vapour pressure are discussed and calculated. The intensity obtained was reduced to the value for a vapour pressure of mercury at 20°; the graph connecting the values of the intensity so obtained and the vapour pressure was not quite horizontal, and on extrapolation to zero vapour pressure gave for the absolute intensity the value $5{\cdot}78 \pm 0{\cdot}13$, a value considerably greater than that obtained by earlier workers. The higher value is due to the elimination of the errors mentioned above. The case of complex structure is investigated. It is shown that it is possible to obtain from observations on widened lines the intensity of the undistorted line. The intensity does not depend on the magnitude of the Doppler widening. The intensity of the line was also determined for higher temperatures of the absorption chamber (up to 305°), and it was found that on extrapolation to zero vapour pressure as before, the same value for the intensity was obtained as when the chamber was at the ordinary temperature. A. J. Mee.

Measurement of radiation from a tungsten lamp. H. C. von Alphen (Ann. Physik, 1928, [iv], **85**, 1058—1088).—The spectral distribution and the intensity curve of radiation from a 6-volt lamp were determined by two methods, one photographic, the other pyrometric. The emissivity of the tungsten in the ultra-violet region was obtained as a function of the wave-length by comparison with a carbon lamp of which the emissivity is known. The agreement between the two methods is good. A. J. Mee.

Continuous emission spectra from the electrodeless discharge. G. Balasse (Bull. Acad. roy. Belg., 1927, [v], **13**, 543—546).—Continuous spectra from electrodeless discharges have been obtained with the elements potassium, rubidium, cæsium, cadmium, mercury, phosphorus, bismuth, sulphur, and iodine. These elements are distributed over five columns of the periodic table, a fact which renders it probable that the continuous spectrum should be obtainable with any element. *A priori*, the passage from one state of ionisation to another is sufficient to account for the production of the spectra. R. A. Morton.

New type of discharge in neon tubes. F. A. Long (Nature, 1928, **121**, 1020).—The nature of the discharge in a neon tube when used as a safety device (Proc. Leeds Phil. Soc., 1927, **1**, 185) differs from that produced in normal use. The investigations will be described elsewhere. A. A. Eldridge.

Arc spectrum of chlorine. O. Laporte (Nature, 1928, **121**, 1021).—Turner's lines (A., 1926, 550) are now identified as follows: 1396·5, $^2P_1$—$^4P_2$; 1389·9, $^2P_2$—$^4P_3$; 1379·6, $^2P_2$—$^4P_2$; 1363·5, $^2P_1$—$^2P_2$; 1351·7, $^2P_2$—$^2P_1$; 1347·2, $^2P_2$—$^2P_2$; 1335·8, $^2P_2$-

$^2P_1$. Although the terms arising from the configurations ($3p^6$) and ($3p^5$, $4s$) are still approximately "normal," the higher term group arising from ($3p^5$, $4p$) is of higher rank. The situation is similar to that in the arc spectrum of argon.

A. A. ELDRIDGE.

New regularities in the band spectrum of helium. W. E. CURTIS (Nature, 1928, **121**, 907—908).—Experimental results in substantial agreement with those just published by Dieke, Takamine, and Suga (this vol., 677) have been obtained. The effective electronic quantum numbers of the new levels are tabulated; the parhelium values are higher than the corresponding orthohelium values. Unambiguous evidence is thus available for the existence of molecular electronic levels which are additional to the ordinary atomic system of levels.

A. A. ELDRIDGE.

Continuous and band spectra of zinc vapour. H. VOLKRINGER (Compt. rend., 1928, **186**, 1717—1719).—A study of the spectra of zinc vapour resulting from an electrodeless discharge at gradually rising temperatures indicates that for low vapour densities the continuous spectrum obtained is due to the passage of free electrons from one orbit to another. For high vapour densities a band spectrum extending from 2975 to 4800 Å. results, and is due to unstable molecules formed from the zinc atoms, some of which have become excited. A number of atomic aggregations probably exist, since the bands and the continuous spectrum (maximum at 2570 Å.) on which they are superimposed have not the same origin, whilst the regions of the tube corresponding with maximum intensity are different in the two cases.

J. GRANT.

Hydrogen rays in the electric arc. (MLLE.) M. HANOT (Compt. rend., 1928, **186**, 1716—1717).—The H_β and H_γ rays have been studied by means of an electric arc between two copper electrodes, of which the anode is fixed whilst the cathode is attached to an electromagnet in series with the arc so that when the arc is broken it falls back on to the anode and re-strikes the arc. The difference in the absorption effects of these two rays is attributed to the difference in their structure previously indicated by a study of the spark discharge (this vol., 209). J. GRANT.

Spark spectra of chlorine and of bromine. L. BLOCH and E. BLOCH (Ann. Physique, 1928, [x], **9**, 554—555).—A correction (cf. *ibid.*, 7, 206; this vol., 98). C. W. GIBBY.

Band spectra of mercury. (LORD) RAYLEIGH (Proc. Roy. Soc., 1928, **A**, **119**, 349—357; cf. A., 1927, 1122).—A mercury band spectrum excited by fluorescence, with the continuous hydrogen spectrum as a source, is described. A remarkable feature of this spectrum is that the narrow band at 2540 Å. is found, although the resonance line 2537 Å. is absent. The band 2540 Å. has never before been obtained in emission without the resonance line accompanying it in much greater intensity. It is also observed that the region of continuous emission on the short-wave side of the bands 2345, 2338, 2334, etc. is traceable as far as 2150 Å., thus extending much beyond the position of the forbidden line 2270 Å. which was in a former investigation (*loc. cit.*) under other conditions the limit of this continuous spectrum. The series of emission bands 2345, 2338, etc. has been examined with large resolving power, using as source a high-tension alternating-current discharge in dense vapour, between mercury electrodes. No trace is observed of the underlying bands of 1 Å. spacing which are seen so clearly in absorption. A remarkable structure is found in the emission band 2482—2476 Å. described by Stark and Wendt as continuous (cf. A., 1913, ii, 647). The proper description of this structure in terms of the quantum theory is, however, problematic. This band does not occur in absorption.

L. L. BIRCUMSHAW.

Stark effect of the fine structure of hydrogen. R. SCHLAPP (Proc. Roy. Soc., 1928, **A**, **119**, 313—334).—An investigation of the influence of an electric field on the fine structure of the levels of the hydrogen atom, by a method embodying the new theory of fine structure which has developed out of the idea of the spinning electron. The work is based on the wave equations of Darwin and Dirac. Attention is directed chiefly to the two extreme cases of weak and strong fields. In weak fields, all the fine-structure levels except the highest split up into several, with separations proportional to the first power of the field; in the highest level the separations are proportional to the square of the field. The fine structure of each of the equidistant levels of the ordinary Stark effect in stronger fields is found. The case of H_α is worked out in detail. L. L. BIRCUMSHAW.

Spark spectrum of copper. A. C. MENZIES (Proc. Roy. Soc., 1928, **A**, **119**, 249—256).—The method of obtaining spectrograms with one very short exposure by the fusion of wires, described previously (this vol., 99), has now been used for copper in the Schumann region, where it has several advantages over the usual arc and spark discharges in a vacuum. The lines 1358·76, 1367·92, and 1472·38 Å. are allocated to (1^1S_0—a^1P_1), (1^1S_0—$a^3D_1{}^1$), and (1^1S_0— respectively. This identifies 1^1S_0, the basic term corresponding with the normal orbit of Cu II, with the term-value −21929·4. Photographs of the spectrum of copper–gold have been taken with a small quartz-prism spectrograph, the source being a Pfund arc. Taking as standards three calculated copper lines, the wave-lengths in the copper–gold spectrum have been measured, and are compared with their values as calculated by Shenstone (A., 1927, 389) and by McLennan and McLay (A., 1926, 875), respectively. The copper and gold wave-lengths are found to be consistent with one another, so that probably Shenstone's scheme of copper spark terms and McLennan and McLay's scheme for the gold arc are both correct. L. L. BIRCUMSHAW.

Structure of the yellow sodium lines (5890, 5896). H. SCHULER (Naturwiss., 1928, **16**, 512—513).—A special form of light source (A., 1926, 215) allows the light from metal vapours to be observed at very low temperatures. This materially reduces the Doppler effect so that finer line structure may be disclosed if electrical disturbances are eliminated. The investigation of the sodium resonance lines at the temperature of liquid air shows that the line 5890 Å.

consists of two components, $\Delta\lambda$ being $0{\cdot}02_1$ Å., and the intensity ratio being approximately 1 : 2·5, the weaker component being towards the violet. The line 5896 Å. also consists of two components, $\Delta\lambda$ being $0{\cdot}02_3$ Å. and the intensity ratio 1 : 2·0. The weaker component is again on the violet side. The fine structure of the *D*-lines has been analysed by means of a Perot–Fabry etalon. This has not hitherto been possible because of excessive pressure and Doppler effect. The new structure is unexpected both from quantum numbers and from the point of view of isotope effects. Nuclear effects are indicated.

R. A. MORTON.

Multiplets in the Co II spectrum. W. F. MEGGERS (J. Washington Acad. Sci., 1928, **18**, 325—330).—A portion of the under-water spark spectrum of cobalt (A., 1927, 910) has been re-measured, and by comparison of their behaviour in the spark and arc, several classes of spark lines have been recognised. Many lines absorbed in the under-water spark are partly self-reversed in the spark in air. A group in the region 2249—2449 Å. has been arranged as a trio of multiplets $^5F'$—$^5(D',F,G')$, whilst a weaker overlapping group (2192—2339 Å.) has been arranged on the basis of line intensities as a second trio of multiplets ^3D—$^3(P,D',F)$. The triplet-*D* term occurs in a strong group of lines 3353—3621 Å., constituting the intersystem combinations ^3D—$^5(D',F)$. The latter appear to be the only set of strong Co II lines lying within the range of solar spectrum transmitted by the earth's atmosphere, nearly all other strong lines being on the ultra-violet side of 2900 Å. Nine lines in the region 3353—3621 Å. are shown to be coincident as regards both intensity and wave-length with absorption lines in Rowland's "Preliminary table of solar spectrum wave-lengths." The very low intensities of these Co II lines in the sun is due to the fact that the lines involve excited states of ionised cobalt atoms.

R. A. MORTON.

Pseudo-spectrum of the energy matrix. A. WINTNER (Z. Physik, 1928, **48**, 731—732).

J. W. SMITH.

Explanation of some properties of spectra from the quantum mechanics of the spinning electron. II. J. VON NEUMANN and E. WIGNER (Z. Physik, 1928, **49**, 73—94).—Mathematical (cf. this vol., 344).

J. W. SMITH.

Absorption by excited hydrogen. N. ROBINSON (Z. Physik, 1928, **49**, 137—145).—Measurements have been made of the light absorption of hydrogen excited by unidirectional pulses of variable frequency obtained by rectifying damped wave trains of oscillations. Absorption takes place when the half-period of the frequency characteristic of the wave train is of the same order of magnitude as the life period of the excited hydrogen atom. The upper limit of the life period thus measured is 10^{-6} sec.

J. W. SMITH.

Spark spectrum of sodium. S. FRISCH (Z. Physik, 1928, **49**, 52—58).—The sodium spark spectrum generated in a discharge tube containing metallic sodium has been surveyed and more than 100 lines have been measured in the range 4000—2500 Å. A number of these lines have been classified in a manner analogous to that employed in the case of neon.

J. W. SMITH.

Series spectrum of sodium, Na II. I. S. BOWEN (Physical Rev., 1928, [ii], **31**, 967—968).—Seventy-four lines in the sodium spark spectrum are classified as combinations between 23 terms of Na II. The ionisation potential is 47·0±0·5 volts.

A. A. ELDRIDGE.

Theory of the excitation of spectra by atomic hydrogen. J. KAPLAN (Physical Rev., 1928, [ii], **31**, 997—1002).—The theory is based on the hypothesis that in a three-body collision two hydrogen atoms can be linked to form a molecule in any one of the vibration states of its normal electronic level. It is postulated that the probability of excitation of the third body is the greater, the nearer the energy required is to the difference between the energy of recombination and that retained by the hydrogen molecule in one of its vibration states.

A. A. ELDRIDGE.

Theory of the electric discharge through gases. P. M. MORSE (Physical Rev., 1928, [ii], **31**, 1003—1017).

Zeeman pattern of the hyperfine structure lines of the resonance line of mercury. W. A. MACNAIR (Physical Rev., 1928, [ii], **31**, 986—996).—The results already published (A., 1927, 804) are essentially correct. In addition, four anomalous perpendicular components have been found.

A. A. ELDRIDGE.

Stark effect and series limits. H. P. ROBERTSON and (MISS) J. M. DEWEY (Physical Rev., 1928, [ii], **31**, 973—982).—Following a consideration of the energy of conditionally periodic and aperiodic orbits in hydrogen-like atoms under the influence of an external electric field, it is concluded that the line spectrum of such an atom must end at a point on the long wave-length side of the normal series limit, and that the continuous spectrum may extend even further within the normal series limit.

A. A. ELDRIDGE.

Multiplet separations. S. GOUDSMIT and C. J. HUMPHREYS (Physical Rev., 1928, [ii], **31**, 960—966).—Formulæ for the separations of normal multiplets, arising from general configurations, are derived from the fundamental assumption that they are due to the interaction energy between spin and orbital magnetism of the electrons.

A. A. ELDRIDGE.

Multiplet separations for equivalent electrons and the Röntgen doublet law. S. GOUDSMIT (Physical Rev., 1928, [ii], **31**, 946—959).—Theoretical. Expressions are derived for the separation of multiplets arising from configurations of equivalent electrons. The properties of Lande's Γ factors are studied.

A. A. ELDRIDGE.

Negative absorption of radiation. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, **122**, 12—13).—When benzene is irradiated by monochromatic light, the radiation scattered by the molecules contains several spectral lines of modified frequencies. The difference between the incident and scattered frequencies is exactly equal to an infra-red frequency of the molecule, so that the process of

modified scattering involves the absorption of radiation by the molecule. Experimental results show the existence in the liquid of molecules at energy levels higher than the normal, and that the incident radiation induces a return to a lower state of energy. A. A. ELDRIDGE.

First spark spectrum of krypton. P. K. KICHLU (Naturwiss., 1928, **16**, 346).—The work of Abbink and Dorgelo (this vol., 338) furnishes material for the completion of the analysis of the first spark spectrum of krypton. The lowest states are ^2P-terms originating from an electron configuration $5N_2$, and these combine with a set of terms $^4P^2P^2D^2S$ coming from $4N_2O_1$. The next set of terms are obtained from $4N_2O_2$ combination. These terms and those from $4N_2O_3$ and $4N_2P_2$ have been obtained and account for about 200 lines. R. A. MORTON.

Structure of the negative bands of nitrogen. G. HERZBERG (Ann. Physik, 1928, [iv], **86**, 189—213).—The electrodeless ring discharge through nitrogen at very low pressures produces the negative bands in purity. On account of this purity of the spectrum, and because of its extent and brightness, it has been possible to observe the inversion point of the degradation of the bands. Tail bands analogous to the cyanogen tail bands appeared. It is concluded from the structure of these latter bands that N_2^+ can be dissociated in any elementary way by high-velocity electrons. W. E. DOWNEY.

Distribution of energy and luminosity in the cross-section of the positive column in neon and helium. G. ZWIEBLER (Ann. Physik, 1928, [iv], **86**, 241—290).—The energy is found to decrease from the middle of the column to the edge, quickly at first but more slowly as the edge is approached. The energy decrease in a section is greater the greater is the energy of the lines emitted from the section. At fixed current density, the energy decrease is, at first, less than proportional to the pressure, but with increasing pressure tends, asymptotically, to a limiting value. The intensity of the individual spectral lines increases at a greater rate than that of direct proportionality to the current strength.

W. E. DOWNEY.

Absorption of the vapour of excited mercury and reversal of the green ray and of its satellites. M. PONTE (Compt. rend., 1928, **187**, 37—39).—For rays of different series no relation exists between the intensity of the rays emitted by excited mercury vapour and that of the absorption of the corresponding arc rays. The rays $^3P_{012}{}^3S$, $^3P_{012}{}^3D_{123}$, $2^1P_1-m^1D_2$, and $2^1P_1-m^3D_2$ show absorption, the latter pair to a slight extent only. The *PS* series is more strongly absorbed than the *PD* series, the absorption of the rays 2^3P_0 and 2^3P_2 being equivalent in the former case, and 2^3P_0 showing a strong absorption in the latter. Reversal of the rays is best studied by the insertion of excited mercury vapour between the plate and a cooled Cotton arc, and was observed for λ 4358, for the green ray, and for six of its satellites, but not for the yellow rays. J. GRANT.

Photo-electric current as a function of the field in air at ordinary pressures. A. BLANC (Compt. rend., 1928, **186**, 1835—1837).—Comparison of the curves obtained for the same metal subjected to different illuminations with those for different metals showed that the form of the curve depends on the nature of the metal. Saturation is attained rapidly in a vacuum, since the number of electrons emitted does not depend on the field. At sufficiently high pressures, however, the electrons ionise the gas in accordance with Thomson's theory, the mean number of ions produced by each increasing with the field in a manner depending on the metal. The initial energy and capacity for ionisation of the electrons depend on the distance they travel in the direction of the field before meeting a molecule. They may even ionise several molecules before uniting with one of them, and saturation is not attained.

J. GRANT.

Resonance line of the iodine atom and the optical dissociation of iodine molecules. L. A. TURNER (Physical Rev., 1928, [ii], **31**, 983—985).—The line 1830·4 Å. is probably the resonance line of the iodine atom, corresponding with a critical potential of 6·75 volts. Strong illumination of iodine vapour apparently causes dissociation into atoms, since light of the above wave-length is more strongly absorbed by illuminated than non-illuminated vapour.

A. A. ELDRIDGE.

New photo-electric observation with thin layers of alkali metals. B. GUDDEN (Naturwiss., 1928, **16**, 547).—An alternative explanation of Suhrmann's work under the above title (this vol., 680) is given. R. A. MORTON.

Photo-electric and thermionic properties of iron. A. B. CARDWELL (Proc. Nat. Acad. Sci., 1928, **14**, 439—445).—The variation of the photo-electric current of iron with time of outgassing was determined. The variation is complex. After a time the photo-electric current increased in steps as the time of heating increased, changing less rapidly as the outgassing became more complete. A thoroughly outgassed specimen showed no fatigue for 12 hrs. after treatment. When this state was reached, the strength of the photo-electric current depended on the rate of cooling of the iron filament. There was a decrease in the photo-electric sensitivity if a filament heated above 910° was suddenly cooled, this being due to the retention of part of the γ-iron. The variation of the photo-electric current with temperature of the filament was investigated for iron which had been outgassed by heat treatment for 150 hrs. The variation is complex. Between about 475° and 768 there is a decrease in photo-electric current due to a pure temperature effect. At 768° (where there is a transition of α- to β-iron) the sensitivity remains constant or increases slightly. Near 910° (transition of β- to γ-iron) there is an abrupt decrease in the sensitivity. The thermionic current was also measured and plotted against heating current. There is an abrupt change in the curve at 910°. The long wave-length limit for thoroughly outgassed iron lies between 2580 and 2652 Å. The work function, obtained by substituting these values in Einstein's photo-electric equation, is 4·72+0·07 volts. The question of whether the abrupt changes in the photo-electric and

thermionic currents are due directly or only indirectly to the crystallographic changes in the iron is discussed. A. J. MEE.

Angular distribution of slow electrons on passing through metal sheets. E. RUPP (Ann. Physik, 1928, [iv], **85**, 981—1012).—The above distribution is photographically investigated. The metals used are chosen from those with cubical, tetragonal, and hexagonal space-lattices. The investigation covers two main effects : (*a*) the scattering of electrons in a sphere about the point of impinging as centre; (*b*) the " diffraction " of electrons into discrete rings. These electron diffraction rings can be fitted in with X-ray observations, using the Debye–Scherrer method. The calculated refractive indices of the metals for electrons always exceed unity. This is in apparent contradiction with the results of Davisson and Germer, who found the indices to be less than unity. If, however, the observations of these investigators for small angles only are taken, these give an index greater than one. The refractive index falls with increasing electron velocity, but for a given velocity is constant for a given metal. The inner lattice potentials are calculated from the values of the refractive indices; these lie between 10 and 20 volts for the metals considered, and within the accuracy of the experiments this potential is independent of the velocity. It appears to be a characteristic constant for any metal. A. J. MEE.

Mobilities of gas ions in sulphur dioxide and mixtures of sulphur dioxide and hydrogen. L. DU SAULT and L. B. LOEB (Proc. Nat. Acad. Sci., 1928, **14**, 384—393; cf. this vol., 453).—Two sets of values of mobilities were observed at atmospheric pressure in sulphur dioxide. The values for the supposedly less pure sample were 0·34 cm./sec. and 0·32 cm./sec., respectively, for positive and negative ions. For the other sample the values 0·48 cm./sec. and 0·44 cm./sec. on the same scale were observed. Negative electrons could not be detected down to 0·05 cm. pressure of sulphur dioxide in 3·8 cm. of pure hydrogen. The effect of sulphur dioxide at higher concentrations in sulphur dioxide–hydrogen mixtures is similar to the effect of ammonia in ammonia–hydrogen mixtures. At low concentrations the positive mobilities in hydrogen were 22 cm./sec. per volt/cm. W. E. DOWNEY.

Statistical experiments on the motion of electrons in gases. R. D'E. ATKINSON (Proc. Roy. Soc., 1928, **A**, **119**, 335—348; cf. Townsend, A., 1926, 3; Townsend and Focken, *ibid.*, 878).—An attempt to explain Townsend's experiments (*loc. cit.*) on the ionisation of gases by collision and the critical potential of gases on the basis of the quantum theory. The most important conclusion reached is that the ionisation potential of helium is below 25 volts. This result is discussed on the assumption that the gas always contains small quantities of impurities, and with special consideration to collisions of the second kind (*i.e.*, collisions between a normal and an excited, but not necessarily metastable, molecule, such that the potential energy of the excited molecule is wholly or partly removed from it; some of the energy thus made available may be used to put the second molecule into an excited state, and the balance appears in the form of kinetic energy). The production of ions in the gas at a voltage well below the ionisation potential is considered to be firmly established. The fact that above about 60 volts the current rises exponentially may be explained by consideration of the normal diffusion of the metastable atoms between the time of their formation and the collision of the second kind. The distance they will diffuse depends both on the amount of impurity present and on the diameter of the metastable atom. It is shown that α/p is a single-valued function of X/p (where α is the exponential constant of the curves, p is the pressure, and X the field strength), a relation experimentally obtained by Townsend. A somewhat similar verification is found by taking the statistical figure for the average loss of energy on collision. L. L. BIRCUMSHAW.

Direct determination of the magnetic moment of a single electron. T. SEXL (Z. Physik, 1928, **48**, 729—730).—A technique is devised for determining the magnetic moment of a single electron by studying the behaviour of small droplets in a magnetic field. J. W. SMITH.

Electrons and positive ions in pure argon. M. A. DA SILVA (Compt. rend., 1928, **187**, 32—35).—Mobility measurements with alternating in place of direct fields, for effective voltages of from 40 volts/cm., have confirmed the earlier conclusions (this vol., 341) that all the negative ions in pure argon, even at atmospheric pressure, are free electrons. The mobility (K) is related to the critical voltage (V_0), the frequency of the alternating field (n), and the distance between the condenser plates (d) by the expression $K = nd^2/V_0\sqrt{2}$. The critical voltage of the positive ions is also indicated on the curves. J. GRANT.

Attempt to add an electron to the nucleus of an atom. W. D. HARKINS and W. B. KAY (Physical Rev., 1928, [ii], **31**, 940—945).—Electrons with a velocity of $138—145\times10^3$ volts were caused to strike the surface of the liquid mercury anti-cathode of an X-ray tube; no gold was, however, detected. Hence, either too small a proportion of electrons became attached, or the nuclei produced were insufficiently stable. A. A. ELDRIDGE.

Lead isotopes and the problem of geologic time. C. S. PIGGOT (J. Washington Acad. Sci., 1928, **18**, 269—273).—The possibility of determining the ages of rocks by determination of the uranium : uranium-lead and thorium : thorium-lead ratios is discussed. J. W. SMITH.

[Relation between atomic number and] atomic weight. A. VON FISCHER-TREUENFELD (Ann. Physik, 1928, [iv], **85**, 1113—1116).—The following relationship is proposed between atomic number and atomic weight: $3(2n)^{\frac{1}{2}}+5([n-1]/3)^{\frac{1}{2}}+1\approx8w^{\frac{1}{2}}$, where n represents the atomic number and w the atomic weight of an element. The values for the atomic weights obtained by means of this expression agree fairly well with the usually accepted values. The formula is deduced from considerations of the nuclear atom. A. J. MEE.

Preparation of highly concentrated polonium by distillation. E. Rona and E. A. W. Schmidt (Z. Physik, 1928, **48**, 784—789).—Polonium is deposited on a large surface of platinum foil by electrolysis of a solution of radium-*D* in $0{\cdot}1N$-nitric acid, using a current density of 5×10^{-6} amp. per cm.^{2} The electrodes are then cut into thin strips and heated in a quartz tube in a current of hydrogen, the polonium being condensed in a platinum capsule cooled by means of a large copper rod.

J. W. Smith.

Visual observation of H-particles. H. Pettersson (Z. Physik, 1928, **48**, 795—798).—Two arrangements are described. In the first a polonium preparation is enclosed in a glass capillary of 20 μ wall thickness coated inside with a layer of paraffin wax of similar thickness. The α-particles are unable to penetrate the tube, whereas the H-particles generated in the paraffin wax pass readily through it and their paths are rendered visible by Wilson's method. In the second arrangement the polonium preparation is covered by a thin mica sheet, coated on the lower side with a thin layer of paraffin wax. Supported above this is a screen coated with zinc sulphide, scintillations being observed by means of a lens system mounted above the screen. J. W. Smith.

Photographic action of H-particles from paraffin and atomic fragments. M. Blau (Z. Physik, 1928, **48**, 751—764).—It is found that the sensitivity of the photographic plate is unsuitable for quantitative measurement of atomic scattering, but this method may be used conveniently for the qualitative detection of H-particles. J. W. Smith.

Radium content of Stone Mountain granite. C. S. Piggot (J. Washington Acad. Sci., 1928, **18**, 313—316).—The average radium content of Stone Mountain, Georgia, granite is $4{\cdot}826\times10^{-12}$ g. per g. of granite. C. W. Gibby.

[Apparatus for the determination of] the number of ions produced by the α-particles of radium-C' in air. (Mme.) I. Curie and F. Joliot (Compt. rend., 1928, **186**, 1722—1724).—The α-radiation of radium-C' has been compared with a radium standard by means of its γ-radiation and using an apparatus in which the ionisation produced by a known fraction of the total radiation of the source is measured. The low-speed β-rays are eliminated by a magnetic field, and the effect of the γ-rays is determined by measuring the ionisation produced with and without a magnetic field, and after interposing a series of aluminium screens 0·02—0·1 mm. thick. The easily absorbed γ-radiation from radium-*B* or -$C+C'$ has an ionising effect which is negligible compared with that of the α-particles. J. Grant.

Number of ions produced by the α-particles of radium-C' in air. (Mme.) I. Curie and F. Joliot (Compt. rend., 1928, **187**, 43—45).—The authors continue the description of their apparatus (see above) and its use. A final corrected value of 1944 ± 10 *E.S.U.* for the ionisation current produced in the angle 2π by the α-particles emitted from 1 millicurie of radium-C' was obtained, which gives 2·2 or $2{\cdot}36\times10^5$ for the number of ions produced by one α-particle from radium-C', according to the value taken for the number of α-particles from 1 g. of radium (3·7 or $3{\cdot}45\times10^{10}$, respectively). Exact proportionality of ionisation to energy is not obtained for the radiations of radium-C'. J. Grant.

Efficiency of β-recoil of thorium-*B*. K. Donat and K. Philipp (Naturwiss., 1928, **16**, 513).—In an earlier paper (this vol., 3) the efficiency of the β-recoil from thorium-*B* was found to be 2—6·5% of the theoretical. In order to test whether the low yield is due to evaporation of recoil atoms from the collecting surface, the latter has been maintained at low temperatures. At $-90°$ the efficiency was 9—11%, and at $-170°$, 33%. Further work is necessary to determine whether the yield becomes theoretical with extremely low temperatures. R. A. Morton.

Visibility of β-scintillations. H. Pettersson and G. Kirsch (Naturwiss., 1928, **16**, 463).—Polemical against Bothe and Franz (*ibid.*, 204).

W. E. Downey.

Regularity of radioactive disintegration. H. T. Wolff (Z. Physik, 1928, **48**, 745—746).—The relation advanced by Sokolow between the disintegration constant of an α-ray emitter and its number in the radioactive series also follows directly from the equation previously derived by Wolff (A., 1920, ii, 578) in connexion with the Geiger–Nuttall relation.

J. W. Smith.

Atomic fragments, reflected α-particles, and *X*-rays generated by α-particles. W. Bothe and H. Franz (Z. Physik, 1928, **49**, 1—26).—The atomic disintegration, measured by the H-particle emission, when beryllium, carbon, aluminium, and iron were bombarded with α-particles from polonium has been investigated. The values obtained are in agreement with those of Rutherford and Chadwick and show that the results of Kirsch and Pettersson were too high.

J. W. Smith.

Atomic groupings for emanations and mixtures of radioelements. (Mlle.) C. Chamie (Compt. rend., 1928, **186**, 1838—1840).—The author's experiments (A., 1927, 1120) have been extended and have shown that radon, thoron, or actinon liberated in air or dissolved in mercury form groups of atoms, whilst in mixtures of radioelements heterogeneous groups of atoms from both sources, and groups characteristic of atoms all of the same family, are both formed. J. Grant.

Mechanism of the oscillation of electrons. H. E. Hollmann (Ann. Physik., 1928, [iv], **86**, 129—188).—It is possible to obtain simultaneous electron oscillations of different kinds in the same valve. The different kinds of electron oscillation in the Barkhausen–Kurz decelerating field are described. Four frequency ranges are possible: (*a*) Barkhausen–Kurz oscillations; (*b*) Gill and Morrell oscillations; (*c*) by using a grid of finer mesh it is possible to obtain oscillations of higher frequency, which take place, not in the anode–cathode space, but between the anode and grid only; (*d*) by using a valve with electrodes of smaller dimensions it is possible to get oscillations of higher frequency. A. J. Mee.

Refraction quotient of the De Broglie waves of electrons. A. Joffé (Z. Physik, 1928, **48**, 737—738).—

Although the work of Schmidt discussed by Klemperer (this vol., 344) can be explained in a simple manner on the theory of wave mechanics, it by no means proves the latter theory, since the same result can be reached from ordinary electrostatics. J. W. SMITH.

Ionisation in the upper atmosphere of the earth. E. O. HULBURT (Physical Rev., 1928, [ii], **31**, 1018—1037).—A theory of the ionisation of the upper atmosphere of the earth by the ultra-violet light of the sun is based on known laws of pressures and constitution of the high atmosphere, ionic recombination, attachment of free electrons to neutral molecules, and diffusion of ions. A density of 10^4 to 10^5 electrons per cm.^{3}, or 10^9 to 10^{10} ions per cm.^{3}, or a suitable mixture of ions and electrons, seems possible down to 100 km. Ozone may be formed by ultra-violet light of wave-length 1300—1800 Å.

A. A. ELDRIDGE.

Correspondence relationship between matrices and Fourier coefficients in the theory of the hydrogen atom. C. ECKART (Z. Physik, 1928, **48**, 295—301).—Mathematical. R. W. LUNT.

Theory of magnetic electrons. I. D. IWANENKO and L. LANDAU (Z. Physik, 1928, **48**, 340—348).—Mathematical. R. W. LUNT.

Helium nucleus as the foundation of other atom nuclei. H. PETTERSSON (Z. Physik, 1928, **48**, 799—804).—From the point of view of the new at. wt. determinations of Aston, arguments are brought forward against the theory that elements in general are built up from helium nuclei.

J. W. SMITH.

Quantum theory of rotating electrons. F. MÖGLICH (Z. Physik, 1928, **48**, 852—867).—Mathematical. J. W. SMITH.

Dirac's theory of spinning electrons. J. VON NEUMANN (Z. Physik, 1928, **48**, 868—881).—Mathematical (cf. Dirac, this vol., 344, 456).

J. W. SMITH.

Dirac's theory of spinning electrons. A. LANDÉ (Z. Physik, 1928, **48**, 601—606).—Mathematical.

J. W. SMITH.

Application of the Fermi statistics to the distribution of electrons under fields in metals and the theory of electrocapillarity. O. K. RICE (Physical Rev., 1928, [ii], **31**, 1051—1059).—Theoretical. A. A. ELDRIDGE.

Statistical methods in quantum theory. R. J. CLARK and W. H. WATSON (Nature, 1928, **122**, 12).

Evidence for the continuous creation of the common elements out of positive and negative electrons. R. A. MILLIKAN and G. H. CAMERON (Proc. Nat. Acad. Sci., 1928, **14**, 445—450).—The evidence derived from the study of cosmic rays that the more stable and abundant elements (*e.g.* helium, oxygen, silicon, and iron) are being formed at the present time directly out of protons and electrons is summarised. (1) Pilot balloon experiments have shown that there are no strong radiations of wave-length intermediate between those of the γ-rays and the cosmic rays entering the earth's atmosphere. (2) The cosmic-ray spectrum consists of definite bands. Hence the rays cannot be formed in the same way as X-rays, as has been suggested, but are probably produced by definite and continually recurring atomic transformations involving energy changes of a magnitude much greater than any occurring in radioactive processes. (3) Using the Einstein equation and the Dirac formula, it is possible to show that the only transformations which can give rays of the penetrating power of the cosmic rays are those corresponding with the building up of the abundant elements from hydrogen. The complete breaking up of hydrogen might be another possibility, but there are reasons against this. (4) The results of previous work have shown that there are three cosmic-ray bands of absorption coefficients 0·35, 0·08, and 0·04 per m. of water, respectively. The theoretical absorption coefficients if the rays were produced (*a*) by formation of helium from hydrogen, (*b*) by formation of oxygen from hydrogen, (*c*) by formation of silicon from hydrogen, would be 0·30, 0·075, and 0·043, respectively. A. J. MEE.

Wave mechanics of the atom lattice. M. J. O. STRUTT (Ann. Physik, 1928, [iv], **86**, 319—324).—Mathematical. W. E. DOWNEY.

Mechanism of the reaction between sodium vapour and copper halides. II. V. KONDRATÉEV (Z. Physik, 1928, **48**, 310—322).—The reaction between sodium and potassium vapour and the vapour of cupric chloride and bromide in the neighbourhood of 300° has been examined. The spectrum of the light emitted by the reacting vapour is that of the corresponding cuprous halide. Following a discussion of the energy changes taking place with the formation of excited molecules of the cuprous halide, it is concluded that the reaction takes place at the surface of the containing vessel between solid cupric halide and gaseous alkali metal forming gaseous cuprous halide and solid alkali metal halide. Analysis of the solid product of the reaction confirms this view. The distribution of alkali metal halide along the length of the tube in which the alkali metal vapour meets the cupric halide vapour shows a sharp maximum, as also does the distribution of intensity of the light emission, which, however, lies nearer to the source of alkali metal vapour; this result, which also obtains in the reaction between sodium and mercuric chloride vapours, is analogous with that between sodium and iodine vapours.

Earlier experiments indicated that the reaction between sodium and mercuric chloride vapours was homogeneous. This has been confirmed by calculating the rate of formation of sodium chloride from the vapour pressure of the reacting vapours to be $21{\cdot}5\times10^{20}$ mols. per hr., whilst the experimental value is $5{\cdot}5\times10^{20}$. R. W. LUNT.

Afterglow of oxygen and nitrogen in air. K. STOCK (Z. Physik, 1928, **48**, 358—359).—Phenomena essentially similar to those described by Herzberg (this vol., 457) have been observed by examining the discharge in a vacuum tube in the pressure range 2—14 mm. in the direction of the flow of current.

R. W. LUNT.

H_α emission in the positive column. E. LAU (Z. Physik, 1928, **48**, 824—830).—The intensity and

polarisation of the H_α line from the positive column in a discharge tube have been examined with respect to the gas pressure in the range 0·05—0·7 mm. The observed Stark effect is of the same order as that calculated by Sommerfeld's theory. R. W. LUNT.

Spectroscopic analysis of the light obtained by molecular diffusion of a monochromatic radiation by a fluid. J. CABANNES and P. DAURE (Compt. rend., 1928, **186**, 1533—1534).—Spectroscopic measurements have been made of the change in wave-length, the symmetrical enlarging of the exciting ray, and of the diffusion spectra accompanying the Raman effect (this vol., 461) for benzene and ether excited by the rays 4046 and 4358 Å. Contrary to previous theories (this vol., 571, 686), secondary rays of frequency higher than that of the exciting ray were not detected in the diffusion spectra, and the emission of such rays is therefore not symmetrical with respect to the fundamental ray. J. GRANT.

First ultra-violet characteristic frequency of a simple crystal. R. HILSCH and R. W. POHL (Z. Physik, 1928, **48**, 384—396).—The ultra-violet absorption spectra of thallous chloride, bromide, and iodide and of lead chloride and iodide have been observed by mounting a crystal lamina of 1 mμ thickness under pressure between two silica plates. The first characteristic frequencies thus observed agree very well with those of alkali halide phosphors containing these substances in fine division. Additional data for the absorption spectra of crystalline iodine and silver halides are also given.

J. W. SMITH.

Broadening of hydrogen chloride lines by foreign gases. H. W. KUSSMANN (Z. Physik, 1928, **48**, 831—844).—The influence of various indifferent foreign gases has been investigated by absorption measurements, using a quartz lens method of focal separation. Argon, in spite of its atomic symmetry, exerts a strong influence, so the broadening is supposed to be due, not to an intramolecular effect, but to Lorentzian collision damping. Hence for any single foreign gas the absorption change brought about by the broadening of the line is proportional to the increase in the number of collisions, but this proportionality factor differs with different gases.

J. W. SMITH.

Light absorption of some salts. A. HANTZSCH (Z. physikal. Chem., 1928, **134**, 453—455).—The observation of Viterbi (A., 1927, 1122) that solutions of the alkaline-earth halides show marked selective absorption in the ultra-violet is confirmed for barium chloride. The relation between constitution and colour of mercuric iodide and of tin tetraiodide in the solid state and in solution is discussed. The view is maintained that red mercuric iodide is an associated " pseudo-complex salt " in the solid state, but is converted by dissolution into the unimolecular colourless pseudo-salt. O. J. WALKER.

Spectrum of the hydrogen molecule. O. W. RICHARDSON and P. M. DAVIDSON (Nature, 1928, **121**, 1018).—The following are believed to be the final vibrational differences ($1''\rightarrow 0''$, $2''\rightarrow 1''$, etc.) of the lowest rotational levels of the band systems previously examined (A., 1927, 916): 1312·55(4), 1276·60(2), 1242·382, 1209·062, 1176·33(3), 1144·00, 1112·08, 1081·29. Dieke and Hopfield's B states are considered to be identical with the authors' final states. The value $2B_o''=uw_0-31{\cdot}1$ is deduced.

A. A. ELDRIDGE.

Absorption of ultra-violet light by carbohydrates. L. KWIECIŃSKI, J. MEYER, and L. MARCHLEWSKI (Z. physiol. Chem. 1928, **176**, 292—293).—In general, pure sugars do not show selective absorption. A concentrated solution of α-methylglucoside shows a faint band about 2800 Å., but β-methylglucoside does not. Glucosan shows strong absorption. H. BURTON.

Absorption curves of the pulegonenols. J. SAVARD (Compt. rend., 1928, **186**, 1738—1741; cf. Schoû, A., 1927, 751).—The ultra-violet absorption curves of pulegone, pulegonenol, and of their corresponding *iso*-compounds show that replacement of the CO group by the C·OH group involves the disappearance of the first band (at 3000—3200 Å.) attributed to the former group, and the appearance of the first portion of a band in the extreme ultra-violet attributed to the latter. The position of the ethylenic band is not appreciably changed, although the intensity of its absorption maximum is lowered. There is evidence of molecular combination between pulegone and *iso*pulegone or its enol. J. GRANT.

Intermetallic compounds in the vapour state. The spectra of the alkali metals, and of their alloys with each other. J. M. WALTER and S. BARRATT (Proc. Roy. Soc., 1928, **A**, **119**, 257—275).—An apparatus is described for the determination of the vapour density of potassium by the Victor Meyer method at 950°. A special device was employed for the accurate weighing of the potassium (free from oxide) into the steel bottle. The results show that at 935° the ratio $[K_2]/[K]$ does not exceed 5×10^{-2}, and the conclusion is reached that the alkali metals at their b. p. contain not more than 5%, and probably only about 2%, of molecules of the type M_2. The band spectra of the alkali metals lithium, sodium, potassium, rubidium, and cæsium have been re-investigated and a number of new bands are described. Metals which are known to possess a measurable proportion of polyatomic molecules show bands in their absorption spectra, and the observation of such bands is considered a delicate test for the existence of association in the vapours. From an examination of the absorption spectra of the mixed vapours of the alkali metals it is shown that these metals form a complete series of binary molecules with each other in the vapour state. The band systems lie, in general, near the lines of the principal series of the constituent atoms, but the molecules containing lithium are exceptions to this rule. Most of the alkali metal molecules possess a distinct type of absorption spectrum, in addition to these band systems. The second type consists of an isolated diffuse band, which is probably a true continuous spectrum. It is suggested that these regions correspond with the continuous absorption of the halogen molecules, and the heats of formation of the alkali metal molecules have been worked out on this basis.

L. L. BIRCUMSHAW.

Ultra-violet absorption spectrum of chlorophyll in alcoholic solution. E. LEWKOWITSCH (Biochem. J., 1928, **22**, 777—778).—Absorption maxima are shown at 4200 and 3250 Å. No trace could be found of any further minimum or descent of the curve, which rose steeply below a wave-length of 2400 Å. S. S. ZILVA.

Absorption of plane polarised infra-red radiation by calcspar. F. MATOSSI (Z. Physik, 1928, **48**, 616—623).—The absorption of plane polarised infra-red radiation by calcspar, with the optical axis parallel with the electrical vector, has been investigated over the range 2—16 μ. Between 5·3 and 8 μ and round 11·5 μ measurements were also made with the optical axis in different positions. The loss by reflexion was measured and correction applied. Combination relations between the different absorption bands are deduced. J. W. SMITH.

Spectrum of gold chloride. W. F. C. FERGUSON (Physical Rev., 1928, [ii], **31**, 969—972).—Auric chloride vapour was introduced into a stream of active nitrogen, and the spectrum thus excited was examined in the region 7000—2000 Å. Except for certain atomic lines, it consisted of 43 bands comprising, for each isotope of aurous chloride, two intermingled systems in the green; all the bands were shaded towards the red. The vibrational intensity distribution agreed with that anticipated. Attempts to excite the spectra of gold bromide and iodide similarly were unsuccessful. A. A. ELDRIDGE.

Absorption spectrum of vitamin-*A*. R. A. MORTON and I. M. HEILBRON (Nature, 1928, **122**, 10).—Vitamin-*A* concentrates show a prominent absorption band at 328·5 μμ, the intensity of which accords with the potency as determined by the antimony trichloride test. Irradiation results in the disappearance of the chromogenic substance, and the destruction of the vitamin by aeration or oxidation is also confirmed by spectrographic observations. It appears probable that the first decomposition products of vitamin-*A* include a substance possessing an absorption band in the region 275—285 μμ.

A. A. ELDRIDGE.

Secondary radiation observed in the molecular diffusion of light by fluids (Raman effect). P. DAURE (Compt. rend., 1928, **186**, 1833—1835; cf. this vol., 461).—The frequencies of the secondary radiations are given by the formula $N-n_p$, where N is the frequency of the exciting radiation and n_p represents the characteristic constants of the fluid and is probably related to its infra-red absorption spectrum. Values of the latter are given. It has been shown for ether, ethyl alcohol, benzene, toluene, and aqueous salt solutions that spectra of fluids having a common radical contain some rays in common, some different, and some slightly displaced. Rays corresponding with the same molecular frequency have the same degree of polarisation, and the spectrum of a benzene–toluene mixture is the superposition of the constituent spectra (cf. Wood's fluorescence spectra). The intensities probably depend on that of the exciting ray and on the molecular density. J. GRANT.

Chemistry and band spectra. R. MECKE (Naturwiss., 1928, **16**, 521—529).—A lecture.

R. A. MORTON.

Absorption spectra of quinolphthalein and quinolsulphonephthalein. C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, **50**, 1772—1778).—The absorption spectrum of quinolsulphonephthalein in water or alcohol is closely similar to those which it and quinolphthalein exhibit in sulphuric acid and alcoholic hydrogen chloride, but differs entirely in type from the lactonoid spectrum of quinolphthalein or phenolphthalein in alcohol. This confirms the view (cf. *ibid.*, 1730) that free quinolsulphonephthalein is an internal salt, and suggests that all solutions of the first type contain salts of *m*-quinonoid derivatives. Quinolsulphonephthalein dibenzoate is probably also quinonoid, since its absorption spectrum differs in type from that of quinolphthalein dibenzoate. In alcoholic solution 100 mols. of potassium hydroxide convert quinolphthalein into a mixture of the blue di- and colourless tri-potassium salts and quinolsulphonephthalein into the dipotassium salt, whilst smaller proportions of alkali give mixtures of dipotassium salt and unchanged phthalein. In 33% aqueous potassium hydroxide both yield nearly colourless solutions of tripotassium salts. H. E. F. NOTTON.

Fluorescence of mercury vapour. H. NIEWODNICZANSKI (Z. Physik, 1928, **49**, 59—72).—The spectrum of the fluorescence radiation emitted by superheated mercury vapour excited by an aluminium spark has been investigated over the temperature range 245—910°. The bands generally became weaker with rising temperature, except the continuous band with an intensity maximum at about 3300 Å. which attains a maximum intensity at about 500°. In the presence of hydrogen all the lines and bands were much weaker, except the band with a long-wave convergence frequency of 2349 Å., of which the intensity remained unchanged. From the data obtained the carriers of the bands are deduced. The decrease in the intensity of the band with a convergence frequency of 2349 Å. with increasing vapour density in the saturated vapour is attributed to increased band absorption. J. W. SMITH.

Resonance fluorescence of cyanogen. G. HERZBERG (Naturwiss., 1928, **16**, 464—465).—The cyanogen bands occurring in the spectrum of active nitrogen are found to be due to resonance fluorescence excited by the ultra-violet bands.

W. E. DOWNEY.

Fluorescence of electrically [and optically] excited mercury vapour. S. PIENKOVSKI (Compt. rend., 1928, **186**, 1530—1532).—A study of the electrically excited fluorescence of moving mercury vapour of different densities by the use of colour filters has shown that the ray 4358 ($2^3S-2^3P_1$) is principally responsible for its excitation and the rays 4047 ($2^3S-2^3P_0$) and 5461 ($2^3S-2^3P_2$) to smaller extents. Optical excitation is produced principally by the ray 2537, and affects mercury atoms in the state 2^3P_1. The atoms then change into the state 2^3S under the influence of the ray 4358, the emission of fluorescence being connected with the subsequent

return of the atom to its normal state. The fluorescence of atomic mercury shows no appreciable retardation. J. GRANT.

Photo-luminescence of uranium salts. S. J. VAVILOV and V. L. LEVSCHIN (Z. Physik, 1928, **48**, 397—425).—The phosphorescence of uranium salt crystals, uranium glasses, and solutions follows the equation $I=I_0e^{t/\tau}$. Only on excitation by short-wave ultra-violet radiation does a second type of resonance appear, and this is of short duration. The resonance of solutions is dependent on the concentration and to a smaller extent on the temperature. The light emitted is not polarised. It is concluded that the photo-luminescence arises from radiating transformation in the excited molecule. J. W. SMITH.

Tesla luminescence spectra of the halogens. I. Iodine. S. S. BHATNAGAR, D. L. SHRIVASTAVA, K. N. MATHUR, and R. K. SHARMA (Phil. Mag., 1928, [vii], 5, 1226—1239).—The Tesla luminescence spectrum of iodine has been shown to have a continuous luminous background with sharp edges extending over the range λ 4800—2130 Å. A number of electronic emission bands are superimposed on this background. These comprise four systems, of which one has been analysed and shown to agree with the equation $\nu=29078+(710n'-8n'^2)-(213\cdot7n''-0\cdot6n''^2)$, where 29078 is the wave-number of the band at the head of the system. The fluorescence term $(213\cdot7n''-0\cdot6n''^2)$ is shown to arise from emission as the molecule returns from a higher excited state to the metastable $2p_1$ state. The strong bands at $\lambda\lambda$ 4800 and 3440 are discussed and an attempt is made to explain the continuous background. A. E. MITCHELL.

Chemiluminescence by oxidation of dyes with ozone. N. N. BISWAS and N. R. DHAR (Z. anorg. Chem., 1928, **173**, 125—136).—A large number of dyes (*e.g.*, eosin, safranine, thioflavine, etc.) dissolved in various solvents were treated with ozonised oxygen. Many of them emitted radiation in the form of light of definite wave-lengths. No light is seen if oxygen alone is used. It was found impossible to photograph the spectrum of the emitted light owing to its feebleness, but the wave-lengths were measured by means of a quartz spectrograph, and the intensities by a spectrophotometer. The relative intensity of the light for any particular dye depends on the solvent. The intensity is usually less in water than in alcohol. The effect of the addition of various substances (*e.g.*, nicotine, strychnine, benzaldehyde, etc.) to the dyes was investigated. In no case was the light increased by the addition of a foreign substance. Reducing substances suppressed it. The light is equally bright if the substance is fluorescent. The chemiluminescence spectrum does not correspond with the fluorescence spectrum. The relationship between chemiluminescence and fluorescence is discussed from the point of view of the activation of molecules, and the theory is applied to previous work on oxidation. A. J. MEE.

Supposed luminescence of liquids on adiabatic compression. G. TAMMANN and C. KROGER (Z. anorg. Chem., 1928, **171**, 364—366).—The momentary luminescence of liquids when subjected to sudden compression appears in some instances to be due to the compression of air bubbles present in the liquid, but it is not certain that this is always so. R. CUTHILL.

Light emitted by the reunion of iodine [atoms]. V. KONDRATÉEV and A. LEIPUNSKI (Naturwiss., 1928, **16**, 463—464).—The light emitted by heating iodine in air or in a vacuum has been examined by means of a visual spectroscope. Bands are found in the red, yellow, and green regions. It is concluded that the light has its origin in the reunion of an excited iodine atom with a normal atom to form a molecule. W. E. DOWNEY.

Chemiluminescence; energetics, spectra, intensity, and efficiency. E. Q. ADAMS (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 30—40).—For the emission of visible light, some atomic or molecular system must be in a state richer in energy by 37—71 kg.-cal. per mol. than some lower state to which spontaneous transition is possible. Quantitative data for luminescence spectra are surveyed. The efficiency of chemiluminescence reactions is usually far below 1%. CHEMICAL ABSTRACTS.

Chemiluminescence; photochemistry and chemiluminescence; kinetics of chemiluminescence. H. S. TAYLOR (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 41—49).—Chemiluminescence processes, which are the reversal of photochemical and photosensitised processes respectively, are considered generally. CHEMICAL ABSTRACTS.

Chemiluminescence; experimental methods. A. H. PFUND (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 23—29).—A survey. CHEMICAL ABSTRACTS.

Chemiluminescence; types. A. D. GARRISON (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 7—22).—Chemiluminescence reactions are direct or indirect; in the latter the chemical reaction occurs as an intermediate transformation of some other form of energy into light. CHEMICAL ABSTRACTS.

Bioluminescence. E. N. HARVEY (Bull. Nat. Res. Council, U.S.A., 1927, No. 59, 50—62).—A survey of the bioluminescence of *Cypridina*, and its mechanism. CHEMICAL ABSTRACTS.

Phosphorescence in relation to electrical phenomena. R. W. POHL (Naturwiss., 1928, **16**, 477—484).—A crystalline phosphor at a low temperature can store up radiant energy and retain it. Excitation at higher temperatures is accompanied by emission of a part of the absorbed energy during the activation process. The liberation of energy is increased by exposure to infra-red or long-wave radiation. By long-wave radiation is meant those rays which are absorbed by the excited phosphor and not by the unexcited material. Excitation consists in the liberation of electrons by photo-electric effects; luminosity arises from the return of such electrons to the normal state. When it is stated that phosphorescence is a result of photo-electric phenomena, it is not implied that photo-electric conduction is restricted to phosphors. With crystals exhibiting a high refractive index (*e.g.*, >2), a photo-electric primary current is quite general, and with crystals showing a lower refractive index the effect can be obtained by pre-

paring special crystals; *e.g.*, sodium chloride which has been treated with sodium vapour becomes yellow and exhibits photo-electric conduction. The return to its normal position of a photo-electrically displaced electron is not the sole condition determining phosphorescence. The best definition of a phosphor appears to be: an insulating crystalline material with which a minute trace of a highly refracting substance has been incorporated in the molten state. Luminosity is only an accessory phenomenon, and it may be absent in cases where the essentials (light absorption, electrical phenomena, etc.) are present. This view makes the absorption spectra of phosphors very important; in most cases, however, the sintered micro-crystalline powders are difficult to investigate, not only because of their physical nature, but also because the absorption of the phosphorogen may be masked by that of the diluent.

A series of alkali halide phosphors with traces of thallium chloride and lead chloride as phosphorogens has been prepared and has proved amenable to spectroscopic investigation because large crystals can be grown and polished and cut into sections. The thallium phosphors exhibit sharp absorption bands at about 250 and 193 μμ, whilst a lead–potassium chloride phosphor shows bands at 273 and 196 μμ. Pure thallium chloride shows bands at about 250 and 220 μμ, whilst lead chloride has bands at 270 and 220 μμ. These results show that a phosphor can be regarded as a mixed crystal with a very low concentration of one component. Apart from secondary "solvent" shifts, the absorption spectra show that the characteristic frequencies of the ultra-violet dispersion electrons of the substance present in small concentration (phosphorogen) represent the activating rays of the phosphor. R. A. MORTON.

Quantum yield in the photolysis of silver chloride. P. FELDMANN (Naturwiss., 1928, **16**, 530—531).—Gelatin-free silver chloride has been exposed to monochromatic light (365 μμ) under conditions such that the whole of the incident light was absorbed. The halide was immersed in water so that the liberated chlorine would appear as hydrochloric and hypochlorous acids. Analysis of the solution by the method of Lange and Schwartz (A., 1926, 701) indicated that the ratio chlorine atoms/quanta is $0{\cdot}86 \pm 2\%$. The ratio is much lower with silver chloride exposed to light before the experiment. The slight departure from Einstein's law of photochemical equivalence is ascribed to absorption by silver formed in the photochemical reaction.

R. A. MORTON.

Dielectric constant of benzene–toluene mixtures. R. D. SCHULWAS-SOROKINA (Z. Physik, 1928, **48**, 426—437).—Colley (*ibid.*, 1909, **10**, 663) reported that in benzene–toluene mixtures the dielectric constant measured for damped wave trains, in which the train frequency was 10^8 sec.$^{-1}$, when expressed as a function of the toluene concentration exhibited a number of maxima which were attributed to the liberation of photo-electrons by the electric field. In order to investigate this phenomena, determinations of the dielectric constant of such mixtures have been made in undamped alternating electric fields of frequency corresponding with a wave-length of 190 m. No evidence of the phenomena reported by Colley has been observed. R. W. LUNT.

Effect of radioactive radiation on the dielectric constant. G. GUEBEN (Bull. Acad. roy. Belg., 1927, [v], **13**, 509—525).—A more detailed account of work already published (this vol., 460).

Dielectric constants of ammonia, phosphine, and arsine. H. E. WATSON (J. Indian Inst. Sci., 1928, **11A**, 41—61).—An amplified account of work already published (see this vol., 107).

Variation of dielectric constant of liquids with pressure. L. CAGNIARD (Ann. Physique, 1928, [x], 9, 460—553).—A sensitive method for measuring dielectric constants by means of a Wheatstone's bridge is described, having a sensitivity of 1 in 6×10^4. The variation of the pressure coefficient with temperature has been measured for carbon tetrachloride, hexane, *cyclo*hexane, and amyl alcohol, from 1° to 24°. For dipolar dielectrics $\delta\varepsilon/\delta p$ and $[1/(\delta\varepsilon/\delta p)](\delta^2\varepsilon/\delta p\delta T)$ are less, and for other dielectrics greater, than the values calculated from Debye's formula. C. W. GIBBY.

Variation of dielectric constant of some gases with temperature at different pressures. H. A. STUART (Z. Physik, 1928, **48**, 747).—A discussion of Forro's results (this vol., 347).

Dielectric polarisation of liquids. I. Dielectric constants and densities of solutions of the chlorobenzenes in benzene and in hexane. C. P. SMYTH, S. O. MORGAN, and J. C. BOYCE (J. Amer. Chem. Soc., 1928, **50**, 1536—1547).—A capacity bridge suitable for determining the dielectric constants of liquids is described. The constants and densities at 0°, 25°, and 50°, of solutions of chlorobenzene, and *o*-, *m*-, and *p*-dichlorobenzenes in benzene and in hexane are recorded. The curves representing the variation of density, dielectric constant, and polarisation as functions of the mol. fraction of solute indicate that the molecules influence one another more strongly the greater are their moments and their concentrations, and the lower is the temperature.

S. K. TWEEDY.

Dielectric polarisation of liquids. II. Temperature dependence of the polarisation in certain liquid mixtures. C. P. SMYTH and S. O. MORGAN (J. Amer. Chem. Soc., 1928, **50**, 1547—1560).—The dielectric constants and densities of liquid solutions of ethyl bromide, chloroform, and chlorobenzene in hexane are recorded over the maximum temperature range. A special form of pyknometer is described. Approximate values for the polarisation due to the shifts of atoms and groups of atoms are obtained, and Debye's equation is shown to hold for infinitely dilute liquids. As before, the molecules affect one another more strongly the greater are their moments and concentrations and the lower is the temperature (cf. preceding abstract).

S. K. TWEEDY.

Molecular and atomic volumes. XIX. Density of the chlorides of uranium, tungsten, and molybdenum. W. BILTZ and C. FENDIUS (Z. anorg. Chem., 1928, **172**, 385—394).—Details are

given of the preparation and the results of density determinations of the following chlorides: UCl_4, *d* 4·854; UCl_3, *d* 5·440; WCl_6, *d* 3·520; WCl_5, *d* 3·875; WCl_4, *d* 4·624; WCl_2, *d* 5·436; $MoCl_5$, *d* 2·928; $MoCl_3$, *d* 3·578; $MoCl_2$, *d* 3·714. The molecular volume of chlorine in the different compounds at 0° has been calculated and compared with the molecular volume of free chlorine. In the higher chlorides the two agree very closely, but in the lower chlorides the molecular volume of combined chlorine is either above or below that of free chlorine, the largest value being in the lowest, *i.e.*, the most unsaturated chloride. If the molecular volumes of the halides are compared in the uranium, aluminium, and indium chlorides, bromides, and iodides, it is found that, for UCl_4, $AlCl_3$, $InCl_3$, and $InBr_3$ the molecular volumes of the halogens are practically the same in the free and combined states. These substances all form an ionic crystal lattice. For UBr_4, $AlBr_3$, UI_4, AlI_3, and InI_3 the molecular volume of the combined halogen is considerably greater in all cases than that of the free halogen, and the deviation is about the same for each. These substances all form a molecular lattice. The results thus point to a morphological origin for the deviation of molecular volumes from additivity. M. S. Burr.

Molecular and atomic volumes. XX. Density measurements of iodine chlorides. E. Birk (Z. anorg. Chem., 1928, **172**, 395—402).—Density determinations have been made on solid α- and β-iodine monochlorides with air in the pyknometer instead of liquid, the volume of the air being determined by driving it out with a current of carbon dioxide and measuring in a eudiometer. The stable α-form has a molecular volume of 42·1 at 0°, and the labile β-form 44·8, whilst liquid iodine monochloride has a molecular volume of 52·3 at 29°. The results are in agreement with the rule that the labile form of a monotropic substance passes into the stable form with contraction of volume, and also that the molecular volume of the α-form is equal to the product of the factor 0:81 and the molecular volume of the liquid phase in the neighbourhood of the m. p. At 0° Abs. the molecular volume of α-iodine monochloride is corrected to 40·9, and the sum of the molecular volumes of iodine and chlorine is 40·8. The agreement is within the limits of experimental error. The density of solid iodine trichloride has been determined, using liquid chlorine as the pyknometer liquid. The molecular volume at —40° is 72·84. When reduced to 0° Abs. this becomes 70·7, whereas by calculation it is 73·8, indicating that the formation of the trichloride is accompanied by a small contraction. M. S. Burr.

Non-polar linking and atomic refraction. I. R. Samuel (Z. Physik, 1928, **49**, 95—136).—A modification of Lewis' octet theory is suggested by the assumption that even in non-polar combination one electron only is essentially concerned in the union, so that one atom is more positive and the other more negative than its partner. For non-polar inorganic molecules, molecular refraction can be divided into atomic refractions so long as the kind of linking and valency are borne in mind. Thus from atomic refractions the type and strength of the bindings in a non-polar compound can be deduced. J. W. Smith.

Dispersion of magnesium sulphide. M. Haase (Z. Krist., 1927, **66**, 236—238; Chem. Zentr., 1928, i, 1012).—Magnesium sulphide has n_{540} 2·284±0·002, n_{570} 2·277±0·002, n_{615} 2·266±0·001, n_{640} 2·259±0·001, *V* 41±3. A. A. Eldridge.

Potassium, rubidium, cæsium, ammonium, and thallium tetroxalates. M. W. Porter (Z. Krist., 1927, **66**, 217—235; Chem. Zentr., 1928, i, 1015).—Potassium trihydrogen oxalate, $KHC_2O_4,H_2C_2O_4,2H_2O$, has *d* 1·860, and is triclinic, $a:b:c$=0·6001 : 1 : 0·6643, α 86° 2′, β 100° 4′, γ 78° 42′; strong negative double refraction; n_α 1·4152, n_β 1·5364, n_γ 1·5604. The rubidium salt has *d* 2·124, $a:b:c$=0·5909 : 1 : 0·6774, α 85° 20′, β 97° 43·5′, γ 97° 36′ (?); strong negative double refraction; n_α 1·4210, n_β 1·5428, n_γ 1·5595. The ammonium salt has *d* 1·655, $a:b:c$=0·6019 : 1 : 0·6865, α 85° 49′, β 97° 50′, γ 79° 43′; n_α 1·4237, n_β 1·5500, n_γ 1·5687. The cæsium salt has *d* 2·352, $a:b:c$= 0·5826 : 1 : 0·6917, α 85° 23′, β 95° 13′, γ 80° 34′; n_α 1·4365, n_β 1·5523, n_γ 1·5621. The thallous salt has *d* 2·992, $a:b:c$=0·5854 : 1 : 0·6859, α 84° 58′, β 96° 59′, γ 80° 4′; n_α 1·5097, n_β 1·6319, n_γ 1·6538. A. A. Eldridge.

Rotatory dispersion of solutions. R. Lucas (Ann. Physique, 1928, [x], **9**, 381—459).—The rotatory dispersion of tartaric acid and of ethyl and methyl tartrates has been measured in various solvents, for seven wave-lengths between 6780 and 4358 Å. The results can be explained on the assumption that mixtures of three forms, in discontinuous equilibrium, are being dealt with. Stereochemical configurations are proposed in the light of this suggestion, and their consequences applied to anomalous electric and magnetic birefringence and to polymorphism. Similar measurements on camphor and *l-iso*borneol indicate the existence of two forms. C. W. Gibby.

Anomalous rotatory dispersion from the point of view of the Drude equation. C. E. Wood and S. D. Nicholas (J.C.S., 1928, 1671—1696).—The rotatory dispersions of monoacetyl, diacetyl, monobenzoyl, and dibenzoyl derivatives of dimethyl and diethyl *d*-tartrates have been measured together with those of ethyl thionyl-*d*-tartrate and ethyl dichlorosuccinate. For all compounds exhibiting anomaly, inflexion and maxima were confined to the positive region of rotation, and at the crossing of the axis $d\alpha/d\lambda$ was always positive. The interpretations of anomaly in terms of the theories of Wood or Lowry are rejected as being incomplete and it is suggested that anomaly is due to one or more rotations of electronic origin in the ultra-violet, together with a rotation of molecular origin, due to atomic oscillations in the infra-red. The sign of the infra-red term is dependent on the configuration of the molecule and is negative for the *d*-configuration and positive for the *l*-configuration. Lowry's criteria for anomaly (A., 1915, ii, 660) are, therefore, also criteria for relative configuration. F. J. Wilkins.

Rotatory dispersion. Intersections of dispersion curves and of temperature–rotation

curves. C. E. Wood and S. D. Nicholas (J.C.S., 1928, 1696—1712; cf. preceding abstract).—The curves are discussed from the point of view of the evidence which they provide for the decision of problems of relative configuration. If the maxima of positive or negative rotation are to the right of the region of anomaly, then at the crossing of the axis $d\alpha/dT$ is positive for a compound of *d*-configuration and negative for a compound of *l*-configuration, and maxima move to a higher temperature with decrease of wave-length. If the maxima are to the left, the contrary relationships hold. In the absence of anomaly the configuration may be decided by a consideration of the direction of crossing of the axis, and the possibility of the intersection of temperature-rotation curves in the positive region. It is further assumed that the presence and movement of negative minima are temperature relationships for enantiomorphs. These in conjunction with an analogous set of defining conditions to those used with maxima of positive and negative rotation may be employed to solve problems of configuration. F. J. Wilkins.

Anomalous rotatory dispersion of configuratively related compounds. C. E. Wood and S. D. Nicholas (J.C.S., 1928, 1712—1727; cf. preceding abstracts).—The application of anomalous rotatory dispersion to the determination of relative configuration is made according to the criteria established in the previous papers. In this way the configurations assigned to *l*-lactic, *l*-malic, *d*-hexahydromandelic, and *d*-tartaric acids are respectively "*d*," "*l*," "*l*," and "*d*," which is in agreement with the conclusions of other investigators. Further, from a detailed consideration of a series of optically active alcohols it is shown that the distinction between "*d*" and "*l*" normal alcohols depends only on the relative lengths of their chains. Thus an alcohol

$$\mathrm{H}-\overset{\mathrm{R'}}{\underset{\mathrm{R}}{\mathrm{C}}}-\mathrm{OH}$$

belongs to the "*d*" series if R>R′ and to the "*l*" series if R<R′. The relationship of the α-hydroxy-acids to these alcohols is also discussed. The influence of variation of radicals and temperature on the rotatory dispersion of series of alcohols is considered particularly in relation to their bearing on the question of relative configuration.

F. J. Wilkins.

Rotatory dispersion of optically active co-ordination compounds. C. E. Wood and S. D. Nicholas (J.C.S., 1928, 1727—1738; cf. preceding abstracts).—The methods have been applied to a discussion of the configuration of co-ordination compounds in the light of measurements of their rotatory dispersions. The results support Werner's view, as against Jaeger's, that the dextrorotatory rhodium and iridium compounds have the "*l*"-configuration. Whilst the algebraic sign of the hemihedral form of the co-ordination compounds considered indicates the relative configuration, no generalisation can, at present, be made. F. J. Wilkins.

Uniaxial optically active crystals. G. Friedel (Compt. rend., 1928, **186**, 1788—1790).—The author contests the deductions of Burger (A., 1927, 1126), particularly his fundamental supposition that the lattice of uniaxial optically active crystals results from the pseudo-symmetry of the crystal edifice regarded as a whole. He considers that the stability of the edifice does not necessarily depend on periodicity or quasi-periodicity, since a lattice may be formed when the periodicity is interrupted and the edifice composed of a number of homogeneous elements variously oriented. Calcite, in which there is not the least pseudo-symmetry with respect to the plane (110), is cited as an example. J. Grant.

[Rotatory dispersion of alkyl aspartates.] M. L. Pagliarulo (Atti R. Accad. Lincei, 1928, [vi], **7**, 577—579).—A reply is made to Mazza's criticism (A., 1927, 500; this vol., 460) of the author's results (A., 1927, 610), which represent the mean values of large numbers of measurements and may be regarded as accurate. T. H. Pope.

New quantum statistics of distribution phenomena. R. Furth (Z. Physik, 1928, **48**, 323—339).—Mathematical. R. W. Lunt.

Nature of the *cis*- and *trans*-isomerism of platinum salts. A. A. Grinberg (Ann. inst. platine, 1927, **5**, 365—366).—By Kurnakov's reaction with thiocarbamide, the nature of the isomerism of diamminoplatinous thiocyanate is shown to be identical with that of the isomerism of Peyronet's chlorides and other salts, and Reise's second base. Both isomerides are unimolecular.

Chemical Abstracts.

Valency and the rule of eight. W. H. Rodebush (Nature, 1928, **122**, 56—57).—A critical note concerning London's theory of valency (this vol., 344).

A. A. Eldridge.

Constitution rules. F. Wratschko (Pharm. Presse, 1928, **33**, 11—14; Chem. Zentr., 1928, i, 1015).—Two rules, the linking rule and the nucleus rule, are put forward, whereby the structure of organic compounds can be derived from a knowledge of the empirical formula and the density of the liquid substance. A. A. Eldridge.

Electronic theory of valency. VI. Molecular structure of strong and weak electrolytes. (*b*) Reversible ionisation. T. M. Lowry (Phil. Mag., 1928, [vii], **6**, 50—63).—See A., 1927, 1026.

Exact measurements in the *K*-series of tin. J. Stenman (Z. Physik, 1928, **48**, 349—357).—The following values have been assigned to the K α_1, α_2, β_1, β_2, and β_3 lines of tin from measurement with a calcite grating: 489·572, 494·016, 434·297, 424·992, and 434·947 X., respectively. The wave-length of the K absorption limit of bromine is 918·091 X.

R. W. Lunt.

Precision measurements of the *K*-series of iron, cobalt, nickel, manganese, and chromium. S. Eriksson (Z. Physik, 1928, **48**, 360—369).—By using a calcite grating and a new form of precision telescope spectrometer, measurements have been made of a number of lines in the *K*-series of iron, nickel, cobalt, chromium, and manganese. The following values are given: Fe α_1, α_2, β_1, β', β_2, 1932·076, 1936·012, 1753·013, 1756·46, 1740·80; Ni α_1, α_2, β_1, β', β_2, 1654·503, 1658·353, 1497·045, 1499·10, 1485·61; Co α_1, α_2, β_1, β', β_2, 1785·287, 1789·187,

1617·436, 1620·11, 1605·62; Cr α_1, β_1, β_2, 2285·033, 2288·907, 2080·586, 2066·71; Mn α_1, α_2, β_1, β', β_2, 2097·506, 2101·489, 1906·195, 1910·50, 1893·27 X., respectively. R. W. LUNT.

X-Ray examination of celluloid. K. H. UEDA (Z. physikal. Chem., 1928, **133**, 350—356).—If nitrated ramie fibres are caused to take up camphor, two "amorphous" rings, due to the superposition of the interferences of camphor and cellulose nitrate, appear in the X-ray diagram, and with increase in the amount of camphor these become more and more intense, and the original fibre diagram becomes less and less distinct, until ultimately the diagram becomes identical with that of celluloid. With variations in the relative amounts of the components of celluloid, the positions and intensities of the two rings constituting the diagram vary, but the effects observed are merely those which would be expected from a solid solution; there is no indication of compound formation. With celluloid containing 70% of camphor, camphor crystals can be detected, and crystallisation can also be induced by stretching in celluloid containing less camphor. A cellulose nitrate film gives the cellulose nitrate fibre diagram if stretched. R. CUTHILL.

Quantitative X-ray analysis by cold excitation of spectra. R. GLOCKER and H. SCHREIBER (Ann. Physik, 1928, [iv], **85**, 1089—1102).—The various errors attending the use of X-ray analysis for quantitative analysis by finding the intensities of lines in the spectrum can be diminished by using the cold excitation of the characteristic radiation of the substance by means of X-rays. The proportions of two elements in a mixture can then be determined by comparing the intensities of the lines due to each substance. The theory of the method is given, and the relationship between the potential of the tube and the intensities of the lines is investigated theoretically and experimentally using the $K\alpha$ lines of vanadium and titanium. The effect of the mixture of different elements is also worked out. A. J. MEE.

Fluorescence secondary X-radiation and the J-phenomenon. W. H. WATSON (Phil. Mag., 1928, [vii], **5**, 1145—1163).—Previous work (A., 1927, 3) in which evidences of the "J" absorption effect in the transmission of the secondary X-radiation from paraffin wax through aluminium were obtained has been confirmed and extended to absorption by silver and copper. The ratio of the ionisations produced by two secondary beams from a radiator the K-characteristic radiation of which was excited did not change continuously when the amount of absorbing material was increased, but exhibited discontinuities in relation to this thickness which are apparently identical with the J-absorption discontinuities previously observed. Except for the effects of crystal reflexion in the radiator, practically pure monochromatic K-radiation was obtained. The changing of the orientation of the radiator with respect to the primary beam led to the displacement of a discontinuity, necessitating a different thickness of absorbing material for its reproduction. The results show that the J-phenomenon may be of periodical recurrence in absorption without appreciable change in the absorption coefficient of the beam in its passage through the absorber. A. E. MITCHELL.

Modified scattered X-radiation and superposition. The J-phenomenon. VIII. C. G. BARKLA (Phil. Mag., 1928, [vii], **5**, 1164—1171).—The change from unmodified to modified scattered radiations has been shown to occur not by passing through a certain critical average frequency as measured by the average absorption coefficient as shown previously by Barkla and Sale (Phil. Mag., 1923, [vi], **45**, 737) and others, but in this case it has been obtained by the superposition of radiations of the same frequencies in almost exactly the same proportions. The degree of modification, as measured by absorption methods, increased rapidly with the thickness of the scattering medium and approached a limiting value. A. E. MITCHELL.

X-Ray investigation of stannic sulphide, and titanium disulphide, diselenide, and ditelluride. I. OFTEDAL (Z. physikal. Chem., 1928, **134**, 301—310).—The position of the lines and their intensity in the X-ray diagram of titanium disulphide, diselenide, and ditelluride were determined, and it was shown that they could be explained by assuming a structure similar to cadmium iodide. This had already been shown for stannic sulphide. The powder method was used. The intensities calculated agree well with those observed. A table of dimensions of the lattices is given. A. J. MEE.

Structure of stretched synthetic rubber. L. HOCK and W. BARTH (Z. physikal. Chem., 1928, **134**, 271—278).—The Röntgen diagram of stretched synthetic rubber at the ordinary temperature and at −60° was investigated, and compared with that of the natural product. The diagram for stretched and cooled synthetic rubber does not show such clear lines as the diagram for the natural product, but there is a tendency to line formation. The identity period appears to be the same for both the natural and synthetic rubber, but owing to experimental difficulties it was impossible to make any very accurate numerical deductions. A. J. MEE.

Röntgen diagrams of cellulose nitrate and cellulose acetate. S. VON NARAY-SZABÓ and G. VON SUSICH (Z. physikal. Chem., 1928, **134**, 264—270).—The Röntgen diagram of cellulose nitrate was investigated, the distances being measured with a probable error of ±0·1 mm. The value of the "identity period" is 26·6±0·5 Å. The experiments were carried out with cellulose nitrates of varying nitrogen content. Those with nitrogen contents between zero and that required by cellulose trinitrate give diagrams in which the interference due to pure cellulose and that due to cellulose trinitrate are superimposed. It thus appears that the mono- and di-nitrate do not have definite lattices like the trinitrate, and that their existence as well-defined, stable, stoicheiometric compounds is improbable. Cellulose acetate was also investigated, compounds with an acetyl content of from 20% to 42% being used. The "identity period" in this case is 10·3±0·3 Å. Here, too, the positions of the points in the diagram did not vary with the acetyl content. It is

therefore concluded that only the triacetate exists as a well-defined compound with a definite lattice.

A. J. MEE.

Spectrography of γ-rays by crystalline diffraction. M. FRILLEY (Compt. rend., 1928, **186**, 1614—1615).—The author's apparatus (this vol., 215) has been used to study the lines 16, 24, and 29·5 (from radium-*C*) and 26 (from radium-*B*). With these high-frequency rays, a lead filter 0·5 mm. thick may be used to eliminate diffusion of soft *X*-rays without producing a diminution in the sharpness of the spectrum.

J. GRANT.

Crystal structure of thiocarbamide. L. DEMENY and I. NITTA (Bull. Chem. Soc. Japan, 1928, **3**, 128—136).—The crystal structure of thiocarbamide has been determined from Laue photographs and *X*-ray measurements. The unit group is Γ_0, having *a* 5·47, *b* 7·64, *c* 8·54 Å., and contains 4 molecules of $CS(NH_2)_2$; $d_{calc.}$ 1·408. The probable space-group is V_h^{16}, and a possible atomic arrangement, neglecting hydrogen atoms, is indicated. The molecule has one plane of symmetry; the distance carbon—sulphur is 1·81 Å., and carbon—nitrogen is 1·39 Å.

C. J. SMITHELLS.

Dispersion of long wave-length *X*-rays in platinum and calcite. E. DERSHEM (Proc. Nat. Acad. Sci., 1928, **14**, 380—384).—For platinum the dispersion increases with wave-length as far as 7 Å. and probably continues to do so as far as the beginning of the *N*-series of absorption limits. The examination of calcite near the *K*-limit of calcium showed that anomalous dispersion of the type predicted by the theories of Kronig and of Kallmann and Mark takes place near a *K*-absorption limit. The agreement is not quantitative.

W. E. DOWNEY.

Broadening of the Debye–Scherrer lines of cold-worked tungsten wires and strips as a function of the temperature and duration of heating. A. E. VAN ARKEL and W. G. BURGERS (Z. Physik, 1928, **48**, 690—702).—The dependence of the line broadening in the *X*-ray absorption of cold-drawn tungsten wires and cold-rolled tungsten strips on the temperature and duration of heating was investigated by determination of the ratio between the intensity of the strongest line in the copper $K\alpha$ doublets and the intensity in the minimum between the two lines. The sharpness of the doublets increases rapidly with the temperature of heating. It also increases at first with time, but at temperatures where recrystallisation does not markedly occur the ratio soon assumes a constant value for each temperature.

J. W. SMITH.

***X*-Ray investigations on cellulose. IV.** R. O. HERZOG and W. JANCKE (Z. Physik, 1928, **49**, 27—30).—The employment of a monochromatic beam of *X*-rays shows that cellulose has only a single crystal structure (cf. Gonell, A., 1924, ii, 588).

J. W. SMITH.

Fine structure in the *K*-series of copper and nickel and the width of spectral lines. H. PURKS (Physical Rev., 1928, [ii], **31**, 931—939).—At 40 kilovolts and in the first order the widths (X.) at half-maximum were: nickel $K\alpha_{1,2}$ 0·66, copper $K\alpha_{1,2}$ 0·63, molybdenum $K\alpha_{1,2}$ 0·47, $K\beta_{1,2}$ 0·43, silver $K\alpha_{1,2}$ 0·43, $K\beta_{1,2}$ 0·40; in the second order the estimated width of the components of nickel and copper $K\alpha_{1,2}$ and $K\beta_{1,2}$ was 0·4 X. Weak lines were present at displacements 0·42 and 0·35 X. from Cu $K\alpha_2$ and Cu $K\alpha_2$, respectively, and 0·45 and 0·38 X. from Ni $K\alpha_1$ and Ni $K\alpha_2$, respectively. The following separations are recorded: Ag $K\beta_2$—$K\beta_1$ 0·63, Mo $K\beta_2$—$K\beta_1$ 0·58, Cu $K\beta_2$—$K\beta_1$ 0·32, Ni $K\beta_2$—$K\beta_1$ 0·29 X. The variation of the width with potential was studied; a limiting value is approached at 40 kilovolts.

A. A. ELDRIDGE.

***X*-Radiation from gases.** A. BJORKESON (Nature, 1928, **122**, 13—14).—A method is briefly described whereby an *X*-ray spectrum can be obtained with a gas (sodium or sulphur vapour) as radiator.

A. A. ELDRIDGE.

General *X*-radiation from mercury vapour. W. DUANE (Proc. Nat. Acad. Sci., 1928, **14**, 450—458).—An apparatus is described by which the radiation projected from impacts of electrons with mercury vapour atoms can be investigated both in the direction of the electron stream and at right angles to it. The intensity and penetrating power of the radiation were measured by means of the ionising effect. The penetration of the rays was tested with a sheet of aluminium, and it was found that the mercury radiation both in the direction of the electron stream and at right angles to it became more and more penetrating as it passed through successive layers of aluminium, showing that neither beam of rays is homogeneous. The wave-lengths of these inhomogeneous beams are a little longer than that of the short wave-length limit of the *X*-ray spectrum. The intensities of the rays per mercury atom in the direction of motion of the electron stream and perpendicular to it are of the same order of magnitude. Experiments were made from which the amount of radiation that should pass through the test sheet of aluminium could be obtained. The values for the fraction of radiation passing through, determined experimentally, agreed with that calculated from the "inverse square of the wave-length" law.

A. J. MEE.

Secondary electrons from cobalt. M. N. DAVIS (Proc. Nat. Acad. Sci., 1928, **14**, 460—465).—The secondary emission from cobalt was found to be greater than that observed for any other metal. The target of cobalt was given special heat treatment to ensure complete outgassing. The ratio of secondary current to primary current is plotted against the accelerating potential. It is shown that before outgassing the emission was low, but the current began to show maximum and minimum values at certain accelerating voltages as outgassing proceeded. Curves for iron and nickel previously obtained show something of the same form as the curve for cobalt, but the breaks are not so pronounced.

A. J. MEE.

Diffusion of cathode rays, of 100 volts velocity, in gaseous media. O. HOLTZMANN (Ann. Physik, 1928, [iv], **86**, 214—240).—True reflexion of electrons (*i.e.*, large angle deflexion from the original line of travel) is found to occur in hydrogen, nitrogen, helium, neon, and argon. An electron suffering

such reflexion undergoes no loss in velocity. The true reflexion masks the diffusion so that it was possible only in the case of nitrogen to determine the value of the "turbidity factor" in the absorption equation. W. E. DOWNEY.

X-Ray analysis and crystal structure of cadmium–silver alloys. III. G. NATTA and M. FRERI (Atti R. Accad. Lincei, 1928, [vi], 7, 406—410; cf. this vol., 223, 464).—Mainly a discussion of the work of Petrenko and Fedorov on the thermal investigation of cadmium–silver alloys. The authors' *X*-ray investigations of these alloys described in the first two papers appear to render necessary an accurate revision of the thermal analysis. There is a great similarity in crystal structure between copper–zinc and silver–cadmium alloys. All the phases which are present in tempered silver–cadmium alloys are also found with similar lattices in brasses. This is in accord with the homologous positions which silver and cadmium occupy in the periodic system with respect to copper and zinc. O. J. WALKER.

Atomic arrangement in crystals of the alkali thiocyanoplatinates. S. B. HENDRICKS and H. E. MERWIN (Amer. J. Sci., 1928, [v], **15**, 487—494).—The atomic arrangement has been determined in crystals of ammonium, potassium, and rubidium thiocyanoplatinates. Oscillation spectrum (30°) photographs were made with the *a* axis either coincident with or at an angle of 30° to the axis of oscillation. In addition, Laue photographs were made with the incident *X*-ray beam parallel to and making small angles with the normal to (001). The agreement between the observed density and the density calculated assuming that the unit of structure contains $1R_2Pt(SCN)_6$ was satisfactory. The units of structure had the dimensions: (NH_4), *a* 6·77 Å.; *c* 10·45 Å.; (K), *a* 6·73 Å.; *c* 10·26 Å.; (Rb), *a* 6·75 Å.; *c* 10·47 Å. Laue photographs made with the incident *X*-ray beam normal to (001) showed a three-fold axis and three planes of symmetry, and this observation, coupled with crystallographic evidence, leads to two possible atomic arrangements, in either of which the sulphur atom is adjacent to the platinum atom. These crystal structures are compared with that of the cadmium iodide type. R. A. PRATT.

Distances apart of atoms in metals. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1928, **133**, 397—419).—In comparing values of the atomic radii of the elements with the view of discovering relations between the atomic volumes, the figures must relate to lattices which are all of the same type, and for all of which the co-ordination number, *i.e.*, the number of atoms by which each individual atom is immediately surrounded, is the same. As the basis of comparison, either the regular face-centred or the hexagonal most densely packed lattice may be used, or, in fact, both of these, since in respect of inter-atomic distances they are accurately equivalent, and both have the co-ordination number 12. Calculations of atomic radii have been made on these lines, using available *X*-ray data, supplemented by some new determinations, the figures for certain metals not crystallising in the pure state with either of the requisite lattices being derived from measurements on mixed crystals having lattices of the closely-packed hexagonal type. Reduction of the co-ordination number of a particular atom from 12 to 8, 6, or 4 causes the inter-atomic distance to fall by 3, 4, or 12%, respectively. R. CUTHILL.

Crystal structure of the alums. L. VEGARD and E. ESP (Ann. Physik, 1928, [iv], **85**, 1152—1164).—The crystal structure of the alums was investigated by means of the Debye–Scherrer method. The four alums used were ammonium alum, potassium alum, ferric ammonium alum, and chrome alum, and the radiation used was the $K\alpha$ radiation of chromium. The intensity of the lines was estimated. The results of the identification of the lines leading to the determination of the unit cell are in agreement with those obtained by Vegard and Schjelderup. The structure of the alums is discussed, the general result arrived at being that there are six atoms of oxygen from the water next to the univalent metal, then the sulphate group with the base of the tetrahedron towards the water group, and the point directed towards the tervalent metal. The whole forms a compact unit along the trigonal axis, which is terminated at each end by a metallic atom. Diagrams are given. The structure given cannot be regarded as final. A. J. MEE.

Crystal structure of α-manganese. G. D. PRESTON (Phil. Mag., 1928, [vii], 5, 1198—1206).—α-Manganese (d^{25} 7·44) crystallises as a body-centred cube of side 8·894±0·002 Å. Thus 58 atoms must be associated with the crystal unit, a result in agreement with that of Bradley and Thewlis (A., 1927, 814). The crystal is assigned to the space-group T_d. A. E. MITCHELL.

Crystal structure of β-manganese. G. D. PRESTON (Phil. Mag., 1928, [vii], 5, 1207—1225).—β-Manganese, stable above 742°, crystallises in the cubic system, the unit having a side of 6·29 Å., and containing 20 atoms, a result in agreement with that of Westgren and Phragmen (A., 1925, ii, 1035). The space-group may be either of the enantiomorphs O^7 or O^6, it being impossible to distinguish between these by *X*-ray methods. A. E. MITCHELL.

Crystallography and optical properties of β-lactose. E. T. WHERRY (J. Washington Acad. Sci., 1928, **18**, 302—304).—β-Lactose crystals are monoclinic, holoaxial-polar; $a:b:c=0·817:1:0·377$. The optical constants of α-lactose, β-lactose, and sucrose are tabulated, and directions are given for distinguishing between the three. C. W. GIBBY.

Crystal form of atoxyl [sodium *p*-aminophenylarsinate]. G. CESARO (Mem. Soc. Roy. Sci. Liege, 1924, **12**, 1—11).—The results obtained by Melon (A., 1923, i, 407) and by Gilta (A., 1922, i, 961) are discussed in regard to the relationship between the two different orientations of the crystal adopted. W. E. DOWNEY.

Tetrahedral carbon atom and crystal structure of pentaerythritol. K. WEISSENBERG (Naturwiss., 1927, **15**, 995—996; Chem. Zentr., 1928, i, 787).—Polemical against Schleede and Schneider (this vol., 224). A. A. ELDRIDGE.

Tetrahedral carbon atom and the crystal structure of pentaerythritol. A. HETTICH, A. SCHLEEDE, and E. SCHNEIDER (Naturwiss., 1928, 16, 547).—The authors' experimental results can be interpreted only in terms of a tetrahedral molecular structure, as against the pyramidal structure (cf. Weissenberg, this vol., 462). R. A. MORTON.

Molecular symmetry of pentaerythritol. S. B. HENDRICKS (Z. Krist., 1927, 66, 131—135; Chem. Zentr., 1928, i, 638).—A repetition gives space-group S_4^2 or C_4. A sphenoid arrangement of the $CH_2{\cdot}OH$ groups around the central carbon atom is possible. A. A. ELDRIDGE.

Molecular theory of crystal growth. E. BRANDENBERGER (Z. Krist., 1927, 66, 120—130; Chem. Zentr., 1928, i, 878).—A molecular theory of crystal growth, in accord with the lattice theory of crystal structure, is proposed. A. A. ELDRIDGE.

Carrollite (sychnodymite). W. F. DE JONG and A. HOOG (Z. Krist., 1927, 66, 168—171; Chem. Zentr., 1928, i, 896).—Carrollite (sychnodymite), $CuCo_2S_4$, exhibits hexakisoctahedral symmetry (O^7_h, $u{\sim}N^3_8$); length of edge of unit cell 9·458±0·003 Å., distance Cu—S 2·05 Å., Co—S 2·36 Å. A. A. ELDRIDGE.

Structure analysis. H. OTT (Z. Krist., 1927, 66, 136—153; Chem. Zentr., 1928, i, 550—551).—A general method for the determination of the positions of atoms in a lattice without the assistance of the structure theory is based on the extinction of X-ray interference. A. A. ELDRIDGE.

Structure of monticellite, $MgCaSiO_4$. G. B. BROWN and J. WEST (Z. Krist., 1927, 66, 154; Chem. Zentr., 1928, i, 636).—Monticellite contains SiO_2 36·8, FeO 4·75, MnO 1·62, MgO 21·6, CaO 34·31, H_2O 0·95; the edges of the unit cell of four molecules are a 4·815, b 11·08, c 6·37 Å.; space-group V^{16}_h. The relation between monticellite and olivine is discussed. A. A. ELDRIDGE.

Space-group of staurolite. C. GOTTFRIED (Z. Krist., 1927, 66, 103—107; Chem. Zentr., 1928, i, 636).—The unit cell, containing two molecules, has a 7·84, b 16·52, c 5·61; space-group V^{11}_h. A. A. ELDRIDGE.

Crystal structure of zircon and criteria for special positions in tetragonal space-groups. R. W. G. WYCKOFF and S. B. HENDRICKS (Z. Krist., 1927, 66, 73—102; Chem. Zentr., 1928, i, 637).—The unit cell of zircon, containing four molecules, has a 6·60, c 5·88 Å.; space-group D^{19}. A. A. ELDRIDGE.

Morphological and structural relationships of meteoric iron in relation to its evolution. J. LEONHARDT (Fortschr. Min. Kryst. Petr., 1927, 12, 52—55; Chem. Zentr., 1928, i, 897).—Two kinds of meteoric iron are differentiated by means of Laue photographs. Kamazite has in both groups a cubic body-centred lattice with edge of unit cube 2·84 Å. A. A. ELDRIDGE.

Crystal form of artificial vivianite. G. CESARO (Bull. Acad. roy. Belg., 1928, [v], 14, 260—264).—The crystallographic constants of artificial vivianite, prepared by the action of air on a slightly acid solution of ferrous phosphate, $Fe(H_2PO_4)_2$, are practically identical with those of the natural product. C. W. GIBBY.

Fine structure of the felspars. E. SCHIEBOLD (Fortschr. Min. Kryst. Petr., 1927, 12, 78—82; Chem. Zentr., 1928, i, 895).—The monoclinic felspars are basal-face-centred, the edges of the unit cell being parallel with the crystallographic axes a, b, and c. Values of a_0, b_0, and c_0, respectively, are as follows: adularia 8·61, 13·07, 7·26; sanidine 8·42, 12·92, 7·14; microcline 8·44, 13·00, 7·21; hyalophane 8·50, 12·92, 7·12; albite 8·23, 13·00, 7·25; oligoclase 8·16, 12·90, 7·13; labradorite 8·23, 12·91, 7·16; anorthite 8·185, 12·895, 7·09 Å. The space-group for the monoclinic felspars is C^3_{2h}, and for the triclinic, C^1_i. The effect of changes of composition on the dimensions of the unit cell is considered. A. A. ELDRIDGE.

Study of copper alloys by X-ray diffraction. J. LOISEAU (Compt. rend., 1928, 186, 1732—1733).—The Laue radiograms of laminated copper, and brasses containing 33 and 40% of zinc with and without traces of lead, have been studied during and after annealing at 1050°, 900°, and 700°, respectively, and are fully described. The reflecting planes were simple (100) cubic lattices with the dimensions 3·60, 39·98, 93·60$\times10^{-8}$ cm., respectively. The deformations due to lamination are modified by annealing, which induces the orientation of the (100) planes around an axis perpendicular to the laminations. Comparison of the spectrograms, micrographs, and tensile curves showed the existence of the four classic zones. J. GRANT.

Constitution of silicates. W. EITEL (Naturwiss., 1928, 16, 421—423).—A review of the problem from the point of view of chemical constitution, crystalline structure, the vitreous state, and colloidal properties. R. A. MORTON.

Crystal structure of antimony oxides. U. DEHLINGER (Z. Krist., 1927, 66, 108—119; Chem. Zentr., 1928, i, 636—637).—The oxides Sb_2O_3, Sb_2O_4, Sb_6O_{13}, and Sb_2O_5 were examined by the powder method. The trioxide exhibits the senarmontite form; space-group O^7_h, a 11·14 Å., the unit cell containing 8 mols. Sb_4O_6. The tetroxide also has a cubic structure, a 10·22 Å., the senarmontite lattice being contracted by 10%. The oxide Sb_6O_{13} has approximately the same cubic lattice constant as the tetroxide, but double refraction indicates a pseudocubic structure (tetragonal, c/a=3·0). The unit cell consists of three superposed senarmontite cells. The pentoxide is cubic, with the same lattice constant as the tetroxide. A. A. ELDRIDGE.

[Crystal] structure of beryllium oxalate trihydrate. L. HAVESTADT (Z. anorg. Chem., 1928, 171, 351—354).—By the X-ray method it is found that the unit cell of crystals of the above salt contains 4 molecules, and has the values of 6·37, 7·53, and 12·45 Å. for a, b, and c, respectively. The translation group is Γ_0, and the space-group V^{16}_4. R. CUTHILL.

Crystal structure of mercuric cyanide. R. FRICKE and L. HAVESTADT (Z. anorg. Chem., 1928, 171, 344—350).—X-Ray investigation shows the

unit cell of crystals of mercuric cyanide to contain 8 molecules, and to have the dimensions $a=b$, 9·74 Å., and c 8·94 Å. The translation group is Γ'_t, and the space-group is probably V_d^{12}. R. CUTHILL.

Complex structure of the copper–tin intermetallic compounds. J. D. BERNAL (Nature, 1928, **122**, 54).—The three phases δ-, η-, and ε-bronze have been examined by *X*-ray analysis, and found to be more complex than has been assumed. δ-Bronze contains 416 atoms in the unit cell, so that the simplest formula is $Cu_{41}Sn_{11}$; the space-group is T_d^2. η-Bronze has the molecular formula $Cu_{50}Sn_{16}$; the space-group is probably Q_h^{1-}. ε-Bronze contains 250 atoms of tin and 280—300 of copper in the unit cell; the molecular formula Cu_6Sn_5 is given with reserve. A. A. ELDRIDGE.

Diameter of the CH_2 chain in aliphatic acids. C. S. PIGGOT (J. Washington Acad. Sci., 1928, **18**, 330—333).—Within the limits of error, the short dimension in the *X*-ray crystal structure of pentadecoic, palmitic, stearic, and behenic acids is the same, viz., $4·235\times10^{-8}$ cm. This is apparently the diameter of all organic CH_2 chains. R. A. MORTON.

***X*-Ray spectroscopic examination of a cellobiose anhydride.** M. BERGMAN, R. O. HERZOG, and W. JANCKE (Naturwiss., 1928, **16**, 464).—The hexa-acetyl derivative of the cellobiose anhydride described by Bergmann and Knehe (A., 1925, i, 1384) has been examined by means of *X*-rays. The photographs are identical with those given by cellulose triacetate. W. E. DOWNEY.

Distinction between *d*- and *l*-crystals by means of *X*-rays. A. HETTICH (Z. Physik, 1928, **48**, 614—615).—The differentiation between *d*- and *l*-crystals is discussed with particular reference to quartz. J. W. SMITH.

Study of chlorites by means of *X*-rays. C. MAUGUIN (Compt. rend., 1928, **186**, 1852—1855).—The crystal characteristics of the three chlorites studied (pennine, leuchtenbergine, and grochauite) are analogous to those of the micas (this vol., 463, 611) and are due to piled elementary leaflets about 14×10^{-8} cm. thick, separable by cleavage. The Laue diagrams show a well-defined ternary symmetry. The crystalline pattern is always composed of 6 electro-negative oxygen atoms and 6 electro-positive atoms, but it is not possible to assign formulæ to the chlorites in which the atoms are represented by whole numbers. Since the number of hydrogen atoms is always found equal to 8/3, it is thought that *X*-ray examination gives a crystal lattice one third of that actually present, the true lattice containing 18 atoms of oxygen and 8 of hydrogen. J. GRANT.

Reticular-plane contraction at crystal surfaces. W. BRAUNBEK (Naturwiss., 1928, **16**, 546).—The results of Davisson and Germer on the scattering of electrons by nickel single crystals (A., 1927, 492) are in formal agreement with a contraction of the lattice in a direction vertical to the surface. According to Patterson (*ibid.*, 817) the experimental data demand on this basis a contraction of 35% in the first spacing between the like planes as compared with the normal spacing inside the crystal. Bethe (Naturwiss., 1927, **15**, 786; 1928, **16**, 333) has accounted for the electron diffraction by introducing a refractive index for electron waves. The author has calculated the magnitude of the change in spacing for successive like planes in a crystal of the sodium chloride type with a (100) surface plane. The magnitude of the change is of the order 0·3% for the first spacing and very much smaller for the second and subsequent spacings. Even with less rigid lattices in which the contraction (or expansion) may be greater, it would seem that the effect could not exceed the experimental error of measurements. R. A. MORTON.

Atomic arrangement in orthorhombic iodine. P. M. HARRIS, E. MACK (jun.), and F. C. BLAKE (J. Amer. Chem. Soc., 1928, **50**, 1583—1600).—The unit cell has orthorhombic bipyramidal symmetry corresponding with the space-group V_h^{18} (Wyckoff's notation), the atoms being arranged according to scheme (f) with parameter values $u=0·150$, $v=0·117$. The cell contains 8 atoms and has a_0 4·795 Å., b_0 7·255 Å., c_0 9·780 Å., corresponding with a (Groth) axial ratio of 0·661 : 1 : 1·348 and d 4·913. The parameter values were determined by both the structure factor and Fourier series methods; in the latter method the question of crystal perfection is not serious. The atoms are grouped in molecules of I_2, the distance between the atomic centres being 2·70 Å. The conditions of the formation of monoclinic iodine are questioned. S. K. TWEEDY.

Lattice structure transformation in metallic mixed crystals. G. BORELIUS, C. H. JOHANSSON, and J. O. LINDE (Ann. Physik, 1928, [iv], **86**, 291—318; cf. A., 1927, 400).—Temperature–resistance measurements have been made of the metallic additive compounds, Cu_3Au, CuAu, Cu_3Pd, and CuPd. The measurements confirm the view that at low temperatures the atoms in these compounds are in an ordered, stable distribution, but that at higher temperatures there is a disordered distribution of the atoms. The conversion between the ordered and disordered states in the region of Cu_3Au, CuAu, and Cu_3Pd appears continuous. In the case of CuPd, the disordered arrangement of atoms has a face-centred cube lattice, and the ordered state, a body-centred cube lattice, so that the conversion must be discontinuous. W. E. DOWNEY.

Study of the structure of electrolytic copper by means of *X*-rays. J. J. TRILLAT (Rev. Mét., 1928, **25**, 286—288).—The unit cell of electrolytic copper is a face-centred cube, of length 3·68 Å. The presence of gelatin during electrolysis has no appreciable effect on the dimensions of the unit cell. By the Debye–Scherrer method it is shown that copper deposited in the presence of gelatin has a very fine-grained structure, and that much larger crystals are obtained in its absence. C. W. GIBBY.

Constitution of hydroxides and hydrates. I. G. NATTA (Gazzetta, 1928, **58**, 344—358).—The hydroxides of metals which, as bivalent ions, have a radius between 0·77 and 1·10 Å. belong to the isomorphic class of rhombohedric hydroxides; this class includes the hydroxides of calcium, cadmium,

nickel, magnesium, manganese, iron (ferrous), and cobalt (ous), but not zinc hydroxide, since the radius of the zinc ion is less than 0·77 Å. All these hydroxides belong to the holohedral class of the rhombohedral system and have an orthorhombic unit cell defined by the co-ordinates of the atoms: M^{++}—(0, 0, 0), O^{--}=($\frac{1}{3}$, $\frac{2}{3}$, u) ($\frac{2}{3}$, u), the value of the parameter u depending on the magnitude of the metallic ion and increasing from 0·25 to 0·28 as this varies from 0·77 to 1·06 Å. The side of the base of the elementary cell of the rhombohedric hydroxides increases regularly with increase in the radius of the metallic ion, but only a very imperfect relation exists between the value of $c : a$ for crystals of the composition MX_2 and the ratio $R_x : R_m$ for the component ions.

From the distance O—M it is calculated that oxygen has a radius between 1·33 and 1·38 Å., which agrees well with the value determined for the bivalent oxygen ion in other ways; the semi-distance O—O is about 10% greater than this value. The oxygen ion being only slightly deformable, it may be assumed that the hydrogen ion which would occupy the positions ($\frac{1}{3}$, $\frac{2}{3}$, v) and ($\frac{2}{3}$, $\frac{1}{3}$, $-v$) hinders contact between the oxygen atoms. On the assumption that the oxygen and hydrogen ions are spherical, the radius of action of the hydrogen ion is calculated to be 0·3—0·4 Å. If the hydroxyl ion in the lattice is considered as an entity, it would be limited by a non-spherical surface with radii varying from 1·35 to 1·50 Å., and would thus have the form of a strongly deformable ion analogous to that of polarisable ions like iodine, and would form the stratified lattices typical of compounds of polarisable ions.

T. H. POPE.

Electrolytic conduction of solids. E. FRIEDERICH (Z. Physik, 1928, **48**, 446).—A claim for priority over Reis (*ibid.*, **46**, 444). J. W. SMITH.

Electrolytic conduction of solids. A. REIS (Z. Physik, 1928, **48**, 446).—A reply to Friederich (cf. preceding abstract). J. W. SMITH.

Magnetisation of single crystals of iron at high temperatures. K. HONDA, H. MASUMOTO, and S. KAYA (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 111—130).—The magnetisation of a single iron crystal between −190° and 790° was measured in the direction of the principal axes. The variation in saturation value with temperature was almost the same as for a polycrystalline iron rod. At the ordinary temperature the curve is almost straight up to a magnetisation of 1000 c.g.s. units, the slope then changing up to the saturation value of 1707 c.g.s. units. As the temperature is raised the break in the curve occurs at progressively lower fields, and the saturation value decreases until it vanishes at 790°. By extrapolation the saturation value at 0 Abs. is 1752 c.g.s. units. The results are explained on the theory previously advanced by Honda and kubo (*ibid.*, 1916, **5**, 153). C. J. SMITHELLS.

Division of the Faraday effect into two phenomena of different origins. Diamagnetic and paramagnetic rotatory polarisation. J. BECQ RE and DE HAAS (Compt. rend., 1928, **186**, 1720—1722).—Experiments with tysonite, which has a considerable negative rotatory power, at 1·39—4·21 Å. for the wave-lengths 4258·9—6249·5 Å., have proved the existence of a paramagnetic rotatory polarisation proportional to the thickness of the crystal but not to the field strength. The rotation is exactly represented by a hyperbolic tangent, and at saturation, is a function of wave-length and decreases with the temperature for a given wave-length. This explains the deviations from Curie's law. J. GRANT.

Paramagnetism. Magnetic moment of ions of elements of the transition groups. D. M. BOSE and H. G. BHAR (Z. Physik, 1928, **48**, 716—721).—Preliminary measurements have been carried out on the magnetic susceptibility of salts of metals in the transition groups of the periodic system. Their Weiss magneton numbers calculated according to the method developed by Hund (A., 1925, ii, 912) and Bose (A., 1927, 805) are compared. J. W. SMITH.

Electronic theory of metals from the point of view of Fermi's statistics. E. KRETSCHMANN (Z. Physik, 1928, **48**, 739—744).—It is pointed out that the formulæ deduced by Sommerfeld (this vol., 467) for electrical and thermal conductivity are not dependent on the assumption made by him that the mean free path of the electrons is, as a first approximation, independent of temperature. J. W. SMITH.

Theory of the magnetic and electrical properties of metals at 0° Abs. J. FRENKEL (Z. Physik, 1928, **49**, 31—45).—From statistical considerations the paramagnetic susceptibility of metals at 0° Abs. is deduced. Ferromagnetism is qualitatively discussed and calculations are made of the energy of evaporation of electrons from metals, the contact potentials between different metals, and of the density and compressibility of metals. J. W. SMITH.

Paramagnetism of iron in potassium ferricyanide. (MLLE.) P. COLLET and F. BIRCH (Compt. rend., 1928, **187**, 35—36).—Iron in potassium ferricyanide has a moment of 12 magnetons at 0—200°, and probably a moment of 13 magnetons below 0°.

J. GRANT.

Magnetic changes of iron sesquioxide, its solid solutions, and ferromagnetic compounds. H. FORESTIER (Ann. Chim., 1928, [x], **9**, 317—401).—A thermal dilatometric examination of iron (Fe_2O_3, Fe_3O_4, and FeO), aluminium, chromium, and magnesium oxides, compressed into short rods, has been made. When the heating is not continued beyond a certain temperature, which varies from substance to substance (940° for aluminium, 1000° for magnesium oxides), a reversible contraction occurs, but above this temperature the slope of the curve changes abruptly and it is no longer possible to get reversibility no matter at what temperature the material has previously been heated. The curves for magnesium oxide which has been preheated either to 1000° or 2000° both show an abrupt change of direction at 500°. From these results it is deduced that two distinct processes take place: (1) a continuous and irreversible contraction due to the disappearance of the spaces between the grains which runs parallel with changes in the apparent density of the material, (2) the occurrence of plasticity in the

grains after a certain temperature. No allotropic changes occur. The paper gives a detailed account of investigations the results of which have already been summarised (Forestier and Chaudron, A., 1924, ii, 617; 1925, ii, 534, 1159; 1926, 566; 1927, 11).

J. W. Baker.

Mechanical twinning in zinc crystals. E. Schmid and G. Wassermann (Z. Physik, 1928, **48**, 370—383).—The changes in the mechanical properties of single crystals of zinc are shown to be related to the formation of twinned crystals. J. W. Smith.

Influence of the mother-liquor on crystal form. M. Yamada (Japan. J. Phys., 1928, **4**, 159—163).—The effect of mother-liquor on crystal form is investigated, a simple law of atomic action being postulated. The regular arrangement of atoms in the crystal is assumed to have some effect on the atoms of the liquid in the neighbourhood of the surface of the crystal. The atoms of the liquid will themselves be arranged regularly on the surface of the crystal. If the diameter of the atoms (assumed spherical, although ellipsoids or more complicated forms would do as well) of the liquid is greater than that of the atoms of the solid they cannot lie on the surface of the crystal without some heaping up. This means that the mutual potential energy between crystal and liquid is less than when the two diameters are equal. If a step is now made on the surface of the crystal the liquid atoms can come into contact with the surface without any heaping. If steps are made at every place where otherwise there would be heaping the surface energy will be minimal. Protruded atoms will then be regularly arranged, giving rise to surfaces with rational indices. Surfaces of high indices (vicinal planes) may be explained if the atoms of the liquid are only slightly larger than those of the solid. The theory will explain the observation that when a crystal of nickel chloride in a solution of the same substance is placed in a strong magnetic field slightly inclined faces appear on the crystal. A. J. Mee.

Hylotropic-isomeric forms. IV. K. Schaum (Annalen, 1928, **462**, 194—209).—A continuation of previous work (A., 1916, i, 405; 1924, i, 520, etc.). The author classifies cases of polymorphism as follows: (1) Physical polymorphism. Here identical units form different space-lattices; small differences in the molecular anisotropy disappear on destroying the space-lattice, *i.e.*, the liquid obtained by just melting either form is the same. (2) Cryptochemical polymorphism, subdivided into (2*a*) cryptochemical metameric polymorphism and (2*b*) cryptochemical polymeric polymorphism. The fused mass obtained from the two forms shows slight differences in (2*a*) and (2*b*); (2*a*) arises with complex molecules of fairly stable forms caused by intramolecular change, whilst (2*b*) is found with substances which tend to associate. High rates of interconversion are found in cases of (2*b*). (3) Chemical polymorphism. This may be of two kinds, I and II. (3) I is further divided into metameric and polymorphic cases (*a* and *b*). Under (3) I*a* are cases where the two forms in the fused condition are quite different, there being in these cases two distinct chemical isomerides, convertible one into the other. If (3) I*a* is represented by B B′, (3) I*b* is represented by *n*B B_n, where B=unit. In the *b* cases the fusions and interconversion are as in *a*. Chemical polymorphism II, giving very low interconversion velocities, is a limiting case of (3) I, each form containing a mere trace of the unit corresponding with the second form.

A number of substances have been investigated with a view to their classification on the above lines, the main results being as follows: Benzophenone: f. p. depends on the previous history; very high rate of interconversion (*R*). Phenyl *p*-tolyl ketone, low *R*. In these two cases the formation of the metastable form is aided by prolonged heating of the fused substances at relatively high temperatures. Fresh fusions of the different forms show great diversity of behaviour as regards supercooling and crystallisation, and further show small differences in physical constants. Both cases are probably examples of (2*b*), possibly (3) I*b* in addition. *p*-Chloro-, *p*-bromo-, *p*-iodo-, and *p*-hydroxy-benzophenone and *p*-ditolyl ketone are apparently cases of (3) I*b* (*R*, low, measured for the hydroxy-compound). Benzoin: *R*, low, measured. Dibenzoylacetone: case of (3) I*a*; *R*, moderate, measured. Ethyl mesityloxideoxalate (ethyl αγ-diketo-ε-methyl-Δ^{δ}-heptenoate): case of (3) II*a* (*R*, moderate, measured). Benzil-*o*-carboxylic acid: case of (3) I*a* or (3) II*a* with transition temperature about 66° (cf. Vixseboxe in Smits: "Allotropie," 1921); *R*, low, measured. β-Naphthyl salicylate: *R*, measured. 3-Nitro-*p*-acetotoluidide: *R*, low, measured: case of (3) I*a*. 2-Nitro-*p*-toluidine: *R*, measured; the stability of the β-form (m. p. 69·5°) is increased by long heating of 2 : 6-dinitrotoluene: heat treatment of the fused mass has no effect on the transition, occurring at 40·5°. *m*-Nitrobenzoic acid: *R*, moderate, measured. 2 : 6-Dinitro-*p*-chlorophenol: metastable form appears below −3 , passing fairly rapidly into the stable form. α-Nitronaphthalene: a metastable form appears, together with the stable form, at the ordinary temperature, rapidly passing into the latter; at higher temperatures only the stable form is produced. 4-Nitrotriphenylcarbamide has a very low *R*. Triphenylmethane: *R*, high, measured. The transition temperatures and m. p. of the β-forms of other compounds are given as: Tetrabromomethane, 46·7° and 94·3°; succinic anhydride, 110·1° and 120·2°; orcinol, 53·3° and 197·5°; *as*-tetrachloroaniline, 117·8° and 118·1 ; ethyl azoxybenzoate, 112·6° and 119·2°. Other less definite cases are also discussed. E. E. Turner.

Conductivity and Hall effect in sputtered platinum films. A. Riede (Z. Physik, 1928, **48**, 302—309).—The conductivity of platinum films sputtered on glass in the presence of hydrogen is proportional to the thickness of the film in the range 4·7—136 mμ. The Hall effect in such films is constant until the thickness is reduced below 30 mμ, when the magnitude of the effect diminishes rapidly.

R. W. Lunt.

Resistivity of thin metallic layers obtained by cathodic disintegration. F. Joliot (Compt. rend., 1928, **186**, 1526—1528).—The resistance of thin films of platinum deposited on glass at the rate of $0{\cdot}2\times10^{-5}$ g./cm.²/min. from a cathode placed 3 cm.

away from the anode, at 900 volts, and an air pressure of 0·01 mm. of mercury, varies with the thickness of the film according to a curve of an exponential type, and for a constant film thickness, decreases with an increase in voltage. The effect of heat, which changes the resistance and its temperature coefficient in the direction of that of ordinary platinum, is attributed principally to the removal of gas occluded by the film. J. GRANT.

Wiedemann–Franz law. III. A. EUCKEN (Z. physikal. Chem., 1928, **134**, 220—229).—It is shown that the equation connecting the total specific thermal resistance of a metal with its specific electrical resistance proposed by Grüneisen and Goens cannot hold. The observations of Grüneisen and Goens can be utilised more satisfactorily if the fact that the "non-metallic" conductivity will be considerably lowered by deformation of the lattice is taken into account. A new evaluation of the results gives a somewhat better agreement. The Wiedemann–Franz constant for metals at low temperatures is in all cases much below its normal value for high temperatures. This constant seems to show very little dependence on lattice deformation. A. J. MEE.

Electron "free path" and super-conductivity in metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, **14**, 377—380).—Theoretical. The termination of a "free path" is taken to occur when the free electron is captured by a positive ion. The effect of this definition on specific heat, dependence of conductivity on temperature, super-conductivity, and on thermal conductivity at low temperatures is discussed.

W. E. DOWNEY.

Sommerfeld's electron theory of metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, **14**, 370—377).—A critical examination of the conclusions reached by Sommerfeld and others (this vol., 467).

W. E. DOWNEY.

Specific resistance of bismuth crystals and its change in strong magnetic fields and some allied problems. I. Growth of crystal rods with a definite orientation of the crystal planes and the specific resistance of bismuth crystals. II. Method and apparatus for observing the change of resistance of bismuth in strong magnetic fields. III. Change of resistance of bismuth and the time lag in magnetic fields. P. KAPITZA (Proc. Roy. Soc., 1928, A, **119**, 358—386, 387—401, 401—443).—I. A method is developed for growing bismuth crystals in the form of small rods, 3—5 mm. long and about 1 sq. mm. cross-section, in which the cleavage planes are oriented at any desired angle relative to the axis of the rod. An essential condition for the growth of such rods is that no strain must be set up in the bismuth during crystallisation. A small strain set up in the material has the effect of changing the perfect cleavage plane from one of the pseudo-octahedral planes to one of the three remaining planes of the same pseudo-octahedron, according to the nature of the strain. Measurements of the resistance of bismuth rods in a compressed state suggest that during the process of the growth of the crystals, cracks and imperfections are developed in the lattice which account for the variation of the specific resistance in bismuth previously observed. By means of compression the cracks close, and the limiting value of the specific resistance perpendicular to the cleavage plane, reached when all the cracks have closed, is $1{\cdot}39\times10^{-4}$ at 16°. The limiting value parallel to the perfect cleavage plane is $1{\cdot}07\times10^{-4}\pm1\%$ at 16°. The origin of the cracks is studied, and it is found that their development probably occurs almost at the moment when the bismuth passes from the liquid to the solid state. A close relation is observed between the flexibility of the rods and their specific resistance. An ideal bismuth crystal at the ordinary temperature will probably have no well-defined cleavage plane and will be perfectly flexible. To explain the origin of the cracks, the hypothesis is advanced that there are two crystalline bismuth modifications; one of them, at present unknown, but probably cubic, is transformed into the ordinary rhombohedral form at a temperature slightly below the m. p. Since this transformation takes place when the bismuth is in a solid state and must be accompanied by changes in shape, stresses are set up in the crystal lattice which account for the spoiling of the lattice and the formation of "cracks." On the basis of this hypothesis several physical properties of bismuth may be explained.

II. A detailed description is given of a method for measuring the change of resistance of a bismuth crystal when it is placed in a magnetic field which exists for 0·01 sec. only and varies during the whole of this time. The study of the change of resistance is made possible by the fact that large current densities are permitted in the conductor, for such a short time, without heating the conductor, and no specially sensitive apparatus is required. The method adopted was to send a known current through the bismuth crystal and by means of potential leads to observe the difference of potential across the crystal, both the current and the *P.D.* being measured by oscillographs. A special switch is described which permits the current to be sent through the conductor for a very short time during the existence of the magnetic field. The make and break of this switch can be adjusted relative to the current wave through the coil with an accuracy of 1/5000 sec. The elimination of errors and stray effects, due to the *E.M.F.* in the potential leads induced by the variation of the magnetic field and to the heating of the crystal produced by the current, is discussed.

III. A method is described for eliminating the *E.M.F.* in the bismuth crystal which accounts for the time lag phenomenon in the measurement of the change of resistance of bismuth in a magnetic field. Results are given for the change of resistance of bismuth crystals when the current is flowing perpendicular to the magnetic field, for different orientations of the crystal axis relative to the field, at 15°, −80°, and −182°. The presence of impurities and imperfections of the crystal lattice have a marked effect in diminishing the change of resistance of bismuth, particularly in strong fields and at low temperatures. The change of resistance of an ideal crystal in a magnetic field is discussed, and it is shown that in weak fields it follows a square law and in strong fields a linear law. The linear law is

practically independent of the orientation of the crystal relative to the magnetic field. A study has also been made of the case when the current is parallel to the magnetic field, for different orientations of the crystal axis relative to the field. Here the change of resistance is very small and a definite limiting value is reached. The magnitude of the change is little affected by the temperature, but is strongly influenced by imperfections of the crystal, being much larger for imperfect than for perfect crystals. It is suggested that this small change of resistance is due to the imperfection of the crystals and to the defective alinement of the current in the crystal with the lines of force of the magnetic field. An attempt was made to produce perfect bismuth crystals, growing them by means of direct deposition of bismuth vapour on cooled quartz plates in a vacuum. The experiments for obtaining single crystals were unsuccessful, but by studying the change in resistance of the deposits formed in a strong magnetic field, explanations were found for certain phenomena previously observed in thin bismuth layers (cf. Patterson, Phil. Mag., 1902, 64, 562). From a general study of the residual *E.M.F.* developed in bismuth in a magnetic field, it was found that the ratio, residual *E.M.F.*/resistance, is independent of the strength of the magnetic field in the region of investigation but is strongly influenced by the orientation and by the degree of perfection of the crystal. The origin of the residual *E.M.F.* is discussed. The failure of the present theory of metallic conductivity to account for the large change of resistance of bismuth in a magnetic field is considered, and reasons for the discrepancies between theory and experiment are suggested. A mechanism is suggested by means of which several phenomena observed in conductors may be explained. L. L. Bircumshaw.

Interferential method for measuring magnetic susceptibility of liquids. O. Specchia (Atti R. Accad. Lincei, 1928, [vi], 7, 574—576).

Thermoelectric power in cold-worked metals. W. F. Brandsma (Z. Physik, 1928, 48, 703—705).—The thermoelectric power appearing between cold-worked and recrystallised copper rods was found to be reproducible, providing the preliminary treatment was identical. The effect increases with the degree of working. On heating the cold-worked wire to a definite temperature the effect was found to decrease slowly to a value characteristic of the temperature. J. W. Smith.

Temperature of the acetylene–oxygen flame. F. Henning and C. Tingwaldt (Z. Physik, 1928, 48, 805—823).—The temperature in different parts of the acetylene–oxygen flame was determined by Kurlbaum's method of spectral line inversion. Observations were made in the visible region by colouring the flame by means of lithium carbonate and in the infra-red region by measurements on the carbon dioxide band 4·39 μ in the colourless flame, the former giving the temperature in the interior of the flame and the latter that of the outer cone. The hottest point in the normal flame is about 3 mm. above the tip of the luminous cone, where the temperature is about 3100°. J. W. Smith.

Specific heats of liquids and saturated vapours. J. J. van Laar (Z. physikal. Chem., 1928, 134, 311—328).—Mathematical. A. J. Mee.

Specific heats of solid substances at low temperatures. K. Clusius and P. Harteck (Z. physikal. Chem., 1928, 134, 243—263).—The specific heats of gold, zinc, gallium, zinc oxide, copper oxide, zinc sulphide, ammonium carbamate, and silver chloride were determined at temperatures down to about 10° Abs. The apparatus and method of working are described. The results are given and curves drawn showing the variation of atomic heat with temperature. The results are discussed generally. A. J. Mee.

Specific heats at constant pressure and at constant volume of some substances in the solid, liquid, and hypercritical states between 80° and 320° Abs. A. Eucken and F. Hauck (Z. physikal. Chem., 1928, 134, 161—177).—The specific heats of various gases in the condensed state were determined by means of an apparatus previously described by Eucken, but slightly modified for this purpose. The specific heats of carbon dioxide (solid and liquid), nitrous oxide (solid), ethylene (solid and liquid), methyl chloride (solid and liquid), ethane (liquid), air (liquid), and argon (liquid) were determined at constant pressure and at different temperatures. The specific heats of ethane, argon, air, and carbon dioxide were also determined at constant volume, and in the case of the last three above the critical point. The behaviour of the specific heats with temperature was investigated. The specific heat increased only slightly with rise of temperature for ethane, a little more rapidly for carbon dioxide, whilst for air and argon there was a considerable decrease of specific heat with rise of temperature, although the substances were still some distance below the critical point, and therefore still in the liquid state. The results obtained for the specific heat of air at constant volume in the hypercritical state are compared with those of Hausen. A. J. Mee.

Heat conductivity of solid crystalline substances between 0° and —190°. A. Eucken and G. Kuhn (Z. physikal. Chem., 1928, 134, 193—219).—The heat conductivities of a large number of crystalline substances and crystalline aggregates were measured at temperatures from 0° to —190°. The fact previously found by Eucken and Neumann that the conductivity decreased if a substance in the form of large crystals was converted into small crystals holds for calcite, but not for crystalline aggregates of regularly crystallised substances if these are made up of a single component. The formation of mixed crystals was investigated; there was a very considerable decrease in the absolute value of the conductivity as well as in the temperature coefficient. The effect of an impurity on the heat conductivity of a crystal can be expressed by Matthiessen's law. The results for the series of alkali halides are collected; in general the conductivity, as well as the temperature coefficient between 0° and —190°, reaches a maximum when the two atoms composing the molecule are of nearly equal weight. There is a parallelism between heat conductivity and hardness if the

crystals are arranged in groups according to their constitution. The results are discussed in connexion with Debye's theory of heat conductivity of solids.

A. J. MEE.

Theory of specific heat c_v of monatomic liquids at high temperatures. A. EUCKEN and H. SEEKAMP (Z. physikal. Chem., 1928, **134**, 178—189).—Mathematical. It is assumed that the molecules in a liquid have a periodic motion not necessarily harmonic, as has usually been supposed in order to explain the fact that the specific heat at constant volume of a liquid is more nearly equal to $6R/2$ than to $3R/2$, as the kinetic theory indicates. The atom is supposed to be surrounded by an elastic envelope, the repulsive force being expressed by a given law. The molecular heat of liquid argon was calculated at various temperatures and the results were compared with the measured values. There is only a qualitative agreement between the two results.

A. J. MEE.

Allotropic modifications and solid solutions of phosphorus. J. W. NICOLAIEV (Compt. rend., 1928, **186**, 1621—1624).—The mixture of crystals of phosphorus obtained in the Ipatiev bomb was separated by hand under the microscope and shown to consist of purple (1·90, 4·4 mm., 200°), ruby (2·11, 1·4 mm., 346°), and black (2·7, <0·5 mm., 490°) modifications, the figures in parentheses being the corresponding d, vapour pressures at 21°, and inflammation points, respectively. These and white phosphorus form a continuous series of solid solutions, red phosphorus being a mixture of ruby and purple phosphorus, and violet phosphorus a mixture of the ruby and black varieties. Black and purple phosphorus form a eutectic.

J. GRANT.

Critique of the electrical differential method of measuring the specific heats of gases at constant volume. M. TRAUTZ and O. TRAUTZ (Ann. Physik, 1928, [iv], **86**, 1—65).—A comprehensive paper giving a systematic account of the errors in the above method of determining the specific heats of gases at constant volume. The errors are investigated both theoretically and practically. An outline of a complete c_v measurement is given. There is a table of corrections giving their estimated values. It now appears possible to make measurements of c_v correct to 1 part in 2000 parts.

A. J. MEE.

Effect of cold working on specific heat. W. GEISS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1928, **171**, 317—322).—The specific heat of tungsten or nickel in the form of cold-drawn wire is not appreciably different from that of the recrystallised metal, a fact which is in agreement with the relationship previously developed (A., 1925, ii, 372) between cold working and the energy content of metals.

R. CUTHILL.

M. p. and b. p. of homopolar compounds as a function of the distribution of electrons in the molecule. A. DIBROVA (Ukraine Chem. J., 1928, **3**, [Sci.], 1—38).—A consideration of Bohr's theory of the structure of the atom (Ber., 1925, **58**, 1565) and of Remy's conception of molecular structure leads to the conclusion that any physical property g of a homopolar substance may be expressed as a function of N_m, the number of valency electrons, N_a, the number of nuclear electrons not taking part in chemical reactions, N, the number of nuclear charges, and K, a constant depending on given external conditions. A comparison of the m. p. and b. p., T, of members of homologous series of aliphatic hydrocarbons, alcohols, mercaptans, disulphides, tellurides, and mono- and di-basic acids leads to an expression $T{-}f(N.P).N_a/\sqrt{N_m}$, where P represents pressure. Where $P>0$, $f(N,P)$ is a linear function, which, although not constant for different compounds, yet differs little. At pressures below 1 atm. the value of $f(N,P)$ is below 30 for m. p. and below 40 for b. p. Where $P{-}0$, $f(N,P)$ is constant (its value is about 20 for the m. p.), and the m. p. and b. p. equal the quotient, $N_a/\sqrt{N_m}$. Where P is variable, the value of $f(N,P)$ is best expressed as $a[(b-N)P^{1/5}+d]$, where a, b, and d are constants for the given homologous series, and ad=const.=20.

R. TRUSZKOWSKI.

Fusion of *cyclo*hexanol. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 593—599).—*cyclo*Hexanol exhibits dimorphism, transition from transparent to translucent crystals occurring at 21·4°. The latter form has a marked solvent action on atmospheric gases, which are evolved again when the temperature falls below 21·4°. The fusion pressure P of *cyclo*hexanol is determined at temperatures of from 25·10° to 29·22°, and over this range P increases from 27·39 to 127·10 megabars and dP/dt from 18·48 to 29·97. The latent heat of fusion is a linear function of temperature, and amounts at 23·7° to 2·71 g.-cal.

R. TRUSZKOWSKI.

Specific heat of nickel above the Curie point. P. WEISS (Compt. rend., 1928, **187**, 12—14).—The atomic heat of nickel corrected for the heat of demagnetisation in accordance with the theory of the molecular field (cf. Lapp, this vol., 577), increases with temperature from 0 to 550° and remains constant at the Curie point, the rise being equal to that portion of the atomic heat corresponding with the kinetic energy of a degree of freedom. The experimental error is 2·5%. It is probable that the rise is connected with the change of atomic moment from 3 to 8 magnetons shown by nickel at high temperatures, the fourth degree of freedom being represented by the penetration of thermal agitation into the atom.

J. GRANT.

Gaseous state of normal substances. K. WOHL (Z. physikal. Chem., 1928, **133**, 305—349).—The applicability of Wohl's equation of state is considered in the case of normal substances, *i.e.*, those for which RT_c/p_cv_c (where T_c, p_c, and v_c are the critical temperature, pressure, and volume, respectively) has the value 3·5—3·95, and T_c lies between 0° and 300°. Below T_c, the equation is valid for the entire stable gaseous state, and at T_c its validity extends to v_c, the deviations of the pressure from the theoretical value never exceeding 1%. For *iso*pentane, ethyl ether, and carbon dioxide above T_c, the limit of applicability rises to $1{\cdot}7v_c$ and $4p_c$ as the temperature rises to $1{\cdot}75T_c$, the maximum error in the pressure being 2%. Since in these applications of the equation it is necessary to introduce only two

constants which are characteristic of the particular gas considered, viz., T_c and p_c, it follows that the theorem of corresponding states is true over the same range as the equation. Applying the equation to sulphur dioxide, it seems that the experimental data for the volumes of the saturated vapour at low temperatures are incorrect, and that the gas is a normal substance, and not, as previously supposed, associated. Between temperatures of $0·8T_c$ and $2·5T_c$, the equation gives accurate values for the second virial coefficients of all the normal gases, whilst below $0·8T_c$ there are deviations which show that the attraction potential of the molecules is no longer proportional to the inverse power of the temperature, but varies somewhat more rapidly. The possession of a high dipole moment is not in itself sufficient to ensure that a substance shall be associated; it is essential that the orientation polarisation due to the rigid dipole moment shall greatly preponderate over the polarisation depending on the displacement of electrons and atoms in the electric field. The magnitude of the dipole moment or even a very wide variation in the ratio of the two polarisation effects has no effect on the behaviour of the substance in the gaseous state. R. CUTHILL.

Velocity of sound in liquids at high frequencies by the sonic interferometer. J. C. HUBBARD and A. L. LOOMIS (Phil. Mag., 1928, [vii], 5, 1177—1190).—High-frequency vibrations are set up in a column of liquid by means of a quartz piezo-electric vibrator. The resonance lengths of the column are then determined by means of a piston moving at the other extremity of the column. From the frequency of the oscillator the velocity of sound in the liquid is determined. Measurements have been made with mercury, water, and several salt solutions and the thermodynamic coefficients deducible therefrom are in good agreement with those obtained by Bridgman (Proc. Amer. Acad. Sci., 1912, **47**, 549).

A. E. MITCHELL.

Molecular force. I. The change of vapour pressure of a liquid in the presence of compressed gas and its relationship to the van der Waals constant a_{12}. A. EUCKEN and F. BRESLER (Z. physikal. Chem., 1928, **134**, 230—242).—It is shown that the increase of vapour pressure of a liquid through the presence of another substance in the form of a highly compressed gas provides a method of obtaining the van der Waals constant a_{12}, which is proportional to the reciprocal molecular attraction. The substance used was carbon disulphide. The gas (carbon dioxide, nitrogen, or hydrogen) was saturated with the vapour and compressed. The amount of carbon disulphide vapour contained was then determined at atmospheric pressure by means of an interferometer. The a_{12} values were calculated from the results and from those of other observers. The Bertholet relationship a_{12}— where a_1 and a_2 are the values for the single components, was verified. A. J. MEE.

Volume chemistry. III. Oxygen compounds. (2) Carbonyl group. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 456—460; Chem. Zentr., 1928, i, 1001).

Determination of the vapour pressure of scented substances. G. TAMMANN and W. OELSEN (Z. anorg. Chem., 1928, **172**, 407—413).—With a knowledge of the threshold value, or weight of material which can be detected by smell, the vapour pressure of a scented substance at different temperatures may be determined. The sensitiveness to smell of the investigator must first be measured. At a temperature at which the vapour pressure of the scent is known a fixed volume of air v_1 is saturated with it and then diluted by a volume of air v_2 until the scent can only just be perceived. From the dependence of the quotient $(v_1+v_2)/v_1$ on temperature the vapour-pressure curve may be obtained. This was tested and found to be satisfactory for substances with small threshold values by determining the vapour pressures of camphor and butyric acid and comparing with values found by other methods. The method should be employed only at very low pressures, where other methods become difficult. Substances of which the vapour pressure at the temperature of the nose is below the threshold value cannot be perceived by smell. M. S. BURR.

Has aluminium a transition point? A. SCHULZE (Z. Physik, 1928, **49**, 146—154).—Measurements of the electrical resistance of very pure aluminium (99·94%) indicate that no allotropic change occurs in that metal in the neighbourhood of 610°. J. W. SMITH.

Absorption of ultrasonic waves by various gases. T. P. ABELLO (Physical Rev., 1928, [ii], **31**, 1083—1091).—The increase in the absorption coefficient ($cm.^{-1}$) for ultrasonic waves of frequency 612 kilocycles in air containing 1 vol.-% of various gases, compared with air, was: carbon dioxide 0·029, nitrous oxide 0·034, hydrogen 0·014, helium 0·0025; for argon mixtures no absorption was observed.

A. A. ELDRIDGE.

Connexion between the properties of liquids and orthobaric densities. W. HERZ (Z. anorg. Chem., 1928, **172**, 414—416).—From McLeod's relationship $\gamma/(d_l-d_g)^4$, where γ is the surface tension and d_l and d_g are the densities of the liquid and saturated vapour, respectively, is a constant for any one substance independently of temperature, and from certain relationships found by the author between the number of molecules per c.c. and the viscosity, heat of vaporisation, and surface tension, respectively (this vol., 229, 368, 697), the following formulæ have been deduced: $L^{1/1·2}(d_l-d_g)$=const. and $\eta^{1/5·5}/(d_l-d_g)$=const., L being the heat of vaporisation and η the viscosity. The first formula has been tested by reference to the available data for pentane, ethyl ether, and tin tetrachloride over a large range of temperature, and the second by reference to the data for fluorobenzene and methyl acetate. The agreement is satisfactory. M. S. BURR.

Method for measurement of vapour pressure of small quantities of substance. The vapour pressure of chloropicrin. H. BŁASZKOWSKA-ZAKRZEWSKA (Rocz. Chem., 1928, **8**, 219—228).—Using a method based on Smith and Menzies' submerged bulblet method (cf. A., 1910, ii, 1036), together with Swientoslawski's ebullioscopic thermostat, the vapour pressure of chloropicrin has been

determined between 78° and 112°. The constants α, β, and γ are calculated for the formula $\log p=\alpha-\beta/(273+t)-\gamma \log (273+t)$, connecting vapour pressure with temperature. These constants apply to chloropicrin between 0° and its b. p.

R. TRUSZKOWSKI.

Determination of vapour pressure of chloropicrin at about 100°. H. BŁASZKOWSKA-ZAKRZEWSKA (Rocz. Chem., 1928, 8, 210—218).—The vapour pressure of chloropicrin is determined between 98° and 105°, using the air-current method, which consists of determining the loss in weight of chloropicrin after a known volume of air at a given temperature has been passed through the liquid. Swientoslawski's ebullioscopic thermostat, which maintains temperatures constant to within 0·01—0·02°, was used for the above purpose. R. TRUSZKOWSKI.

Influence of glass on vapour pressure. J. RINSE (J.C.S., 1928, 1442—1449; cf. McHaffie and Lenher, A., 1925, ii, 854; 1926, 898; 1927, 198; Frazer, Patrick, and Smith, A., 1927, 722).—The vapour pressure–temperature curves of mercuric iodide, bromide, and chloride and iodine, when measured with a glass-spring indicator which had been heated previously at above 500°, instead of changing abruptly to the linear form on passing the saturation point, were continuous. Mercury and mercurous chloride did not behave in this way. Experiments with carefully dried materials indicated that water was not the cause of this effect. The addition of glass powder considerably augmented it. Further, the effect is not to be explained either in terms of adsorption, for the adsorbed layers would have to be at least 500 molecules thick, or in terms of a reaction between glass and the substance; experiment failed to reveal such a reaction.

F. J. WILKINS.

Dissociation of ammonium chloride vapour. H. BRAUNE and S. KNOKE (Z. physikal. Chem., 1928, 135, 49—62).—Accurate measurements of the vapour density of ammonium chloride at temperatures between about 200° and 400° indicate that complete dissociation takes place, in contradiction to the work of Smith and others. H. F. GILLBE.

Cohesion and intermolecular repulsion. R. K. SCHOFIELD (Phil. Mag., 1928, [vii], 5, 1171—1176).—Cohesion is defined as the quantity $(dU/dv)_T$ in the relation $(dU/dv)_T=T(dp/dT)_v-p$, where U is the internal energy of the substance under consideration. No effect of chemical union is considered and effects due to translational kinetic energy are ignored. The magnitude of this quantity has been calculated for a number of liquids up to pressures of 3000 atm. As the volume is reduced the cohesion first increases to a maximum and then decreases. The results are not in accordance with the view that molecules resemble rigid spheres. They are readily explainable if the molecular fields are of the complex type considered by Lennard-Jones (A., 1926, 888), the force between two molecules being repulsive when they are very close together and attractive when they are farther apart. A. E. MITCHELL.

Diffusion problem for a solid in contact with a stirred liquid. H. W. MARCH and W. WEAVER (Physical Rev., 1928, [ii], 31, 1072—1082).—Mathematical. The problem considered is that of the one-dimensional flow of heat which occurs when a solid is in contact with a stirred liquid. Its connexion with material diffusion is shown. A. A. ELDRIDGE.

Density of fused mixtures of cadmium and potassium chlorides. R. LORENZ and H. ADLER (Z. anorg. Chem., 1928, 172, 372—374).—The density of fused mixtures of cadmium and potassium chlorides has been determined at different temperatures by a modification of Tammann and Brunner's method (cf. A., 1904, ii, 244). The results are tabulated. At constant temperature the variation of density with composition is approximately linear. M. S. BURR.

Binary azeotropic mixtures containing a lower alcohol as one component. Y. TANAKA and T. KUWATA (Chem. News, 1928, 137, 13—14).—From observations on azeotropic mixtures containing a lower alcohol as one component it is deduced that a rise of temperature or an increase of pressure causes an increase in the proportion of that component of the mixture which has the greater heat of vaporisation, and that two substances which have the same heat of vaporisation at the same temperature cannot form an azeotropic mixture. A. R. POWELL.

Peculiar results in hardness tests of lead–antimony alloys. L. O. HOWARD (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 90, 5 pp.).—Fall in hardness was observed at 40% and 50% Sb in two series. Reported differences in hardness are ascribed to different thermal treatments.

CHEMICAL ABSTRACTS.

Structure of tin–antimony alloys. W. BRONIEVSKI and L. SLIVOVSKI (Compt. rend., 1928, 186, 1615—1616).—Measurements of the electrical conductivity, thermo-electric power, electrode potential, coefficient of expansion, and hardness, and of their respective temperature coefficients, for tin–antimony alloys reheated at 200° for 1200 hrs. suggest that Sn_3Sb_2 is the only compound formed. Thermal analysis confirms this result and shows that such crystals are deposited from a liquid of the composition Sn–Sb. This is said to explain the supposed formation of the compound SnSb in commercial alloys containing 25% of antimony. J. GRANT.

Structure of silver–aluminium alloys with a high content of aluminium. M. HANSEN (Z. Metallk., 1928, 20, 217—222).—Examination of a series of silver–aluminium alloys containing 0—60% Ag by thermal and micrographic methods has confirmed the position of the liquidus and eutectic composition as found by Petrenko (A., 1905, ii, 635), but the m. p. of the eutectic is now found to be 558°. The solubility of silver in solid aluminium is about 0·45% at 20° and 0·75% at 200°; with further rise of temperature the solubility increases remarkably rapidly to a maximum of 48% Ag at the eutectic temperature. Thus all alloys containing more than about 0·5% Ag exhibit age-hardening properties when quenched from above 300° and tempered at a temperature below the solid solution line. A. R. POWELL.

Solubilities and mol. wt. determinations in liquid chlorine. K. H. BUTLER and D. MCINTOSH

(Proc. Nova Scotian Inst. Sci., 1927, **16**, 198).—The solubilities in liquid chlorine were obtained by measuring the rise in b. p. caused by addition of the solute. Fifty-nine of the commoner salts were found to be insoluble at the b. p. Sulphur, arsenic, silver, copper, and zinc did not react with the liquid chlorine, whilst aluminium, iodine, phosphorus, and tin reacted, but only the last caused any rise in b. p.

S. J. GREGG.

Grain growth in metals caused by diffusion. F. C. KELLEY (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 89, 7 pp.).—Rapid grain growth results from diffusion, the direction of grain being parallel to that of diffusion. The diffusion of chromium and manganese in iron is discussed. Iron diffuses into nickel, but not nickel into iron.

CHEMICAL ABSTRACTS.

Solubility of thallous chloride in water and aqueous solutions of magnesium sulphate and lanthanum nitrate at 25°. M. RANDALL and K. S. CHANG (J. Amer. Chem. Soc., 1928, **50**, 1535—1536).—The solubility of thallous chloride is 0·01611 mol. per 1000 g. of water, the solution having sp. gr. 1·0034 and *d* 1·0004. S. K. TWEEDY.

Vapour pressure of mixtures of benzene and *cyclo*hexane. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 562—583).—Measurements of the vapour pressures of mixtures of benzene and *cyclo*hexane at temperatures between 30° and 80° give values almost identical with those calculated from Antoine's formula (Compt. rend., 1888, **107**, 681). At all temperatures mixtures of maximum vapour pressure exist, their composition depending on temperature. The vapour-pressure curves of benzene and *cyclo*hexane cut at 50°; below this temperature the vapour pressure of the latter exceeds that of the former, whilst above 50° the contrary is the case. The 50° isotherm is strictly symmetrical, with a maximum value at 50% of benzene; at higher temperatures the summit is shifted in the direction of *cyclo*hexane. This affords a confirmation of Konovalov's law (J. Russ. Phys. Chem. Soc., 1884, **16**, 11). The properties of the above mixture are not additive at temperatures below the b. p. R. TRUSZKOWSKI.

Vapour pressures of mixtures of toluene and *cyclo*hexane. I. I. NAGORNOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 584—593).—The vapour pressure of mixtures of toluene and *cyclo*hexane rises steadily at all temperatures as the proportion of *cyclo*hexane increases; at all concentrations the observed vapour pressure is greater than the arithmetic mean of those of the constituents. The observed vapour pressures agree well with Antoine's formula (Compt. rend., 1888, **107**, 681). R. TRUSZKOWSKI.

Equilibrium of solutions of barium and lead chlorides dissolved in aqueous hydrochloric acid. P. A. VOLKOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 704—724).—The solubility of lead chloride at 25° and at 0° has a minimum value when 7—8 mols. of barium chloride are present per 100 mols. of water and a maximum value at the saturation concentration of barium chloride. The first effect is due to the increase in concentration of chlorine ions and the second probably to the formation of complex salts. Similar results have been obtained for the system lead chloride–hydrochloric acid–water (Ende, Z. physikal. Chem., 1903, **16**, 162). In presence of concentrated hydrochloric acid the solubility of barium chloride is unaffected by the presence of lead chloride; the solubility of the latter salt is greatly increased by the addition of hydrochloric acid, whilst that of barium chloride becomes very small. The use of this reaction is recommended for the separation of traces of lead from radium. R. TRUSZKOWSKI.

Diffusion of hydrogen through iron. W. E. DEMING (Phil. Mag., 1928, [vii], **5**, 1081—1084).—It is shown with the aid of the results of Borelius (A., 1927, 727) and of Bartlett (*ibid.*, 404, 927) that the rate of diffusion of hydrogen through iron is represented by an equation of the form $dP^{1/n}/dt = K_1/c\Delta^2P^{1/n}$, where P is the pressure of the gas and c the amount adsorbed per unit volume under unit pressure. For the steady state this becomes $dm = K_1A\Delta P^{1/n}dt$, where dm is the amount of hydrogen diffusing through an area A of thickness dx with pressures P and $P+dP$ in time dt. These equations are exactly similar in form to those representing the conduction of heat by metals. A. E. MITCHELL.

Solubility of oxygen in iron, and in ferrous oxide (oxoferrite, wüstite). C. BENEDICKS and H. LOFQUIST (Z. anorg. Chem., 1928, **171**, 231—238).—Schenck and Dingmann's value for the solubility of oxygen in solid iron (A., 1927, 1030) is much in excess of the values to be found in the literature, and also in their diagram for the system iron–oxygen the ferrous oxide region of homogeneity is displaced towards much higher concentrations of oxygen. It seems probable, however, that in these authors' experiments the mixture of metal and oxides became contaminated with alumina from the vessels used to contain it, so that the previously accepted values are possibly substantially correct. R. CUTHILL.

Fractional crystallisation of radioactive substances. III. Distribution of radium between solid crystalline barium chloride dihydrate and its saturated aqueous solution at 0° and 35°. W. CHLOPIN and A. POLESSITSKY (Z. anorg. Chem., 1928, **172**, 310—320; cf. A., 1927, 1133).—The distribution of radium between solid barium chloride and its saturated solution is strictly in accordance with the simple partition law. The partition coefficient at constant temperature and concentration of the liquid phase remains constant for large variations in the relative quantities of the two solvents and also for large variations, *e.g.*, $2·628\times10^{-8}$—$2·816\times10^{-5}M$, in the concentration of the radium salt. The distribution coefficient varies with temperature, the temperature coefficient being $-0·516$ per degree between 0° and 35° and $-0·275$ per degree between 35° and 57·5°. Hence fractional crystallisation of the chlorides, and also of the bromides, is the more effective the lower is the temperature at which the crystallisation takes place. There are considerable differences between the partition coefficients found by different investigators, but these may probably be explained by variations in temperature and acid concentration. M. S. BURR.

Influence of viscosity on the rate of absorption of carbon dioxide by neutral sodium carbonate. P. Riou and P. Cartier (Compt. rend., 1928, **186**, 1727—1729).—An extension of the authors' viscosity experiments (this vol., 702) to ethylene glycol, methyl and ethyl alcohols, lactose and acetaldehyde has shown that although viscosity has a certain influence on the rate of absorption of a gas by a liquid, it is not the principal factor, the chemical nature of an added non-reacting organic crystalloid substance playing a far more important part and increasing the viscosity and rate of absorption to an extent which suggests a catalytic effect. J. Grant.

Important factors in the investigation of adsorption from solutions. K. C. Sen (Z. anorg. Chem., 1928, **171**, 275—280).—From the Freundlich adsorption isotherm $x/m=KC^n$, it follows that if K and n actually remain constant independently of the volume of the solution and the weight of adsorbent, m, then for a given concentration C of the solution, x/m should also be independent of m, and of the volume and initial concentration of the solution. For adsorptions in which there is no possibility of chemical reaction, *e.g.*, the adsorption of acetic acid by animal charcoal (Pavlov, A., 1924, ii, 833), this is in agreement with the experimental results. Where, on the other hand, forces of a chemical nature may be involved, as in the adsorption of ions by colloids, this is no longer true. Thus in the adsorption of copper sulphate by manganese dioxide, the values of K and n are not independent of m and of the initial concentration of the solution. R. Cuthill.

Adsorption from solution by ash-free adsorbent charcoal. V. Adsorption from buffer solutions as a means of determining the iso-electric point for charcoal. E. J. Miller and S. L. Bandemer (J. Physical Chem., 1928, **32**, 829—842; cf. A., 1927, 929).—Adsorption from Sorensen's standard buffer solutions by blood, wood, and sugar charcoals, purified by treatment with hydrofluoric acid (A., 1926, 898), and by unpurified blood charcoal has been studied. Adsorption produces the changes in reaction which are to be expected from previously-established facts of adsorption by pure adsorbent charcoals (cf. A., 1926, 1090). Pure charcoal decreases the acidity of acid buffer mixtures by adsorption of acids and increases the alkalinity of less alkaline buffers by hydrolytic adsorption of acid from salts with the liberation of alkali. The alkalinity of highly alkaline buffers is not reduced. Unpurified blood charcoal reduces the alkalinity of the more alkaline buffers owing to the presence of acid impurities in the charcoal. Pure charcoal carrying adsorbed acids acts in a similar manner. Decomposition or elimination of acid impurities by ignition of the unpurified charcoal removes this effect. The method of adsorption from buffer solutions is unsuitable for the determination of the isoelectric point for charcoals, and the results bear no relation to the isoelectric point determined electrokinetically. Data are given. L. S. Theobald.

Adsorption in binary systems. (Mlle.) L. S. Lévy (Compt. rend., 1928, **186**, 1619—1621; cf. this vol., 118).—The adsorption from solutions containing iron and nickel or copper and nickel has been studied with manganese dioxide as the adsorbent, the concentration of one metal being kept constant and the other varied. The results agree with Freundlich's adsorption formula. Values for the constants of the formula are obtained, and it is shown that equal concentrations of copper and nickel have the same influence on the adsorption of iron, but the concentration of iron which is required to produce the same effect on the adsorption of copper is only 0·0017 as great as the corresponding nickel concentration. J. Grant.

Adsorption in solutions. XIII. Adsorption from mixed solutions of electrolytes. M. Dubinin (Z. physikal. Chem., 1928, **135**, 24—35).—The adsorption by pure activated wood and sugar charcoal from mixed aqueous solutions of electrolytes has been studied quantitatively. A linear relationship exists between the quantities of each component adsorbed from a binary mixture. From the ratio between the number of molecules of each component in the adsorbed layer, the extent to which the adsorption of one component is diminished by the second may be calculated by a method applicable to such widely differing mixtures as hydrochloric and nitric acids, hydrochloric and oxalic acids, and hydrochloric acid and acetone; in the first case poisoning of the catalyst occurs, in the second there is ordinary partition, and in the third independent adsorption of the two components takes place. Such differences are purely qualitative, and all these cases are susceptible of the same general treatment. H. F. Gillbe.

Adsorption of electrolytes by crystalline surfaces. A. Pinkus and (Mlle.) L. de Brouckère (Bull. Acad. roy. Belg., 1927, [v], **13**, 415—440).—The adsorption of an electrolyte A_mB_n at a crystalline surface in contact with water has been investigated. The electrolytes chosen were hydrochloric acid, and the chlorides of potassium, lithium, copper, and nickel, whilst the surface consisted of microcrystalline, pure barium sulphate presenting a surface area of $8{\cdot}45\times10^5$ cm.^{2} per g. Solutions of the various electrolytes, saturated with barium sulphate, were agitated with known weights of barium sulphate for 5—10 hrs. at 25°, the solid was washed, and the amounts of adsorbed electrolytes were determined by various direct and indirect methods. The same equilibrium conditions could be obtained under defined conditions, starting either from pure barium sulphate or from crystals bearing an excess of adsorbed electrolyte.

The reversibility of the adsorption and the equivalent adsorption of cations and anions is quantitatively demonstrated. Errors arising from capillary absorption are negligible. Adsorption isotherms $\log x=f(\log c)$ are plotted, x being the equilibrium concentration in g.-equivalents per g. of barium sulphate, and c the equilibrium concentration of the solution in g.-equivalents per litre. The curves cease to be linear at higher concentrations.

The expression $x=p/Ax^\nu+Bp$ has been deduced theoretically and fully verified. The terms in the expression follow from $A=Na/S$, $B=4N\theta/mnS$, and $f(x)=ax^\nu$, where a and ν are constants, p is the

osmotic pressure, N is Avogadro's number, S is the adsorbing surface in cm.^{2} per g., and θ is the surface in cm.^{2} occupied by a single adsorbed particle. The verification does not apply to the nickel and copper chlorides, as the activity coefficients are not known.

R. A. MORTON.

Absorption of ammonia, carbon dioxide, and vapours of benzene and acetone by gels of titanium dioxide and stannic oxide. N. J. NIKITIN and W. J. JURÉEV (Z. anorg. Chem., 1928, **171**, 281—284).—The absorption of the above gases and vapours by titanium dioxide and stannic oxide at the ordinary temperature has been studied. Titanium dioxide readily absorbs ammonia, and at $-16°$ under 1 atm. takes up about 8·5% of its weight of the gas; stannic oxide is less active, and several other oxides manifest very little activity. In respect of the absorption of benzene vapour, titanium dioxide gel is comparable with ordinary inactive silica gel.

R. CUTHILL.

Surface tension of a mixture of ethyl alcohol and water. I. K. I. ALEKSEEVA (Z. physikal. Chem., 1928, **134**, 467—474).—The surface tension of mixtures containing 99·7—87% of ethyl alcohol has been measured by the maximum bubble pressure method. The change in surface tension is directly proportional to the change in concentration.

O. J. WALKER.

Variation with time of surface tension of plasma. G. HOMES (Bull. Acad. roy. Belg., 1927, [v], **13**, 555—572).—A slow decrease in the surface tension of colloidal liquids over a period of about 2 hrs. has been demonstrated, and shown to be independent of evaporation. Both dynamic and static surface tension are little affected by the nature of the anticoagulant used. A full theoretical discussion is appended.

R. A. MORTON.

Capillary action of mercury in the absence of gas-grown skins. J. J. MANLEY (Phil. Mag., 1928, [vii], **5**, 958—962).—If the gas-grown skin which normally occurs on the surface of a charged barometer tube be removed, the convexity of the mercury surface is changed to concavity. The same effect is obtained with any mercury surface which has been treated, either by electric discharge or by boiling, so as to remove the gas-grown skin. The difference between the reduced reading of a standard barometer and that of a treated column was found to be +3·1 mm. This capillary effect is four times as great as that shown by water.

W. E. DOWNEY.

Surface action in chemical phenomena. R. DUBRISAY (Bull. Soc. chim., 1928, [iv], **43**, 625—641).—A lecture delivered on May 11, 1928.

Reflecting power and colour sequences shown by metals on activation. F. H. CONSTABLE (Nature, 1928, **122**, 57).—It has been verified that a burnished metal surface becomes duller on activation, the accompanying colour phenomena being also less pronounced.

A. A. ELDRIDGE.

Formation of surface films on palladium by heating in air and by anodic polarisation. G. TAMMANN and J. SCHNEIDER (Z. anorg. Chem., 1928, **171**, 367—371).—The rate of increase with the time, t, of the thickness of the surface film of oxide produced on palladium when heated at 500—750° in air is represented by the equation $t=ae^{by}-a$ (cf. A., 1922, ii, 831), y being the thickness of the equivalent film of air, and log b decreasing in an approximately linear manner with rise in temperature. The same relation applies to the anodic polarisation, but here when y has reached a certain magnitude, which depends on the current strength, both a and b abruptly assume new values.

R. CUTHILL.

Determination of surface-development of foaming drugs. R. DIETZEL and U. PANKOW (Apoth. Ztg., 1928, **43**, 44—45; Chem. Zentr., 1928, i, 1076).—A photomicrographic method is described. The increase of surface caused by a spuman preparation was 260-fold at 20°, 390-fold at 37°.

A. A. ELDRIDGE.

New interference method of measuring the surface area of film catalysts. I. Theory. II. Nickel. Preparation of the film, apparatus for activation, and study of the surface area. F. H. CONSTABLE (Proc. Roy. Soc., 1928, **A**, **119**, 196—201, 202—213).—I. Spectrophotometric measurements of the intensity and wave-length of the light reflected from oxidised surfaces of iron, nickel, and copper show that interference is the main cause of production of the colour sequences, so that the colour of these films uniquely determines their thickness when the order of the colour and the refractive index of the film is known. This supplies a method of evaluating the surface area of metallic film catalysts if the full data are available. Five methods are outlined, involving (1) measurements of the mass of the film and spectrophotometric observations on the light reflected from the coloured film; (2) data on the spectrophotometric analysis of the reflected light and the conductivity of the film; (3) observation of the surface colour expressed in terms of the equivalent air thickness of the covering film and the mass of the film; (4) simultaneous observations of the surface colour and the electrical conductivity of the metallic film; and (5) determination of the initial values of the oxidation constants from observations of the surface colour, and of the mass of oxide produced, or the change in conductivity of the metallic film.

II. Experimental details are given for the preparation of uniform graphite films on china clay rods, and an electrical method of deposition of nickel on the graphite-coated rods is described. The metal films were activated by alternate oxidation and reduction at 580°, and then reduced at the lowest possible temperature by hydrogen. They were then oxidised at 330°, the conductivity of the film being measured at intervals during the oxidation, and the surface area was determined from spectrophotometric and visual observations of the surface colour. Curves show the relation between the fall of conductivity with time and the thickness of the oxide film. The area on activation passes through a minimum and then rises. This effect is accompanied by a fall in the conductivity due to cracking in the film, the strain set up by the alternate oxidation and reduction being sufficient to break up the film. Raising the

temperature to 563° after activation, with alternate oxidations and reductions, showed that two consecutive oxidations and reductions were necessary before the film would settle down to an equilibrium state. The terminal area was less than that shown by metal reduced at the lowest possible temperature.

L. L. BIRCUMSHAW.

Dialysis. III. Temperature coefficient of dialysis. H. BRINTZINGER and B. TRŒMER (Z. anorg. Chem., 1928, **172**, 426—428).—The relation between c_0 and c_t, the concentration of a dialysable substance before and after dialysis for a time t, is expressed by the equation $c_t=c_0\times e^{-\lambda t}$, where λ is a coefficient typical for each substance and dependent on the membrane, the size of surface, concentration, presence of other substances, temperature, etc. (this vol., 121). Experiments have been made at different temperatures, but under otherwise comparable conditions, and λ has thus been found to vary linearly with temperature. $\lambda_{T'}=\lambda_T[1+a(T'-T)]$, where a is the temperature coefficient. a appears to be of the order of magnitude of the temperature coefficient for diffusion without a membrane.

M. S. BURR.

Electro-osmosis and electrolytic transport of water in solutions of alkali chlorides. J. BABOROVSKÝ and J. VELISEK (Chem. Listy, 1928, **22**, 265—267).—Measurements of the proportion of solutions of sodium, potassium, or lithium chloride transported by one faraday, of the electrolytic transport of water in these solutions, of the transport of these salts themselves, and finally of the transport numbers of their cations in normal solution show that these are linear functions of the concentration in g.-equivalents. This confirms the work of Hepburn on other electrolytes (A., 1926, 1100; 1927, 422).

R. TRUSZKOWSKI.

Electro-osmosis and anion effect. A. RABINERSON (Kolloid-Z., 1928, **45**, 122—129).—Experiments have been performed to determine the drop in electrokinetic potential at a surface of talc in various electrolyte solutions, and to determine the influence of various anions. Variations were noticed in the electro-osmotic velocity at high concentrations of electrolyte, a result which is ascribed to the great adsorbing surface of talc. At these concentrations, the Helmholtz formula is inapplicable and the falling branch of the curve relating electro-osmotic velocity with concentration does not give a true representation of the change of electrokinetic potential, and the antagonistic effect of mixtures of electrolytes cannot be studied quantitatively. Sulphate and citrate ions produce a higher negative charge than chloride ions, and similarly alkali salts give a higher negative charge than acids. Antagonistic effects were observed in experiments on the reversal of charge by addition of multivalent cations in presence of other electrolytes. The concentration of ferric chloride or of thorium nitrate required to reverse the charge was raised by addition of sulphate or citrate ions, but was unaltered by chloride or nitrate ions.

E. S. HEDGES.

Electrodialysis of serum. G. ETTISCH, R. BRADFIELD, and W. EWIG (Kolloid-Z., 1928, **45**, 145).—Undiluted serum can be rapidly electrodialysed with a current density of 20—30 milliamp./cm.[2] by using a parchment membrane for the cathode and a collodion membrane soaked in albumin from suitably treated serum for the anode. The latter may consist of a collodion membrane containing hæmoglobin. The liquid in the middle cell changes gradually from its initial hydrogen-ion concentration to the value p_H 5·0. Contrary to the views of Reiner (A., 1926, 1205), immersion of a collodion membrane in serum-albumin for a short time is insufficient to cause it to behave as an albumin membrane, and the supposition that the albumin membrane acts as a valve cannot be maintained. During the course of the electrodialysis, the anode membrane is surrounded by a liquid with acid reaction, whilst the liquid round the cathode membrane has an alkaline reaction.

E. S. HEDGES.

Phenomenon of stratification in electrodialysis as an electrophoretic phenomenon. F. BLANK and E. VALKÓ (Biochem. Z., 1928, **195**, 220—227).—The separation into layers during electrodialysis of colloidal solutions using Pauli's apparatus is explained as an electrophoretic phenomenon. The upper layer arises at the membrane and, owing to the migration of colloid particles, is colloid-free and of smaller density and therefore rises to the surface.

P. W. CLUTTERBUCK.

Influence of lipoids on the diffusion of acids and alkalis in gels. S. I. AFFONSKY (Biochem. Z., 1928, **195**, 387—395).—Usually cholesterol accelerates and lecithin retards the diffusion process of acids and alkalis (sulphuric and acetic acids, sodium hydrogen carbonate and hydroxide, etc.) through agar and gelatin gels, but when the lipoid concentration becomes high, then both cholesterol and lecithin inhibit, but the latter more strongly than the former.

P. W. CLUTTERBUCK.

Diffusion rings and regions of crystallisation. G. LINCK and E. KORINTH (Z. anorg. Chem., 1928, **171**, 312—316).—If a solution of sulphur in carbon disulphide thickened with rubber or Canada balsam is allowed to evaporate, the sulphur first appears as a cloudiness consisting of globulites of about 1 μ in diameter. Some of these increase in size at the expense of their neighbours, and regions free from globulites are thus formed. When a crystal is formed it grows in the same way, the drops in its vicinity moving towards it, probably carried by the streaming of the more concentrated solution to the crystal. In the course of the crystallisation, the formation of a pale yellow tetragonal modification of sulphur has been observed, this passing spontaneously into a pale yellow liquid modification. The formation of diffusion rings in gases (cf. König, A., 1920, ii, 594) does not occur in the dark and in absence of vibration.

R. CUTHILL.

Secondary periodicity in Liesegang's rings. B. DOGADKIN (Kolloid-Z., 1928, **45**, 136—140).—The secondary systems of Liesegang rings described by Dunin and Schemjakin (A., 1926, 675) cannot be explained in terms of any of the usual theories. The apparent analogy between these secondary ring systems and the secondary systems reported by Küster ("Über Zonenbildung in Kolloiden Medien," Jena, 1913) is purely an outward resemblance. Experiments in gelatin purified by electrodialysis

showed that the secondary rings described by Küster are due to chlorides and phosphates present as impurities in the original gel. On the other hand, the secondary periodicity reported by Dunin and Schemjakin is due to the alteration of various external factors affecting the solubility of the product during the course of the diffusion. Such factors are changes in temperature, concentration of the diffusing electrolyte, consistency of the gel, and in some cases intensity of illumination. In the precipitation of silver chromate, secondary systems of rings have been produced by varying the intensity of illumination. E. S. HEDGES.

Chemical changes of acids and salts in solution based on refractometric data. A. HANTZSCH and F. DURIGEN (Z. physikal. Chem., 1928, **134**, 413—452).—The attempts to explain the change on dilution of the molecular refraction of electrolytes in aqueous or non-aqueous solution by physico-chemical theories, *e.g.*, dissociation, association, electrostriction, deformation, are rejected in favour of a chemical explanation in terms of Hantzsch's views (following abstract). The refractivity of acids and salts in aqueous solution is in general influenced by two chemical changes which have opposite effects—firstly, the conversion of homopolar substances into heteropolar substances, which brings about an increase in refraction, and secondly, hydration or solvation, which lowers the refraction. The observed molecular refraction gives the net result of these two processes, which may occur simultaneously in certain concentration regions. These changes may be followed by another optical method, viz., by investigation of the absorption in the ultra-violet, and also by means of conductivity determinations. The latter method is applicable only to dilute solutions, whilst the optical methods are of value mainly for concentrated solutions. The chemical changes brought about by the action of water on acids are most readily observed in the case of nitric acid. The molecular refraction of this acid increases regularly up to a dilution of 90 mols. of water to 1 mol. of acid, and then remains constant. Similarly, the absorption reaches a constant value at this dilution. This is explained by a complete displacement of the equilibrium $[O_2N\cdot OH]_2 \rightleftharpoons 2[NO_3]'[H_3O]^+$ towards the right, *i.e.*, towards the side of the hydroxonium salt. The changes which homopolar acids and homopolar pseudo-salts undergo by the action of water can be represented by the general scheme :

Pseudo-acid.	Pseudo-acid hydrate.		Hydroxonium salt.
XH	$XH\cdot OH_2$	$\xrightarrow{nH_2O}$	$X[H_3O]$
XM	$XM\cdot OH_2$		$X[(H_2O)_nM]$
Pseudo-salt.	Pseudo-salt hydrate.		Aquo-salt.
I	II		III

Salt hydrate.	
$X[H_3O]\cdot nH_2O$	Ion
$X[(H_2O)_nM]nH_2O$	hydrates
Aquo-salt hydrate.	
IV	V

The refraction and absorption may vary during the changes I$\longrightarrow$II$\longrightarrow$III$\longrightarrow$IV, but are not affected during the change IV$\longrightarrow$V. True salts are converted on dissolution directly into aquo-salts, which may then become further hydrated according to the above scheme.

The foregoing conclusions are based partly on the refractometric data of other workers and partly on new observations. O. J. WALKER.

Constitution of acids and salts, and their chemical changes in solvents. A. HANTZSCH (Z. physikal. Chem., 1928, **134**, 406—412).—A further summary of the author's views on the constitution of acids and salts (cf. A., 1927, 327, 1011). O. J. WALKER.

Dielectric constants of aqueous amino-acid solutions. G. HEDESTRAND (Z. physikal. Chem., 1928, **135**, 36—48).—The increase of the dielectric constant of water produced by glycine, α- and β-alanines, and taurine is linearly proportional to the concentration of the solute; *o*-, *m*-, and *p*-aminobenzoic acids decrease the dielectric constant. Neutral salts decrease equally the dielectric constants of water and of aqueous glycine solutions. H. F. GILLBE.

Unprotected uniform silver hydrosols. III J. VOIGT and J. HEUMANN (Z. anorg. Chem., 1928, **173**, 27—44).—The effect on the sols of the addition of various quantities of sodium carbonate solution to the silver solutions before reduction was investigated. The reducing agents used to prepare the sols were hydrazine sulphate, hydrazine hydrate, and formaldehyde. The first gave the finest sol, the last the coarsest. The effect of addition of ammonia was also studied. It was found that the number of sub-microns per mm.^{3} of the sol varies with the amount of alkali added, the colour of the sol changing. If the number of particles in a definite volume of sol be plotted against the volume of alkali a curve is obtained which shows a peak. The position of this peak varies with the reducing agent used. The colour of the sol was investigated. Two samples of silver sol inoculated with gold, one containing 0·0005% of silver, the other 0·001%, were successfully concentrated by ultrafiltration. Whilst there was relatively no change in the number of particles present, there was a change of colour. The concentrated solution was diluted so as to contain about the same number of particles per unit volume as the original sol, and it was then compared with it as regards coagulation. It was shown that the ultrafiltered solution contained no protective colloid. The colour changes on coagulation of sols prepared in different ways were studied. It was found that uniform silver sols free from protective colloid, having a diameter less than 30 μμ, pass through different series of colour changes on coagulation by electrolytes. This behaviour seems to depend to some extent on the mode of preparation of the sol and also on the electrolyte used. It appears that dilution of a pure silver sol is accompanied by an increase in the silver ion content of the sol. A. J. MEE.

Colloid chemistry. XXIII. Physico-chemical investigation of thorium oxide sol. W. PAULI and A. PETERS (Z. physikal. Chem., 1928, **135**, 1—23).—Pure concentrated thorium oxide sols, with

chlorine as contra-ion, have been prepared by peptisation in hot and cold solution. The chlorine and thorium oxide contents have been determined potentiometrically and measurements of the conductivities of the sols have been carried out. Sols obtained by hot peptisation yield very low values for the activity of the chlorine ion, an effect attributed to reciprocal interionic forces between the chlorine ions and the colloid particles. The activity coefficients and the dilution–equivalent conductivity relationship exhibit marked anomalies, which can be explained in terms of modern views, whereas the classical theory leads to very improbable values for the colloid-ion mobilities. Substitution of the contra-ion by the addition of various silver salts indicates that complex asymmetric univalent ions have a greater effect than simple ions in changing the activity coefficient. H. F. GILLBE.

Electrochemistry of colloids. I. Colloidal silicic acid. A. J. RABINOVITSCH and E. LASKIN (Z. physikal. Chem., 1928, **134**, 387—405).—A quantitative investigation has been made of the increase in the dissociation constant of weak acids when these pass from the state of true solution to the colloidal state (cf. Rabinovitsch, A., 1925, ii, 778). Silicic acid sols containing from 0·25 to 0·53% SiO_2 were prepared by Graham's method. The total and the free hydrogen-ion concentration of these sols was determined from (*a*) conductometric and (*b*) potentiometric titration curves using alkali solutions. The results for the two methods agree satisfactorily. The dissociation constant of colloidal silicic acid derived from the potentiometric data is found to be 2×10^{-4} and is much higher than the value of 10^{-9} found by Hagg for true solutions (A., 1926, 924). This increase is probably due to the weakening of the attractive force between the hydrogen ion and the acid anion owing to adsorption of the latter by the colloidal particle. By diluting the silicic acid sols the number of free hydrogen ions increases and becomes greater than the total quantity of hydrogen ion of the undiluted sol. This effect is so large that the sol acts as a buffer solution, and is explained by a hydration of the silica molecules in the interior of the colloid particles. O. J. WALKER.

Role of dielectric constants, polarisation, and dipole moments in colloid systems. II. Stability relations of weakly solvated pure organosols. WO. OSTWALD (Kolloid-Z., 1928, **45**, 114—122).—A theory is advanced for the stability relations found experimentally by Svedberg for organosols prepared by electrical disintegration, according to which the orientation of polarisation of the dispersion medium is the chief factor in the stability. The theory agrees with all the known experimental details. The sols discussed are considered as examples of disperse systems which are stabilised, not by electrolytes, but by dipoles of a purely organic nature. The stability depends not only on the value of the dipole moment, but also on the number of dipoles present. The strong stabilising influence of small quantities of water on these systems is discussed and it is pointed out that water has a very high dipole moment and may confer a polar property on a non-polar organic liquid. This view is extended to a consideration of the catalytic effect of water on gaseous chemical reactions and the change in the properties of liquids with intensive drying. In connexion with the latter, it is pointed out that all the liquids used by Baker have smaller dipole moments than water. E. S. HEDGES.

Combined water of colloids. J. AMAR (Compt. rend., 1928, **186**, 1147—1149).—Measurements of the velocity of evaporation of aqueous solutions of ovalbumin (water content 85%) indicate that 47% of the total solvent is more firmly absorbed by the colloid. From these and similar figures (Davis and Eyre, A., 1923, ii, 838; Mayer and Plantefol, A., 1924, i, 809) the size of the water envelope (which is smaller when the continuous phase contains inorganic salts) surrounding the average colloid particle may be calculated. G. A. C. GOUGH.

Influence of salts on the viscosity of linseed oil. M. S. DUNIN and F. M. SCHEMJAKIN (Kolloid-Z., 1928, **45**, 146—152).—The aqueous extract of linseed has a high viscosity, which is decreased by addition of the following salts at concentrations of 0·2—0·04N: sodium, potassium, and calcium chlorides, sodium and potassium sulphates and nitrates. Small quantities of magnesium sulphate (0·0001—0·1N) lower the viscosity, but a slow rise is produced by higher concentrations. Potassium, ammonium, and zinc sulphates, and calcium chloride behave similarly to magnesium sulphate, but to a smaller extent. The specific effect of magnesium sulphate is related not only to the role of magnesium in the chlorophyll of plants, but also to the effect of magnesium on the swelling of plant colloids. E. S. HEDGES.

Alteration of hydrogen-ion concentration of stable kaolin suspensions by mechanical working in capillaries. A. JEPPESON (Kolloid-Z., 1928, **45**, 156—158).—Suspensions of kaolin in water containing a small amount of sodium hydroxide showed on keeping an increase in viscosity and a decrease in hydroxyl-ion concentration. Experiments showed that the adsorption of hydroxyl ions is accelerated by the process of drawing through the capillary tube in the measurement of the viscosity. E. S. HEDGES.

Form and structure of soil particles. G. I. POKROVSKI (Kolloid-Z., 1928, **45**, 158—161).—Particles of soil have a plate-like form and are consequently difficult to measure. An optical method of measurement is described; this shows that the particles in the soil are oriented, giving horizontal layers. E. S. HEDGES.

Thermodynamic theory of the colloidal state. A. MARCH (Kolloid-Z., 1928, **45**, 97—112).—A theoretical paper in which thermodynamic principles are applied to systems of any degree of dispersion. The known laws relating to molecular solutions are derivable from the general theory, which is also applicable to colloids. E. S. HEDGES.

Colloidal heat-indicator. R. E. LIESEGANG (Kolloid-Z., 1928, **45**, 112—114).—A temperature indicator can be made by dissolving 0·4 g. of novocaine

hydrochloride in 20 c.c. of 20% sodium sulphite solution. This solution is clear at the ordinary temperature, but becomes turbid at 32°. A less satisfactory indicator is obtained when quinine is used in place of novocaine. The indicator has been applied to the study of the temperature distribution in banded liquids. When a concentration gradient is set up in a tube (*e.g.*, by placing solid sodium chloride at the bottom of a test-tube of water and leaving for some days) and the tube is subsequently plunged quickly into hot water, a series of bands or zones is observed, differentiated from each other by the refractive power. In presence of the temperature indicator, the experiment gives banded turbidities, which are shown to be rings, the cool contents of the middle of the tube remaining clear. The formation of layers is ascribed to the sinking of this middle liquid, which does not travel to the bottom of the tube, but stops when it reaches a warmer layer of higher concentration and the same density.

E. S. HEDGES.

Soaps as colloidal electrolytes. J. W. McBAIN (J. Amer. Chem. Soc., 1928, **50**, 1636—1640).—Linderstrøm-Lang's view that soap solutions are completely dissociated is criticised (A., 1927, 109). Ultrafiltration, migration, viscosity, and hydration phenomena are directly at variance with this view. The data agree, however, with the author's micelle theory and show that the ionic micelle does not conform to the rule of ionic strength.

S. K. TWEEDY.

Relation between the properties and composition of soaps. IV. Surface tension and emulsifying power of palmitic, oleic, and lauric soaps. M. HIROSE (J. Soc. Chem. Ind. Japan, 1927, **30**, 823—827).—The emulsifying powers in petroleum of the sodium salts of palmitic, oleic, and lauric acids have been compared by reference to the drop numbers using Hillyer's stalagmometer. The measured values for mixtures are much larger than those calculated from the simple mixture rule. In the case of the surface tension, the deviations of the measured from the calculated values are small; at 60—80° the two series are nearly coincident. At temperatures below 60°, the lowering of the surface tension is greater for the mixed soaps above mentioned than for the corresponding mixed soaps derived from stearic and oleic acids or from stearic, oleic, and lauric acids. At temperatures higher than 70°, the reverse is true.

Y. NAGAI.

Relation between the properties and composition of soaps. V. Drop number and the surface tension of lauric–oleic acid soaps. M. HIROSE (J. Soc. Chem. Ind. Japan, 1928, **31**, 156—159).—A 0·5% solution of sodium oleate was mixed with a sodium laurate solution of the same concentration in various proportions and the drop number and surface tension were determined at 40°, 60°, and 80°. It was found that the drop number of the mixtures deviates markedly from the simple mixture rule, a maximum being obtained at 30% of laurate solution. This deviation is less at higher temperatures. The surface tension of a laurate solution is increased by the admixture of a small amount of oleate solution, whilst the reverse holds when a small amount of laurate solution is added to the oleate solution.

Y. NAGAI.

Relation between the properties and composition of soaps. VI. Viscosity, lathering power, and washing power of stearic–oleic–lauric acid soap solutions. M. HIROSE (J. Soc. Chem. Ind. Japan, 1928, **31**, 160—166).—The viscosity, lathering power, and washing power of 0·5% solutions of stearic–oleic–lauric acid soaps have been measured and compared. The relation between these properties, surface tension, and drop number is also discussed.

Y. NAGAI.

Soap. VII. Viscosity and hydration of soap solutions. M. NONAKA (J. Soc. Chem. Ind. Japan, 1927, **30**, 828—835).—The viscosity at 25—30° of solutions of the sodium salts of oleic, palmitic, and stearic acid has been measured at various concentrations by means of an Ostwald–Auerbach pressure viscosimeter. At small pressures all the soap solutions show "structure viscosity," whilst at higher pressures turbulence occurs. The Hagen–Poiseuille rule holds only for mean pressures. Using the relation between viscosity and hydration suggested by Hatschek, the hydration of the micelle is calculated. Thus the concentration of the soaps in the micelle was found to be about 30%, about 1·7%, and about 2·0% for the solutions of the oleate at 25°, of the palmitate at 26°, and of the stearate at 30°, respectively.

Y. NAGAI.

Silica gels. P. BARY (Rev. Gén. Colloid., 1928, **6**, 85—89).—Silica gels containing 27—35% of water suffer disintegration when placed in water. A similar, although much less marked effect is observed with ether, benzene, and toluene, but not with carbon tetrachloride. It is suggested that liquid is sucked into the pores of the gel by capillary attraction, which, by compressing the air they contain, engenders disruption.

F. J. WILKINS.

Structure of gels. I. Colloidal solutions of a photo-polymerisation product of vinyl chloride, giving solid, waxy masses and gels. G. FLUMIANI (Kolloid-Z., 1928, **45**, 152—155).—A product of the photo-polymerisation of vinyl chloride gave either elastic gels or waxy, vaseline-like masses, according to the solvent from which it was obtained. The elastic gel was obtained from solutions in aniline, Peru balsam, rosemary oil, tetralin, bromoform, and ethylene dibromide, and the wax-like material from solutions in castor oil, cedar oil, terpentine, pine oil, origanum oil, camphor, and copaiba balsam. The principal difference between the two forms seems to be the order of magnitude of the smallest particles of the disperse phase, which determines the attraction between these particles and the solvent particles.

E. S. HEDGES.

Barophoresis in gels. H. SOBOTKA and A. B. SABIN (J. Amer. Chem. Soc., 1928, **50**, 1561—1572).—Data are given in support of the relations $d=k\sqrt{t}$ and $(c_1/c_2)^n=k_1/k_2$, where d is the distance a coloured salt solution (concentration c) diffuses into a gelatinous medium in time t, k being a constant. Diffusion may occur with adsorption (methylene-blue) or without (picric acid, sodium dichromate). The temperature

coefficient of diffusion tends to rise when adsorption occurs. The rates of diffusion are usually greater when the diffusing salt moves against gravity ("barophoresis"; cf. Peskoff, Kolloid-Z., 1924, **33**, 215), but at and above the "critical concentration" of the diffusing substance the sense of barophoresis is reversed, *i.e.*, the diffusion becomes more rapid in the direction of gravity. The densities of the intermicellular liquids, indirectly determined, coincide with the densities of the solutions at the corresponding critical concentrations, thus demonstrating that the diffusion against gravity is really a convection current between the intermicellular liquid and the less dense solution.

S. K. TWEEDY.

Optical activity and colloidal behaviour of aqueous gelatin dispersions. E. O. KRAEMER and J. R. FANSELOW (J. Physical Chem., 1928, **32**, 894—911; cf. A., 1925, ii, 1057; 1927, 621).—The influence of p_H, temperature, nature of electrolyte, and gelatin concentration on the optical rotation of dilute aqueous dispersions of electrodialysed, de-ashed gelatin has been studied. Above 30°, the specific rotation is independent of these factors over somewhat wide limits, but minimal rotations may appear at p_H 1, 5, and 8·5, with rapid falls in rotation at the two extremes. Heating at 100° in sealed tubes results in irreversible changes in rotation owing to hydrolysis. Below 25°, maximal rotations occur near p_H 1, 5, and 8·5, and with low gelatin concentrations at low temperatures the maxima and minima are pronounced, but tend to disappear at higher concentrations. The specific influence of electrolytes is not marked at moderate concentrations. Above 30°, the adjustment of rotation to temperature is immediate, but below 25°, the speed of adjustment is measurable. Optical behaviour and colloidal behaviour run closely together. Gel formation is invariably accompanied by pronounced mutarotation and a high specific rotation, and any factor which prevents the latter prevents gel formation as well. This appears to be characteristic of optically active systems capable of forming gels. It is suggested that the intermicellar cohesion which accompanies the incipient precipitation responsible for gel formation modifies indirectly the intramolecular structure by exercising a "distributed stress," which in the special case of gelatin is more effective in controlling rotatory power than the more localised stresses associated with acid or base combination. Curves summarising the data obtained are given.

L. S. THEOBALD.

Ionic activity of gelatin. H. S. SIMMS (J. Gen. Physiol., 1928, **11**, 613—628).—Titration curves have been determined for solutions of gelatin free of electrolytes and containing definite concentrations of sodium and magnesium chlorides and potassium and magnesium sulphates, and the influence of these salts on the dissociation constants of the gelatin and on its activity has thus been found. From the relation between the ionic strength and the activity of a multivalent ion, the dissociating groups of which are separated by finite distances, the average distance between like charges on the gelatin molecule has been calculated and is found to be 18 Å. The structure of the gelatin molecule is discussed (cf. A., 1926, 681).

W. O. KERMACK.

Nature of the ionisable groups in proteins. H. S. SIMMS (J. Gen. Physiol., 1928, **11**, 629—640).—The titration curve for gelatin deaminised by treatment with nitrous acid has been determined. The resulting data are analysed along with the titration curves for gelatin and for ovalbumin. These curves are in general such as are to be expected from the amino-acid content of the protein except that the place of arginine appears to be taken by a group referred to as "prearginine" which shows itself at p_H 4·6 (cf. A., 1926, 681).

W. O. KERMACK.

Combination of salts and proteins. III. The combination of cupric, magnesium, calcium, aluminium, lanthanum, and potassium chlorides, silver nitrate, and sodium sulphate with gelatin. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1928, **11**, 481—493).—A gelatin solution contained within a membrane is allowed to come into equilibrium with a salt solution on the other side of the membrane and the electrical potential between the liquids on two sides of the membrane is measured. The concentration of the salt ions in the liquid external to the membrane is found by analysis, and from this the concentration of the free salt ions within the membrane is calculated from the theory of the Donnan membrane equilibrium. The total concentration of ions within the membrane is found by analysis, so that the quantity of ions combined with the gelatin may be calculated by difference. In the case of cupric chloride 0·9 millimol. of copper combines with 1 g. of gelatin, but gelatin deaminised by treatment with nitrous acid combines with only 0·4—0·5 millimol. of copper per g. In presence of acid, less copper combines with gelatin, but the sum of the copper ions and hydrogen ions which combine with gelatin remains constant and equal to 0·9 millimol. per g. The chloride ion combines with gelatin whether deaminised or not. Similar results are found for aluminium, lanthanum, magnesium, and calcium chlorides, but in these cases deamination of the gelatin does not alter the power of combining with the cation. For lithium, sodium, and potassium chlorides no combination with the cations appears to take place, but only with the chloride ion, so that the gelatin is negatively charged and not positively as with the preceding salts. In the case of silver nitrate some combination with the silver ion takes place, but the nitrate ion is uncombined, whilst with sodium sulphate no combination occurs, the gelatin remaining unchanged.

W. O. KERMACK.

Influence of inorganic ions on the dispersion of ovalbumin and hæmoglobin at various hydrogen-ion concentrations. V. SCHRODER (Biochem. Z., 1928, **195**, 210—219).—By counting the number of particles visible ultramicroscopically in solutions of ovalbumin and hæmoglobin, it is shown that at a definite p_H, the addition of salts (0·05—0·1M) displaces the precipitation optimum, anions displacing to the acid side in the order $SO_4 < HPO_4 < Cl, Br, I < SCN$ and the cations $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ to the alkaline side.

P. W. CLUTTERBUCK.

Lipin–protein complexes. I. Lecithin–caseinogen complexes. T. R. PARSONS (Biochem.

J., 1928, **22**, 800—810).—The percentage of lecithin in precipitates obtained by the addition of a mixture of lecithin and caseinogen to buffer solutions of graded acidity increases with increasing hydrogen-ion concentration of the medium. When mixtures of caseinogen and progressively increasing quantities of lecithin are added to the same buffer solution the initially rapid increase in the percentage of lipin in the several precipitates becomes more and more gradual until a stage is reached at which very considerable further increase of the total proportion of lecithin added produces but slight increase in the percentage of the constituent in the precipitated complex. The results are explained in terms of the mutual precipitation of two colloids with opposite charges which vary in intensity with the hydrogen-ion concentration of the dispersion medium.

S. S. Zilva.

Plasticity. IV. Plastic masses with silica. O. Ruff and B. Hirsch (Z. anorg. Chem., 1928, **173**, 14—26).—The preparation of plastic masses from which articles can be moulded from powdered quartz is described. The starting material was Swedish quartz of which the particles varied in size from 2μ to 8μ. By washing, centrifuging, etc. various fractions of the quartz were obtained. The effect of alkali on the plasticity was determined; it was not possible to make a vessel from this paste. One sample of a neutral paste, where the silica was merely mixed with water, was suitable for working, and a vessel was made, dried, and burnt. For acid pastes, the silica was first mixed with hydrochloric acid of various concentrations. The effect of acid concentration, size of particles, and temperature on the degree of plasticity was shown. Addition of acid improves the plastic properties of a quartz–water paste. Experiments were also carried out with pastes acidified with nitric, sulphuric, oxalic, phosphoric, or acetic acid, respectively, and with pastes to which solutions of neutral salts as well as hydrochloric acid had been added. The vessels moulded were burnt at about 1500°. The pastes contained in all cases a certain amount of quartz gel and sol. The assumption that the increased plasticity is due to adsorption of the acid, which has been put forward to explain the similar effects with alumina and zirconia, is tested, and it is found that the amount of hydrogen-ion adsorption is only small and is difficult to determine. The hydrogen-ion concentration of the quartz hydrated surface is p_H 4·85. A hypothesis is put forward to explain the facts, based on the assumption of a diffusion equilibrium between the hydrogen ions which find their way inside the quartz particle and those in the dispersion medium, and the formation of a polar layer of molecules on the surface of the quartz particle.

A. J. Mee.

Dispersoidological investigations. XVIII. General methods of obtaining fibrous precipitates of any substance; the structure of fibres in general and of cellulose fibres in particular. P. P. von Weimarn (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **8**, 7—17).—Precipitates of a fibrous structure may be obtained by several methods. A precipitate AC, produced by the interaction of two very concentrated solutions of AB and CD (Kolloid-Z., 1908, **2**, 306), consists of fibres the walls of which represent a gelatinous membrane of the substance AC and the adsorbed soluble reaction product DB. Within the fibres is a solution of AB or CD. Similar fibres are obtained under suitable conditions if the solution becomes separated into two layers. The process is accompanied by the formation of practically insoluble membranes on the surface of streams arising during this separation, *e.g.*, the effects observed during the separation into two layers of aqueous colloidal solutions of silk fibroin (A., 1927, 309) or casein by the addition of alcohol, salts, etc. A third method of obtaining fibrous precipitates depends on whether the crystals are "negative," *i.e.*, drawn out to a large extent in one direction forming needles, or not. The ends of the microcrystals drawn out in one direction possess the greatest velocity of growth, and when in the mother-liquor easily grow together, forming long fibres. The movement of the mother-liquor from the crystals in a definite direction promotes the formation of such fibres. Cellulose fibres are more complex in structure than precipitate fibres. Microscopic and ultramicroscopic examination of cellulose fibres, under different conditions of swelling, shows that the fibre consists of a number of concentric tubes. The outer hard cuticle or skin consists of a mixture of wax-like and grease-like substances the chemical nature of which has not yet been clearly defined. Then follows a transition layer of cuticulated cellulose, a tube chiefly of cellulose, a second transition tube of plasmated cellulose, and finally an inner tube which contains the central canal or lumen and represents a plasmatic formation. The cellulose tube consists of a number of very thin concentric tubes the walls of which are of unequal thickness and consist of ultramicroscopically thin fibres arranged parallel to each other along the length of the tubes. During dispersion the fibre is divided into long thin fibrils which ultimately break up across the length of the fibre.

M. S. Burr.

Dispersoidological investigations. XX. Microscopic investigation of coarse-cellular or membranous jellies in polarised light. P. P. von Weimarn (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **8**, 41—66).—The method of studying barium sulphate precipitates in polarised light is described, and a number of photomicrographs which have been taken are reproduced. The results support the conclusions reached in numerous earlier publications, viz., that the "aggregate fluid-crystalline" state is a perfectly universal state of matter. M. S. Burr.

Dispersoidological investigations. XXI. Caoutchouc-like state of matter in connexion with a microscopic investigation of silk coagula in natural and polarised light. P. P. von Weimarn (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **8**, 67—80).—The microstructure of a silk coagulum and its action on polarised light have been examined during the changes in consistency and elastic properties which accompany dehydration and ageing; similar observations were also made with threads of natural silk during the process of swelling to a syrupy consistency in hot concentrated sodium iodide solu-

tion. As the threads swell they are seen to be composed of the thinnest ultramicro-fibrils, which, in the course of swelling, gradually become curled in spirals. When the thread has the consistency of a viscous syrup, several of these spiral curls coalesce into oblong drops. In the reverse process, threads drawn out of a silk coagulum, precipitated by a concentrated neutral aqueous solution of sodium citrate, ultimately display properties identical with those of natural silk threads, including the appearance of interference colours. In the state in which the curled fibrils are evident, the silk coagulum displays elastic caoutchouc-like properties. It is therefore inferred that the high elasticity of caoutchouc must be due to the presence of similar spirally curled fibrils in an interfibril, viscous, or plastic dispersion medium which permits the fibrils, after the stretching out of the system, to become more or less straightened, as well as to become curled again after the system has been released from tension. These conclusions have been confirmed by the examination, in polarised light, of a thread of rubber alternately stretched and contracted. In the precipitation of silk coagula the aggregate fluid-crystalline state is observed as in the case of barium sulphate (cf. preceding abstract). M. S. Burr.

Does the theory of complexity of micelles find application in the study of cellulose ? I, II. M. Catoire (Bull. Soc. Chim. biol., 1928, **10**, 714—726; 727—735; cf. A., 1927, 412, 511).—I. The deflocculation accompanied by swelling indicates that the structure of cellulose breaks down, through less complex polymerides, to the monoses in a number of stages. Fractional precipitation of an acetic acid solution of cellulose acetate with water shows that the inorganic matter (particularly silica) is probably present in a state of combination and not merely as an impurity. It is suggested that the smaller micelles contain less silica and that silica is essential to the polymerisation of the monoses. Partial removal of the mineral matter from cotton renders it more susceptible to deflocculation after conversion into cellulose nitrates, whilst the addition of various salts during, or after, treatment with nitric and sulphuric acids leads to the formation of a less soluble product. Treatment of cellulose acetates of small inorganic content (slightly soluble in acetone) with aqueous solutions of sodium hydroxide of increasing concentration leads first to an increase in the solubility and then to insolubility after drying.

II. The application of the theories of complexity and micelles is discussed. G. A. C. Gough.

Coagulation of strongly solvatised sols by organic substances and salts. I. B. Jirgensons (Biochem. Z., 1928, **195**, 134—141).—A medium containing a mixture of an organic substance (*iso*propyl and ethyl alcohols, acetone) and an inorganic salt (calcium, strontium, potassium chlorides) coagulates caseinogen and albumin sols more rapidly than either substance added separately. When the mixture was added in large quantity (30—50 vols. % of alcohol with 0·2—1·2M-solution of inorganic salt per litre) it was found that the coagulation time was lengthened with organic substances of small dielectric constant (*iso*propyl alcohol). The degree of stabilisation increases with increasing concentration of the organic and inorganic substances. P. W. Clutterbuck.

Coagulation of colloids by electrolytes. V. Pure silicic acid sols. E. Laskin (Kolloid-Z., 1928, **45**, 129—136).—Pure silicic acid was prepared by adding sodium silicate to hydrochloric acid, dialysing in a collodion thimble, and finally subjecting to electrodialysis and concentrating by evaporation. Such sols are very stable and strongly acid in reaction, having a of about 3·5. The coagulation of the sol by electrolytes was followed by conductometric and potentiometric methods. In some preparations, coagulation can be brought about only by saturated potassium chloride solution, whilst in others, saturated solutions of lithium chloride, barium chloride, and acids are also effective. It is believed that the principal factor in the coagulation of the sols is the dehydration of the colloid particles by ions with strong hydrating tendencies. Basic colouring matters coagulate the sol readily, even when in very dilute solution, the cations of the substance being adsorbed by the colloid particles. Acid colouring matters are not adsorbed by the sol and do not effect coagulation. The degree of dispersion of the colouring matter plays no part. During coagulation the acidity of the sol increases, resembling in this respect the behaviour of mastic sols, but differing from that of sols of arsenious sulphide and tungstic acid.

E. S. Hedges.

Coagulation. G. Wiegner [with P. Tionta and H. Müller] (Z. Pflanz. Düng., 1928, **A 11**, 185—228).—The Smoluchowski rule for the rapid perikinetic coagulation of monodisperse systems may be considered as an extension of the laws governing the reactions of gold sols. Kaolin particles in monodisperse systems are coagulated according to the same rule. The slow perikinetic coagulation of monodisperse systems is examined by ultramicroscopic methods. Relationships between this process, ion hydration, and base exchange in colloids are examined and discussed. The Müller formula is applied to the rapid perikinetic coagulation of polydisperse systems and is applicable to clay particles. Polydisperse systems coagulate more rapidly than monodisperse systems involving the same number of ultimate particles. The mass of the particles in polydisperse systems is one thousand times as great as in corresponding monodisperse systems. Formulæ are developed which represent the course of rapid and slow orthokinetic coagulation. By the electrical discharge of the particles it is possible to differentiate between their sizes. Orthokinetic coagulation is frequently more important than perikinetic in soil analysis by sedimentation or elutriation methods. It is shown that the Wiegner elutriation apparatus may be arranged so that by observations of deposition curves at different heights the original dispersion characteristics can be calculated. A. G. Pollard.

Stabilisation of albumins by globulins. V. Bergauer (Bull. Soc. Chim. biol., 1928, **10**, 576—580).—In order to determine whether the protecting action of natural globulin against the coagulation of serum-albumin by alcohol is due actually to the globin or to lipins contained in the usual preparation,

the coagulating actions of alcohol on (*a*) serum-albumin alone, (*b*) serum-albumin protected with globulin, with lipin-free globulin, and with a lipin emulsion have been investigated. Whilst globulin itself has a small effect, the lipin-containing globulin and the lipin emulsion show much greater protection. It is suggested that the protecting action of the lipin-free globulin is due to a small amount of chemically combined lecithin. G. A. C. GOUGH.

Colloidal dissolution of composite (high-molecular) compounds by means of substances which possess a large true solubility and are inclined to great solvation. P. P. VON WEIMARN (Japan. J. Chem., 1928, **3**, 71—87).—See A., 1927, 725. M. S. BURR.

Free energy and fugacity in gaseous mixtures of hydrogen and nitrogen. A. R. MERZ and C. W. WHITTAKER (J. Amer. Chem. Soc., 1928, **50**, 1522—1526).—The fugacities and free energies of nitrogen and hydrogen in mixtures of these gases are calculated from the compressibility figures of Bartlett (A., 1927, 927). The maximum deviation from the behaviour of a perfect mixture does not exceed 20% for pressures up to 1000 atm. S. K. TWEEDY.

Strength of acetamide as an acid. G. E. K. BRANCH and J. O. CLAYTON (J. Amer. Chem. Soc., 1928, **50**, 1680—1686).—By plotting the conductivities, Λ, at 25° of acetamide solutions of constant concentration (C) containing small, varying concentrations (c) of barium hydroxide against c, $L=(\partial\Lambda/\partial c)_C$ is obtained. The variation of L with C was measured, and, from conductivity measurements for acetamide solutions containing sodium chloride (for which L is a linear function of C), was corrected for the influence of acetamide on the mobilities of the acetamide and hydroxyl ions. The value 12±2 is recorded for the hydrolysis constant of the acetamide ion, and $K=8{\cdot}3\times10^{-16}$ for the acid dissociation constant. Measurements with benzamide, which were unsatisfactory owing to the low solubility of this substance, gave K between 10^{-14} and 10^{-15}, in disagreement with the accepted value. S. K. TWEEDY.

Electrolytic dissociation of dibasic acids. IV. Dissociation constants of some thiolmonocarboxylic acids. E. LARSSON (Z. anorg. Chem., 1928, **172**, 375—384).—As unsymmetrical dibasic acids monothiolmonocarboxylic acids, OH·CO·R·SH, must have two first and two second dissociation constants, K_1', K_1'', and K_2, K_2'', respectively. These cannot be determined separately, but only the total values, $K_1=[H^+]\times([^-O{\cdot}CO{\cdot}R{\cdot}SH]+[OH{\cdot}CO{\cdot}R{\cdot}S^-])\div[OH{\cdot}CO{\cdot}R{\cdot}SH]$ and $K_2=[H^+]\times[^-O{\cdot}CO{\cdot}R{\cdot}S^-]/([^-O{\cdot}CO{\cdot}R{\cdot}SH]+[OH{\cdot}CO{\cdot}R{\cdot}S^-])$. $K_1=K_1'+K_1''$, and $1/K_2=1/K_2'+1/K_2''$ or $K_2=K_2K_2''/(K_2+K_2'')$. Actually K_1 is practically equal to the dissociation constant of the carboxyl group of the acid and K_2 the dissociation constant of the thiol anion $^-O{\cdot}CO{\cdot}R{\cdot}SH$. K_1 has been determined at 25° by conductivity measurements, correction being made on the assumption that the activity coefficient of the ions may be calculated from the formula valid for acetic acid. K_2 has been determined colorimetrically by indicators, the degree of accuracy being approximately 0·1 of p_H. The values of K_1 for thioglycollic, α-thiol-lactic, β-thiol-lactic, and α-thiol*iso*butyric acid are $2{\cdot}1\times10^{-4}$, $2{\cdot}0\times10^{-4}$, $0{\cdot}46\times10^{-4}$, and $1{\cdot}26\times10^{-4}$, respectively, and of K_2, $2{\cdot}1\times10^{-11}$, $2{\cdot}0\times10^{-11}$, $2{\cdot}9\times10^{-11}$, and $0{\cdot}48\times10^{-11}$, respectively. M. S. BURR.

Ionisation of solutions of hydrogen sulphide. M. AUMERAS (Compt. rend., 1928, **186**, 1724—1726; cf. this vol., 711).—It is shown theoretically and confirmed by the experiments of the author and of others that the solubility product of cadmium sulphide in water corresponds with the equilibrium $CdS+H_2O \rightleftharpoons CdOH^{\cdot}+HS'$ and not with $CdS \rightleftharpoons Cd^{\cdot\cdot}+S''$. If this is taken into account, the second dissociation constant of hydrogen sulphide has a value of $0{\cdot}59-0{\cdot}37\times10^{-15}$ at 25° which is of the same order as that found by an independent method by Knox (A., 1906, ii, 608). J. GRANT.

Dilution and neutral salt errors of buffer mixtures. C. MORTON (J.C.S., 1928, 1401—1415).—Electrometric measurements have been made which show the influence of dilution and the addition of neutral salts on half-neutralised solutions of acetic and cacodylic acids, one fourth neutralised solutions of aspartic acid and of arginine, three fourths neutralised solutions of *o*-phthalic and α-monoglycerylphosphoric acids, and mixtures of sodium pyrophosphate and hydrochloric acid in the molecular proportions 2 : 3 and 2 : 1. The relations (between the p_H limits 4—10) are expressed by Debye and Hückel's equation, $p_H=p_K-\log[\text{acid}]/[\text{salt}]-A\sqrt{u}+Bu$. The value of A is approximately $(n-0{\cdot}5)$, where n is the valency of the buffer electrolyte, and agrees with that calculated on Debye and Hückel's theory.

The Van Slyke (A., 1922, ii, 893) unit of buffer capacity describes only the resistance of the buffer solution to p_H changes on addition of alkali or acid. It is suggested that this unit should be supplemented by a factor $\pi=dp_H/d\sqrt{\mu}=2\beta\sqrt{u}-A$ which is a measure of the dilution and neutral salt errors. As the second term is the greater, especially in dilute solution, π will increase rapidly with the valency of the buffer electrolyte. The values obtained for the thermodynamic dissociation constants are: aspartic acid, $pk_a=3{\cdot}895$; acetic acid, $pk=4{\cdot}735$; cacodylic acid, $pk_a=6{\cdot}247$; *o*-phthalic acid, $pk_2=5{\cdot}333$; glycerylphosphoric acid, $pk_2=6{\cdot}744$; pyrophosphoric acid, $pk_3=6{\cdot}704$, $pk_4=9{\cdot}880$; arginine, $pk_{b_1}=5{\cdot}178$. F. J. WILKINS.

Influence of dilution on the p_H of buffer mixtures. I. M. KOLTHOFF (Biochem. Z., 1928, **195**, 239—247).—The influence of dilution on the p_H of ordinary (phthalate, acetate, phosphate, and hydrogen carbonate–carbonate) buffer solutions may be accurately calculated using the equations of Debye and Hückel for the activity coefficients of the ions and assuming a mean ionic diameter of 4×10^{-8} cm. With citrate buffer, better results are obtained by assuming a diameter of $6{\cdot}5\times10^{-8}$ cm. With boric acid–borate mixtures, the calculation breaks down, due to formation of complex boric acid–borate ions. P. W. CLUTTERBUCK.

Pinachrome as a one-colour indicator. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1928, **50**, 1604—1608).—A solution of pinachrome in alcohol is a suitable indicator for use near the neutral point

(p_H 5·8—7·8). At low electrolyte concentrations the salt error is very small; at higher concentrations the acidity indicated is too great. Alkaline solutions of the indicator are unstable. A simple test is described whereby the adsorption of a substance at the air–water interface may be demonstrated.

S. K. TWEEDY.

Influence of the so-called higher terms in the Debye–Hückel theory of solutions of strong electrolytes. T. H. GRONWALL, V. K. LAMER, and K. SANDVED (Physikal. Z., 1928, **29**, 358—393; cf. A., 1927, 314, 828).—The Debye–Hückel theory is discussed at length with special reference to the theoretical side of recent developments. An analytical integration is given for the Poisson equation forming the basis of the theory and determining the electrostatic potential ψ of an ion. This gives a complete statistical expression for the electrical density as a function of ψ, instead of using merely the first linear term as in the approximate calculation given by Debye and Hückel. Hence the free energy as well as the activity coefficient remain in the form of infinite series progressing in powers of $1/D$, D being the dielectric constant. For very low concentrations asymptotic expressions are obtained, from which it follows that the Debye limiting law is valid not only for the Debye approximation, but also quite generally. For the case of pairs of ions of equal valency, numerical values have been worked out for terms up to $1/D^5$ inclusive. Comparison with experimental data shows very good agreement even in the case of small ionic diameters where the Debye approximation fails.

R. A. MORTON.

Solubility of lead bromide in aqueous salt solutions and the calculation of the activity coefficient from solubility measurements. M. RANDALL and W. V. A. VIETTI (J. Amer. Chem. Soc., 1928, **50**, 1526—1534).—The solubility at 25° of lead bromide in solutions of lead and barium nitrates and cadmium and potassium bromides is measured. The solubility in pure water is 0·02683 mol. per 1000 g. of water. A graphical method for calculating the Lewis and Randall "proportionality factor" from the graph of the log. of the reciprocal of the mean molality against the square root of the ionic strength is given, and illustrated by application to thallous chloride (*ibid.*, 1535) and lead bromide. The method is satisfactory when the saturating salt is "non-associated" in the Bjerrum sense, or when the solubility is very small, but it may lead to considerable errors with fairly soluble "associated" substances such as lead bromide.

S. K. TWEEDY.

Solubility of lead monoxide and basic lead carbonate in alkaline solutions. M. RANDALL and H. M. SPENCER (J. Amer. Chem. Soc., 1928, **50**, 1572—1583).—The solubilities at 25° of the tetragonal (red) and orthorhombic (yellow) varieties of lead monoxide in dilute potassium hydroxide solution are recorded. The standard free energy change for the reaction $PbO+OH'=HPbO_2'$ is 1903 g.-cal. and 1740 g.-cal. for the red and yellow oxides, respectively. From the corresponding solubilities of hydrated lead monoxide and basic lead carbonate the standard free energies are: $PbO,\frac{1}{3}H_2O(s)+OH'=HPbO_2'+\frac{1}{3}H_2O(l)$, 1512 g.-cal; $Pb_3(CO_3)_2(OH)_2(s)+7OH'=3HPbO_2'+2CO_3''+3H_2O(l)$, 6961 g.-cal. The activity coefficient of the plumbite ion is approximately equal to that of the nitrate ion in dilute solutions. Berl and Austerweil's work is criticised (A., 1907, ii, 457).

S. K. TWEEDY.

Reduction potential of selenious acid and the free energy of aqueous selenic acid. M. S. SHERRILL and E. F. IZARD (J. Amer. Chem. Soc., 1928, **50**, 1665—1675).—The equilibrium $X_2+H_2SeO_3+H_2O=H_2SeO_4+2HX$, where X=Cl or Br, was investigated. From the equilibrium constants the reduction potential of the reaction $H_2SeO_3+H_2O(l)=3H^{\cdot}+HSeO_4'+2\ominus$ was calculated to be −1·088 volts. The free energy, ΔF, of $HSeO_4'$ is thus −107,710 g.-cal. at 25°. Data representing the solubility of gaseous chlorine in hydrochloric acid at 25° and 1 atm. and the distribution of bromine between carbon tetrachloride and aqueous hydrobromic acid solutions are recorded. The equilibrium constant $[Br_3']/[Br_2][Br']$ increases with rising hydrobromic acid concentration.

S. K. TWEEDY.

Thermomagnetic study of magnetic iron sesquioxide. J. HUGGETT and G. CHAUDRON (Compt. rend., 1928, **186**, 1617—1619).—A thermomagnetic study of Malaguti's magnetic iron sesquioxide has shown that at a sufficiently high temperature it is transformed irreversibly into the non-magnetic form, with the liberation of heat. The reversibility obtained with the impure oxide is due to the elevation of this temperature above the point of magnetic transformation. The magnetic properties of the oxide therefore depend on the method of preparation.

J. GRANT.

Metallic nitrides and hydrides. I. I. SHUKOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 600—640; cf. *ibid.*, 1926, 3, 14).—The equilibrium pressures for hydrogen in contact with various metals at various temperatures have been determined. The following hydrides are formed: sodium hydride, NaH; cerium hydride, CeH_2, which is capable of dissolving hydrogen to yield a solid solution, and palladium hydride, Pd_2H. The curve for rhodium is similar to that for palladium, indicating a large absorptive power for hydrogen, but in the case of iridium, compound formation does not appear to occur although considerable quantities of hydrogen are absorbed.

R. TRUSZKOWSKI.

Systems iron–silicon, iron–chromium, and iron–phosphorus. C. KREUTZER (Z. Physik, 1928, **48**, 556—566).—The influence of silicon and chromium on the α—γ and γ—δ changes of iron has been investigated by means of X-ray spectra. With silicon concentrations up to 2·2% the α-phase changes into the δ-phase through γ-iron. With 2·2—2·5% of silicon there is a region in which α- and γ-iron can coexist, but above 2·5% the α-phase changes directly into the δ-phase. Similarly, the α—δ change occurs directly in the presence of more than 15% Cr. With phosphorus up to 1·7%, mixed crystals are formed, but at greater concentrations the phosphides Fe_3P, Fe_2P, and a third of unknown composition are produced.

J. W. SMITH.

Critical points in chromium–iron alloys. A. B. KINZEL (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 100, 7 pp.).—With addition of chromium up to 10% the A4 transformation is gradually lowered from 1400° to 1250°; further addition causes more abrupt lowering, and at 12·25% the A4 and A3 transformations are practically coincident. The A3 transformation is not affected. The "austenite" loop in the chromium–iron system ends at 12·37% Cr.
CHEMICAL ABSTRACTS.

α-Phase boundary of the copper–nickel–tin system. W. B. PRICE, C. G. GRANT, and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 103, 12 pp.).—The ternary isotherm was determined for mixtures containing less than 25% Sn. The α-phase boundary fluctuates but little. A series of hardenable alloys is described.
CHEMICAL ABSTRACTS.

Aluminium–beryllium alloys. R. S. ARCHER and W. L. FINK (Amer. Inst. Min. Met. Eng. Tech. Pub., 1928, No. 91, 27 pp.).—Brinell hardness numbers for chill-cast and heat-treated aluminium–beryllium (0·013—0·75%) alloys show an ageing effect, maximal for the alloy containing 0·75% Be. The solid solubility of beryllium is about 0·075% at 639°, 0·05% at 631°, and <0·013% at the ordinary temperature. The constitutional diagram was re-examined up to 1·7% Be; the eutectic point is at 0·87% Be and 645°. The density is additive. The effect of beryllium on the properties of aluminium-copper alloys was investigated; the corrosion resistance is not improved. CHEMICAL ABSTRACTS.

Hydrates, transition temperatures, and solubility of sodium iodate. H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1928, [v], **16**, 68—72).—The stable hydrates of sodium iodate are the penta- and mono-hydrates; the hydrate $NaIO_3,1{\cdot}5H_2O$ reported by Meerburg (A., 1905, ii, 508) could not be detected. The transition temperatures corresponding with $NaIO_3,5H_2O \rightarrow NaIO_3,H_2O$ and $NaIO_3,H_2O \rightarrow NaIO_3$ are 19·85° and 73·4°, respectively. The change at 73·4° is slow enough to permit the solubilities of the metastable and stable forms to be determined. Solubility data for sodium iodate in water from 0° to 90·3° are given. The solubility, S, of the monohydrate from 20° to 50° is represented by the equation $\log S = 3{\cdot}6344 - 802{\cdot}8/T$ and that of the pentahydrate between 0° and 15° by $\log S = 7{\cdot}7793 - 2019/T$.
L. S. THEOBALD.

System lithium perchlorate–water. J. P. SIMMONS and C. D. L. ROPP (J. Amer. Chem. Soc., 1928, **50**, 1650—1653).—According to the solubility curve between 0° and 170° the tri- and mono-hydrates are the only compounds formed. The transition points are: $LiClO_4,3H_2O$ (m. p. 95·1°) $\rightleftharpoons LiClO_4,H_2O$, 92·53°; $LiClO_4,H_2O$ (m. p. 149°) $\rightleftharpoons LiClO_4$, 145·75°. The solubility of anhydrous lithium perchlorate is 37·48 g. per 100 g. of solution at 25°; the densities of the saturated solutions are recorded from 0° to 40°. S. K. TWEEDY.

F. p. of ethyl alcohol–water mixtures. D. N. TARASSENKOW (Z. angew. Chem., 1928, **41**, 704).—The f. p. of mixtures of ethyl alcohol and water containing from 5·1 to 74·7% of alcohol by weight have been determined, the freezing-mixture being contained in a Dewar flask. With higher concentrations of alcohol the solution is too viscous for accurate measurement. The freezing curve indicates the separation of a crystalline hydrate.

The following data are recorded, the figures in parentheses being wt.-% of alcohol: (5·1) −2·1°, (9·3) −4·1°, (14·2) −6·7°, (17·8) −10·2°, (24·4) −15·2°, (29) −19·1°, (33·3) −24·2°, (37·6) −28·4°. (43·0) −33°, (46·7) −35·4°, (51·9) −38°, (56·3) −42°, (61·4) −45°, (66·1) −48°, (70·2) −56°, (74·7) −67°.
R. BRIGHTMAN.

System aluminium oxide–water. G. F. HÜTTIG and E. VON WITTGENSTEIN (Z. anorg. Chem., 1928, **171**, 323—343).—The properties of various preparations of hydrated alumina and also of some of the naturally occurring forms have been investigated by gradually removing the water, and at each stage of the dehydration observing the temperature, t, at which the pressure of water vapour over the product is 10 mm. (cf. A., 1926, 798). Aluminium hydroxide precipitated in the cold with ammonia from solutions of the chloride and washed until almost free from chloride is a true amorphous colloid, and the curve representing the variation of t with the water content, N, is exactly similar to those for other oxides, not related chemically to alumina, in the same state. With increasing age, the dispersity decreases, the arrangement of the molecules becoming at the same time more orderly, and the system tends to pass into hydrargillite or its dehydration products. If hydrargillite crystals are dehydrated at 192°, decomposition is complete when the residue has the composition Al_2O_3,H_2O, this being the upper limit, in respect of water content, of the series of continuously homogeneous hydrates lying between Al_2O_3,H_2O and Al_2O_3. If the cold-precipitated hydroxide, aged in air to the composition $Al_2O_3,2{\cdot}95H_2O$, is dehydrated to the composition Al_2O_3,H_2O, the N–t diagram for the removal of the last molecule of water is essentially the same as that for the complete dehydration of the monohydrate prepared from hydrargillite, except that the water is retained rather more firmly, although not firmly as in bauxite. Both preparations seem to be amorphous colloids starting to change into bauxite. The curve for bauxite itself is closely similar to that for diaspore, so that the affinity of the transformation of one form into the other must be nearly zero. By ageing the precipitated hydroxide under water, a product is obtained which seems to contain the dihydrate (cf. Guichard, A., 1927, 475). A hydroxide prepared by precipitating aluminium sulphate at 48° with ammonia in presence of ammonium chloride and ageing for a long time in a closed vessel gives the X-ray interferences corresponding with the isomeride of hydrargillite discovered by Bohm (*ibid.*, 113), and "aloton" seems to be similar. Since, however, hydrargillite itself is the stable isomeride, the colloidal system alumina–water must ultimately pass into this form. The dehydration curve of diaspore is not greatly affected by variations in the fineness of division, and yields no indications of the existence of definite lower hydrates. If hydrargillite is heated at 370° under 20 atm. pressure of water vapour, it is converted into crystalline bauxite, whereas diaspore

undergoes no change when treated in this way. From a consideration of the general behaviour of the system aluminium oxide–water, it seems that here the laws of constant and multiple proportions may possess something of an ideal character, the chemical forces which give rise to compounds with strictly stoicheiometric compositions being accompanied by forces of diffusion, which are independent of stoicheiometric considerations. The usual stoicheiometric formulæ do not, in general, therefore, represent the actual compositions, but only the limiting states which the system approaches more or less closely in the stable pure state. The activity of a preparation of aluminium oxide depends on the distance by which it is removed from the final equilibrium state.

R. CUTHILL.

Lowering of the eutectic temperature in binary mixtures. V. Determination of mol. wt. from the position of the eutectic temperature. E. KORDES (Z. anorg. Chem., 1928, **173**, 1—13).—The formation of mixed crystals raises the position of the eutectic temperature. This may possibly be due to the attractive force tending to form a compound. The mol. wt. of a substance can be found if it is mixed with another of known mol. wt. and the position of the eutectic temperature and the composition of the eutectic mixture are determined. In applying the method, regard must be had to certain causes of error, such as the formation of mixed crystals etc. Many systems have been investigated by this method, the results giving approximate values for the mol. wts. of the same order of accuracy as might be obtained by vapour-density determinations. In many cases, polymerisation is indicated. Aluminium bromide appears to dissolve as $(AlBr_3)_2$ in arsenic tribromide. Sulphur dissolved in naphthalene and in iodine separates in the monoclinic form and gives for its mol. wt. values corresponding with the formulæ $S_{8\cdot5}$ and S_9, respectively. Since other determinations have given values corresponding with S_7 to S_9 for this form, it is highly probable that the correct formula is S_8. For grey selenium a value corresponding with Se_4 is obtained. Experiments with water as one of the components indicate that the water is not polymerised. This does not agree with determinations by other methods. The method is of use for strong electrolytes. Since the mol. wt. is always found to be the same when the same crystalline form of a substance separates, it is assumed that the value obtained represents the mol. wt. of the substance in the crystalline state.

A. J. MEE.

Solid solutions and compound formation. A. LEHRMAN (Chem. News, 1928, **136**, 401—403).—It is suggested that the vertical line drawn through the point corresponding with the composition of the compound in a f.-p. diagram consists of two lines, which represent two solid solutions, so close together that the ordinary methods of analysis do not permit of their separation. Similar considerations are applied to three-component systems.

C. W. GIBBY.

Separation of mixed crystals from solutions. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1928, **173**, 73—80).—The conditions of separation of mixed crystals from a solution are discussed. Mixed crystals are not in equilibrium with the solution from which they separate, so that special diagrams must be drawn to express conditions of separation. Three methods of drawing such diagrams are given, and the differences between hydrated and anhydrous mixed salts are demonstrated. The differences can be referred to a different type of growth of the two types of crystals. Protection of one component by the other is also studied. Experiments on protection were carried out by placing mixed crystals of potassium permanganate and potassium perchlorate in a saturated solution of potassium perchlorate. If the potassium permanganate content of the mixed crystal was less than 9% a small amount dissolved, but the composition of the residue was the same. If, however, the permanganate content was greater, more dissolved, and the amount of permanganate in the residue fell to 8—11%. Similar results were obtained by using mixed crystals of potassium chromate and potassium sulphate and a solution of potassium sulphate.

A. J. MEE.

Systems with retrograde melting curves. I. System sodium selenate–water. II. System magnesium sulphate–water. A. SMITS (Z. physikal. Chem., 1928, **135**, 62—72, 73—84).—I. [With W. M. MAZEE.]—Theoretical.

II. [With J. RINSE and L. H. LOUWEKOOYMANS.] —The systems sodium selenate–water and magnesium sulphate–water have been investigated from 76° to 372° and from 60° to 95°, respectively. The former system has a continuous melting curve, partly retrogressive and having a vertical tangent, whilst the melting curve of the latter is retrogressive and has a critical end-point. A curve having two vertical tangents, a possibility discussed in I, has not yet been obtained experimentally.

H. F. GILLBE.

Equilibria between metals and salts in the molten state. X. Equilibria in the molten state with aluminium as one component. R. LORENZ and G. SCHULZ (Z. anorg. Chem., 1928, **171**, 258—260; cf. this vol., 594).—The reactions $3Mg+2K_3AlCl_6=2Al+3(MgCl_2,KCl)+3KCl$, $3Ca+2(AlCl_3,3NaCl)=2Al+3(CaCl_2,2NaCl)$, and $4Al+3Na_2SiF_6+6NaF=4Na_3AlF_6+3Si$ in the molten state seem to occur entirely from left to right.

R. CUTHILL.

Equilibria between metals and salts in the molten state. XI. Tin, cadmium, stannous chloride, cadmium chloride. R. LORENZ, W. FRAENKEL, and P. WOLFF (Z. anorg. Chem., 1928, **171**, 355—363; cf. preceding abstract).—The equilibrium $Sn+CdCl_2 \rightleftharpoons Cd+SnCl_2$ at 600° (A., 1927, 518) is displaced slightly towards the right by the addition of bismuth, which is miscible with both metals and indifferent towards the salts; dilution of the salt phase with lithium chloride or an equimolecular mixture of sodium and potassium chlorides has the reverse effect. In respect of the applicability of the mass law, the systems containing bismuth are intermediate between condensed systems and dilute solutions.

R. CUTHILL.

Thermodynamics of iron oxides. M. TIGERSCHIOLD (Jernkont. Annaler, 1923, **107**, 67—105; Chem. Zentr., 1928, i, 886).—Equilibria in the systems

iron–oxygen–carbon and iron–oxygen–hydrogen are determined. Ferrous oxide decomposes below 534° into iron and ferrosoferric oxide; ferrous and ferrosoferric oxides are more readily reduced by carbon monoxide below 800° and by hydrogen above 800°. The dissociation pressures of ferrous, ferric, and ferrosoferric oxides are computed. The reactions $3Fe_2O_3+CO=2Fe_3O_4+CO_2$ and $3Fe_2O_3+H_2=2Fe_3O_4+H_2O$ are practically irreversible. Heats of formation are calculated to be (kg.-cal.): ferrous oxide 66·3, ferrosoferric oxide 217·0, ferric oxide 197·1. A. A. ELDRIDGE.

Equilibria in the reduction, oxidation, and carburation of iron. VI. R. SCHENCK and T. DINGMANN (Z. anorg. Chem., 1928, **171**, 239—257).—Experiments in which iron was caused to take up oxygen by being heated in carbon dioxide, under conditions admitting no possibility of contamination of the reacting system with substances derived from the containing vessel, have given values for the solubility of oxygen in iron which approximate to that previously obtained by the reduction method (A., 1927, 1030). Benedicks and Löfquist's explanation of the discrepancy between this value and values to be found in the literature (Z. anorg. Chem., 1928, **171**, 231) is therefore to be regarded as untenable; it is probably the latter values which are affected by the material of the containing vessel. Further, a comparison of the diagram for the cementation of iron with carbon monoxide calculated from the data for cementation with methane and the diagram obtained directly by experiment shows that in the latter the austenite area is depressed by about 130°, and is different in form, which can be explained only by postulating a considerable solubility of oxygen in iron. R. CUTHILL.

Heterogeneous equilibrium $CdBr_2+H_2S \leftarrow CdS+2HBr$ at higher temperatures. K. JELLINEK and L. ZUCKER (Z. anorg. Chem., 1928, **171**, 271—274).—The above equilibrium has been studied at 300—500° by the method applied to other sulphides (cf. following abstract). Except at the highest temperature, the values of the equilibrium constant are in fairly good agreement with Nernst's approximate formula. R. CUTHILL.

Heterogeneous equilibrium between metallic chlorides and hydrogen sulphide, and between metallic sulphides and hydrogen chloride at higher temperatures. K. JELLINEK and G. VON PODJASKI (Z. anorg. Chem., 1928, **171**, 261—270).—The following equilibria have been measured over the temperature ranges indicated in parentheses: $CdCl_2+H_2S \leftarrow CdS+2HCl$ (232—352°), $MnCl_2+H_2S \rightleftharpoons MnS+2HCl$ (407—583°), and $2AgCl+H_2S \rightleftharpoons Ag_2S+2HCl$ (230—419°), by passing hydrogen sulphide over the chloride or hydrogen chloride over the sulphide at various rates, and extrapolating the composition of the emergent mixture of gases to zero rate of flow. The values of the equilibrium constants are not in agreement with Nernst's approximate formula, the reason being that it is not permissible to neglect the molecular heats. Vologdin and Penkievitsch's value of 62,900 g.-cal. for the heat of formation of manganous sulphide (A., 1914, ii, 247) is irreconcilable with the present results. R. CUTHILL.

Reduction of silver sulphide by means of carbon. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], **7**, 367—369).—The tension of carbon disulphide in the reaction $2Ag_2S+C=4Ag+CS_2$ at 1015° and 1050° has been calculated (*a*) from determinations of the sulphur tension and of the ratio p_{S_2}/p_{CS_2} (cf. this vol., 480, 594), and (*b*) from the equilibrium data obtained from the reduction of silver sulphide by hydrogen and the dissociation constant of carbon disulphide. The agreement between the two methods is satisfactory. O. J. WALKER.

Chemical equilibrium and space [geometry]. N. S. KURNAKOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 525—552).—The application of three-dimensional geometry to chemical problems is discussed and illustrated. R. TRUSZKOWSKI.

[Equilibrium models.] V. I. NIKOLAEV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 553—561).—The space-model for the four-component system H_2O–N_2O_5–Na_2O–EtOH in the form of a triangular prism is described; solutions saturated with sodium nitrate are represented by two curved surfaces which intersect at the median line of the triangle and run parallel to the axis of the prism. R. TRUSZKOWSKI.

Generalisation of the method of residues; determination of hydration of solid phases in the equilibrium of systems. V. P. SHISHOKIN (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 746—749).—Schreinemakers' residue method (A., 1893, ii, 260) for the determination of the composition of solid phases in heterogeneous systems may be extended to any number of solid phases. This is illustrated by reference to the system magnesium chloride, sodium sulphate, water. R. TRUSZKOWSKI.

Method of radiation calorimetry, and the heat of fusion or of transition of certain substances. L. E. STEINER and J. JOHNSTON (J. Physical Chem., 1928, **32**, 912—939).—A method is described for determining the heats of fusion or transition of substances, or the heat of reaction of certain irreversible processes. The new, electrically-heated, radiation calorimeter permits the time–temperature curves for small amounts of poorly-conducting materials to be rapidly obtained, and the heat of reaction can then be found by graphical methods preferably from the heating curve with an error not greater than 5% from the mean of a series. The heats of fusion of phenol and benzophenone found are 2690 and 4600 g.-cal., respectively, and those of the polymorphous forms of monochloroacetic acid are α 4630, β 4450, and γ 3790 g.-cal. The heat of transition of red–yellow mercuric iodide is 640 g.-cal. and of ammonium nitrate III—II 310, and II—I 980 g.-cal., respectively. The interpretation of time–temperature curves and the theoretical basis of the method are fully discussed and details of the apparatus are given. L. S. THEOBALD.

Heat of formation of partly miscible water–alcohol mixtures. P. BRUN (Compt. rend., 1928, **186**, 1729—1731).—Mixtures of ethyl and *iso*amyl

alcohols and water intended to simulate fusel oils have been studied calorimetrically by Berthelot's method, exothermic and endothermic mixtures being associated with a decrease and an increase in volume, respectively (cf. A., 1926, 895). Biron's law is found to apply except for mixtures near the miscibility limit. The thermal diagrams show breaks characteristic of the critical miscibility and an attempt is made to explain the contradictory results of Mondain-Monval (Bull. Soc. chim., 1928, [iv], **43**, 145) on the assumption of molecular association which modifies the thermal properties of certain mixtures. J. GRANT.

Ratio of the heats of combustion of benzoic acid and salicylic acid. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1928, **47**, 709—714).—By means of combustions of naphthalene, methyl racemate, and hydrobenzoin it has been confirmed that the heats of combustion determined by Berner (A., 1926, 116) contain a small systematic error. The heat of combustion of salicylic acid found by him is too low. A redetermination of this quantity gave the value 5241·3 g.-cal. (15°) per g. (air) at constant volume, in agreement with the authors' previous determination (A., 1925, ii, 39). O. J. WALKER.

Effect of certain corrections on the results obtained for the heat of combustion of organic compounds. W. SWIENTOSLAWSKI and H. STARCZEWSKA (Rocz. Chem., 1928, **8**, 195—209).—Corrections for the isothermal heat of combustion of a number of organic substances are given, as well as for the temperature coefficient. These corrections are so small as to be negligible except in those cases where the heat of combustion of the given compound is small; in the latter case the correction is negligible where the temperature variation is of the order of 1°. If the combustions take place within the temperature limits 15—21°, the correction for the temperature coefficient may also be neglected. When an ice-calorimeter is used, or when the deviations from the usual calorimetric temperature of 15—21° are considerable, the application of the correction for the temperature coefficient du/dt is necessary.
R. TRUSZKOWSKI.

Swientoslawski's method for the correction of the older thermochemical data. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1928, **47**, 701—708; cf. this vol., 712).—A further criticism of Swientoslawski's method for correcting the thermochemical data of Zubow, Swarts, Richards, and others. It is considered that the only result of these corrections is to replace incorrect data by data the trustworthiness of which is doubtful. O. J. WALKER.

Characteristics of homogeneous, exothermic gas reactions. R. N. PEASE and P. R. CHESEBRO (Proc. Nat. Acad. Sci., 1928, **14**, 472—475).—Although it is usually found that a glass surface acts as a catalyst, experiments are described which point to inhibition by glass surfaces. A 1 : 1 methane–oxygen mixture was passed through a pyrex tube poisoned with potassium chloride, heated at 650°. It was found that 5% of the mixture was oxidised in a contact time of 3 secs. When, however, the tube was packed with broken pyrex glass, poisoned as before with potassium chloride, only 10% oxidation occurred in a contact time of 20 sec. It thus appears that the glass packing inhibited the reaction. It is inferred that the reaction is homogeneous. The potassium chloride is not essential for this inhibiting effect. Clean glass fragments have a similar, but smaller, effect. Other reactions, such as the oxidation of hydrogen and of *iso*butane, have been shown to be inhibited in similar circumstances. It is suggested that reaction centres are developed in the body of the gas, these centres being associated with extremely large amounts of energy. Some of the energy of the reaction centres will be absorbed by the glass walls, and hence a tube packed with broken glass limits the development of the reaction centres by decreasing the volume available for their formation, and the glass acts as a temporary reservoir for their excessive energy. This accounts for the inhibition of the reaction. A. J. MEE.

Conductivities of sodium and potassium derivatives of β-ketonic compounds in alcoholic solution. (MISS) E. WHITE (J.C.S., 1928, 1413—1415).—The molecular conductivities of sodium and potassium derivatives of ethyl acetoacetate, acetylacetone, benzoylacetone, ethyl *iso*butyl- and *iso*amyl-acetoacetate, and also of sodium and potassium ethoxides and potassium iodide have been determined in alcoholic solution at 25° at dilutions of 4—1024 litres. The conductivities of the β-ketonic derivatives are only slightly less than that of potassium iodide.
F. J. WILKINS.

Liquid hydrogen sulphide as an ionising medium. H. R. CHIPMAN and D. MCINTOSH (Proc. Nova Scotian Inst. Sci., 1927, **16**, 189—195).—Of the fifteen substances examined, iodine, tri*iso*butylamine, tripropylamine, and antimony trichloride were found to give solutions in liquid hydrogen sulphide which possessed appreciable conductivity over a considerable concentration range. The conductivity of iodine increased on dilution, indicating that it ionises into positive and negative ions, whilst that of the other three increased on concentration, indicating the formation of compounds with the solvent which then dissociate. In the case of antimony trichloride the compound $SbSCl_3$ is probably formed.
S. J. GREGG.

Electrical conductivity of calcite. W. J. JACKSON (Proc. Nova Scotian Inst. Sci., 1927, **16**, 46—53).—A constant *E.M.F.* of the order of 300 volts was applied to a crystal of calcite and the current was found to vary approximately exponentially with temperature; a displacement current and a conduction current were both indicated and there was a polarisation effect due possibly to a space change near the electrodes or throughout the crystal. The conductivity is directional. Exposure of the crystal to *X*-rays increases the conductivity, but it returns to a normal value in 1—2 hrs. S. J. GREGG.

Electrical conductivity of solids. G. MAYR (Nuovo Cim., 1927, **4**, cxxv—clvi; Chem. Zentr., 1928, i, 885).—A review. A. A. ELDRIDGE.

Electrical conductance of nickel sulphate solution. Ionic conductance of nickel. K. MURATA (Tech. Rep. Tohoku, 1928, **7**, 1—7).—See this vol., 595.

Electrode potential of nickel. I. Measurements in an atmosphere of hydrogen and reduced nickel powder. K. Murata (Tech. Rep. Tôhoku, 1928, **7**, 9—25).—See this vol., 596.

Electrometric titration curves of dibasic acids. I. Normal acids. R. Gane and C. K. Ingold (J.C.S., 1928, 1594—1600).—The chemical evidence supporting the theory that the angles between the valencies of a carbon atom are modified by the space requirements of the attached groups may be confirmed by the measurement of the second dissociation constant of normal dibasic acids. Bjerrum's relation (cf. A., 1923, i, 1059) connecting the first and second dissociation constants of symmetrical dibasic acids with the distance between the ionising groups is not adequate for all purposes. It is important to measure both dissociation constants by the same method and in the same experiment. The first and second dissociation constants and the apparent distance between the ionising centres are calculated for homologous normal dibasic acids from oxalic acid to azelaic acid. The causes of the systematic deviations of the apparent from the real distances are discussed, and it is shown that in glutaric acid and in the higher acids, but not in malonic acid or succinic acid, deviations due to internally propagated polar effects are negligible. R. A. Pratt.

Limiting potential of sugar solutions. R. Wurmser and J. Geloso (Compt. rend., 1928, **186**, 1842—1844; cf. A., 1927, 316).—At 7 the limiting potential (E) of a gold or platinum electrode in a solution of pure dextrose is attained after 30 days at 40°, 9 hrs. at 75°, and 2 hrs. at 90°, and corresponds with the expression $E = -0{\cdot}0002TpK$. The constant K includes the term r_H, which has a temperature coefficient of $\pm 0{\cdot}5$ in a phosphate buffer. In the absence of buffers the potential first passes through a minimum. Dyes (up to a maximum concentration of 6×10^{-4} g./100 c.c.) do not affect the final potential but influence the rate at which it is attained, the leuco-compounds of janus-green and phenosafranine, which are more electronegative than dextrose, being oxidised by the latter. J. Grant.

Volta effect. E. Dubois (Compt. rend., 1928, **186**, 1832—1833).—The Volta effect, measured in water vapour, between a fixed, electrically heated, cylindrical spiral electrode of the metal studied, and a cool mobile cylindrical electrode, shows differences of about 0·1 volt for iron, nickel, molybdenum, aluminium, or copper, but none for gold, silver, or platinum (cf. A., 1927, 832). The metal becomes more electropositive, and the change is a qualitative indication of the action of water vapour on the metal. J. Grant.

Solid cells, particularly thermoelectric cells with solid electrolytes. H. Reinhold (Z. anorg. Chem., 1928, **171**, 181—230).—Measurements with the cells $Ag|AgCl|Cl_2$, $Ag|AgBr|Br_2$, $Pb|PbCl_2|Cl_2$, and $Pb|PbCl_2|AgCl|Ag$ with solid electrolytes at temperatures up to about 500° show that the *E.M.F.* may be calculated from the thermal data for the processes occurring at the electrodes with the aid of the Gibbs–Helmholtz equation and Nernst's heat theorem. It thus follows that the heat theorem is valid over the whole range of temperature investigated, and it becomes possible to represent as a function of the temperature the heat effects and affinities of the reactions $Ag+\frac{1}{2}Cl_2=AgCl$, and $\frac{1}{2}Pb+\frac{1}{2}Cl_2=\frac{1}{2}PbCl_2$ up to the m. p. of the chlorides, and of the reaction $\frac{1}{2}Pb\ \ AgCl=\frac{1}{2}PbCl_2+Ag$ up to the eutectic temperature of the mixture of chlorides. In the thermoelectric cells $Ag|AgI|Ag$, $Ag|AgCl|Ag$, $Ag|AgBr|Ag$, $Pb|PbCl_2|Pb$, $Cl_2|AgCl|Cl_2$, $Br_2|AgBr|Br_2$, and $Cl_2|PbCl_2|Cl_2$, in which a difference of temperature is maintained between the electrodes, it appears that the changes which occur are of exactly the same nature as in the above isothermal cells, so that here also the heat theorem is true, and may be used to calculate the *E.M.F.* resulting from the chemical changes which take place in the cells. The values calculated in this way, however, prove, in general, to be different from the actually observed values, except in cases in which the electrolyte is a purely anionic conductor, as with lead chloride, where there is fairly satisfactory agreement. With the cells containing silver halides, indeed, the direction of the current is the reverse of what would be expected. It seems therefore that there is a component of the *E.M.F.* of the thermoelectric cells with cationically conducting electrolytes which is opposite in sign to the *E.M.F.* calculated from the electrode processes and exceeds this in magnitude; for cells with anionic conductors any such *E.M.F.* is negligible. This residual *E.M.F.* may be considered as arising from a Benedicks effect, *i.e.*, an *E.M.F.* produced in a homogeneous conductor by a temperature gradient, these effects for the metal and electrolyte respectively being of the same order of magnitude, and in opposite directions for cells containing anionic conductors and in the same direction for cells containing cationic conductors. The Benedicks effect in metals is calculated to be equal to about half the residual *E.M.F.* in the latter type of cell. It seems that the methods used in calculating the *E.M.F.* of the above thermoelectric cells may also be applied to cells in which both anions and cations conduct the current, provided that the transport numbers are known. R. Cuthill.

Magneto-electrolytic potentials. E. O. Holmes, jun. and A. Handy (J. Amer. Chem. Soc., 1928, **50**, 1303—1314).—When a salt solution is allowed to flow through a constant magnetic field, a *P.D.* is set up at right angles both to the direction of flow and to the field. These magneto-electrolytic potentials are investigated for copper and zinc sulphate solutions (Scarpa, A., 1925, ii, 128). The *P.D.* is independent of the nature and concentration of the electrolyte, but is proportional to the velocity of flow and the field strength. Experiment shows that the magnetic field produces neither dissociation nor ionic displacement. An equation for the *P.D.* is derived, which is shown to correspond with the equation representing the electro-magnetic effects which are involved in the operation of the dynamo, with the addition of a very small osmotic term. S. K. Tweedy.

Reduction of niobic acid. I. S. J. Kiehl and D. Hart (J. Amer. Chem. Soc., 1928, **50**, 1608—1620).—The solubility at 25° of niobic acid is 8·34 g. of niobium pentoxide per 100 g. of solution containing

88·11% of sulphuric acid, or 15·43 g. in 100 c.c. of solution. The solution must contain at least 3*M*-sulphuric acid and not more than 0·038*M*-niobium pentoxide to remain stable for 3 days; higher oxide concentrations require greater acid concentrations. Niobium, in 0·00032*M*-solution, may be detected in presence of tantalum by the blue or pale green colour obtained on reducing a dilute solution of "niobic acid" with zinc. At a mercury cathode niobic acid in sulphuric acid solution is almost completely reduced to the tervalent state. In 3*M*-sulphuric acid the reduced solution is blue; in 6*M*- and 10*M*-sulphuric acid it is reddish-brown, but turns blue on dilution with water, indicating complex formation rather than valency change. S. K. TWEEDY.

Theory of combustion. N. SEMENOV (Z. Physik, 1928, **48**, 571—582).—From a higher development of the Arrhenius theory expressions are deduced for the velocity of chemical reactions and for the conditions of explosion. These are found to be in agreement with experimental observation (A., 1927, 122; this vol., 483). J. W. SMITH.

Gaseous combustion at high pressures. X. The co-volume corrections, maximum temperatures, and dissociation of steam and carbon dioxide in explosions. D. M. NEWITT (Proc. Roy. Soc., 1928, A, **119**, 464—480).—A review of data accumulated in researches on high-pressure explosions of hydrogen–air, carbon monoxide–air, etc. mixtures, relating to the effects of density and temperature on the internal energies of gaseous media and the dissociation of steam and carbon dioxide (cf. Bone, Newitt, and Townend, A., 1924, ii, 398; 1925, ii, 800). A revision of the previous estimates of maximum temperatures and dissociation has been carried out. The revised figures for the maximum temperatures reached in theoretical hydrogen– and carbon monoxide–air explosions are almost identical with those estimated previously in cases where the initial pressure (P_i) did not exceed 25 atm., but for all higher pressures the revised figures are lower than the old, the divergence increasing with increase of P_i. This is due to the fact that a co-volume correction is now applied to the maximum pressure (P_m) attained during explosion. The revised figures in general confirm the original estimates for the dissociation of steam and carbon dioxide. The fact that the "corrected" P_m/P_i ratios were found to show an unexpectedly large increase with the initial pressure was previously ascribed to the increasing opacity of the gaseous medium to the radiation emitted during the explosion. It is now found that about 50% of the effect in the case of the carbon monoxide explosions, and about 75% in the hydrogen explosions, may be accounted for by the probable increase in the co-volume factor with temperature and pressure. L. L. BIRCUMSHAW.

Inflammability of hydrogen. VI. Influence of tin tetramethyl and lead tetramethyl on the limits of inflammability of hydrogen. Y. TANAKA and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1928, **31**, 20—23; cf. A., 1927, 1145).—Tin tetramethyl and lead tetramethyl have mol. refraction for the *D* line 36·40 and 40·13, respectively; the atomic refractions of tin and lead are 13·53 and 17·26, respectively. S. OKA.

Least energy required to ignite mixtures of air and ethyl ether vapour. Y. NAGAI and M. FURIHATA (J. Soc. Chem. Ind. Japan, 1927, **30**, 781—786).—See A., 1927, 943.

Effect of ethyl bromide on the least energy required to ignite mixtures of air and ethyl ether vapour. Y. NAGAI and M. FURIHATA (J. Soc. Chem. Ind. Japan, 1927, **30**, 786—791).—See A., 1927, 943.

Carbonyl bromide. I. Thermal decomposition. S. LENHER and H. J. SCHUMACHER (Z. physikal. Chem., 1928, **135**, 85—101).—At the ordinary temperature the equilibrium $CO+Br_2 \leftarrow COBr_2$ is established in the dark very slowly, and only about 10% of carbonyl bromide is formed. In the light equilibrium is established in a few hours, at a bromine concentration of about 200 mm. and a carbon monoxide concentration of about 560 mm. The thermal decomposition is a surface reaction of the first order, and is independent of added gases. The decomposition velocity is greater in borosilicate glass than in soda glass, and greater still in quartz vessels. Carbonyl bromide is stable at temperatures up to 150°. Between 210° and 230° the temperature coefficient of the reaction velocity in borosilicate vessels is 1·8 for 10° rise of temperature.

H. F. GILLBE.

Kinetics of nitrous acid. III. Kinetics of the decomposition of nitrous acid. E. ABEL and H. SCHMID (Z. physikal. Chem., 1928, **134**, 279—300).—A method and an apparatus are described for the investigation of the decomposition of nitrous acid according to the equation $3HNO_2=H^{\cdot}+NO_3'+2NO+H_2O$. The reverse reaction is neglected. The velocity is proportional to the fourth power of the concentration of undissociated acid, and inversely proportional to the square of the concentration of nitric oxide. Considering the distribution equilibrium between gas and liquid phases, the velocity of decomposition was inversely proportional to the square of the partial pressure of nitric oxide. The velocity coefficient rises with increasing ionic concentration, the relationship between the two being almost linear. Mathematical expressions are given for the velocity coefficient. Since the concentration of nitrous acid appears in the velocity expression to the fourth power the degree of dissociation of the acid appears particularly great if there is no excess of hydrogen and nitrite ions present which depress the dissociation. If sulphate ions are also present the reaction is still further complicated. An expression is deduced for the case where the nitrous acid is practically undissociated. The mechanism of the decomposition is discussed. The reaction involves the hydrolysis of nitrogen tetroxide as a part-reaction. The velocity of this reaction can be expressed by the equation $-d[N_2O_4]/dt=2\times10^4 p_{N_2O_4}$, where represents the partial pressure of the gas. A. J. MEE.

Absorption kinetics for molecules attached at more than one point. R. E. BURK and D. C. GILLESPIE (Proc. Nat. Acad. Sci., 1928, **14**, 470—472).—A theoretical paper in which the kinetics of desorption of molecules attached to the surface by two linkings are considered and compared with the

kinetics of desorption of molecules attached by only one linking. By considering the probability that a molecular vibration would break one or both linkings, the rate of desorption is calculated. It is shown that singly and doubly attached molecules would come off at the same rate if $M(\alpha+\beta)=2$, where M is the number of vibrations of the underlying surface atoms (assumed all alike) per second, α is the average time after breaking one linking that the end of the molecule thus set free returns to the surface, and β is the corresponding time for the other end of the molecule.

A. J. MEE.

Reaction velocity at a liquid–liquid interface. R. P. BELL (J. Physical Chem., 1928, **32**, 882—893).—The velocity of reaction at the liquid–liquid interface between a solution of benz-*o*-toluidide in benzene and of potassium permanganate in water has been measured at 14·90° and 25° (approx.) for varying concentrations of the reactants, and the interfacial tension between water and benzene solutions of benz-*o*-toluidide has been measured by the drop-weight method. The reaction results from collisions between the permanganate ions and an adsorbed layer of benz-*o*-toluidide, and the velocity is independent of diffusion from solvent to solvent. Comparison of surface tension with velocity confirms the Gibbs–Helmholtz adsorption equation.

L. S. THEOBALD.

Reaction regions. XVIII. Velocity of propagation of the reaction in iron–sulphur mixtures. W. P. JORISSEN and C. GROENEVELD. **XIX. Reaction regions in which one of the substances is guncotton.** W. P. JORISSEN and H. A. STARINK (Rec. trav. chim., 1928, **47**, 737—742, 743—751).—XVIII. The velocity of propagation of the reaction between iron and sulphur induced by a piece of burning magnesium ribbon in a finely-divided mixture of these two elements shows a maximum when plotted against the composition of the mixture. The top of the curve, which is somewhat uncertain, appears to lie to the right of the ratio for complete transformation, *i.e.*, 1S : 1Fe (100% sulphur being on the left).

XIX. The reaction regions of mixtures of guncotton (12·12% N) with salts and with organic substances have been investigated. It is shown that mixtures with definite times of reaction can be prepared.

O. J. WALKER.

Mechanism of hydrogen-ion catalysis. E. MÜLLER (Z. physikal. Chem., 1928, **134**, 190—192).—By making use of the electronic theory of the structure of the molecule, the mechanism of hydrogen-ion catalysis of ester formation is investigated. According to Goldschmidt the hydrogen ion forms a complex ion by addition to a neutral molecule. It is shown that in the uncatalysed reaction it is necessary for 4 atoms to come into contact at the same time, whereas if the catalysis takes place according to the theory of Goldschmidt, it is sufficient if 2 atoms in the molecules collide. The probability of the second reaction occurring is therefore many times greater than that of the first.

A. J. MEE.

Rate of oxidation of hydrogen peroxide by bromine and its relation to the catalytic decomposition of hydrogen peroxide in a bromine–bromide solution. W. C. BRAY and R. S. LIVINGSTON (J. Amer. Chem. Soc., 1928, **50**, 1654—1665).—Experimental results are recorded which prove that the rate of oxidation follows the equation: $-d[H_2O_2]/dt=K[Br_2][H_2O_2]/[Br'][H^{\cdot}]$. An apparatus is described for measuring reaction rates having half-times of 0·5—6 sec.; the solutions are mixed at two jets and the reaction is stopped by adding to the mixture a third solution which reacts with, and so removes, one of the reacting components with great rapidity. The hypobromous acid mechanism for the reaction between hydrogen peroxide and bromine and for the catalytic decomposition of hydrogen peroxide is in agreement with experimental results. The hypobromite-ion mechanism suggested by Christiansen (A., 1927, 1035) is unsatisfactory. Hydrogen peroxide may be determined by pipetting a quantity into potassium iodide solution containing 0·2*N*-sulphuric acid, and, after keeping in the dark for 40 min., titrating with thiosulphate.

S. K. TWEEDY.

Oxidation of some dicarboxylic acids by hydrogen peroxide in the presence of certain catalysts. J. H. WALTON and D. P. GRAHAM (J. Amer. Chem. Soc., 1928, **50**, 1641—1648).—A continuation of previous work (A., 1926, 918). Owing to the large number of uncontrollable factors a quantitative relation between structure and ease of oxidation could not be deduced. Experiments were carried out with oxalic, succinic, malic, lactic, and tartaric acids, and also glycerol, formic acid, and ethylene glycol. The carbon dioxide content of the solution has a large influence on the nature of the reaction, and increase in acidity tends to increase the decomposition rate of the peroxide and the oxidation rate of the acid. Oxalic acid forms a stable complex containing equimolecular quantities of ferric and oxalate ions. In presence of the lactic acid structure the concentration of the copper salt catalyst has practically no influence on the oxidation or the rate of decomposition of hydrogen peroxide. Introduction of hydroxyl groups into succinic acid increases the rate of oxidation of the acid but decreases the power to inhibit the decomposition of hydrogen peroxide. Primary alcohol groups exert a protective action on formic acid and reduce the rate of oxidation.

S. K. TWEEDY.

Theory of acid and basic catalysis. Mutarotation of dextrose. J. N. BRONSTED and E. A. GUGGENHEIM (J. Amer. Chem. Soc., 1927, **49**, 2554—2584).—The conception, previously advanced (A., 1926, 797), that molecules, independently of their electric charge, should be regarded as acids or bases according as they tend to lose or to unite with a hydrogen nucleus is developed to include acid and basic catalysis. The new theory ascribes the catalytic effect not particularly to hydrogen and hydroxyl ions, but generally to acid and basic molecules as defined above. Dilatometric measurements at 18° of the mutarotation of dextrose under the influence of acids and bases of various electrically-charged types support the new theory. The velocity coefficient at 18° when water only is present has the value $(5·30\pm0·10)\times10^{-3}$/min. at p_H 4—6, the range of minimum

velocity, and the neutral salt effect is negligible for salts up to an ionic strength of 0·2. The effect of the oxonium ion (OH_3^+), determined in aqueous solutions of perchloric acid, is proportional to its concentration and primary salt effect is again undetectable. Data for 13 weak, monobasic, organic acids buffered to p_H 4—6 by their corresponding salts show the anions of these acids to be catalytically active in proportion to their concentrations. With the strongest bases, the trimethylacetate, propionate, and acetate ions, the effect is greater than one fifth that of the oxonium ion. Catalysis by the undissociated acid is established in the case of formic, glycollic, and mandelic acids; with weaker acids, the smallness of the catalytic effect makes its detection uncertain. Catalysis by acid and basic molecules increases regularly with an increase in strength of the acid or base. A mechanism for the mutarotation of dextrose is suggested, and previous work is discussed. Finally, it is pointed out that the laws of mutarotation conform to those previously discovered for the decomposition of nitroamide (A., 1925, ii, 982). L. S. THEOBALD.

Autoxidation and antioxygenic action. Catalytic properties of phosphorus. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1928, **186**, 1673—1677).—It has been shown by manometric determinations of the oxygen absorbed that about 1% of white phosphorus inhibits the autoxidation of furfuraldehyde, but increases that of benzaldehyde, styrene, or turpentine. Elaborate precautions were taken and in the last case it is shown that the oxygen absorption obtained was not due to oxidation of the phosphorus, although it may have been due partly or completely to the catalytic effect of one of its oxidation products. Red phosphorus has analogous but less marked effects, and inhibits or accelerates the oxidation of sodium sulphite solution according as the latter is slightly alkaline or acid, respectively. J. GRANT.

Heterogeneous catalysis and adsorption. II. C. F. VAN DUIN [in part with H. G. SNIJDER] (Rec. trav. chim., 1928, **47**, 715—736; cf. A., 1921, ii, 392).—The acceleration of the reaction between αβ-dibromopropionic acid and inorganic iodides by the addition of carbon, previously observed by Kruyt and the author, has been confirmed. An acceleration was also observed for the sodium salt of the acid. The velocities of hydrolysis of methyl *m*- and *o*-sulphobenzoate, methyl *iso*valerate, monoacetin, methyl hydrogen succinate, methyl hydrogen *d*-tartrate, and methyl mesotartrate, and of the inversion of sucrose are all retarded by the addition of carbon. The unimolecular reaction *r*-dibromosuccinic acid ⟶ bromofumaric acid + hydrobromic acid is also retarded by addition of carbon, a result which supports the hypothesis that adsorbed molecules are in a less favourable condition to meet other molecules and to take part in a reaction. On the other hand, the velocity of the termolecular reactions *r*-(or meso-) dibromosuccinic acid + 2KI = maleic (or fumaric) acid + 2KBr + I_2 is greatly increased by the presence of carbon. This result supports the hypothesis that adsorption can cause positive catalysis only where the orientation of the adsorbed molecules is such that the reacting groups are turned away from the adsorbent and towards the surrounding liquid. This orientation must be so favourable that the primary decrease of the velocity of the reaction, caused by the adsorption itself, is overcome. Experiments were also carried out using a colloidal suspension of tin oxide as adsorbent. The velocity of hydrolysis of methyl hydrogen *d*-tartrate is decreased in presence of tin oxide, but with methyl mesotartrate the velocity is unaffected. In the former case the retarding influence due to the adsorption itself preponderates, whereas in the latter case this retarding influence is just compensated by the accelerating influence due to the favourable orientation of the molecules.

O. J. WALKER.

Catalytic activity of titania in the reduction of nitro-compounds. G. ETZEL (J. Physical Chem., 1928, **32**, 852—860).—The catalytic activity of titania obtained by reduction in hydrogen of the hydroxide, prepared from the chloride by precipitation with ammonia, on the reduction of nitrobenzene has been studied. The yield of amines increases with the amount of catalyst; the optimum temperature for reduction to aniline is 282° and the best yield obtained was 94·4% with a catalyst reduced at 302°. A higher temperature of reduction favours the formation of azobenzene and hydrazobenzene, whilst a lower (260°) increases the yield of *cyclo*hexylamine and diphenylamine formed. The optimum rates of flow of hydrogen and nitrobenzene for production of aniline are 14 litres/hr. and 4·05 g./hr., respectively. Continuous or intermittent feeding of the latter has little effect. The activity of the catalyst is poor initially, but soon increases to a constant value, and the use of asbestos as a support had no effect. Small amounts of manganese (5%) in the titania do not increase the yield of aniline, but prevent the formation of azobenzene and give a product of a better colour. The aniline produced was slightly yellow with the catalyst reduced at 260° and cherry-red with those reduced at higher temperatures. L. S. THEOBALD.

Catalytic oxidation of aromatic hydrocarbons and their derivatives by means of air. E. B. MAXTED.—See B., 1928, 473.

Catalytic oxidation of nitro- and halogen derivatives of toluene by means of air. E. B. MAXTED and A. N. DUNSBY (J.C.S., 1928, 1439—1442; cf. A., 1907, ii, 273).—The catalytic oxidation of *p*-nitrotoluene, *o*-nitrotoluene, *o*-bromotoluene, and *o*-chlorotoluene, using tin vanadate as catalyst, is described. Air was passed at a known speed through a suitably heated wash-bottle containing the substance to be oxidised before entering the catalyst tube, and the products were collected in a weighed receiver. The products from *p*-nitrotoluene were *p*-nitrobenzoic acid, *p*-nitrobenzaldehyde, and unchanged *p*-nitrotoluene, the maximum yield of acid being 16% at a catalyst temperature of 285° and a carburettor temperature of 93°. With *o*-nitrotoluene, much decomposition occurred and practically no acid was isolated. With *o*-bromotoluene, the maximum yield of *o*-bromobenzoic acid was 24·3% at a catalyst temperature of 290° and a carburettor temperature of 60°. With *o*-chlorotoluene, the maximum yield of *o*-chlorobenzoic

acid was 13·8% with a catalyst temperature of 287° and a carburettor temperature of 60°.

R. A. Pratt.

X-Ray examination of iron catalysts for the ammonia synthesis. O. Eisenhut and E. Kaupp (Z. physikal. Chem., 1928, **133**, 456—471).—The X-ray diagram of the catalyst for the ammonia synthesis prepared from ferrosoferric oxide according to G.P. 249,447 shows that when the activity is maximal the lattice is identical with that of α-iron. Similarly it seems that in the formation of a catalyst from potassium aluminium ferrocyanide (cf. Mittasch and Kuss, this vol., 605) α-iron is present actually from the commencement of the reduction, although where local excessive temperatures occur γ-iron may be formed. The admixture of potassium chloride with the ferrocyanide has no appreciable effect on the process of formation. Even in catalysts prepared according to B.P. 253,122 (B., 1927, 481) or Norwegian Patent 43,263 α-iron is still the essential constituent.

R. Cuthill.

Ammonia synthesis with catalysts obtained from complex cyanides of iron. A. Mittasch and E. Kuss.—See B., 1928, 522.

Influence of arsenic on the catalytic activity of platinum for the oxidation of sulphur dioxide. E. B. Maxted and A. N. Dunsby (J.C.S., 1928, 1600—1603; cf. A., 1903, ii, 639; 1926, 365).—The activity of a progressively poisoned platinum catalyst and its arsenic content are correlated. Dry electrolytic oxygen and sulphur dioxide were allowed to react at 300°±2° in the presence of platinum prepared by the reduction of platinic chloride with hydrogen. Unconverted sulphur dioxide was collected and determined iodometrically. The catalyst was progressively poisoned with a standard arsenic solution and the corresponding decreases in activity were recorded. The poisoning curve showed that, in the first stages of poisoning, the catalytic activity varies approximately linearly with the arsenic content. This initial portion is followed by a region in which the continued addition of arsenic affects the activity to a far smaller degree. The addition of about 0·0016 g. of arsenic reduced the activity of 1 g. of platinum to half its original value, but a total arsenic content of about 0·03 g. per g. of platinum reduced this only to 26% of its original activity.

R. A. Pratt.

Catalytic action in the oxidation of sulphides and arsenides. F. Carmichael (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 47—53).—Chalcocite, pyrrhotite, and nickeliferous pyrrhotite were not oxidised more rapidly in presence of platinum-black, pyrite, or manganese dioxide. Polydymite gave 11·4% S, and a residue of iron hydroxide. The reaction was accelerated by platinum-black. The oxidation of rammelsbergite was promoted by each of the catalysts.

Chemical Abstracts.

Hygroscopic and catalytic properties of gelatinated electrolytic copper. C. Marie and P. Jacquet (Compt. rend., 1928, **187**, 41—43).—The desiccation and moisture-absorption curves of copper deposited electrolytically in the presence of gelatin (A., 1927, 840) have the same slope as that of gelatin alone under the same conditions. Such deposits will catalyse the synthesis of water at 100°, and have an activity and structure (as shown by X-ray examination) comparable with those of finely-divided copper obtained by the reduction at 220° of copper oxide prepared from the nitrate.

J. Grant.

Reduction of sodium sulphate to sulphide, particularly by hydrogen and carbon monoxide in presence of catalysts. P. P. Budnikov and E. Shilov.—See B., 1928, 481.

Catalytic refining of bromine. P. T. Danilitschenko and M. Ravitsch.—See B., 1928, 482.

Electrodeposition of tellurium. F. C. Mathers and H. L. Turner (Amer. Electrochem. Soc., Sept. 1928, **54**. Advance copy. 8 pp.).—Tellurium can be deposited in smooth, thick layers with theoretical current efficiency from a bath containing 300 g. of tellurium dioxide (49·6% TeO_2, 46·1% Na_2TeO_3), 500 g. of 48% hydrofluoric acid, and 200 g. of sulphuric acid per litre at the ordinary temperature, using 1·6 amp./dm.² at a lead cathode. With tellurium anodes the bath voltage was about 1 volt, and 0·9% of selenium contained in the anodes remained entirely in the slimes, showing that this bath can be used for refining tellurium. The deposited tellurium is light grey and very brittle. Baths consisting of hydrochloric–sulphuric acid solutions of tellurium dioxide gave somewhat less satisfactory deposits.

H. J. T. Ellingham.

Electrolytic preparation of the borides of calcium, strontium, and barium. L. Andrieux (Compt. rend., 1928, **186**, 1537—1539).—In the method previously described (A., 1927, 216, 844) the electrolytic bath may be replaced by a mixture in suitable proportions of powdered boric anhydride with the oxide or carbonate, and the fluoride, of the corresponding alkaline-earth metal, heated at 1000°. Direct electrolysis of the metallic borates gives amorphous boron, and a much smaller yield of boride, particularly in the case of barium.

J. Grant.

Electrolytic separation of copper from cuprous chloride solutions. P. P. Fedotéev [with N. P. Fedotéev] (Z. anorg. Chem., 1928, **173**, 81—91).—The form of deposit obtained by electrolysing cuprous chloride solution under various conditions is examined. Incidentally the solubility of cuprous chloride in hydrochloric acid and in sodium chloride solution at 19° was found, and also the solubility in cupric chloride solution. The solutions of cuprous chloride in hydrochloric acid and in sodium chloride were electrolysed under different conditions. Using solutions of cuprous chloride in hydrochloric acid and a current density of 80 amp./m.², with increase of cuprous chloride content the deposit became more uniform and had a fine crystal structure. The same was observed for solutions of the salt in sodium chloride. On the whole, using the same conditions, the deposit from the acid solution was more uniform and of finer structure than that from the sodium chloride solution. The effects of other conditions such as current density, temperature, stirring, and addition of colloids were also studied. The crystal form of the deposit was investigated. It is quite

possible to obtain a compact cathode deposit of copper from cuprous chloride solutions at the ordinary temperature and with ordinary current densities.

A. J. Mee.

Effect of colloids in the electro-deposition of silver from silver nitrate solutions. S. Wernick (Trans. Faraday Soc., 1928, **24**, 361—366).—The "silver numbers" of a number of colloids commonly used to reduce grain-size were determined. Silver deposits were obtained from neutral silver nitrate solutions containing the different colloids, and photomicrographs of these deposits were taken. The number of crystals per unit area was determined, and taken as a measure of the fineness of the deposit. With the exception of dextrin, it was found that there was a rough relationship between silver number and fineness of deposit; the larger the silver number the more closely grained was the deposit.

L. F. Gilbert.

Precipitation of gold and silver from their dilute solutions. M. Yasuda (Bull. Chem. Soc. Japan, 1928, **3**, 113—118).—A coherent plate is obtained by compressing and hammering a mixture of powdered lead and manganese. When immersed in dilute solutions of gold or silver, such as sea water, the precious metals are deposited on the surface and recovered by cupellation. From solutions containing 37 mg. of gold per m.^{3} the yield was 10^{-6} g./cm.^{2} of surface in 100 hrs. A plate containing 5% Mn is most suitable.

C. J. Smithells.

Crystallographic *X*-ray study of the structure of simultaneous electrolytic depositions of two metals. A. Roux and J. Cournot (Compt. rend., 1928, **186**, 1733—1736).—The *X*-ray diffraction spectra of simultaneous electrolytic deposits of copper with zinc on steel, and of cadmium with silver, tin, or nickel on duralumin are not due to the superposition of the spectra of the constituent metals, and therefore indicate that these have either combined or formed solutions.

J. Grant.

Electrolytic production of heavy metals from fused electrolytes. II. G. Neuendorff and F. Sauerwald.—See B., 1928, 526.

Electro-deposition of iron-nickel alloys. II, III. S. Glasstone and T. E. Symes (Trans. Faraday Soc., 1928, **24**, 370—372, 372—378; cf. A., 1927, 633).—II. Anions and cations appear to exert little influence on the relative tendencies for iron and nickel to deposit from solutions containing simple ions of both metals.

III. Experiments performed at higher temperatures than previously employed confirm the conclusion that the relative tendencies of iron and nickel to deposit in the form of an alloy are independent of the hydrogen-ion concentration of the electrolyte. In accordance with a previous theory (A., 1927, 24), at higher temperatures the deposits from a given solution contain less iron than at lower temperatures, and the increase of the proportion of iron with increase of current density is much more gradual. The influence of dilution and stirring is similar to that observed at the ordinary temperature, but is not so marked, on account of the increased rate of diffusion. Diffusion of the ions is so rapid at 90° that depletion of the electrolyte near the cathode probably does not occur to any appreciable extent. There is a minimum iron content of the electrolyte from which the initially deposited alloy contains relatively less iron than does the electrolyte. This minimum is decreased as the temperature is raised.

L. F. Gilbert.

Application of electrical resistance measurements to the study of atmospheric corrosion of metals. J. C. Hudson.—See B., 1928, 488.

Experimental technique of photochemistry. V. Reflexion losses in the optical system of the Hilger ultra-violet monochromatic illuminator. H. N. Ridyard and D. W. G. Style (J. Physical Chem., 1928, **32**, 861—867; A., 1925, ii, 809).—The apparatus and method used in measuring the reflexion of mercury lines by the mirror in this illuminator are described. The reflexion losses at the various quartz surfaces in this instrument have been calculated together with the total transmissions of the mercury lines. Factors by which galvanometer deflexions should be multiplied to reduce all lines to the standard of 579 $\mu\mu$ are also given.

L. S. Theobald.

Photo-decomposition of an iron-carbon monoxide compound and the law of photochemical equivalence. O. Warburg and E. Negelein (Naturwiss., 1928, **16**, 387).—Cremer has shown that aqueous solutions of ferrocysteine absorb 2 molecules of carbon monoxide for every atom of iron in the complex. Irradiation of the solution effects the dissociation of the compound formed. The use of monochromatic light (mercury) shows that Einstein's law is valid, since 4 molecules of carbon monoxide are liberated per quantum absorbed over the region 366—580 $\mu\mu$. The photochemical effects supply a method of obtaining the absorption spectrum which yields data in excellent agreement with direct measurements. The work is of value in confirming the validity of other work on the absorption spectrum of the respiratory enzyme (cf. this vol., 537).

R. A. Morton.

Chemical actions of radiations. P. Villard (Compt. rend., 1928, **186**, 1669—1673).—The author compares his experiments and theories with those of Belliot (B., 1927, 174; A., 1927, 323) and claims priority. Experimental evidence favours the hypothesis that the impressions produced on a plate by radiations of very different frequencies have not the same properties and can co-exist independently on the same plate. The relation between solarisation and the slight blackening which accompanies it in the case of silver bromide is also discussed. Solarisation is probably a relative effect, the theory of atomic levels indicating that a plate solarised for one frequency cannot be acted on by another which affects a lower atomic level.

J. Grant.

Effect of light on indigo-dyed [cotton] fabric. R. Haller, J. Hackl, and M. Frankfurt.—See B., 1928, 479.

Purification of potassium dihydrogen phosphate. R. Holcomb and R. R. McKibbin (J. Amer. Chem. Soc., 1928, **50**, 1695—1696).—The sediment produced on keeping potassium dihydrogen phosphate solutions consists of a mixture of colloidally aggre-

gated aluminium and ferric compounds, sometimes accompanied by alkaline-earth metal salts. The phosphate may be purified by keeping a 0·2*M* solution at 75—85° for 24 hrs. in a sealed flask. After filtration, the liquid is either evaporated to dryness and the residue recrystallised, or is concentrated and precipitated with alcohol. S. K. TWEEDY.

Dehydration of gypsum. A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 24—27).—Gypsum loses >99% of water when heated at 115° for 22 hrs. A study of the optical properties and water content in all stages of the manufacture of plaster of Paris shows that this is not a definite compound but a mixture of bassanite and gypsum (3 — 2 : 1). The hemihydrate was prepared only by wet methods. CHEMICAL ABSTRACTS.

Behaviour of calcium carbide towards free halogens and sulphur. E. BIESALSKI and H. VAN ECK (Z. angew. Chem., 1928, **41**, 720—723; cf. B., 1928, 522).—Bromine and calcium carbide react slowly at the ordinary temperature, about 80—90% of hexabromoethane being formed after 3·5 months. At higher temperatures little or no hexabromoethane is formed, the carbide being decomposed with production of free carbon. Low temperature favours the production of hexachloroethane from calcium carbide and chlorine, although the yield is small (3—5%). A certain amount of carbon is produced, but the carbide is attacked very slowly, 80—90% remaining after 6 months. Very little reaction occurs between iodine and calcium carbide at the ordinary temperature, but 35—37% of tetraiodoethylene, together with considerable amounts of free carbon, is obtained after heating at 100—160° in sealed tubes for some hours. A 20% yield of carbon disulphide and much carbon are obtained when calcium carbide and sulphur are heated at 270°. Traces only of carbon disulphide are formed at 500°.

The first reaction, which is probably preceded by adsorption, is the formation of calcium halide or sulphide and carbon. The latter can either polymerise or react with the agent to form halogen compounds or carbon disulphide. The yield of halogen compound or carbon disulphide is determined by the rates of the three reactions concerned. If the polymerised carbon accumulates the carbide becomes coated with a layer of carbon and the first reaction is prevented. The formation of a layer of calcium halide may also prevent further attack on the carbide. This latter effect is not of considerable magnitude with bromine and iodine, since these readily form complex compounds with the corresponding halides. J. S. CARTER.

Composition of the precipitate formed by the action of potassium ferrocyanide on calcium salts in presence of acetic acid. I. TANANAEV (Z. anorg. Chem., 1928, **172**, 403—406).—In presence of a sufficient quantity of acetic acid a saturated solution of potassium ferrocyanide forms a precipitate even with a very dilute solution of a calcium salt. The nature of this precipitate has been examined when formed in presence of (1) excess of ferrocyanide and (2) excess of calcium salt. The complex salt obtained could be completely decomposed by repeated evaporation to dryness with concentrated nitric acid. In both cases the composition of the precipitate agreed with the formula $K_2CaFe(CN)_6$. An oxalate method for the determination of potassium in the presence of calcium is described. M. S. BURR.

Action of aqueous ammonia on mercurous chloride. H. S. KING (Trans. Nova Scotian Inst. Sci., 1927, **16**, 115—125).—The formula Hg_2Cl_2 is preferred for mercurous chloride since the formula HgCl cannot be reconciled with the electron structure of the mercury atom. The unsymmetrical form $Hg{:}HgCl_2$ agrees best with the chemical properties of the compound. The mechanism of the reaction is described as follows: $Hg{:}HgCl_2 \leftarrow Hg+HgCl_2$; $HgCl_2 + NH_3{}^+ = Cl{\cdot}Hg{\cdot}NH_2{}^+ + Cl^-$; $Cl{\cdot}Hg{\cdot}NH_2{}^+ + NH_3{=}Cl{\cdot}Hg{\cdot}NH_2 + NH_4{}^+$; $xCl{\cdot}Hg{\cdot}NH_2{=}(Cl{\cdot}Hg{\cdot}NH_2)_x$. It is impossible to separate the isotopes of mercury by this reaction. S. J. GREGG.

Preparation of boric anhydride and its efficiency as a drying agent. J. H. WALTON and C. K. ROSENBAUM (J. Amer. Chem. Soc., 1928, **50**, 1648—1650).—The oxide is prepared by dehydrating boric acid at not above 800°; the mass is poured into carbon tetrachloride at 0° and powdered. If the dehydration temperature exceeds 800°, the product exhibits an induction period, probably due to the formation of molecular complexes. The oxide is a rapid and efficient drying agent until it contains 25% of its weight of water (metaboric acid stage). S. K. TWEEDY.

Elucidation of [the nature of] hydrated alumina by the ammonia extraction method. W. BILTZ and G. A. LEHRER [with K. MEISEL] (Z. anorg. Chem., 1928, **172**, 292—309).—The action of liquid ammonia on samples of hydrated alumina of different origin has been studied, and the results have been compared with those obtained by Willstatter (A., 1924, ii, 615; 1926, 34) by acetone drying. An *X*-ray examination of the different products has also been made. The results may be explained by dividing the hydrates into two classes. Hydrates of the first class have a special lattice distinguished by its great stability. They therefore occur as minerals. Only two of this type have been examined, viz., hydrargillite, $Al_2O_3,3H_2O$, and bauxite, Al_2O_3,H_2O. These substances cannot unite directly with water or ammonia. There are, however, bauxite compounds of the second kind which may be called bauxite hydrates and bauxite ammines, and most of the compounds examined belong to this class. In addition to other hydrates, a bauxite dihydrate, $[Al_2O_3,H_2O],2H_2O$, may be obtained isomeric with hydrargillite. It will take up a molecule of ammonia with which it is only loosely combined. Hydrates of the second class, formed by precipitation from aluminium salt solutions, do not consist of completely formed crystals, but of crystals in process of formation. By varying the conditions, intermediate forms, more or less similar to hydrargillite in water content and lattice structure, are obtained. M. S. BURR.

Indium. III. A. THIEL and H. LUCKMANN (Z. anorg. Chem., 1928, **172**, 353—371; cf. A., 1904, ii, 618; 1906, ii, 169; 1910, ii, 413).—It has been shown by dialysis against an indium-free ammonia solution

that the solution of precipitated indium hydroxide in concentrated ammonia solution is not colloidal. Pure metallic indium can be obtained by electrolysis in sulphuric or tartaric acid solution, but the separation is not quantitative. The determination of indium as In_2O_3, by precipitating and calcining the hydroxide, has been shown to be inexact, since, if the oxide is heated at a sufficiently high temperature to remove all traces of water, partial decomposition takes place. Satisfactory results may, however, be obtained by heating the oxide in a current of carbon dioxide and hydrogen sulphide, and weighing the resulting sulphide, In_2S_3. The purest form of the oxide, In_2O_3, is obtained by heating the hydroxide at 850° to constant weight, and then heating for 0·5 hr. in air at 1000°; it has *d* 6·75±0·01. The oxide is yellow, but usually appears white, due to a thin superficial layer of the volatile oxide In_2O. The latter has been obtained by the action of a reducing gas on In_2O_3 at 500°, followed by sublimation in a high vacuum at 650—700°. In thin transparent layers the lower oxide is yellow, black in thicker ones, brittle and hard. It is stable towards cold water, but dissolves readily in hydrochloric acid with evolution of hydrogen. When heated in air it glows suddenly and passes into the yellow In_2O_3; it has *d* 6·31±0·03. In the preparation of In_2O a residue not readily volatile is left behind as a dirty white, bulky powder. Its composition agrees with the formula InO. Since, unlike In_2O_3, it is not hygroscopic, and is also light-coloured, it cannot be a mixture of the other two oxides. The sulphide, In_2S_3, is yellow or brown according to its method of preparation. At 850° it is markedly volatile and, in a closed tube, has m. p. 1050+3°. The fused product is black or, when finely powdered, red; *d* 4·90±0·01. The sulphide In_2S is prepared similarly to the corresponding oxide, and is also similar in appearance and properties; it has m. p. 653±5°, *d* 5·92±0·01. By heating together atomic proportions of indium and sulphur at 650° a slate-grey powder of the approximate composition InS is obtained. At 850°, in a vacuum, it rapidly volatilises, giving In_2S and sulphur. Sintering points and m. p. of mixtures of indium and sulphur have been plotted against composition, and the form of the curve points to the existence of a compound InS and suggests also the possibility of the formation of a sulphide In_4S_5. In_2O and In_2S are fairly strongly paramagnetic, InO and InS are less so, and In_2O_3 and In_2S_3 are indifferent. An *X*-ray examination of the different products has also been made, but the differences in the interference diagrams are not sufficient to settle the question of the individuality of InO and InS. M. S. Burr.

Fractional separation of neodymium and samarium. L. Rolla and L. Fernandes (Atti R. Accad. Lincei, 1928, [vi], 7, 370—372).—The separation and purification of neodymium from samarium and *vice versa* can be readily carried out by fractional crystallisation of the double nitrates with magnesium and manganese, which have the composition $2R(NO_3)_3,3Mg(NO_3)_2,24H_2O$ and $2R(NO_3)_3,3Mn(NO_3)_2,24H_2O$, R representing an atom of the rare element O J Walker.

Reduction of metallic sulphides by carbon. N. Parravano and G. Malquori (Gazzetta, 1928, 58, 279—289; cf. this vol., 479, 480, 594, 844).—The reaction $2MS+C=2M+CS_2$ is considered from the static point of view in comparison with the analogous reduction of metallic oxides by carbon. Since with the sulphides the reducing gas, carbon monoxide, is absent, it is necessary that the particles of carbon must be immersed in the mass to be reduced and that the sulphide must diffuse into this mass with a certain velocity in order that they may reach the carbon. These considerations explain the greater difficulty of reduction of metallic sulphides. T. H. Pope.

Separation on iron of carbon from carbon monoxide and light petroleum. U. Hofmann (Ber., 1928, 61, [*B*], 1180—1195).—Thermal decomposition of hydrocarbons does not permit the preparation of the "series of black, crystalline carbons" at temperatures below 700° (cf. Hofmann and Hofmann, B., 1927, 802; Koch-Holm, this vol., 464). This may be effected by passing carbon monoxide over reduced or powdered iron, electrolytic iron, or reduced cobalt; wrought iron and steel foil are ineffective. Below 400°, activity is too small, whilst above 700° the equilibrium $2CO \rightleftharpoons C+CO_2$ is so far displaced towards the left that little separation of carbon occurs. Between 700° and 900°, light petroleum is a suitable source of carbon. The reaction commences at some particular spot at which, probably, the iron is particularly finely divided. Thence the catalyst becomes continuously disaggregated, so that the rate of separation attains a maximum and then falls until the catalyst becomes exhausted. The carbon thus prepared contains about 4—5% of iron which can be removed completely only by repeated extraction with boiling, 10% nitric acid. The pure, black carbon is pronouncedly crystalline, the size of the crystallites increasing uniformly with the temperature of production independently of the source of the carbon. Chemical properties, density, and general behaviour show no sudden change when light petroleum is substituted for carbon monoxide. The individual crystallites are only loosely arranged, so that the carbon, prepared at low temperatures, is a loose, voluminous powder resembling soot. Above 700°, it becomes more compact and granular, whilst at 900° it is noticeably hard. Parallel with the temperature of preparation, the density of the compressed product increases from 2·00 to 2·17. Simultaneously the resistance to oxidising agents increases, although all specimens ultimately yield graphitic acid. Carbon, prepared at 400° and activated by carbon dioxide, has an adsorptive power of 8—10% measured towards 1% phenol; this decreases with rising temperature of preparation to 0·5% at 900°. The unusually large size of the crystallites and the observation that in the same porcelain tube lustre carbon can be prepared from light petroleum at 900° and a much more coarsely crystalline carbon product formed on iron indicate that the metal does not play merely the part of an accelerator. Röntgen examination of finely-divided iron which has been treated with carbon monoxide at 400° until deposition of carbon has just commenced establishes the presence

of cementite. In the intermediate and final preparations of unpurified carbon, lines are observed due to some unidentified product, termed provisionally "*carbide* X." These lines disappear when the carbon is purified with dilute nitric acid. The change probably consists in the initial production of cementite, $2CO+3Fe=Fe_3C+CO_2$, which with more carbon monoxide affords carbide X; decomposition of the latter substance yields carbon. This change controls the rate of the total reaction. When, as with carbon monoxide at 400° or light petroleum at 700°, the carbide X is itself very stable, the rate of separation of the carbon is remarkably small. H. WREN.

Elucidation of [the nature of] silica hydrates by the ammonia extraction method. W. BILTZ and E. RAHLFS (Z. anorg. Chem., 1928, **172**, 273—291).—By tensimetric methods (cf. A., 1927, 1157), the action of liquid ammonia on non-gelatinous silica hydrates, obtained by treating with acid, under varying conditions, solid crystalline synthetic alkali silicates, vitreous alkali silicates, and silicate minerals respectively, has been examined. In the case of the hydrated silica obtained from crystalline sodium metasilicate, the nature of the resulting products suggests that the ammonia first exerts a dehydrating action on the hydrate, removing two thirds of the water. Ammonia molecules are then added on to the silica molecule in stages, the resulting products being $6SiO_2,2H_2O$ with 1, 2, 3, or 4 molecules of ammonia, and the smallest molecular entity of the original product appears to be $6SiO_2,6H_2O$. The latter is crystalline and gives a definite X-ray pattern. Dehydration under reduced water vapour pressure gives only the metasilica trihydrate, $6SiO_2,3H_2O$, which has the same composition as disilica hydrate, but, unlike it, loses a molecule of water on treatment with liquid ammonia. The metasilica hydrate from vitreous metasilicate differs from the one described, since, although it is dehydrated by liquid ammonia to the same extent, it does not take up ammonia in stages but continuously, and the smallest molecule has the composition $3SiO_2,3H_2O$. It is an amorphous powder with no X-ray pattern. The disilica hydrate, from crystalline sodium disilicate, is not dehydrated by ammonia, but takes up in a continuous manner an amount of ammonia equivalent to the water present. It gives water up in stages when the pressure is isothermally reduced and is crystalline with a definite X-ray pattern. Its least molecule is $6SiO_2,3H_2O$. The product obtained from vitreous disilicate is similar, but gives up water continuously and not in stages, under suitable conditions. It is a powder with no X-ray pattern and its least molecule is $2SiO_2,H_2O$. The disilica hydrate from the mineral heulandite is identical with a loosely aggregated disilica hydrate from crystalline sodium disilicate. Silica gels prepared in various ways have also been examined. They may perhaps be definite hydrates, but it is doubtful. At low temperatures large adsorption of ammonia takes place. As the gel ages the adsorptive power diminishes. M. S. BURR.

Hydroxysiloxens. H. KAUTSKY and H. THIELE (Z. anorg. Chem., 1928, **173**, 115—124).—Directions are given for the preparation of monohydroxysiloxen, $Si_6O_3H_5{\cdot}OH$, by the hydrolysis of monobromosiloxen with alcohol containing 20% of water. The hydrolysis is a reversible reaction. The higher hydroxysiloxens can be obtained similarly, except the penta-derivative, which does not appear to have been prepared. Monohydroxysiloxen is yellow; the dihydroxy-derivative, $Si_6O_3H_4(OH)_2$, is brownish-red; the trihydroxy-derivative, $Si_6O_3H_3(OH)_3$, is red; the tetrahydroxy-derivative, $Si_6O_3H_2(OH)_4$, is brownish-violet; and the hexahydroxy-derivative, $Si_6O_3(OH)_6$, is black. The hydroxysiloxens function as weak bases. They can also be obtained by the action of sulphur dioxide dissolved in acetone on siloxen. Hexahydroxysiloxen is extremely explosive in air; the tendency to explode increases in this series of compounds with increasing number of SiOH groups, and with increasing number of Si–Si linkings. A. J. MEE.

Preparation and properties of a boride of cerium. L. ANDRIEUX (Compt. rend., 1928, **186**, 1736—1738; cf. this vol., 850).—Cerium boride (CeB_6) is best prepared by the electrolysis for 2 hrs. at 950—1000° by a current of 20 amp. of a molten bath having the composition $0{\cdot}1CeO_2+2B_2O_3+Li_2O(Li_2CO_3)+LiF$. Lower yields are obtained with the oxides and/or fluorides of other alkali or alkaline-earth metals, whilst borax alone gives compounds richer in boron. The boride forms aggregates of small, hard, violet-blue, cubic or prismatic crystals, d^{15} 4·6, and is attacked only by dilute or concentrated nitric acid, concentrated sulphuric acid, or by fused alkalis. It burns with difficulty in air, but reacts violently in the hot with lead or sodium peroxides and is similar in properties to the borides of the alkaline-earth metals. J. GRANT.

Electrical synthesis of hydrazine. G. BREDIG and A. KOENIG (Naturwiss., 1928, **16**, 493).—By passing pure gaseous ammonia through a strongly cooled high-tension arc, and cooling the vapour at once with liquid air, hydrazine is formed in appreciable quantities, and has been detected by the formation of weighable quantities of benzylideneazine. The reaction mechanism is the union of NH_3 and –NH, rather than the union of two NH_2 groups, because the probability of collision between two NH_2 groups (with ammonia in great excess) can only be very small. In support of this view, Raschig's detection of hydrazine among the products obtained by burning oxygen in ammonia is cited. Further support is forthcoming from the catalytic synthesis of hydrogen cyanide from carbon monoxide and ammonia at 600—700°, which may occur as follows: $2CO \longrightarrow C+CO_2$; $NH_3 \longrightarrow NH+H_2$; $C+NH \longrightarrow HCN$. R. A. MORTON.

Nitrogen trifluoride. O. RUFF, J. FISCHER, and F. LUFT (Z. anorg. Chem., 1928, **172**, 417—425).—Nitrogen trifluoride has been obtained by electrolysing fused anhydrous ammonium hydrogen fluoride. It is a colourless gas at the ordinary temperature, and, according to analysis and density measurements, has a formula NF_3. It is condensed by liquid air to a colourless mobile liquid which boils under atmospheric pressure at −119° and freezes below −210°. Vapour-pressure measurements have been made between

$-125°$ and $-194°$, and the molecular heat of vaporisation is calculated to be 2400 g.-cal. Nitrogen trifluoride is insoluble in water and unattacked by water or hydrogen, but a reaction takes place if an electric spark is passed through a mixture of the gas with water vapour, and hydrogen fluoride and oxides of nitrogen are formed. With hydrogen under the same conditions the reaction is very violent, nitrogen and hydrogen fluoride being obtained. The gas is remarkably stable; it does not react with mercury, manganese dioxide, potassium hydroxide solution, or glass at the ordinary temperature. M. S. BURR.

Reduction of nitrites, nitrates, and nitric acid with magnesium amalgam: a new method of preparing hyponitrites. P. NEOGI and B. L. NANDI (J.C.S., 1928, 1449—1455; cf. A., 1899, ii, 656; 1900, ii, 16; 1903, ii, 426).—The reducing action of magnesium amalgam on metallic nitrates and nitrites affords a convenient method for the preparation of hyponitrites. The following *hyponitrites* have not hitherto been described: cadmium, zinc, lithium, rubidium, and cæsium; magnesium hyponitrite was identified in solution only. The reduction of nitrates by this amalgam proceeds in stages to produce nitrites, hyponitrites, ammonia, and hydroxylamine, the last-named being often produced in considerable quantities. Sodium and potassium hyponitrites were prepared by reducing the corresponding nitrites, but all the others by reduction of nitrates. In general, magnesium amalgam was added slowly to a concentrated solution of the salt, at 5° or below. After a short time, magnesium hydroxide was removed, and the reduction similarly repeated until the solution was free of nitrate and nitrite. Concentration is carried out in a vacuum desiccator containing sulphuric acid, and the product generally extracted with alcohol. The zinc salt was obtained by reduction in acid solution. During the preparation of cadmium hyponitrite (d_4^{20} 2·121) the explosive *oxyhyponitrite*, Cd(OH)NO, was formed. When heated in a vacuum, cadmium hyponitrite suddenly decomposes at 185° with formation of cadmium oxide and nitrous oxide. Oxyhyponitrite was also formed in the reduction of lead nitrate. The reduction of nitric acid in the presence of sulphuric acid resulted in a 60% yield of hydroxylamine sulphate of 97·8% purity. No hyponitrites were formed on reducing mercuric and mercurous nitrates and the nitrates of copper, cobalt, nickel, silver, and ammonium. R. A. PRATT.

Nitronium or nitracidium salts and the cationic migration of nitric acid. A. HANTZSCH and K. BERGER (Ber., 1928, **61**, [*B*], 1328—1334; cf. A., 1925, ii, 634).—The formation of additive compounds from perchloric and nitric acids gives rise to compounds previously designated nitronium mono- and di-perchlorate in analogy with the hydroxonium perchlorate from perchloric acid and water. As the nomenclature is liable to lead to confusion with azylium and oxylium compounds, it is proposed to term cations formed by addition of hydrogen atoms to acids acidium cations, *e.g.*, nitracidium, acetacidium, etc. Multivalent cations formed by further addition of hydrogen atoms are distinguished by the addition of "hydro-". Thus, nitronium perchlorate and nitronium diperchlorate are to be termed nitracidium perchlorate and hydronitracidium perchlorate.

The structure $\left[O_2N{-}O{<}^{H}_{H}\right]'$ is assigned to the acidium ion, since it exhibits much more feeble absorption than the corresponding acid. Electrochemical evidence of the salt-like nature of nitracidium and hydronitracidium perchlorate is deduced from observations of their electrical conductivity in nitromethane, freed from water and hydrocyanic acid by distillation over mercury oxide and freshly sublimed phosphoric oxide. The limiting conductivity of the two salts is of the order of magnitude required for a binary and ternary electrolyte, respectively. Further analyses of the anodic and cathodic solutions after electrolysis of solutions of the salts establishes the cathodic wandering of the nitric acid. H. WREN.

Application of the spectrographic and spectrophotometric methods to the study of the hydrolysis of some alkaline salts. P. JOB (Compt. rend., 1928, **186**, 1546—1548).—The author's spectrographic and spectrophotometric methods (A., 1926, 791) for the study of the formation of complexes may be applied to any reaction between substances in solution, so long as the absorption spectrum of the reaction products differs sufficiently from that of the reactants. The hydrolysis constants of phenol, *p*-chlorophenol, and the nitrophenols have been determined approximately, and the principal reaction between solutions of sodium chromate and sulphuric acid has been shown to be $CrO_4'' + H^{\cdot} \rightleftharpoons HCrO_4'$, which in strong solutions is probably followed by the reaction $2HCrO_4' \rightleftharpoons Cr_2O_7'' + H_2O$. J. GRANT.

Migration of masked sulphate groups in chrome alum liquors. W. SCHINDLER and K. KLANFER.—See B., 1928, 533.

Chrome tanning. VI. Properties and behaviour of various pretreated chromium sulphate solutions. E. STIASNY and O. GRIMM.—See B., 1928, 494.

Chrome tanning. VII. Hydrolysis and tanning action of sulphatochromium sulphates. E. STIASNY and D. BALANYI.—See B.. 1928, 495.

Selenium tetrafluoride. E. B. R. PRIDEAUX and C. B. COX (J.C.S., 1928, 1603—1607).—Lebeau's preparation of selenium tetrafluoride (A., 1907, ii, 540) may have contained the hexafluoride, oxyfluoride, and even the dioxide dissolved in hydrofluoric acid (cf. A., 1907, ii, 613, 679). The authors have prepared selenium tetrafluoride (yield 73·5%) by the action of selenium tetrachloride on silver fluoride, thus precluding the presence of water, hydrofluoric acid, or a higher fluoride. The compound has *d* 2·77, b. p. 93°, and m. p. $-13·2°$, and hence is clearly distinct from the oxyfluoride. The tetrafluoride reacted immediately with silicon in the cold to give silicon tetrafluoride and a red deposit of selenium. Sulphur did not react in the cold. Some tetrafluoride containing a little oxyfluoride reacted strongly with red phosphorus to give selenium dioxide, selenium, and apparently a mixture of phosphorus fluoride and oxyfluoride. A comparison of the

properties of the lower fluorides of selenium and of a solution of the dioxide in hydrofluoric acid showed that, although the tetrafluoride and the oxyfluoride are similar in their chemical reactions, they are not identical. R. A. PRATT.

Double salts of selenic acid. J. MEYER and W. AULICH (Z. anorg. Chem., 1928, **172**, 321—343).—The properties of the selenates of potassium, sodium, magnesium, and calcium, and the solubility isotherms at 25° of the double salt systems potassium–magnesium, sodium–magnesium, potassium–calcium, sodium–calcium, and potassium–sodium selenates have been investigated and compared with those of the corresponding sulphates. The simple selenates are very similar to the simple sulphates, except that potassium selenate is very much more soluble than potassium sulphate. No magnesium selenate dodecahydrate was obtained, but there is, apparently, a dihydrate. Unstable forms of both selenate and sulphate heptahydrates are obtained. Calcium selenate, in addition to the hemihydrate which behaves similarly to plaster of Paris, forms also a hydrate, $CaSeO_4,1\cdot5H_2O$. Sodium selenate resembles sodium sulphate very closely. The transition temperature of the decahydrate to the anhydrous form is 31·8°. The sodium selenate decahydrate effloresces similarly to Glauber's salt, and the solubility falls with rise of temperature after the transition point is reached. The potassium selenate–magnesium selenate solubility isotherm at 25° indicates the existence of selenate-schönite, $K_2SeO_4,MgSeO_4,6H_2O$, and there is transition to the tetrahydrate, selenate-leonite, at 33·1°. At 25° sodium and magnesium selenates do not form a double salt, but at 28·1° a mixture of equimolecular proportions of the two salts gives selenate-astrakhanite, $Na_2SeO_4,MgSeO_4,4H_2O$. Potassium and calcium selenate form a compound, $K_2SeO_4,CaSeO_4,2H_2O$, whereas the double sulphate is a monohydrate. The sodium calcium double selenate contains 2 molecules of water, but by drying at 100° the anhydrous selenate-glauberite is obtained. No double salt of sodium and potassium selenate has been obtained. The sulphates, however, form glaserite, $2K_2SO_4,Na_2SO_4$. M. S. BURR.

Different states of iron in relation to its chemical behaviour. O. BAUDISCH (Naturwiss., 1928, **16**, 542—545).—Earlier work is summarised. Ferrous hydroxide, precipitated by hydrolysis or by the action of hydroxyl ions from a solution of ferrous hydrogen carbonate reacts in the nascent state with molecular oxygen to form a compound exhibiting a very high oxidation and reduction potential. The reduction has been studied in detail for the system potassium nitrate–potassium nitrite. R. A. MORTON.

Existence of ferrous chloride hexahydrate. G. AGDE and F. SCHIMMEL (Z. anorg. Chem., 1928, **173**, 111—114).—A neutral solution of ferrous chloride saturated at 10° was cooled to —15°, when the hexahydrate $FeCl_2,6H_2O$ separated. The transition temperature between the hexahydrate and the tetrahydrate is 12·3°. Lescœur's observation that when hydrogen chloride is passed into ferrous chloride solution only the tetrahydrate crystallises is not confirmed. A. J. MEE.

Ferric nickel acetate and similar compounds; a lower basic ferric acetate. R. WEINLAND and H. HOLTMEIER (Z. anorg. Chem., 1928, **173**, 49—62).—Salts of the type $Fe_3Ni(OAc)_8(OH)_3,6H_2O$ have been prepared in which the nickel is replaced by cobalt, manganese, zinc, cadmium, and magnesium. They may be obtained by mixing solutions of ferric chloride or nitrate, a salt of the metal to be introduced, and sodium acetate in the right proportions. Directions are given for the preparation of the following *acetates*: $Fe_3Ni(OAc)_8(OH)_3,6H_2O$; $Fe_3Co(OAc)_8(OH)_3,8H_2O$; $Fe_3Mn(OAc)_8(OH)_3,5H_2O$; $Fe_3Zn(OAc)_8(OH)_3,5H_2O$; $Fe_3Cd(OAc)_8(OH)_3,7H_2O$; $Fe_3Mg(OAc)_8(OH)_3,10H_2O$; $Fe_9Ni_4(OAc)_{26}(OH)_9,23H_2O$; $Fe_9Co_4(OAc)_{26}(OH)_9,23H_2O$; $Fe_9Zn_4(OAc)_{26}(OH)_9,18H_2O$. Salts of the second type will combine with pyridine, and isomorphous *compounds* of the formulæ $Fe_6Ni_3O_3(OAc)_{17}(OH),12C_5H_5N$ and $Fe_6Co_3O_3(OAc)_{17}(OH),12C_5H_5N$ are described. The *benzoates* $Fe_6Mg_3(OBz)_{18}(OH)_6,12C_5H_5N$ and $Fe_6Ni_3(OBz)_{18}(OH)_6,12C_5H_5N$ are also described. If sodium perchlorate solution is added to a solution of the salt $Fe_3Mg(OAc)_8(OH)_3,10H_2O$ a yellowish-brown *basic ferric acetate*, $Fe_3O(OAc)_4(OH)_3,7H_2O$, is obtained. A. J. MEE.

[Hydrate of cobaltic fluoride.] E. BIRK (Z. anorg. Chem., 1928, **171**, 372).—A reply to Barbieri and Calzolari (this vol., 495). R. CUTHILL.

Cyanogen compounds of the platinum metals. II. Cyanogen compounds of ruthenium. F. KRAUSS and G. SCHRADER (Z. anorg. Chem., 1928, **173**, 63—72).—The blue cyanide of ruthenium of which the constitution was previously supposed to be $Ru(CN)_2$ or $Ru(CN)_3$ is shown to be a complex compound of the formula $Ru_2(CN)_5,H_2O$. Directions are given for the preparation of this compound from $K_4[Ru(CN)_6],3H_2O$. It is practically insoluble in the usual solvents. With concentrated ammonia solution, however, it gives a complex *salt* of the formula $NH_4[Ru_2(CN)_5,4NH_3]$, which dissolves in water with a yellowish-brown colour. By the addition of solutions of salts of heavy metals to a solution of this ammonium compound, precipitates are obtained with characteristic colours. In this way the *nickel* and *copper* compounds, $Ni[Ru_2(CN)_5,4NH_3],7H_2O$ and $Cu[Ru_2(CN)_5,4NH_3]_2,5H_2O$, respectively, were prepared. The *cyanide* $Ru(CN)_3,5H_2O$ can be obtained from $K_4[Ru(CN)_6],3H_2O$ by the action of chlorine, and then sulphuric acid. This also gives a complex *compound*, $Ru(CN)_3,H_2O,2NH_3$, with ammonia. Both these compounds, in which the ruthenium is tervalent, are probably non-electrolytes, the co-ordination numbers being 4 and 6. Their constitutions are discussed. A. J. MEE.

Recovery of pure platinum. E. H. REERINK (Z. anorg. Chem., 1928, **173**, 45—48).—The fact that when a current of carbon monoxide is passed over heated platinum chloride a volatile platinum carbonyl chloride is formed is employed in the separation of platinum from other metals of the same series which do not form such compounds under the same conditions. The platinum carbonyl chloride decomposes at about 300° with the formation of platinum, carbon

monoxide, chlorine, and carbonyl chloride. In order to obtain the platinum in the compact form, a platinum wire is heated at about 600° in the vapour of the compound, when the platinum formed grows round the wire. A. J. MEE.

Use of filters of known weight in quantitative analysis. B. ORMONT (Ukraine Chem. J., 1928, **3** [Sci.], 47—58).—If 9 cm. filter papers weighing from 0·4 to 0·6 g. are dried to constant weight, the mean error in the latter amounts to 1·2 mg. Such dry filters are exceedingly hygroscopic, so that if, after drying to constant weight at 100—105°, they are left at 75°, they absorb 3·7 mg. of moisture within 90 min., and 0·4 mg. at 95°. If the moisture content be made constant by drying in a desiccator, calcium chloride cannot be used, as it acts too slowly. Phosphorus pentoxide is better, but it also does not give constant weight within 48 hrs., although less moisture remains than after drying at 75° for 1 hr. or at 105° for 30 min. Leaving in the desiccator for a further 48 hrs. leads to a loss of 0·3—0·7% more than after the first 48-hr. period, a mean absolute error of 0·23% as compared with 0·12% for the method of drying to constant weight. Under experimental conditions, however, and in the presence of precipitates the former method is preferable. R. TRUSZKOWSKI.

Use in analysis of the mercury dropping cathode. E. BAYLE and L. AMY (Compt. rend., 1928, **186**, 1610—1612).—Heyrovsky's mercury dropping cathode (A., 1927, 1159) has been improved for the purposes of analysis by the use of a fine capillary tube allowing the flow of 4—5 c.c. of mercury/min., the oscillations and other fluctuations in current being thereby eliminated. The end of the tube is kept at a constant distance from the mercury level. Since the current intensity is independent of the concentration of one of a mixture of two salts, so long as the *P.D.* is less than a critical value (beyond which the intensity is a linear function of concentration so long as the latter is small), it is possible to determine each salt in succession, using suitable *P.D.* An accuracy of 1% was obtained for mixed solutions of bismuth and cadmium sulphates using 0·25 mg. of salt.

J. GRANT.

Following the course of the reaction in potentiometric titrations. F. L. HAHN, M. FROMMER, and R. SCHULZE (Z. physikal. Chem., 1928, **133**, 390—396).—It may be shown mathematically that in a potentiometric titration the turning point on the titration curve occurs before or after the true end-point according as the number of molecules, U, of the substance being titrated which react with one molecule of the reagent is greater or less, respectively, than 1. This error may be quite appreciable even when U diverges only moderately from 1. By the method previously described (A., 1927, 743), however, it is possible to calculate from the potentials at various stages of the titration both the true end-point and the value of U. R. CUTHILL.

Apparatus for measuring hydrogen-ion concentrations. P. HANSEN.—See B., 1928, 505.

Colorimetric determinations. II. Hydrogen-ion concentration and p_H. A. L. CALDWELL (J. Amer. Pharm. Assoc., 1928, **17**, 529—534).

Determination of hydrogen-ion concentrations in phosphate and borate mixtures by means of the quinhydrone electrodes. E. BIILMANN, A. KLIT, and T. SWAETICHIN (Biochem. J., 1928, **22**, 845—854).—The simple quinhydrone, the quinoquinhydrone, and the hydroquinhydrone electrodes have been examined and compared with hydrogen electrodes by determining the potentials for phosphate mixtures of p_H 5·90—8·04 and for borate mixtures of p_H 7·34—8·05. The simple quinhydrone electrode gave correct p_H values in phosphate mixtures up to 7·73 and still very good values at p_H 8·04; in borate mixtures it gave correct values. The quinoquinhydrone electrode gave correct values in phosphate mixtures up to p_H 7·38. In more alkaline phosphate mixtures and in the borate mixtures the potentials were very drifting. The hydroquinhydrone electrode gave very stable potentials in the phosphate mixtures but too low p_H values, because of the acid influence of the hydroquinhydrone. Owing to the acid influence of quinol, corrections must be introduced in the measurements of Biilmann and Katagiri (A., 1927, 516) with hydroquinhydrone electrodes in phosphate and hydrogen carbonate solutions. The acid influence of quinol may affect the measurements of Grossman (A., 1927, 488) in phosphate and borate in such a manner that the correction formula introduced may hold only for special cases. S. S. ZILVA.

Behaviour of indicators in certain titrations. R. T. THOMSON (Analyst, 1928, **53**, 315—321).—In the titration of ammonia, methyl-orange is the only satisfactory all-round indicator, particularly for determining the acidity or alkalinity of ammonium salts. For sodium and calcium phosphates the alkalinity of the pyrophosphate corresponds with that of the dibasic phosphate with bromophenol-blue, methyl-orange, methyl-red, or bromothymol-blue, but a large increase was shown with the other indicators, and in using phenolphthalein, for example, hydrolysis by boiling must be carried out before titrating. Calcium phosphate cannot be accurately determined by titration methods, since basic phosphate is produced both when sodium hydroxide is used with excess of calcium chloride, and when no excess of calcium is present. Methyl-orange is the best indicator for methylamines in the presence of carbonic acid, since the general behaviour of indicators is the same as with ammonia. Congo-red was used as a satisfactory indicator for alkalinity in pyridine. Other indicators did not give very good end-points; thymol-violet gave an acid result (0·24% sulphuric acid). Sofnol No. 1 is seriously affected by carbonic acid, and where larger quantities of boric acid than 0·2 g. are being titrated methyl-orange is preferable. D. G. HEWER.

Use of the centrifuge in quantitative analysis. [Determination of sulphur.] A. GUNDER (Z. anal. Chem., 1928, **73**, 441—444).—The precipitation with barium chloride is carried out in a weighed silica tube and the precipitate separated from the solution by centrifuging and decanting. Washing is effected also by centrifuging. The tube with the precipitate adhering tightly to its walls is dried in a steam oven, heated to redness, and weighed. Separation of the mother-liquor and washings from the precipitate after

treatment for 5 min. in the centrifuge is readily effected without loss by the use of a small siphon. A similar procedure is useful for collecting silver chloride, calcium oxalate, ammonium phosphomolybdate, etc. Platinum tubes must be used if calcium oxalate is to be converted into oxide for weighing. A. R. POWELL.

Determination of sulphur dioxide in small amounts in the atmosphere. R. J. McKAY and D. E. ACKERMAN.—See B., 1928, 482.

Volumetric determination of sulphate in potable water. F. G. GERMUTH.—See B., 1928, 504.

Determination of ammonia. K. TAUFEL and C. WAGNER.—See B., 1928, 522.

Analysis of a mixture of water, nitric acid, and sulphuric acid by thermometric titration. T. SOMIYA (Chem. News, 1928, **137**, 14).—Addition of fuming sulphuric acid to a mixture of water, nitric acid, and sulphuric acid results in a well-defined temperature maximum when the water is converted into sulphuric acid and the nitric acid into $OH{\cdot}SO_2{\cdot}ONO_2$. Further addition of the fuming acid gives a less well-marked temperature maximum when the nitric acid is converted into $(SO_3)_4N_2O_5$. A. R. POWELL.

Analysis of [natural] phosphates [according to the official French method.] A. SANFOURCHE and F. BLÉ (Bull. Soc. chim., 1928, [iv], **43**, 680—683).—Sources of error inherent in the official method are pointed out. Individually these errors are small, but their cumulative effect may lead to final errors of the order of 1%. Since decomposition of the phosphate with hydrochloric acid is not followed by evaporation to dryness to fix silica, the resulting solution is apt to contain appreciable amounts of silicic acid, part of which is usually contained in the precipitate of magnesium ammonium phosphate. This and other errors leading to high results may be avoided when ammonium citrate is present in amounts greater than those indicated by the official method. When precipitation and washing are carried out at 35° the amount of pyrophosphate finally weighed is appreciably less than when these are effected at 18—20°. The ignited pyrophosphate is often grey, due to the presence of carbon, but no appreciable error is thereby introduced. The practice of treating grey pyrophosphate with nitric acid to remove carbon is condemned. There appears to be a lack of uniformity regarding the conversion factor to be applied.
J. S. CARTER.

Determination of small amounts of arsenic. H. KLEINMANN (Deut. Z. ges. gerichtl. Med., 1927, **11**, 61—71; Chem. Zentr., 1928, i, 945).—The arsenic is converted, after separation as trichloride, into a nearly neutral solution of the pentoxide, and the precipitate formed on addition of a reagent containing cocaine and molybdic acid is determined nephelometrically. A. A. ELDRIDGE.

Rapid method for determination of carbon in iron and steel. N. M. MILOSLAVSKY and V. F. VEPRITZKA (Ukraine Chem. J., 1928, **3** [Tech.], 31—35).—A description of de Nolly's method for the determination of carbon in iron and steel (Bull. Soc. Ind. Min., 1910, **13**, 4). R. TRUSZKOWSKI.

Volumetric determination of carbon and carbon dioxide in rock products by electrical incandescence. W. J. PITT (Chem. Eng. Min. Rev., 1928, **20**, 167—170).—The substance, together with an oxidiser if necessary, is placed in a transparent quartz tube the rubber stopper of which carries (*a*) a nickel tube reaching nearly to the bottom and carrying a resistance wire, (*b*) a tube for the ingress of oxygen or air, (*c*) a gas-exit tube. The substance is mixed with a catalyst and heated at 950°; the carbon dioxide is absorbed preferably in barium hydroxide, and determined volumetrically, water also being absorbed in the usual way. The method is applicable to the determination of carbon and hydrogen in organic material. CHEMICAL ABSTRACTS.

Complete gas analysis by the simultaneous oxidation of methane, carbon monoxide, and hydrogen. H. VON JUPTNER (Instruments, 1928, **1**, 55—57).—Of the residual gas after determination of the carbon dioxide, heavy hydrocarbons, and oxygen, 15 c.c. are exploded with 75 c.c. of air, and the carbon dioxide and excess of oxygen determined. The calculation is discussed. CHEMICAL ABSTRACTS.

Determination of hydrocyanic acid in gaseous mixtures. G. E. SEIL, J. S. SKELLY, and H. A. HEILIGMAN (Gas Age Rec., 1927, **60**, 179—180, 223—224, 259—260).—The most satisfactory method consists in removal of ammonia with 10% sulphuric acid, conversion of hydrogen cyanide into ammonium hydrogen sulphate by concentrated sulphuric acid, and determination of the nitrogen by Kjeldahl's method. CHEMICAL ABSTRACTS.

Helium. I. Detection of very small quantities of helium [and neon]. F. PANETH and K. PETERS (Z. physikal. Chem., 1928, **134**, 353—373).—By a systematic investigation of the sources of error the apparatus for the spectroscopic detection of helium and neon has been improved so that 10^{-10} c.c. of either of these gases can be detected with certainty. A table is given showing the single spectral lines which are observed using quantities of helium and neon from 10^{-5} to 10^{-10} c.c. The smallest quantity of air which can be detected by this means from the appearance of the neon lines is 10^{-5} c.c. With this method it is possible to detect spectroscopically the formation of helium from the invisible active deposit of thorium.
O. J. WALKER.

Zirconium sulphate as a reagent for the detection of potassium. R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1928, **50**, 1515—1522).—To the solution at 0° an equal volume of concentrated (20·96%) zirconium sulphate solution is added. Solutions containing in the absence of sodium 0·53 mg. of potassium, and in the presence of sodium 1·76 mg. of potassium, yield a white precipitate. In more concentrated solutions large amounts of sodium sulphate retard the reaction. The test is as delicate as the sodium cobaltinitrite test only when the solution is kept for 1—2 hrs. At certain dilutions comparison blank tests are necessary. Zirconium sulphate solutions of half the above strength are equally sensitive in the absence of sodium, and in the presence of the latter will detect 0·7 mg. of potassium.
S. K. TWEEDY.

Volumetric determination of potassium. O. PFUNDT (Z. anal. Chem., 1928, **73**, 439—440).—To obtain accurate results by titration with sodium perchlorate (Jander and Pfundt, A., 1927, 1046) a motor-driven glass propeller should be used to keep the solution stirred thoroughly during the addition of the reagent. A convenient form of apparatus is illustrated. A. R. POWELL.

Determination of potassium as chloroplatinate. M. McCURDY (Proc. Nova Scotian Inst. Sci., 1927, **16**, 142—143).—The precipitate of potassium chloroplatinate can be ignited to platinum over a Fischer-Meker burner instead of being dried at 100°, without any loss of accuracy. S. J. GREGG.

Determination of potassium ferrocyanide. P. P. BUDNIKOV.—See B., 1928, 522.

Specific reagent for the rapid gravimetric determination of sodium. H. H. BARBER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1928, **50**, 1625—1631).—Experiments are described demonstrating the use of uranyl zinc acetate reagent (Kolthoff, A., 1927, 436) for the gravimetric determination of sodium in the form of the compound $(UO_2)_3ZnNa(OAc)_9,6H_2O$ (not $9H_2O$). Less than 50 mg. of potassium chloride in the solution causes only a small error; lithium and strontium must be absent. Barium, calcium, magnesium, and zinc do not interfere. Phosphoric acid, and large amounts of oxalic and tartaric acids, must be absent. S. K. TWEEDY.

Decomposition of silicates by strontium salts in metals. J. KAVINA (Chem. Listy, 1928, **22**, 267—270).—Strontium chloride or a mixture thereof with ammonium chloride is used for fusion with silicates in the determination of alkali metals in the latter. This fusion mixture corrodes platinum vessels; nickel crucibles cannot be used. Precipitation of strontium as carbonate from aqueous extracts of the fused mass is not as complete in the presence of alkali chlorides as in their absence, 0·1 mg. of strontium being, however, readily precipitable from 3 c.c. of a solution containing 0·2 g. of alkali chlorides. Strontium chloride used alone does not yield satisfactory results. R. TRUSZKOWSKI.

Qualitative analysis of the group magnesium, sodium, potassium. H. S. KING (Proc. Nova Scotian Inst. Sci., 1927, **16**, 30—34).—The filtrate from the alkaline-earth group is evaporated until crystals appear, and 4*N*-phosphoric acid and excess of ammonia solution are added; the precipitate is extracted with dilute sulphuric acid and alcohol and the magnesium again precipitated as magnesium ammonium phosphate. The filtrate is evaporated to dryness, ignited, dissolved in water, and the last traces of ammonium salts are eliminated (as nitrogen) by passing in a mixture of nitric oxide and nitrogen peroxide (from the interaction of starch and nitric acid). After boiling, portions of the solution are tested for potassium and sodium with sodium cobaltinitrite and potassium antimonate, respectively. S. J. GREGG.

Potentiometric determination of silver as ferrocyanide. W. SPEYER (Z. anal. Chem., 1928, **74**, 108—113).—The potentiometric titration of silver with potassium ferrocyanide gives results which are more than 1% too low, but reasonably accurate results are obtained with lithium or sodium ferrocyanide, although the potential limits between which the steepest fall in the curve occurs vary in different tests. A. R. POWELL.

Rapid method for the determination of calcium and magnesium present together. N. M. MILOSLAVSKY and E. A. VILENKO (Ukraine Chem. J., 1928, **3** [Tech.], 37—41).—Willstatter and Waldschmidt's-Leitz's method (A., 1923, ii, 258) for the determination of calcium and magnesium present together is verified and certain slight improvements are suggested. R. TRUSZKOWSKI.

Qualitative separation of the metals of the alkaline-earth group. C. B. NICKERSON (Proc. Nova Scotian Inst. Sci., 1927, **16**, 25—29).—The filtrate after separation of barium as chromate from the solution of acetates is treated with acetic acid, ammonium sulphate, and a large excess of ammonia solution, whereby the strontium (*e.g.*, 3 mg.) is precipitated as sulphate. The calcium (*e.g.*, 400 mg.) is precipitated from the filtrate as oxalate. S. J. GREGG.

Modification of the Schneider-Finkener method for the determination of zinc. I. MAJDEL (Arhiv Hemiju Farm., 1928, **2**, 127—136).—The solution, which should contain a moderate amount of ammonium sulphate and be distinctly acid, is neutralised with ammonia, using Congo-red paper as indicator. After addition of 4 c.c. of *N*-sulphuric acid the solution is diluted to 300 c.c. and treated for ½ hr. at 70° with hydrogen sulphide. After 1 hr. the solution is filtered. The washed precipitate is heated with sulphur in a Rose crucible in a current of hydrogen. The method is applicable to quantities of zinc not exceeding 0·2—0·3 g. The presence of chlorides in the solution is not desirable. J. S. CARTER.

Quantitative spectral analysis of lead in gold, and a new method of analysis by emission spectra. IV. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1928, **173**, 92—103).—A method is described by which as little as 0·001% of lead can be detected and determined in a mixture of lead and gold. Various errors are described. It is necessary to spark between new electrodes for 1—2 min. before taking a photograph. For the analysis the 3684 and 2614 lines of lead can be used, the intensities of the lines being compared with those given by standard mixtures. In a preferable method the spectrogram of the gold containing lead is photographed a number of times in succession with equal exposures, and then a secondary spectrogram of cadmium with 10% of tin is photographed, with exposures increasing in geometrical progression. The secondary spectrogram is photographed superposed on that of the gold-lead mixture. The tin lines are relatively near those of gold. The photograph in which the 3684 lead line is equivalent in intensity to the 3656 tin line is found, and then by comparison of lines of gold and tin in this photograph the lead content can be calculated from a table. The effect of heating the electrodes on the intensity of the

lines when only a small percentage of lead is present is investigated by finding how the intensity varied with the time of passing the spark. A. J. MEE.

Spectroscopic method of finding the position of an impurity in a metal. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1928, **173**, 104—110).—The spectro-analytical method described in the preceding abstract can be used to discover the location of an impurity in a metal, and consequently whether it is distributed uniformly or not. The method applied to a lead–gold mixture shows that for concentrations of lead between 0·04% and 1% the impurity lies on the boundary of the gold crystal. A. J. MEE.

Microtitration of lead cations and of chromic anions by centrifugo-volumetry. R. F. LE GUYON and R. F. AURIOL (Compt. rend., 1928, **186**, 1551—1553).—The author's centrifugo-volumetric method (A., 1926, 927) has been applied to the determination of lead or chromium by precipitation of solutions of lead nitrate by solutions of potassium chromate, the end-point being denoted by the appearance of a yellow colour and the failure to produce a precipitate when the latter is added drop by drop to the former and centrifuged. A slight error is introduced for solutions which are not exactly equivalent, but otherwise quantitative results are obtained in neutral or acetic acid solutions and in the absence of other ions which might be precipitated with the lead. J. GRANT.

Potentiometric determination of copper as cupric ferrocyanide. S. TAKEGAMI (Z. anal. Chem., 1928, **74**, 39—41; cf. this vol., 499).—Following the unsatisfactory results obtained by the potentiometric titration of copper with potassium and lithium ferrocyanides, the corresponding salts of sodium and magnesium were examined. On plotting *P.D.* against concentrations, neither the sodium nor the magnesium salt gave a sharply marked turning point corresponding with any known stoicheiometric proportion. Results with the magnesium salt in alcohol gave characteristic maxima corresponding fairly well with the equivalent-line for cupric ferrocyanide, but the method was not sufficiently accurate or convenient to be of practical importance. Small hope was seen of extension of the method in any simple way by use of other ferrocyanides. R. A. PRATT.

Electrolytic apparatus for determination of copper in insecticides and fungicides. E. B. HOLLAND and G. M. GILLIGAN.—See B., 1928, 498.

Determination of mercuric cyanide and oxycyanide. E. RUPP and F. LEWY (Apoth.-Ztg., 1928, **43**, 228).—A modification of the official German procedure for determining mercuric cyanide in oxycyanide tablets. CHEMICAL ABSTRACTS.

Determination of traces of mercury. III. Determination of mercury in urine and fæces and the influence of medication. N. E. SCHREIBER, T. SOLLMANN, and H. S. BOOTH (J. Amer. Chem. Soc., 1928, **50**, 1620—1625).—The method previously described (A., 1926, 929) may be used to determine mercury in urine; the result is usually about 0·01 mg. too low. Prolonged keeping of the urine at 0° without freezing does not affect the method, and the following may be present: bismuth, chloral hydrate, salvarsan, "barbital," and small amounts of bromides and hexamethylenetetramine. Sodium salicylate, "cinchophen," and large amounts of hexamethylenetetramine should be absent. Bromides in large quantities and iodides must be removed by addition of sodium nitrite after oxidation. The organic matter in fæces must be destroyed by oxidation with potassium permanganate and concentrated nitric acid. S. K. TWEEDY.

Ceric sulphate in volumetric analysis. IV. Potentiometric titration of vanadyl ion alone or in presence of ferric and chromic ions. Stability of vanadyl solutions. N. H. FURMAN (J. Amer. Chem. Soc., 1928, **50**, 1675—1680; cf. this vol., 499).—Vanadyl salt solutions at 50—60° may be titrated potentiometrically with ceric sulphate, even in the presence of large quantities of ferric and chromic salts. When ferrous iron is present, the first end-point obtained on titrating in the cold corresponds with the quantitative oxidation of the iron, and the second end-point, in the hot, to that of the vanadium. Dilute vanadyl salt solutions containing free acid are quite stable for 1 year. S. K. TWEEDY.

Cerium salts as oxidising agents in electrometric titrations. II. J. A. ATANASIU and V. STEFAVESCU (Ber., 1928, **61**, [*B*], 1343—1347).—An acid 0·1*M*-solution of ceric sulphate, obtained by electrolytic oxidation of the mixture of cerium sulphates derived by dissolution of cerium oxide in concentrated sulphuric acid, is used. Such a solution can be preserved unchanged for months if reducing agents are excluded. It is a very energetic and useful reagent for oxidative reactions when potentiometric methods are employed. In 0·1*M*- to 0·01*M*-solution ceric sulphate is remarkably insensitive to external physical influences and chemical reagents which frequently induce errors in titrations with permanganate. Experiments with nitrites, oxalic acid, ferrocyanides, hydrogen peroxide, ferrous iron, arsenic, tin, and titanium are described. H. WREN.

Silicate analysis. J. ROBITSCHEK (Chem. Obzor, 1927, **2**, 325—326; Chem. Zentr., 1928, i, 1074).—8-Hydroxyquinoline is used for the precipitation of aluminium and magnesium. The precipitate, $M(C_9H_6ON)_3$, may be weighed or titrated with bromine in hot hydrochloric acid: $C_9H_7ON+Br_2=C_9H_5ONBr_2+2HBr$. A. A. ELDRIDGE.

Use of mercury ammonium salts in quantitative analysis. I. Quantitative separation of aluminium and nickel. B. ŠOLAJA (Arhiv Hemiju Farm., 1928, **2**, 136—142).—Aluminium is precipitated quantitatively from solutions of its salts by addition of "fusible white precipitate," $HgCl_2(NH_3)_2$. The precipitate is ignited to alumina. In presence of sulphates aluminium and nickel may be separated by the use of this reagent. J. S. CARTER.

Quantitative separations and determinations by volatilisation with hydrogen chloride. VI. Determination of oxide in aluminium alloys. G. JANDER and W. BROSSE (Z. angew. Chem., 1928, **41**, 702—704).—The method recently described (B.,

1927, 527) for the separation of aluminium, silicon, and magnesium etc. in aluminium alloys can be used for the accurate determination of the aluminium oxide present in such alloys, if not less than 0·02% is present. Under the prescribed conditions of drying, moisture is sufficiently eliminated from the gaseous hydrogen chloride, and further drying by cooling to −78° to −80° with ether and solid carbon dioxide is unnecessary. An internal reaction temperature of about 275° is used instead of 200—220° as originally recommended. R. BRIGHTMAN.

Potentiometric determination of gallium. H. D. KIRSCHMAN and J. B. RAMSEY (J. Amer. Chem. Soc., 1928, **50**, 1632—1636).—The potentiometric ferrocyanide titration in presence of ferricyanide previously described is applicable to slightly acid gallium chloride solutions (cf. Bray and Kirschman, this vol., 38). The precipitate has the composition $Ga_4[Fe(CN)_6]_3$. The accuracy is about 0·3%. S. K. TWEEDY.

Determination of ferrous iron in silicate rocks. I. B. A. SOULE (J. Amer. Chem. Soc., 1928, **50**, 1691—1694).—Improvements in Cooke's method are described. The sample may be dissolved in boiling hydrofluoric and sulphuric acids in a Pyrex flask, and the solution titrated with permanganate (observing the usual precautions) without transference to a second vessel. The method of determining the factor necessary to correct for the reduction caused by material dissolved from the glass is given. S. K. TWEEDY.

Volumetric determination of ferrous ion by means of potassium iodate. G. B. HEISIG (J. Amer. Chem. Soc., 1928, **50**, 1687—1691).—To the ferrous salt solution 6 c.c. of iodine chloride solution (Jamieson, "Volumetric Iodate Methods," 1926, 8), 6 c.c. of carbon tetrachloride, and excess of hydrochloric acid are added in turn. After cooling, the mixture, which must contain 50 vol.-% of hydrochloric acid, is titrated with standard potassium iodate solution until the carbon tetrachloride layer is decolorised. If the end-point is exceeded, the excess of potassium iodate may be determined by a potassium iodide solution which has been standardised against potassium iodate; in fact, this back-titration method may be used to carry out the determination. The determination is unaffected by acetic, succinic, and tartaric acids, ethyl alcohol, formaldehyde, and filter paper. S. K. TWEEDY.

Gravimetric determination of molybdenum. E. WENDEHORST (Z. anal. Chem., 1928, **73**, 452—457).—In neutral or slightly alkaline solutions the mercurous molybdate method gives slightly high results due to adsorption of alkali salt. In acid solutions the results are more nearly correct by compensation of errors. The barium molybdate method gives low results owing to the solubility of the salt (1 : 14,000 of water). Precipitation of molybdenum as trisulphide and conversion into disulphide for weighing gives poor results, but conversion into trioxide yields excellent results. A. R. POWELL.

Potentiometric analysis of binary, ternary, and quaternary tin alloys. H. BRINTZINGER and F. RODIS.—See B., 1928, 488.

Use of liquid amalgams in volumetric analysis. X. Determination of vanadium, chromium, and nitro-compounds. K. SOMEYA (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 131—139).—See this vol., 387.

Potentiometric analysis of the hardening elements in special steels. II. Determination of chromium and vanadium in iron alloys and superior steels. E. ZINTL and P. ZAIMIS.—See B., 1928, 525.

Determinative mineralogy. IV. P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (Amer. J. Sci., 1928, [v], **15**, 455—460).—Micro-methods for the determination in minerals of gold and sulphur respectively are described. The method for gold is based on the formation of pleochroic crystals of gold pyridine bromide. The test is specific for this element (limit, 0·02 μg.), some forty elements as ions being examined for interference. Special instructions are given for minerals containing cadmium, zinc, and lead.

Two tests are described for sulphur. The first depends on the colour change of an alkaline solution of bromocresol-green by the action of sulphurous acid formed during the heating of the metallic mineral in a specially designed tube. The second test, applied to non-metallic or to metallic minerals, depends on the decolorisation of a starch–iodine solution by the sulphur dioxide evolved on heating the mineral. The test is specific for sulphur. The limit in each case is 0·2 μg. R. A. PRATT.

Separation of the platinum metals. ANON. (Chem. Eng. Min. Rev., 1928, **20**, 142—143, 170—171).—Concentrated hydrochloric acid (7—8 c.c.) is added to the chloride solution (100 c.c., 0·3 g. of each metal, but less of osmium) and the palladium precipitated with 1% alcoholic dimethylglyoxime; the precipitate is collected, washed with cold, very dilute hydrochloric acid, dried at 105°, and ignited (finally in hydrogen). The filtrate is boiled for 30 min. with furildioxime (2% solution) and alcohol (10%), the precipitate being washed with very dilute alcohol, and after ignition weighed as platinum. The filtrate is evaporated to one third of its volume and boiled with 5 c.c. of concentrated hydrochloric acid and 5 g. of sodium chlorate for each 100 c.c. After addition of an equal volume of alcohol to the chlorine-free solution, rhodium is precipitated with potassium nitrite, the precipitate being washed with 50% alcohol and the filtrate used for determining ruthenium, osmium, and iridium. The precipitate is dissolved in aqua regia, the excess of acid removed, the chloride reduced with magnesium or zinc, and the rhodium washed with dilute hydrochloric acid and ignited in hydrogen. The filtrate is evaporated to remove nitrous fumes, and concentrated hydrochloric acid (10 c.c. per 100 c.c.) is added, and evaporation continued until solids separate, when 2—3 vols. of water are added, followed by sodium hydroxide to alkalinity, and alcohol to 33 vol.-%. The precipitated ruthenium oxide is dissolved in hydrochloric acid, the metal precipitated with magnesium or zinc, and ignited in hydrogen. The filtrate is evaporated to remove alcohol; the osmium and iridium are precipitated with zinc dust and washed with very dilute

hydrochloric acid. The iridium is dissolved from the filter in sodium hypochlorite solution, the osmium being ignited in hydrogen. Zinc and hydrochloric acid are added to the iridium solution, the iridium being dried at 190° before being heated in hydrogen.
CHEMICAL ABSTRACTS.

Ultra-violet light filter. F. SAUNDERS (J. Opt. Soc. Amer., 1928, **16**, 362).—One mm. of a solution of potassium hydrogen phthalate containing 40·836 g. per litre transmits uniformly up to 3000 Å., and cuts off sharply at that wave-length. The salt should be recrystallised several times. C. W. GIBBY.

Experiments on Geiger ion counters. R. D. BENNETT (J. Opt. Soc. Amer., 1928, **16**, 339—354).—The sensitivity of this instrument has been investigated with varying dimensions, voltage, and gas pressure. It is very sensitive for detecting single ions, but only moderately so for ultra-violet light, as its efficiency is low. Quantitative use is possible only if the sensitivity can be kept constant over long periods. C. W. GIBBY.

Projection electroscope for standardising radium preparations. L. F. CURTISS (J. Opt. Soc. Amer., 1928, **16**, 363—366).—For standardising strong radium preparations the ordinary gold-leaf electroscope observed through a microscope involves danger to the operator, and eyestrain. An instrument is described in which a quartz fibre attached to the gold leaf is projected (×100) on a ground-glass scale.
C. W. GIBBY.

Vacuum stopcock. A. P. H. TRIVELLI (J. Opt. Soc. Amer., 1928, **16**, 367—369).—Greater security in mercury sealed stopcocks for vacuum work may be obtained by having a ring of mercury round the centre of the barrel, filled from a small funnel sealed on the outside. C. W. GIBBY.

Automatic colorimeter. G. BAGANZ (Chem. Fabr., 1928, 358).—The apparatus is designed for the control of the chlorination of town's water by the use of benzidine and potassium iodide as colorimetric indicators, but is capable of adaptation. It consists of an electrical arrangement for the taking of samples, addition of indicators, and washing out of the apparatus at regular time intervals, the observation only being left to the attendant. C. IRWIN.

Selenium cells as colorimeters. A. MICKWITZ (Z. anorg. Chem., 1928, **171**, 285—311).—In order to study the absorption of light by a solution, the effect of the transmitted light on the resistance of a selenium cell, measured by the current passing when a constant *P.D.* is applied, may be compared with the effect obtained by using as absorbent a layer of water of the same thickness, and the same source of light. In order to eliminate the effect of variations in the properties of the cell with the time and also hysteresis effects in the resistance, the cell is exposed to the light transmitted by the water and the light transmitted by the solution for alternate periods of 20 sec. each, each period of illumination being separated from the following period by 40 sec. of darkness, and this is continued until the current corresponding with each kind of light becomes constant. The absorption by the solution is then expressed numerically by the ratio x of the quantity (current passing through the cell when illuminated by the light transmitted by the solution — current passing in darkness) to the corresponding quantity for the water. Absorption curves constructed in this way for solutions of copper sulphate and copper nitrate may be used for the colorimetric determination of these salts, the mean error with the sulphate being ±1·5%. As the value of x is affected considerably by variations in the *P.D.* applied to the cell, this should be kept constant for all the measurements. Iron may be determined colorimetrically in the form of colloidal ferrous sulphide, the oxidation of which, with consequent change of colour, is delayed by addition of sodium sulphite; the mean error is ±2·5%. Experiments of this kind show that a saturated solution of ferrous sulphide at the ordinary temperature contains 0·0028 g. of iron/litre.
R. CUTHILL.

Still for preparation of pure water. H. S. KING (Proc. Nova Scotian Inst. Sci., 1927, **16**, 176).—A simple adaptor for fitting a tin condenser on to the neck of an ordinary flask is described. S. J. GREGG.

Application of an electromagnetic force to the thermobalance. Z. SHIBATA and M. FUKUSHIMA (Bull. Chem. Soc. Japan, 1928, **3**, 118—123).—If the sensitivity of Honda's thermobalance (cf. Sci. Rep. Tohoku Imp. Univ., 1915, **4**, 97) is increased its range is reduced and errors due to hysteresis in the spring are increased. This is overcome by attaching an iron rod, on the axis of a solenoid, to the wire connecting the beam to the spring. Movement of the beam is counteracted by passing a current through the solenoid, the change in weight being calculated from the value of the current. Accuracy equal to that of a chemical balance is obtained.
C. J. SMITHELLS.

Apparatus for analysis of solutions, especially bleach liquors containing chlorine. K. HINTZMANN.—See B., 1928, 478.

Physical methods in chemical laboratories. III. Production of intense magnetic and electric fields. H. GEHLEN (Z. angew. Chem., 1928, **41**, 714—716).—Modern methods for the production of intense magnetic and electric fields are briefly described. J. S. CARTER.

Pumice impregnated with anhydrous magnesium perchlorate as a drying agent. J. H. YOE, R. W. MCGAHEY, and W. T. SMITH (Ind. Eng. Chem., 1928, **20**, 656—657).—Pumice granules are soaked for 24 hrs. in 35% magnesium perchlorate solution, heated at 175° to dehydration, and further heated at about 240° in a slow current of dry (P_2O_5) air, at rates of flow from 1·5 to 3·5 litres per hr. The material has greater capacity than phosphorus pentoxide; it can be repeatedly reactivated and does not become sticky on handling or form channels through use. It contracts on absorbing water and is neutral. At rates higher than 5 litres per hr. the agent is less effective than phosphorus pentoxide.
D. G. HEWER.

Automatic apparatus for determination of small concentrations of sulphur dioxide in air. M. D. THOMAS and R. J. CROSS (Ind. Eng. Chem., 1928, **20**, 645—647).—The air sample is drawn continuously by a Nelson pump delivering about 30 litres in

2 min., corresponding with approximately 1 g.-mol. vol. under conditions of operation, and the absorber consists of a standard "salvarsan tube" containing about 1 g. of starch, 2 g. of potassium iodide per litre, and the necessary iodine. Its strength is determined by titration with $0{\cdot}002N$-sodium thiosulphate, 1 c.c. of which corresponds with 1 in 10^6 of sulphur dioxide for 1 g.-mol. vol. of air. The method is automatic to the point of titration; a diagram of the apparatus is given. A modification for field work uses the intake manifold of the conveying motor-car for obtaining suction. The method was tested by comparison with the Selby method with satisfactory results, and concentrations of sulphur dioxide as low as 1 in 10^7 of air were dealt with since a $0{\cdot}000075N$-solution of iodine did not change when 400 litres of air were aspirated through it. With high concentrations of iodine incomplete absorption of sulphur dioxide and volatilisation of iodine may occur, but the method is trustworthy up to 6 in 10^5. D. G. HEWER.

Regulation of flow of carbon dioxide through a combustion train. J. C. RICE (Ind. Eng. Chem., 1928, **20**, 627).—A positive pressure may be impressed on a small Kipp apparatus by fixing a slightly inflated rubber balloon to a small glass tube through the top orifice of the generator. Backing of the acid in the Kipp apparatus is thus avoided and the slightest pressure on the balloon will counterbalance the suction caused by the column of mercury in the nitrometer. D. G. HEWER.

Apparatus for determining m. p. S. AVERY (Ind. Eng. Chem., 1928, **20**, 570).—A Thiele tube, lengthened for the use of an Anschütz total-immersion thermometer and modified to permit mechanical circulation by a propeller driven by a small fan motor, is used for the determining of m. p. It is suitable for use with petrolatum, glycerol, or with a glass propeller and shaft and lead bearing for sulphuric acid. The tube is heated in the same way as a Thiele tube, and the temperature can be very accurately regulated, fluctuation of the thermometer with slow heating being avoided. D. G. HEWER.

Extraction apparatus especially for use with liquids. P. H. PRAUSNITZ (Chem. Fabr., 1928, 346—347).—The use of a perforated glass filter in the extraction of aqueous solutions with ether in the bottom of the extraction tube is of great value in producing effective distribution. The extraction tube should be cylindrical and the space beneath the filter plate as small as possible. Several different arrangements of extraction apparatus are described and times required for complete extraction of a given solution determined. C. IRWIN.

Stand for electrolysis with a rotating electrode. A. GUNDER (Z. anal. Chem., 1928, **73**, 444—445).—The stand comprises a heavy cast-iron tripod with enlarged foot pieces and a thick glass central rod carrying a movable cast-iron arm on one side of which are the driving pulleys and on the other the rotating gear operating in a mercury contact cup on one branch of the arm. A. R. POWELL.

Moving flames. W. PAYMAN (J.C.S., 1928, 1738—1740; cf. this vol., 729).—A "flame-speed" camera and a "wave-speed" camera are described. These are used in determining the speeds of flames, and examining their mode of propagation, use being made of the abrupt change in refractive index of a gas mixture at the surface of a flame passing through it. R. A. PRATT.

Equilibrator; device for determination of the distribution ratio of a volatile solute between two miscible solvents. G. JONES and B. B. KAPLAN (J. Amer. Chem. Soc., 1928, **50**, 1600—1603).—Two closed bulbs are so mounted and connected together by tubes that on rotation gas or vapour is forced to bubble continuously and consecutively through two separated liquids. S. K. TWEEDY.

Nomography. III. Logarithmic and exponential functions. O. LIESCHE (Chem. Fabr., 1928, 359—361, 392—394).—The use of logarithmic scales facilitates the graphical solution of numerous problems. Various examples are given of the combination of a logarithmic scale and an equally divided scale or of two logarithmic scales arranged either parallel or "projectively" at an angle for the graphical determination of the breaking down of mesothorium, the variation of a reaction velocity with the temperature, the iodometric determination of antimony, etc. C. IRWIN.

Visual method of showing high temperature coefficient of resistance of metals as compared with alloys. P. ROOD (J. Opt. Soc. Amer., 1928, **16**, 357—359).—An experiment suitable for lectures. C. W. GIBBY.

Rational nomenclature of chemical compounds. A. SEMENTZOV (Ukraine Chem. J., 1928, **3** [Sci.], 39—45).—It is proposed to base Ukrainian chemical nomenclature on international names, as opposed to national. R. TRUSZKOWSKI.

Geochemistry.

Spectroscopic proof of the presence of boron in the sun. S. B. NICHOLSON and N. G. PERRAKIS (Compt. rend., 1928, **186**, 1523—1524; cf. this vol., 340).—Boron has been shown to be present in the sun by the identification of 26 out of 81 of the most intense rays in the spark spectrum of boric acid in the region 4645—5137 Å., the remainder being unidentifiable on account of the proximity of other strong solar rays, some of which showed the Zeeman effect. The mean and maximum disagreements were 0·005 and 0·013 Å., respectively. J. GRANT.

Nocturnal fluctuations of ozone. D. CHALONGE (Compt. rend., 1928, **186**, 1856—1858; cf. this vol., 389).—Daily and nightly determinations at Paris of the thickness of the layer of ozone in the upper atmosphere from October 1927 to April 1928 have shown that when suitably corrected for the absorption

coefficients of ozone for the spectral regions used, the results confirm those of other workers (cf. Buisson, this vol., 611). A mean nightly value of 3·35 mm. (under conditions of normal temperature and pressure) was obtained, there being no seasonal variation and very little deviation from determinations made in the daytime. J. GRANT.

Chemical characters of waters of Florida. W. D. COLLINS and C. S. HOWARD (U.S. Geol. Survey, Water-Supply Paper 596 G, Feb. 17, 1928, 177—233).

Organic content of the water of small lakes. E. A. BIRGE and C. JUDAY (Proc. Amer. Phil. Soc., 1927, **66**, 357—372).—A study of lakes in N.E. Wisconsin. A low proportion of inorganic matter is associated with a low content of organic matter, but a high proportion of inorganic matter may be associated with a low or high organic matter content.
CHEMICAL ABSTRACTS.

Radioactivity of water from various sources in Poland. S. GRABIANKA (Rocz. Chem., 1928, **8**, 183—194).—The radioactivity of water from nine different sources of mineral water varies from 1·98 to 9·72 Mache units. R. TRUSZKOWSKI.

Necessity of the physical-chemical study of the reaction $2CaCO_3+MgSO_4 \rightleftharpoons CaCO_3,MgCO_3+CaSO_4$. B. P. KROTOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 662—682).—The importance of Heydinger's reaction (Trans. Roy. Soc. Edinburgh, 1827, 36) for the study of the formation of deposits in salt lakes is pointed out. Dolomite and magnesite may be among the ultimate products of this reaction, the direction of which depends on the concentration of other salts in solution, as well as on that of its substrates, and on the temperature of the water.
R. TRUSZKOWSKI.

Systematics of salt lakes. B. P. KROTOV (Ann. Inst. Anal. Phys. Chem., 1927, **3**, 641—662).—An historical and theoretical review of the reactions taking place in salt lakes, on the basis of which a new classification of such lakes is proposed.
R. TRUSZKOWSKI.

Sulphur-bearing waters of Helouan-les-Bains; their composition and therapeutic value. S. NARKIRIER (J. Egypt. Med. Assoc., 1928, **11**, 57—72, 114—128).

Base exchange and the formation of coal. E. McK. TAYLOR.—See B., 1928, 509.

Occurrence of iodine in phosphate beds. E. WILKE-DÖRFURT, J. BECK, and G. PLEPP (Z. anorg. Chem., 1928, **172**, 344—352).—In continuation of previous work (A., 1927, 642), the iodine in a very large number of phosphate minerals has been determined, using several different methods. The results are recorded. Attempts to prepare an iodoapatite have been unsuccessful, and no appreciable quantity of iodine has been found in apatites from different sources. The iodine found in the different phosphate beds is attributable to a biological origin. The large variations in iodine content are no doubt due to differences in geological history and climatic conditions since formation. M. S. BURR.

Tremolite, clinohumite, stromeyerite, natron, and hexahydrite. T. L. WALKER and A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 15—24).—Tremolite, *d* 2·96, from Faraday, Ont., contained (analyses by RICKABY): SiO_2 57·36, TiO_2 0·14, Al_2O_3 1·04, Fe_2O_3 0·21, FeO 0·72, CaO 12·41, MgO 25·22, Na_2O 1·49, K_2O 0·47, H_2O 0·44, total 99·50%. Clinohumite from Chaffey's Locks, *d* 3·17, contained SiO_2 37·42, TiO_2 1·14, Fe_2O_3 0·46, FeO 1·27, MgO 56·32, MnO 0·10, H_2O 0·56, F 5·04, less O 2·12, total 100·19%. Stromeyerite from Cobalt and Gorvganda, Ont., *d* 6·26, contained Cu 31·00, Ag 53·31, S 16·02, total 100·33%. Natron from Clinton, B.C., *d* 1·34, contained Na_2O 21·23, CO_2 15·46, H_2O 63·59, total 100·28%. Hexahydrite from Oroville, Washington, *d* 1·71, contained MgO 17·88 (Al_2O_3,Fe_2O_3) 0·10, SO_3 34·64, H_2O 47·32, insol. 0·03, total 99·97%. CHEMICAL ABSTRACTS.

Bytownite and huronite. T. L. WALKER and A. L. PARSONS (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 5—11).—Bytownite (crushed and granulated anorthosite) contains SiO_2 54·30, Al_2O_3 27·49, Fe_2O_3 1·27, CaO 10·21, MgO 0·50, Na_2O 4·77, K_2O 0·84, H_2O 0·79, total 100·17%. Huronite (75% muscovite and some zoisite) contains SiO_2 46·70, Al_2O_3 31·60, Fe_2O_3 1·41, FeO 0·57, CaO 6·90, MgO 0·64, MnO 0·05, K_2O 6·96, Na_2O 1·45, H_2O 3·63, CO_2 0·40, total 100·31%. (Analyses by RICKABY.) CHEMICAL ABSTRACTS.

Cohenite from Ovifak, Greenland. E. THOMSON (Univ. Toronto Stud., Geol. Ser., Contrib. Can. Min., 1927, No. 24, 41—43).—Cohenite contains Fe 78·12, S 16·40, insol., 3·86%, corresponding with the formula Fe_2S, but the residue examined was not a pure mineral. CHEMICAL ABSTRACTS.

Serpentine and chlorite. N. KURNAKOV and V. CERNYH (Mem. Soc. Russ. Min., 1926, **55**, 183—194; Chem. Zentr., 1928, i, 1013—1014; cf. this vol., 268).—The formula $H_2Mg_3Si_2O_8$ fairly accurately expresses the composition of many serpentines; if alumina (up to 8·2%) is present, the chlorites are approached. The nature of the heating curves is discussed. With increase in the alumina content the orthochlorites show conversion into corundophilite and amesite. A. A. ELDRIDGE.

Crystallography of aurichalcite, danburite, cerussite, etc. H. BUTTGENBACH (Mém. Soc. Roy. Sci. Liege, 1924, [3], **12**, No. 9).—A review is given of the literature on the crystallography and optics of aurichalcite. A new crystal-form is noted on danburite from Switzerland. Twinned crystals of cerussite from Tunisia are figured and described. Crystallographic data are given for *m*-xylylhydrocotarnine, *o*-, *m*-, and *p*-tolylhydrocotarnine, tin dibromodi-*p*-tolyl, tin tetratolyl (*o*-, *m*-, and *p*-), tin tetra-α-naphthyl. L. J. SPENCER.

Louisite. T. L. WALKER (Proc. Nova Scotian Inst. Sci., 1927, **16**, 35—37).—Louisite consists of an aggregate of radiating spherules of quartz in cleavable apophyllite. S. J. GREGG.

Anorthoclase in caucasites. D. S. BELIANKIN (Bull. Acad. Sci. Russ., 1927, 1115—1123).—The author classifies the anorthoclases with orthoclases

and distinguishes the four series: potassium and sodium anorthoclases, either with low or medium values of $2V$, or with high values of $2V$. It is suggested also that the anorthoclases with low or medium $2V$ be termed potassium sanidine (or simply sanidine) and sodium sanidine respectively. Potassium sanidine occurs widely in igneous rocks, principally in intruded materials and mostly in those of recent age.

T. H. POPE.

Minerals from new veins in Belgian Congo. H. BUTTGENBACH (Mem. Soc. Roy. Sci. Liege, 1927, [3], **14**, No. 4).—Accounts are given of several minerals from veins of copper ore in limestone near intrusive rocks recently discovered at several places along the tributaries of the Lubi river. Massive stromeyerite contains Cu 20·45, Ag 60·00, S 15·65, Fe 0·26, insol. 2·56, total 98·92%. Plancheite intermixed with shattuckite and chrysocolla gave SiO_2 41·24, CuO 50·67, CaO trace, H_2O 5·54, moisture 0·85, insol. 1·36, total 99·66%. Crystals of willemite, baryte, libethenite, and volborthite are figured and described.

L. J. SPENCER.

New mineral [berthonite] from Tunis. H. BUTTGENBACH (Ann. Soc. geol. Belg., 1927, **46**, 212; Chem. Zentr., 1928, i, 1013).—Berthonite, d 5·49, hardness 4—5, contains Pb 21·83, Cu 23·68, Sb 32·45%, corresponding with the formula $5PbS,9Cu_2S,7Sb_2S_3$.

A. A. ELDRIDGE.

Two scapolites from the banks of the Slioudianka River. S. SMIRNOV (Mem. Soc. Russe Min., 1927, **55**, 354—361; Chem. Zentr., 1928, i, 1014).

Mineralogy of the bauxites of the Fenouillet region. J. DE LAPPARENT (Compt. rend., 1928, **186**, 1560—1561; cf. *ibid.*, 1927, **185**, 658).—The bauxites examined were all essentially of the diaspore (Al_2O_3,H_2O) type, and contained about 50% in the form of numerous, very small, flat macleated crystals situated along the optical axes, the macles being similar to those of manganite. The crystals were distributed throughout the mass of the rock, sometimes in the pure state, but usually associated with clays, gibbsite, or vegetable tissues and then forming a succession of crusts. Bœhmite, which is often associated with diaspore, was not observed.

J. GRANT.

Apophyllite. S. DI FRANCO (Atti Acc. Gioenia Sc. Na. Catania, 1926, **15**, No. 7; Chem. Zentr., 1928, i, 1013).—A specimen of apophyllite contained SiO_2 52·75, CaO 25·43, K_2O 4·73, Na_2O 0·43, H_2O 16·8% and had d^{15} 2·375.

A. A. ELDRIDGE.

Analcime. S. DI FRANCO (Boll. Soc. Geol. Ital., 1926, **45**, 1; Chem. Zentr., 1928, i, 1013).—A specimen of analcime contained H_2O 8·22, SiO_2 54·10, Al_2O_3 23·68, CaO 0·45, Na_2O 13·40, K_2O 0·34%, and had d 2·249.

A. A. ELDRIDGE.

Successive treatment of mined platinum from Tagil with dilute aqua regia. B. C. KARPOV (Ann. inst. platine, 1927, **5**, 363—364).—Successive treatment of a grain of crude platinum with portions of aqua regia showed that the outer layers contained more iron and copper than the nucleus.

CHEMICAL ABSTRACTS.

Minerals. H. COLLINS (Chem. News, 1928, **136**, 385—387).—Data for twelve minerals are given (see this vol., 613).

Organic Chemistry.

Cholesterol as parent of petroleum. II. N. D. ZELINSKI and K. P. LAVROVSKI (Ber., 1928, **61**, [*B*], 1291—1294; cf. B., 1927, 865).—The various fractions of the hydrocarbons obtained by the action of aluminium chloride on cholesterol (*loc. cit.*) have been subjected to catalytic dehydrogenation and the products treated with fuming sulphuric acid. The "artificial petroleum" is shown to consist of a complicated mixture of hydrocarbons containing only very small amounts of aromatic substances. It consists chiefly of paraffins and *cyclo*paraffins, mainly derivatives of *cyclo*hexane. The fractions are readily dehydrogenated and the products, after removal of the aromatic hydrocarbons, consist either exclusively of compounds, C_nH_{2n+2} (octanes, nonanes, decanes), or mixtures of these with *cyclo*paraffins (naphthenes) of hexahydroaromatic character.

H. WREN.

Electrosynthesis. M. Z. YOVITCHITCH (Bull. Acad. roy. Belg., 1927, [v], **13**, 365—370; cf. A., 1925, 406).—The sum of the percentages of carbon and hydrogen in the products obtained by the action of a silent electric discharge on ethylene and benzene (both normally, but not rigorously purified and dried) is considerably below 100. Since these products, unlike those previously investigated, lose in weight on exposure to air it is assumed that this deficiency is due entirely to the action of the electric discharge itself. A similar deficiency is found in the case of the products from acetylene which has been in contact with the air only for the minimum possible time.

J. W. BAKER.

Polymerisation of olefines. R. VAN WINKLE (J. Amer. Pharm. Assoc., 1928, **17**, 544—547).—The harmful impurities in propylene for anæsthetic purposes are probably higher ethylenic hydrocarbons formed during the dehydration of *iso*propyl alcohol. It was hoped to remove these by polymerisation; contrary to the view of Lebedev, however, propylene also polymerises in the cold when under pressure in contact with activated floridin (a commercial silicate). After 2 months, a liquid containing bi- and termolecular polymerides, b. p. about 70° and 100°, respectively, is obtained. After a year a mixture of products is obtained, of which three volatile fractions and a residue are examined by the depression of f. p. of benzene; the empirical formulæ are $(C_3H_6)_3$, b. p. 35·5—37·5°/7 mm. (15%); $(C_3H_6)_4$, b. p. 60—64·5°/7 mm. (30%); $(C_3H_6)_5$, b. p. 82—85°/3 mm. (15%), and higher polymerides (40%).

*iso*Butylene when passed through a short column of catalyst forms some dimerides; with a long

column, only $(C_4H_8)_3$, b. p. 43—46°/7 mm. (62·5%); $(C_4H_8)_4$, b. p. 75—79°/5 mm. (13·3%), and higher polymerides (24·2%) are formed. E. W. WIGNALL.

Action of the silent electric discharge on hydrocarbons of the ethylene series. N. D. PRIANISCHNIKOV (Ber., 1928, 61, [*B*], 1358—1363; cf. A., 1927, 336).—The most volatile fractions obtained by the polymerisation of *iso*butylene under the action of the silent electric discharge contain more hydrogen than is required for the composition C_nH_{2n}, so that the process is accompanied by re-distribution of the hydrogen atoms. The saturated hydrocarbons are concentrated in the fractions of lower b. p. Polymerisation is also accompanied by fission and re-arrangement of alkyl groups, thus explaining the production of fractions, b. p. 32—52° and 75—85°, with mol. wt. corresponding with C_6 and C_7 compounds in which about 20—30% of hydrocarbons C_nH_{2n} and 70—80% of compounds C_nH_{2n+2} are present. Addition of bromine and reduction of permanganate prove the presence of unsaturated linkings, but polymethylene derivatives can be present only in small amount. The low b. p. and density of the C_6 fraction indicate a highly-branched structure of the hydrocarbons. The first fraction probably contains ββ-dimethylbutane and ββ-dimethylbutylene, whilst βδ- and ββ-dimethylpentanes and ββγ-trimethylbutane are probably present in the second fraction. The products of higher b. p. are notably richer in unsaturated hydrocarbons and contain also naphthenes. After treatment with chromic acid mixture their composition corresponds with 60% of C_nH_{2n} and 40% of C_nH_{2n+2}; lack of additive power indicates the presence of naphthenes. The presence of aromatic compounds appears unlikely. The action of the silent electric discharge on ethylenic hydrocarbons is closely similar to that of high temperature and pressure. The character of the products depends largely on conditions, prolongation of the action causing increase in the quantity of highly-polymerised, non-volatile substances. Increase in electric tension does not influence the process to the same degree, whereas the structure of the original hydrocarbon greatly affects the rate of reaction. H. WREN.

Action of bromine water on certain olefinic hydrocarbons and ethers. J. READ and W. G. REID (J.C.S., 1928, 1487—1493).—The action of bromine water on styrene, a number of related aromatic ethers, and other ethylene derivatives has been investigated. With styrene, anethole, safrole, and *iso*safrole the yield of bromohydrin (determined by titration of the hydrobromic acid produced with sodium hydrogen carbonate solution) is increased and that of the dibromide decreased by raising the temperature to 90° and by dilution. At concentrations between about 0·1 and 0·2 mol./litre the percentage yields of the bromohydrin at 90° and at the ordinary temperature are as follows: styrene 77·9 and 96·7, anethole 47·9 and 76·1, safrole 65·2 and 69·2, *iso*safrole 67·0 and 72·8, amylene (trimethylethylene) 78·9,—, *dl*-Δ^3-menthene 62·9,—; yields of more than 90% with ethylene, sodium maleate and fumarate, indene, itaconic, cinnamic, methylcoumaric, and methylcoumarinic acids, more than 85% with maleic acid and allyl alcohol, and 51·5% with oleic acid. By application of this method are obtained β-*hydroxy*-β-*phenylethyl bromide*, b. p. 109—110°/2 mm., 1·5800, d_4^{20} 1·4994, which when shaken with concentrated ammonia for 10 hrs. yields β-hydroxy-β-phenylethylamine; dl-β-*hydroxy*-β-p-*methoxyphenyl*iso*propylamine*, m. p. 84° (*hydrochloride*, m. p. 182°; *benzoyl* derivative, m. p. 159°; *benzylidene* derivative, syrupy; d-α-*bromocamphorsulphonate*, crude, m. p. 103°), is similarly obtained by the action of ammonia on anethole bromohydrin. This base is resolved by fractional crystallisation of the *d*-camphorsulphonate, the d-β-*hydroxy*-β-p-*methoxyphenyl*iso*propylamine* d-*camphorsulphonate*, m. p. 194—195°, $[\alpha]_D$ +20·5°, separating, from which is obtained d-β-*hydroxy*-β-p-*methoxyphenyl*iso*propylamine*, m. p. 80—81°, $[\alpha]_D$ +4·6° (water), +13·9° (methyl alcohol), +18·4° (ethyl alcohol), +22·9° (benzene), +21·7° (acetone) (*hydrochloride*, m. p. 171—172°, $[\alpha]_D$ +14·7°; *benzoyl* derivative, m. p. 153—154°). From safrole is obtained the *dibromide*, m. p. 87°. *iso*Safrole bromohydrin, when treated with ammonia, yields β-*amino*-α-*hydroxydihydro*iso*safrole*, $CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2$ (*hydrochloride*, m. p. 154°), whilst amylene bromohydrin similarly yields γ-*amino*-β-*hydroxy*-β-*methylbutane*, b. p. 60—62°/16 mm. (*chloroplatinate*, m. p. 186°; *benzoyl* derivative, oil; p-*nitrobenzoyl* derivative, m. p. indefinite about 65°; d-α-*bromocamphorsulphonate*, m. p. 170°; d-*camphorsulphonate*, m. p. 144°). When amylene bromohydrin is heated with aqueous potassium hydroxide for 0·5 hr. it is converted into trimethylethylene oxide, which is converted by the action of dilute sulphuric acid into methyl *iso*propyl ketone and the corresponding glycol, the ketone being best obtained by heating the bromohydrin with litharge and lead chloride in a sealed tube at 200° for 7 hrs. *dl*-Δ^3-Menthene is conveniently prepared by the action of phosphorus trichloride on *dl*-menthol at 80° for 1 hr. (Robertson). J. W. BAKER.

Reactions of simultaneous reduction and oxidation, and isomeric transformations. A. E. FAVORSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 369—414).—The alcoholic fermentation of dextrose (cf. A., 1926, 500) appears to consist of a series of associated reactions of reduction and oxidation, occurring in the following sequence. A molecule of dextrose decomposes, giving two molecules of glyceraldehyde, one carbon atom at the point of attack being reduced to give a primary alcoholic group and the other oxidised to give an aldehydic group. The glyceraldehyde, like α-glycol, gives up water and forms methylglyoxal. With the participation of water (1 mol.), glyceraldehyde (1 mol.) and methylglyoxal (1 mol.) yield glycerol (1 mol.) and pyruvic acid (1 mol.), the last decomposing to form acetaldehyde and carbon dioxide. With the aid of water (1 mol.), acetaldehyde (1 mol.) and methylglyoxal (1 mol.) react, giving ethyl alcohol and pyruvic acid.

[With VASILIEV.]—Favorski (A., 1913, i, 12) showed that, when treated with phosphorus pentachloride, ketones give, according to their structure, either products formed by replacement of the carbonyl oxygen atom by chlorine or, with preliminary enolisation, chloroketones. Pinacolin reacts in the

first way, and ethyl *tert.*-butyl ketone in the second, giving *α-chloroethyl* tert.-*butyl ketone*, b. p. 84°/53 mm., d_4^{20} 0·9814, d_0^0 0·9993, which reduces Fehling's solution and, when heated with potassium formate and methyl alcohol, is converted into (1) trimethylacetylmethylcarbinol, $OH\cdot CHMe\cdot CO\cdot CMe_3$, which is mostly isomerised into acetyl-*tert.*-butylcarbinol, $OH\cdot CHAc\cdot CMe_3$, b. p. 108—111°/100 mm., 0·9523, d_4^{20} 0·9352 (cf. Aschmarin, A., 1913, i, 15), in the conditions of the experiment; conversion of the last-named compound into the glycol, ββδ-trimethylpentane-βγ-diol (cf. Prileschaeff, A., 1904, i, 795), m. p. 64·5—65°, may be effected by treatment with magnesium methyl bromide, and oxidation of this diol yields oxoctenol; (2) *δδ-dimethylpentane-βγ-diol*, m. p. 54°. [V. V. Dolivo-Dobrovolski. ββδ-Trimethylpentane-βγ-diol forms crystals of two types, one in small plates of quadratic outline incapable of measurement, and the other in prismatic crystals of the monoclinic system, $a:b:c = 2{\cdot}306:1:0{\cdot}675$, $\beta=97°$.] Treatment of trimethylacetylmethylcarbinol with magnesium phenyl bromide gives *γ-phenyl-δδ-dimethylpentane-βγ-diol*, m. p. 94°, and *β-phenyl-δδ-dimethylpentane-βγ-diol*, m. p. 82·5°.

[With A. I. Umnova.]—The action of alcoholic potassium hydroxide on *iso*propyl α-bromo*iso*propyl ketone (cf. A., 1913, i, 13) yields *iso*butyryldimethylcarbinol (*semicarbazone*, m. p. 178—179°); treatment of the carbinol with magnesium phenyl bromide gives *γ-phenyl-βδ-dimethylpentane-βγ-diol*, m. p. 75—76°, oxidation of which yields phenyl *iso*propyl ketone and acetone. *iso*Butyryldimethylcarbinol, also obtained from *iso*propyl α-chloro*iso*propyl ketone (*loc. cit.*), undergoes isomerisation on prolonged treatment with alcoholic potassium hydroxide or when heated with alcoholic sulphuric acid, yielding *acetylmethyl*iso-*propylcarbinol*, b. p. 161—164°, d^0 0·9045—0·9230, which is also formed by oxidation of dimethyl*iso*propylethylene. When heated in a sealed tube with alcohol and a small quantity of sulphuric acid, oxoctenol is converted into *acetylmethyl*-tert.-*butylcarbinol*, $OH\cdot CMeAc\cdot CMe_3$, b. p. 176—178°/746 mm., d_0^0 0·9505, d_0^{20} 0·9362 (semicarbazone, m. p. 190—190·5°), which yields pinacolin and acetic acid on oxidation.

[With E. Kotschergina.]—When either heated in a sealed tube with alcohol and a small amount of sulphuric acid or introduced into a sucrose solution undergoing fermentation by brewers' yeast, benzoylmethylcarbinol isomerises into acetylphenylcarbinol. The author considers that the formation of acetylphenylcarbinol from benzaldehyde in a fermenting liquid, observed by Neuberg (Biochem. Z., 1920, **115**, 282), is due to isomeric change of benzoylmethylcarbinol formed from the benzaldehyde.

[With E. D. Vénus-Danilova.]—Bromination of dipropyl ketone yields propyl α-bromopropyl ketone, $CHBrEt\cdot COPr$, b. p. 82—83°/17 mm., d_0^0 1·2717, d_4^{20} 1·2433, which attacks the mucous membrane, and di-α-bromopropyl ketone, b. p. 100—101°/17 mm., d_0^0 1·5572, d_4^{20} 1·5234. Treatment of the monobromo-compound with aqueous potassium hydroxide or with water and freshly precipitated calcium or barium carbonate yields (1) *butyrylethylcarbinol*, b. p. 181—182 or 75—76°/18 mm., d_0^0 0·9488, d_4^{20} 0·9309 (*semicarbazone*, m. p. 117—118°), and (2) propionylbutyryl diketone [*disemicarbazone*, m. p. 253—255° (decomp.)]. Reduction of butyrylethylcarbinol by means of magnesium *tert.*-butyl (or amyl) chloride yields s-*ethylpropylethyleneglycol*, $OH\cdot CHEt\cdot CHPr\cdot OH$, m. p. 98—99°, b. p. 117·5—118°/21 mm. Butyrylethylcarbinol undergoes decomposition when distilled, even under diminished pressure, giving a compound, $C_7H_{12}O_2$, b. p. 146—148° or 58—61°/25 mm. [*semicarbazone*, m. p. 253° (decomp.)], together with compounds of higher b. p. which could not be separated, and a precipitate, which does not distil. The last evidently represents a condensation product and when subjected to prolonged heating with continuous stirring with 2% sulphuric acid solution on a water-bath, yields propionylpropylcarbinol (*semicarbazone*, m. p. 121—122°) and the *anhydride*, $O(CHEt\cdot COPr)_2$, b. p. 151—152°/20 mm., which gives a *semicarbazone*, $C_{16}H_{32}O_3N_6$, m. p. 178—179°. When heated with alcohol in presence of sulphuric acid, butyrylethylcarbinol undergoes isomerisation into propionylpropylcarbinol, which, by treatment with magnesium methyl bromide, is converted into *α-methyl-α-ethyl-β-propylethylene glycol* (β-ethylhexane-βγ-diol), b. p. 101—102°/12 mm., d_0^0 0·9548, d_4^{20} 0·9404. Oxidation of the latter with chromic acid yields methyl ethyl ketone, *butyrylmethylethylcarbinol*, b. p. 93—96°/30 mm. (*semicarbazone*, m. p. 143—144°), butyric acid, and a small amount of acetic acid, apparently formed by further oxidation of the methyl ethyl ketone.

[With E. D. Venus-Danilova.]—When heated with alcohol in presence of sulphuric acid, propionylmethylcarbinol undergoes isomeric change to *acetylethylcarbinol*, b. p. 147—148°/761·5 mm., d_0^0 0·9673, d_4^{20} 0·9500, which gives a *semicarbazone*, m. p. 216—217°, and, on treatment with magnesium methyl bromide, yields *αα-dimethyl-β-ethylethylene glycol*, b. p. 122°/112 mm., d_0^0 0·9764, d_4^{20} 0·9627. Oxidation of the latter gives acetone and propionic acid, together with a small amount of acetic acid, probably formed by oxidation of the acetone. T. H. Pope.

Transformation of propionylmethylcarbinol into acetylmethylcarbinol. [Mme.] E. Vénus-Danilova (Bull. Soc. chim., 1928, [iv], **43**, 582—586).—*Ethyl α-bromoethyl ketone*, b. p. 62—64°/28 mm. (from diethyl ketone, yield 67%), with barium carbonate is converted into propionylmethylcarbinol, b. p. 60—60·5°/20 mm., 152·5°/761 mm., d_4^{20} 0·9742 [*semicarbazone*, m. p. 208—209° (decomp.)] (cf. Pechmann, A., 1890, 1234), together with traces of a diketone and a glycol anhydride. (See also preceding abstract.) R. Brightman.

Transformation of butyrylethylcarbinol into propionylpropylcarbinol. [Mme.] E. Vénus-Danilova (Bull. Soc. chim., 1928, [iv], **43**, 575—592).—See above (Favorski and Venus-Danilova).

Action of polyhydric alcohols on periodic acid. L. Malaprade (Bull. Soc. chim., 1928, [iv], **43**, 683—696).—See this vol., 269.

α-Glucoheptulitol. G. Bertrand and G. Nitzberg (Compt. rend., 1928, **186**, 1773—1776).—α-Glucoheptulitol (this vol., 620) has $[\alpha]^{20}$ −2° 42′, in 5% aqueous solution. The value is much greater in the absolute sense than that for heptitols in general.

Acetylation with acetic anhydride and zinc chloride at the b. p. yielded an *acetyl* derivative, m. p. 116—117°, α_D about +2′ in chloroform (l=2·2). Theoretically α-glucoheptulose should yield on reduction the two active β-glucoheptitols, but proof of the identity of α-glucoheptulitol with one of the β-glucoheptitols is lacking. The rotation value of the *d*-form of the latter (A., 1912, i, 607) is not in agreement with that for α-glucoheptulitol. J. D. FULTON.

Derivatives of glycerol containing sulphur. E. FROMM, R. KAPELLER, and I. TAUBMANN (Ber., 1928, **61**, [*B*], 1353—1358).—The compound obtained by the action of sodium hydrogen sulphite on epichlorohydrin and regarded as derived from the sulphonic acid, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3H$, yields sodium sulphite when boiled with sodium hydroxide and hence is the *sulphurous* ester, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}SO_2H$. Normal sodium sulphite and epichlorohydrin, however, afford sodium β-hydroxypropyl-αγ-disulphonate.

Benzyl mercaptan, sodium hydroxide, and epichlorohydrin or dichlorohydrin afford *αγ-dibenzylthiol*iso*propyl alcohol*, $OH{\cdot}CH(CH_2{\cdot}S{\cdot}CH_2Ph)_2$, m. p. 59°. The products derived from it by the action of hydrogen chloride, benzoyl chloride, or acetic anhydride are non-crystalline, but the *acetate* is oxidised to *αγ-dibenzylsulphonyl*iso*propyl* β-*acetate*, m. p. 159—160°. Oxidation of αγ-dibenzylthiol*iso*propyl alcohol by potassium permanganate unexpectedly affords *αγ-dibenzylsulphonyl*iso*propyl alcohol*, m. p. 208° (*monohydrate*, m. p. 215°); conversion of the alcohol into the corresponding ketone is not effected by potassium dichromate and concentrated acids, which substantially cause loss of water of crystallisation and separation of the anhydrous alcohol. αγ-Dichloroacetone and benzyl mercaptan in presence of alcoholic sodium hydroxide afford *αγ-dibenzylthiolacetone*, oxidised by permanganate in acid solution to *αγ-dibenzylsulphonylacetone*, m. p. 182°; the ketone is transformed by alcoholic sodium hydroxide and subsequent treatment with benzyl chloride into dibenzyl sulphone, m. p. 148°. αγ-Dibenzylsulphonylacetone is indifferent towards phenylhydrazine, hydroxylamine, or hydrazine hydrate. The presence of the carbonyl group is established by treatment with benzyl mercaptan and hydrogen chloride and oxidation of the mercaptol to the crystalline *tetrasulphone*, $(SO_2{\cdot}CH_2Ph)_2C(CH_2{\cdot}SO_2{\cdot}CH_2Ph)_2$, m. p. 198°. H. WREN.

Quantitative study of the oxidation of methyl oleate and elaidate by hydrogen peroxide in presence of acetic acid. T. P. HILDITCH and C. H. LEA (J.C.S., 1928, 1576—1583).—Methyl oleate and elaidate were oxidised in glacial acetic acid with 35% hydrogen peroxide solution at 15—20°, 75—80°, and 95° and the products investigated quantitatively. Three types of oxidation products are formed: (1) a methyl dihydroxystearate, (2) a monoacetyl derivative of (1) formed by the addition of peracetic acid and not by acetylation, and (3) an oily product which liberates iodine from acidified potassium iodide solution, and when heated at 100° under reduced pressure evolves an acrid, acid vapour (not peracetic acid) and the iodine absorption of the resulting product is increased. This oily product is probably a very unstable molecular or peroxide complex, $-CH-CH-$, formed by the direct combination of molecular oxygen with the unsaturated system. No oxido-compounds (cf. Böeseken, A., 1927, 39) could be detected. The ικ-dihydroxystearic acid derivatives produced from methyl oleate are exclusively those of the acid of m. p. 95°, whilst methyl elaidate yields only derivatives of the corresponding acid, m. p. 132°. These results combined with those previously obtained (A., 1926, 938) suggest that various oxidising agents yield the dihydroxystearic acid directly related to the ethylene derivative oxidised without change of configuration, whilst the formation of the isomeric acid, m. p. 132°, by oxidation of oleic acid with potassium permanganate results from inversion during oxidation in the excessively alkaline medium which is essential for the quantitative production of this dihydroxystearic acid. J. W. BAKER.

Cerebrosides. VII. Hydroxy-acids of brain cerebrosides. E. KLENK (Z. physiol. Chem., 1928, **174**, 214—232; cf. A., 1927, 691).—Besides cerebronic acid there is present in cerebroside fractions an unsaturated hydroxy-acid which on catalytic hydrogenation takes up two atoms of hydrogen and yields cerebronic acid. Oxidation of cerebronic acid with potassium permanganate yields a tricosoic acid, $C_{23}H_{46}O_2$, and not lignoceric acid, $C_{24}H_{48}O_2$, as stated by Levene and Taylor (A., 1922, i, 714). The hydroxy-acid yields pelargonic acid, $C_9H_{18}O_2$ on oxidation with ozone, and on further oxidation of the other products with potassium permanganate, dodecane-αμ-dicarboxylic acid, $C_{14}H_{26}O_4$, is produced. The unsaturated hydroxy-acid is probably $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_{12}{\cdot}CH(OH){\cdot}CO_2H$ and cerebronic acid is probably $C_{24}H_{48}O_3$ and not $C_{25}H_{50}O_3$ as usually given. There are evidently several fatty acids with C_{24} in cerebrosides and phosphatides. Since kephalin contains acids of the C_{18} series, the fatty acids of brain lipins appear to be multiples of C_6. A. WORMALL.

Conversion of pyruvic acid into alanine. AUBEL and BOURGUEL (Compt. rend., 1928, **186**, 1844—1846).—The conversion has been effected by stirring pyruvic acid (1 mol.) and ammonia (2 mols.) in an atmosphere of hydrogen for 5—6 days, and employing colloidal palladium stabilised by starch paste as catalyst. Previous attempts with platinum-black proved unsuccessful. The fixation of hydrogen is very slow. On evaporation of the reaction mixture in a vacuum, the catalyst and starch are precipitated by boiling alcohol, the whole being then filtered and evaporated to a small volume. Hot absolute alcohol is again added, followed by ether, which slowly precipitates the alanine in crystalline form. Further purification is effected by adding a concentrated aqueous solution of alanine to boiling absolute alcohol, when a pure, crystalline product is obtained. J. D. FULTON.

Properties of conjugated compounds. V. Hydrogenation of certain extended heterogeneous systems. J. T. EVANS and E. H. FARMER (J.C.S., 1928, 1644—1650).—Reduction of ethyl

muconate with aluminium amalgam in moist ether yields exclusively the Δ^{β}-dihydro-ester (cf. Farmer, J.C.S., 1923, **123**, 2531). Crotylideneacetone, by reduction with the same reagent, yields mainly (80%) a *substance*, b. p. 169—178°/23 mm., which is regarded as 5-*acetyl*-1-*methyl*-3 : 4-*dipropenyl*cyclo*pentan*-1-*ol* (yielding acetaldehyde on ozonolysis and succinic acid on oxidation with chromic acid), together with an unsaturated pinacol-like substance (not identified). Reduction of sorbic acid with sodium amalgam in glacial acetic acid, or of sodium sorbate in aqueous solution with aluminium amalgam or with sodium amalgam, with or without the passage of carbon dioxide, yields a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids, the proportion of the Δ^{γ}-acid under the three conditions mentioned being 40, 35, and 30%, respectively. J. W. BAKER.

Colouring matter from saffron. IV. P. KARRER and H. SALOMAN (Helv. Chim. Acta, 1928, **11**, 711—713).—The formula for α-crocetin is now deduced to be $C_{17}H_{20}(CO_2H)_2$ (A., 1927, 571; this vol., 644). Hydrogenation of γ-crocetin yields tetradecahydro-γ-crocetin, thus demonstrating the presence of seven conjugated double linkings and not eight as previously assumed. α-Crocetin is formulated as γηλ-trimethyltetradecaheptaene-αʼ-dicarboxylic acid. H. BURTON.

Conjugated unsaturated compounds. VI. Colouring matter from Chinese *Gardenia*. Occurrence of conjugated unsaturated colouring matters in plants. R. KUHN, A. WINTERSTEIN, and W. WIEGAND (Helv. Chim. Acta, 1928, **11**, 716—724).—Gardenidin, the colouring matter of *Gardenia grandiflora*, L. (cf. Munesada, A., 1923, i, 77), and α-crocetin (Karrer, preceding abstract) are identical. α-Crocetin has been isolated from the petals of *Crocus luteus*, and is probably identical with nyctanthin (Hill, J.C.S., 1907, **91**, 1501; Perkin, *ibid.*, 1912, **101**, 1538). α-Crocetin (γηλ-trimethyltetradecaheptaene-αξ-dicarboxylic acid) is postulated as being derived from three isoprene residues and 2 mols. of glyoxylic acid, whilst bixin, $C_{25}H_{30}O_4$, m. p. 198° (corr.), is formulated as γηλο-tetramethyloctadecanonaene-ασ-dicarboxylic acid, derived from four isoprene units and 2 mols. of glyoxylic acid. A list of the colour reactions of bixin and gardenidin with various acids is given. H. BURTON.

Physical and chemical properties of bismuth sodium citrate and bismuth sodium tartrate. W. F. VON OETTINGEN, T. SOLLMANN, and H. H. SCHWEID (J. Amer. Pharm. Assoc., 1928, **17**, 540—543).—Solutions of bismuth sodium citrate are neutral, are not precipitated by p_H changes within physiological limits, are precipitated by calcium chloride (but stabilised by sodium citrate), and may be sterilised by boiling. Solutions of bismuth sodium tartrate are alkaline (p_H of 10% solution, 8·2—8·4), are precipitated by acidity above p_H 7·6, by many salts, by Locke's solution, by serum, and by heating. E. W. WIGNALL.

Walden inversion. XII. Oxidation of β-thiolvaleric and γ-thiolvaleric acids. P. A. LEVENE and T. MORI (J. Biol. Chem., 1928, **78**, 1—22).—The sulphonic acids obtained by oxidation of *l*-β- and *l*-γ-thiolvaleric acids show the same change in rotation on passing into the salts as do the corresponding thiol-acids; the anomalous behaviour of *l*-β-thiol- and *l*-β-sulpho-butyric acids in this respect (A., 1926, 1225) remains, therefore, an isolated phenomenon. The present work confirms the hypothesis that substitution of halogen by a hydroxyl or thiol group is accompanied by Walden inversion. *d*-β-Hydroxyvaleronitrile, with thionyl chloride or phosphorus pentachloride, gave l-β-*chlorovaleronitrile*, b. p. 69—70°/10 mm., $[\alpha]_D^{20}$ −10·5° in ether, and, with alcoholic hydrogen chloride, *ethyl* l-β-*hydroxyvalerate*, b. p. 77—79°/10 mm., $[\alpha]_D^{20}$ −14·7° in ether; the latter ester, with thionyl chloride or phosphorus pentachloride, yielded *ethyl* d-β-*chlorovalerate*, b. p. 66—67°/10 mm., $[\alpha]_D$ +6·65°, and, with phosphorus pentabromide, *ethyl* d-β-*bromovalerate*, $[\alpha]^{20}$ +16·1°, which, on hydrolysis with fuming hydrobromic acid in the cold, gave d-β-*bromovaleric acid*, b. p. 117—119°/10 mm., $[\alpha]^{20}$ +11·0°, *sodium* salt $[\alpha]^{20}$ +8·5°, both in 35% alcohol. Ethyl *d*-β-bromovalerate, with potassium hydrogen sulphide, gave *ethyl* l-β-*thiolvalerate*, b. p. 72—76°/10 mm., $[\alpha]_D^{20}$ −5·2° in ether, which, however, could not be hydrolysed; *d*-β-bromovaleric acid yielded -*thiolvaleric acid*, b. p. 112—113°/10 mm., $[\alpha]^{20}$ −15·5° (*sodium hydrogen* salt, $[\alpha]_D^{20}$ −8·75°; *sodium* salt, $[\alpha]_D^{20}$ −11·2°, all in 20% alcohol); ethyl *l*-β-thiolvalerate, on oxidation, yielded l-β-*sulphovaleric acid*, $[\alpha]^{20}$ −7·87° (*barium hydrogen* salt, $[\alpha]_D^{20}$ −7·16°; *barium* salt, $[\alpha]_D^{20}$ −5·06°, all in water). *Ethyl* l-γ-*chlorovalerate*, b. p. 71—73°/9 mm., $[\alpha]_D^{20}$ −19·7° in ether, with potassium hydrogen sulphide, gave a mixture of lactone and ester from which, by hydrolysis with potassium hydroxide, was obtained d-γ-*thiolvaleric acid*, b. p. 121—122°/10 mm., $[\alpha]_D^{20}$ +5·14° (*sodium hydrogen* salt, $[\alpha]_D^{20}$ +1·56°; *sodium* salt, $[\alpha]_D^{20}$ +1·36°, all in 20% alcohol). On treatment with dilute sulphuric acid, this acid yielded l-γ-*thiolvalerolactone*, b. p. 69—70°/10 mm., $[\alpha]^{20}$ −78·3° in ether, and, on oxidation, l-γ-*sulphovaleric acid*, $[\alpha]_D^{20}$ −1·94° (*barium hydrogen* salt, $[\alpha]_D^{20}$ −1·31°; *barium* salt, $[\alpha]_D^{20}$ −1·68°, all in water). C. R. HARINGTON.

Disulphosuccinic acid. H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1928, **47**, 776—781).—When potassium acetylenedicarboxylate is heated at 100° in a sealed tube with 2 mols. of potassium hydrogen sulphite, and the solution treated with hydrochloric acid, an 80% yield of *tripotassium hydrogen disulphosuccinate* (+1H_2O, decomp. 180°) is obtained. The free acid (+4H_2O), which loses water at 120—130° and decomposes at 163°, yielding carbon dioxide and sulphur dioxide, is probably the αα′-disulpho-acid. The following normal salts are described: *potassium* (+4H_2O), sodium (+2H_2O), thallium (anhydrous, decomp. 285°; cf. A., 1927, 856), *calcium*, dehydrated at 190°, *barium* (+3H_2O, lost at 240—250°), *silver*, and lead. With silver nitrate the tetrapotassium and tetrasodium salts yield double salts, the composition of which depends on the excess of silver nitrate present. In the preparation of acetylenedicarboxylic acid from dibromosuccinic acid, yields of 92% of the potassium hydrogen salt are obtained if absolute alcohol is used; dibromosuccinic acid is prepared from fumaric acid in 87% yield by the action of bromine (5% excess) in aqueous

solution in sunlight: maleic acid is previously transformed (yield 93%) by treatment with bromine water in sunlight. R. BRIGHTMAN.

Aldehydes from acetylenic carbinols. II. βζ-Dimethyloctenaldehyde, β-methyl-β-*tert.*-butylacraldehyde, and experiments with the acetylenic carbinol from acetophenone. H. RUPE and L. GIESLER (Helv. Chim. Acta, 1928, **11**, 656—669).—Treatment of methyl *iso*hexyl ketone with sodamide in ether and subsequent reaction of this product with acetylene affords methyl*iso*hexylethinylcarbinol, which is converted by hot formic acid (cf. this vol., 640) into a mixture of βζ-*dimethyl*-Δ^{β}-*octenaldehyde* (I), b. p. 94°/13 mm. (90%; *semicarbazone*, m. p. 170°; *oxime*, b. p. 131—132°/11 mm.; *phenylhydrazone*), and βζ-*dimethyl*-Δ^{α}-*octenaldehyde*, b. p. 98—100°/11 mm. (10%; *semicarbazone*, m. p. 122°). Oxidation of (I) with alkaline potassium permanganate affords *iso*hexoic acid (p-*toluidide*, m. p. 61—62), whilst catalytic reduction yields βζ-*dimethyloctaldehyde*, b. p. 78—79°/11 mm. (*semicarbazone*, m. p. 97°; *oxime*, b. p. 131—132°/17 mm.). Similar treatment of methyl-*tert.*-butylethinylcarbinol (cf. Wouseng, A., 1924, i, 823) gives β-methyl- -butylacraldehyde, d_4^{20} 0·8822, n_D^{20} 1·46718 [semicarbazone, m. p. 193° (cf. Wouseng, *loc. cit.*); *oxime*, b. p. 131°/10 mm.], together with γγ-*dimethyl*-β-*methylenevaleraldehyde*, b. p. 150° (*semicarbazone*, m. p. 148—149°). If sodamide is used in the preparation of sodium acetophenone the product of the reaction with acetylene is *phenylmethylethinylcarbinol* (10%), b. p. 102—103°/12 mm., m. p. 49°, but when sodium is employed the product is acetophenonepinacol. Treatment of the carbinol with formic acid gives a small amount of β-*methylcinnamaldehyde*, b. p. 122—130°/12 mm. (*semicarbazone*, m. p. 201°). H. BURTON.

Catalytic hydrogenation of oximes and their conversion into β-hydroxylamines. G. VAVON and M. KRAJCINOVIČ (Arhiv Hemiju Farm., 1928, **2**, 119—127).—See this vol., 398.

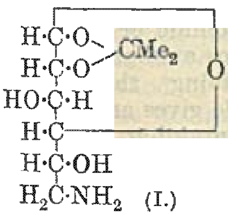
Determination of methylglyoxal in alkaline iodine solution, and the mechanism of the reaction. F. FISCHLER and R. BOETTNER (Z. anal. Chem., 1928, **74**, 28—32; cf. A., 1926, 1170).—The ability of methylglyoxal to form iodoform is used as a basis for its determination. The reaction has been expressed by the equation $CH_3\cdot CO\cdot CHO+3I_2+5KOH=CHI_3+2H\cdot CO_2K+3KI+3H_2O$; the possible formation of oxalic acid is, however, accounted for by a reaction $CH_3\cdot CO\cdot CHO+4I_2+7OH'=CHI_3+C_2O_4''+5I'+5H_2O$. A volumetric method was devised to determine the correct relationship of methylglyoxal to iodine. The substance was treated with a known excess of 0·1*N*-potassium iodide solution followed by a known amount of *N*-sodium hydroxide solution, agitated, kept for 30 min., acidified with an amount of *N*-hydrochloric acid equal to 25% in excess of the alkali added, and the excess of iodine was titrated with thiosulphate. The excess of acid remaining was found by back titration using phenolphthalein. The method of calculating the result is explained. The amount of oxalic acid and iodoform produced and the increase in alkalinity indicate that the relationship was $CH_3\cdot CO\cdot CHO=8I$. R. A. PRATT.

Polymerisation and condensation. III. Acetocondensation of dihydroxyacetone. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1928, **78**, 23—33).—An old sample of dihydroxyacetone was extracted first with a mixture of equal parts of alcohol and ether and then with acetone. The alcohol–ether-soluble portion was distilled up to 110°/0·2 mm., and yielded volatile fatty acids, methylglyoxal, unimolecular dihydroxyacetone, m. p. 82°, and a residue which, on acetylation, yielded diacetyldihydroxyacetone and *diacetyldihydroxyacetonyldihydroxyacetone*, b. p. 138—150°/0·5 mm. The acetone-soluble portion was similarly distilled and gave again unimolecular dihydroxyacetone, together with a residue from which was isolated a *substance*, $C_9H_{14}O_7$, m. p. 258°. From the insoluble residue was obtained a crystalline *substance*, $C_6H_{10}O_5$, m. p. 164°. It thus appears that, when kept at the ordinary temperature, dihydroxyacetone undergoes true autocondensation; whether this is preceded by polymerisation remains uncertain. C. R. HARINGTON.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. II. Ring–chain tautomerism in its relation to the mutarotation of the sugars. J. W. BAKER (J.C.S., 1928, 1583—1593).—Carefully purified specimens of tetra-acetyl- and tetramethyl-glucose which show an arrest of mutarotation (Lowry and Richards, A., 1925, i, 886) in pure ethyl acetate and acetone at 24° and 44° mutarotate rapidly in the fused state under identical aseptic conditions. The effect of structural influences on the velocity of mutarotation of a series of *p*-substituted tetra-acetylglucose anilides, containing the ring–chain tautomeric system $\underbrace{O\text{——}C\cdot NHR}_{(C)_4} \rightleftharpoons \underbrace{HO\quad C{:}NR}_{(C)_4}$, in ethyl acetate containing either hydrochloric or acetic acids as a catalyst at 24° has been studied. As R is varied the unimolecular velocity coefficient (*k*) decreases in the order $C_6H_4OMe(p)>C_6H_4Me(p)>C_6H_5>C_6H_4Cl(p)>C_6H_4Br(p)$. The value of the ratio k/K_b, where K_b is the dissociation constant of the substituted anilide RNH_2 as a base, approximates to a common value. These results are in agreement with the predictions of the electronic interpretation of the ring–chain mechanism of mutarotation (Baker, Ingold, and Thorpe, A., 1924, i, 262), but are opposed to those of an extension of the duplex theory of catalysis suggested by Lowry (A., 1925, i, 886). The mechanism of the action of the catalyst is discussed. The tetra-acetylglucose *p*-substituted anilides are prepared by the action of the appropriate substituted aniline on tetra-acetylglucosidyl bromide and thus are obtained: p-*toluidide*, m. p. 147°, p-*anisidide*, m. p. 129°, p-*bromoanilide*, m. p. 160°, p-*chloroanilide*, m. p. 147°; N-*methylanilide*, m. p. 102°. The last does not exhibit mutarotation even in the presence of acid catalysts. J. W. BAKER.

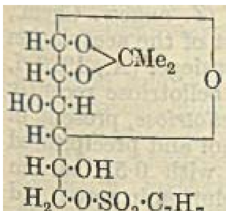
Acetone [*iso*propylidene] compounds of sugars and the products of their transformations. IX. Transformation of monoacetoneglucose [glucose *iso*propylidene ether]. H. OHLE and L. VON VARGHA (Ber., 1928, **61**, [*B*], 1203—1208; cf. A., 1926, 151).—*p*-Toluenesulphonylglucose *iso*propylidene

ether, m. p. 108°, readily loses its acyl group under the influence of alkali hydroxide, giving only traces of glucose *iso*propylidene ether. With methyl-alcoholic ammonia it is transformed into a nitrogen-free, non-crystalline material and a mixture of ammonium *p*-toluenesulphonate and the p-*toluenesulphonate* of ζ-*aminoglucose* iso*propylidene ether*, m. p. 176—177° (decomp.), $[\alpha]_D^{20}$ −7·02° in water. The isolation of the last compound is best effected by treating the crude mixture with sodium carbonate, thus giving the *carbamate*, $C_{19}H_{34}O_{12}N_2[R\cdot CH_2\cdot NH\cdot CO_2H,NH_2\cdot CH_2R]$, m. p. 80° (decomp.) when rapidly heated, $[\alpha]_D^{20}$ 0° to −6·25° in water during 2 days, which is subsequently acted on by *p*-toluenesulphonic acid. The amino-sugar is converted by nitrous acid into glucose *iso*propylidene ether. The carbamate is transformed by dilute sulphuric acid into ζ-amino-*d*-glucose, which yields a non-crystalline *carbonate*, m. p. 96—98° (decomp.), $[\alpha]_D^{20}$ +12·5° in water, a very hygroscopic p-*toluenesulphonate*, $[\alpha]_D^{20}$ +31·68° in water, and a well-defined *picrate*, incipient decomp. 140°, $[\alpha]_D^{20}$ +7·4° in water; it is most definitely characterised as the p-*toluenesulphonate* of its *phenylhydrazone*, m. p. 182—183°, $[\alpha]^{20}$ +6·8° to +1·3° in alcohol during 16 hrs. The position of the amino-group follows from the identity of this salt with that prepared from the aminomethylglucoside hydrobromide of Fischer and Zach (A., 1911, i, 117). The constitution (I) is therefore ascribed to ζ-aminoglucose *iso*propylidene ether. Since γ-*p*-toluenesulphonylglucose *iso*propylidene ether is already known, its crystalline isomeride, m. p. 108°, must have the acyl group in position ε or unless it be assumed that the oxygen bridge forms the α and ζ carbon atoms. A decision between these possibilities cannot at present be made.



H. WREN.

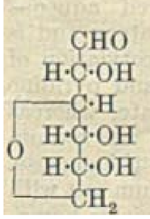
Acetone [*iso*propylidene] compounds of sugars and the products of their transformations. X. New *p*-toluenesulphonylglucose di*iso*propylidene ether. H. OHLE and L. VON VARGHA (Ber., 1928, **61**, [*B*], 1208—1210; cf. preceding abstract).—Repetition of the work of Ohle and Dickhäuser (A., 1926, 151) shows that *p*-toluenesulphonylglucose *iso*propylidene ether, if purified by means of toluene instead of light petroleum, does not react with acetone in presence of copper sulphate. If sulphuric acid is used, p-*toluenesulphonylglucose di*iso*propylidene ether*, m. p. 87°, $[\alpha]^{20}$ +27·1° in chloroform, is produced, which differs from the γ-*p*-toluenesulphonyl derivative of Freudenberg and Ivers (A., 1922, i, 523). If the constitution (I) be assigned to the mono*iso*propylidene ether, the action of the acid involves the shifting of the oxygen bridge, whereas if the isomeric form with the acyl group attached to the ε-carbon atom is adopted, acyl migration must necessarily occur. The compound obtained by Ohle and Spencker (A., 1926, 1126) by the action of hydrogen bromide in glacial acetic acid is not 6-*p*-toluenesulphonyl-2 : 3-triacetyl-β-methylglucoside, since it is not identical with the product isolated by Helferich and others (A., 1927, 1174); hydrolysis of it gives ill-defined compounds. There is no evidence to show that hydrogen bromide and glacial acetic acid cause structural changes similar to those produced by sulphuric acid, since the new *p*-toluenesulphonylglucose di*iso*propylidene ether, when treated with the reagent and subsequently with methyl alcohol and silver carbonate, does not yield *p*-toluenesulphonyltriacetyl-β-methylglucoside, m. p. 155°.

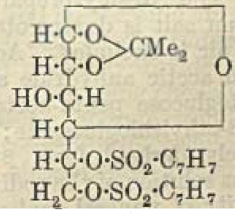


(I.)

H. WREN.

Acetone [*iso*propylidene] compounds of sugars and the products of their transformations. XI. Conversion of glucose *iso*propylidene ether into γζ-anhydro-*d*-glucose. H. OHLE, L. VON VARGHA, and H. ERLBACH (Ber., 1928, **61**, [*B*], 1211—1216; cf. preceding abstracts).—Di-*p*-toluenesulphonylglucose *iso*propylidene ether, m. p. 160° (cf. Ohle and Dickhäuser, A., 1926, 151), is converted by treatment with 1 mol. of alkali hydroxide or by restricted treatment with an excess of the reagent into the compound, m. p. 132°, obtained in limited yield by treatment of glucose *iso*propylidene ether with 3 mols. of *p*-toluenesulphonyl chloride in pyridine at 100° (*loc. cit.*) and erroneously regarded as a third *p*-toluenesulphonylglucose *iso*propylidene ether. Fresh analyses show the compound to contain 1 mol. of water less than required by theory. It is hydrolysed by alkali hydroxide to *anhydro*-d-*glucose* iso*propylidene ether*, m. p. 56—57°, $[\alpha]_D^{20}$ +29·33° in water, from which it is smoothly regenerated by *p*-toluenesulphonyl chloride in pyridine; the corresponding *benzoyl* compound, m. p. 58—59°, $[\alpha]_D^{20}$ +22·28° in chloroform, and *acetyl* derivative, b. p. 125—130°/0·05 mm., $[\alpha]_D^{20}$ +35·7° in chloroform, are described. Hydrolysis of anhydro-*d*-glucose *iso*propylidene ether by acids affords the anhydro-*d*-glucose of Fischer and Zach (A., 1912, i, 678), identified also as the phenylhydrazone and phenylosazone. The production of the anhydro-sugar by this and Fischer's methods leads to the structure (I) (expressed as the aldehydic form). The readily removable *p*-toluenesulphonyl group of di-*p*-toluenesulphonylglucose *iso*propylidene ether must be present in the ζ-position (II). The constitution (III) is ascribed to the *p*-toluenesulphonylanhydro-*d*-glucose *iso*propylidene ether. Di-*p*-toluenesulphonylglucose *iso*propylidene ether behaves towards alcoholic ammonia in much the same manner as towards alkali hydroxide, but in certain circumstances appears to yield an amino-compound in small amount.





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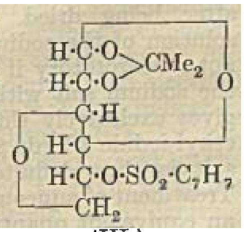


(III.)

The toluenesulphonyl group appears to affect the properties of the sugar residue more deeply than the

benzoyl or acetyl group and to render possible reactions which do not otherwise occur; similar results are to be expected from the biochemically important sulphuric and phosphoric acid residues. H. WREN.

Thio-sugars and their derivatives. XII. Xanthoglucose and its fission to glucothiose [α-thioglucose]. W. SCHNEIDER, R. GILLE, and K. EISFELD (Ber., 1928, **61**, [*B*], 1244—1259; cf. A., 1914, i, 668, 669, 977).—Acetobromoglucose is converted by potassium ethyl xanthate in anhydrous alcohol into *ethylxantho*-d-*glucose tetra-acetate*, $C_6H_7O_5Ac_4$·S·CS·OEt, $[\alpha]^{20}$ +30·8° in *s*-tetrachloroethane, which also exists in an unstable *modification*, slender needles, lowest observed m. p. 74—76°, with a somewhat lower specific rotation. It is hydrolysed by a saturated solution of hydrogen chloride in methyl alcohol at 0° to *ethylxantho*-d-*glucose*, $C_6H_{11}O_5$·S·CS·OEt, m. p. 92—98° after softening at 87°, $[\alpha]_D^{20}$ −50·5° in water (*dihydrate*, m. p. 63—65°, $[\alpha]^{20}$ −45·4° in water). Hydrolysis of the tetra-acetate by ammonia gives α-thioglucose with the properties recorded previously, but invariably containing a low percentage of sulphur; acetylation of the products thus obtained yields only amorphous substances from which thioglucose penta-acetate cannot be isolated, so that mixtures of acetyl derivatives are present. Under certain conditions the acetate of diglucosyl disulphide is obtained; its formation is presumably due to atmospheric oxidation, but even when air is completely excluded the sulphur content of the product remains low. Optical observation of the course of hydrolysis shows the xanthate residue to be considerably more readily removed than the acetyl groups. Thioglucose tetra-acetate must therefore be formed initially; its isolation in substance has not been effected, but acetylation of the product of incomplete hydrolysis affords thioglucose penta-acetate in almost quantitative yield (cf. Schneider and Wrede, A., 1914, i, 977). Hydrolysis of the latter compound by alcoholic ammonia gives products similar to those obtained from the xantho-compound. On the other hand, Zemplén's method affords smoothly the *sodium* compound, $C_6H_{11}O_5$·SNa,$2H_2O$, m. p. 173—174° (decomp.) after darkening. The salt is stable in air when dry and unexpectedly stable in aqueous solution in the absence of air. It can be titrated with acid in the presence of methyl-orange but not of phenolphthalein. In aqueous solution it is oxidised slowly by air, or immediately by hydrogen peroxide, to diglucosyl disulphide. The corresponding silver compound, prepared by means of ammoniacal silver acetate, resembles that described previously, but loses its ability to dissolve in water after being dried. The freshly-prepared aqueous solution of the sodium salt is dextrorotatory and is not mutarotatory if air is excluded. Acetylation of the sodium salt with acetic anhydride and pyridine gives exclusively thioglucose penta-acetate, whereas ethyl iodide affords β-ethylthioglucoside; the sodium salt is thus definitely derived from β-thioglucose. Treatment of aqueous solution of the sodium salt with an equivalent quantity of mineral acid yields homogeneous β-thioglucose, initial $[\alpha]_D^{23}$ +17·62° in water. The specific rotation increases slowly during about 10 days, during which sufficient decomposition occurs to influence the final value even when air is excluded. If a slight excess of mineral acid is used, this decomposition is excluded and the equilibrium value for the α- and β-forms ($[\alpha]_D^{20}$ +58·4° in water) is observed. If the solution is evaporated and the residue acetylated in pyridine, the product can be separated by crystallisation into β-thioglucose penta-acetate and *α-thioglucose penta-acetate*, m. p. 126—127°, $[\alpha]^{20}$ +120·2° in *s*-tetrachloroethane. It follows therefore that α-thioglucose must have a high, positive specific rotation and hence that sinigrin, which according to Wrede gives an initially lævorotatory thioglucose, cannot be derived from it. The nature of the thioglucose from sinigrin remains unexplained.

H. WREN.

Thio-sugars and their derivatives. XIII. Addition of acetobromoglucose to thiocarbamides; S-glucosido-ψ-thiocarbamides. W. SCHNEIDER and K. EISFELD (Ber., 1928, **61**, [*B*], 1260—1263; cf. preceding abstract; Fischer, A., 1914, i, 662; Helferich and Kosche, A., 1926, 273).—Acetobromoglucose reacts with thiocarbamide in boiling toluene yielding *tetra-acetyl*-d-*glucosido*-S-*thiuronium bromide*, $C_6H_7O_5Ac_4$·S·C(NH_2)(:NH),HBr, m. p. 192°, $[\alpha]_D^{20}$ −8·72° in water; the corresponding, unstable *hydrogen carbonate*, $C_{16}H_{24}O_{12}N_2S$, m. p. 92° (decomp.) after softening at 84°, and the *hydrogen oxalate*, $C_{17}H_{26}O_{13}N_2S$, m. p. 159° (decomp.), are described. Hydrolysis of the bromide or hydrogen carbonate with methyl-alcoholic ammonia yields non-crystalline products containing thioglucose; methyl-alcoholic hydrogen chloride gives amorphous, very hygroscopic materials containing dextrose. Acetobromoglucose and phenylthiocarbamide in boiling benzene afford *phenyl-ψ-thiocarbamido*-d-*glucose tetra-acetate*, $C_6H_7O_5Ac_4$·S·C(NH_2)(:NPh), m. p. 150°, $[\alpha]_D$ ±0° in *s*-tetrachloroethane, $[\alpha]_D^{?}$ +19·15° in ethyl acetate (*hydrogen oxalate*, m. p. 146°, $[\alpha]_D$ −15·55° in 50% alcohol). Hydrolysis by methyl-alcoholic ammonia gives thioglucose, whereas the use of sodium methoxide leads to the sodium derivative of the thio-sugar. The product obtained by use of methyl-alcoholic hydrogen chloride contains notable amounts of the *hydrochloride* of phenyl-ψ-thiocarbamido-*d*-glucose, from which the free glucoside or other of its salts could not be obtained. Acetobromoglucose does not appear to react with thiocarbanilide; with allylthiocarbamide it gives amorphous, non-homogeneous products. H. WREN.

Preparation, by sorbose bacteria, of a new reducing sugar with seven carbon atoms. G. BERTRAND and G. NITZBERG (Bull. Soc. chim., 1928, [iv], **43**, 663—667).—See this vol., 510.

New *iso*cellotriose. H. OST (Z. angew. Chem., 1928, **41**, 696—698).—The product of the acetylation of cotton cellulose by Ost and Prosiegel (A., 1920, i, 423) contains in addition to the cellotriose recently described (A., 1926, 1127) an *isocellotriose*, present in the portion freely soluble in alcohol and precipitated with *iso*cellobiose on hydrolysis with 0·5*N*-barium hydroxide. It is purified by dissolution in water and precipitation wth alcohol, the triose separating under these conditions as oily drops which rapidly solidify to a mass having $[\alpha]_D$ +15·6°, reducing power 29

(dextrose 100), ash 0·75%. It contains about 0·5 mol. of water of crystallisation (lost at 115—120°), forms no osazone, has no sweet taste, and is not fermented by yeast. It is only slowly hydrolysed to dextrose by 2·5% hydrochloric acid, conversion being incomplete after 8—10 hrs. and considerable amounts of humic substances formed. Acetylation with acetic anhydride and zinc chloride affords an *undeca-acetate*, m. p. 120—150°, $[\alpha]_D$ +2·4° (chloroform), which is somewhat more soluble than the similarly prepared *undeca-acetate* of the isomeric cellotriose, m. p. 200—220°, $[\alpha]_D$ +2·2 to 6·2°, the latter being contaminated with a little of the octa-acetates, m. p. 222° and 192°, of the isomeric cellobiose. iso*Cellobiose acetate*, m. p. 115—125°, $[\alpha]_D$ +4° in chloroform, was similarly prepared from *iso*cellobiose, being much more readily soluble than the cellobiose octa-acetate, m. p. 220°, which is also formed. R. BRIGHTMAN.

Konjmannan. T. OHTSUKI (Acta Phytochim., 1928, 4, 1—39).—The carbohydrates present in the mannan prepared from "konjak powder" have been investigated. *d*-Mannose and *d*-glucose are present only in the ratio 2 : 1, confirming the results of Mayeda (A., 1922, i, 694). The results of Miyake (J. Coll. Agr. Imp. Univ. Hokkaido, 1927, **12**, 164), who finds that lævulose, dextrose, and mannose are present in the ratio 1 : 2 : 3, are criticised. Lævulose is present in the crude "konjak powder," but not in the purified mannan, whilst the calculations of Miyake are based on the assumption that the hypoiodite method of Willstatter and Schudel is applicable to the determination of all aldoses; mannose, however, is oxidised to the extent of 59·42% only, and Miyake's figures when corrected support the view that lævulose is absent. By the action of takadiastase on konjakmannan, a product, "lævidulinose," has been isolated and this is probably identical with Mayeda's trisaccharide "lævidulin" obtained by the action of bacteria on mannan (*loc. cit.*). This trisaccharide contains mannose and dextrose in the ratio 2 : 1. The nature of the micelle of the mannan has been studied by heating the substance with anhydrous glycerol at 235° and by acetylation, and the conclusion is reached that *d*-mannose anhydride and *d*-glucose anhydride (in the ratio 2 : 1) are parent substances of the mannan micelle. The preparation, purification, and the properties of the mannan and the properties of "lævidulinose" and of various derivatives formed by liquefaction (by takadiastase, dried yeast, and acetylation) and by heat dissociation, are given. A. WORMALL.

Preparation of glucosides of the α-series. Crystalline α-methylfructoside. H. H. SCHLUBACH and G. A. SCHROTER (Ber., 1928, **60**, [*B*], 1216—1222).—Chlorotetra-acetyl-lævulose (cf. Brauns, A., 1920, i, 713), $[\alpha]_D$ −155·5° in chloroform, is more stable in solution but less stable in substance than β′-chloroacetylglucose. On account of its susceptibility to water it cannot be satisfactorily transformed into the methylfructoside by silver carbonate and silver oxide in methyl alcohol, although addition of anhydrous sodium sulphate or copper sulphate effects marked improvement. When its ethereal solution is added to a methyl-alcoholic solution of silver nitrate in the presence of silver carbonate or, preferably, pyridine (to unite with the liberated nitric acid), silver chloride is immediately and almost quantitatively precipitated and *tetra-acetyl-α-methylfructoside*, m. p. 112°, $[\alpha]_D^{20}$ +45° in chloroform, is obtained. Hydrolysis of the latter compound is best effected with barium hydroxide; crystalline products are obtained with difficulty or not at all when methyl-alcoholic ammonia or sodium methoxide is employed. Crystallisation of *α-methylfructoside* is difficult, the most suitable solvent being *iso*butyl or *iso*amyl alcohol; the data, m. p. 96—97°, $[\alpha]_D^{20}$ +44° in water, must therefore be regarded as provisional. The adherence of α-methylfructoside to the stable fructose series is established by methylation with methyl sulphate and alkali hydroxide and subsequent hydrolysis of the pentamethylfructoside to αγδε-tetramethylfructose.

A satisfactory explanation of the course of the reaction between silver nitrate and alkyl halides in the presence of alcohols cannot yet be given, but the occurrence of a Walden inversion in the case recorded above appears to exclude further the possibility of a double exchange. H. WREN.

New constitutional formula for cellulose. G. ODDO (Gazzetta, 1928, **58**, 301—309).—The suggested formula for cellulose is based on the uniform concatenation of four molecules of dextrose with elimination, also uniform, of four molecules of water. The mechanism of the union of the dextrose molecules is that already suggested for polysaccharides, and consists in addition of a dextrose molecule by means of the alcohol group of the ε-carbon atom, as in cellobiose, to the aldehydic group of the next molecule, with formation of the alcoholate or semi-acetal, with subsequent closure of the hydrofuran nucleus in the sugar molecule where the addition occurs, by elimination of 1 mol. of water from the α- and δ-carbon atoms. The formula is considered to interpret simply and completely the fundamental facts concerning cellulose and its physical and chemical behaviour.
T. H. POPE.

Acetic ester of cellulose xanthate. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1928, **31**, 94—100).—The acetic ester of cellulose xanthate was produced by the treatment of viscose with chloroacetic acid, and its properties and method of analysis are given. Y. TOMODA.

Metallic complexes of cellulose nitrates. A. APARD (Mém. Poudres, 1928, **23**, 63—68).—See this vol., 276.

Celluloseglucolic acid. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1928, **31**, 67—73).—Methods of preparation and purification are described. Celluloseglucolic acid can be determined accurately by dissolving it in alkali hydroxide solution and titrating the excess of alkali, using phenolphthalein as indicator, by decomposing sodium celluloseglucolate by sulphuric acid, precipitating celluloseglucolic acid by the addition of alcohol, filtering, and then titrating the excess of mineral acid in the filtrate, or by igniting the sodium salt and determining the alkalinity of the ash. Conductometric titration can also be used, whereas potentiometric titration does not give a sharp

end-point. Celluloseglucolic acid is insoluble in water or organic solvents. Hydrolysis does not occur when the acid is heated with acid and alkali. Its sodium salt is soluble in water and forms a homogeneous solution with viscose. With barium chloride, zinc or copper sulphate, or silver nitrate the corresponding *salt* was precipitated. Celluloseglucolic acid can be dyed using basic dyes. Y. NAGAI.

Additive compounds of halides of bivalent metals with organic bases. V. G. SCAGLIARINI and E. BRASI (Atti R. Accad. Lincei, 1928, [vi], 7, 411—413; cf. A., 1927, 137).—By the action of mercuric halides on hexamethylenetetramine in acetone solution the following *compounds* have been obtained: (with excess of the base) $2HgCl_2,C_6H_{12}N_4$; $HgBr_2,2C_6H_{12}N_4$; $HgI_2,C_6H_{12}N_4$, and (with excess of the halide) $3HgCl_2,2C_6H_{12}N_4$; $HgBr_2,C_6H_{12}N_4$, and $3HgI_2,2C_6H_{12}N_4$ (yellow). O. J. WALKER.

General reaction of amino-acids. H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, 78, 91—105).—On warming α-amino-acids with acetic anhydride and pyridine, carbon dioxide is eliminated and two acetyl groups are introduced, one attaching itself to nitrogen and the other to the α-carbon atom so that the product is an α-acetamido-ketone; the reaction is not confined to amino-acids, since, *e.g.*, phenylacetic acid yields similarly benzyl methyl ketone, and it is thought that, as in the case of the reaction observed by Perkin (J.C.S., 1886, 49, 317), it proceeds through intermediate formation of a β-ketonic acid. Proline, alkylamino-acids, and amino-acids which contain no replaceable hydrogen in the α-position undergo simple acetylation only. Phenylalanine gave *acetamidobenzylacetone*, m. p. 98—99° (*semicarbazone*, m. p. 103—104°), tyrosine yielded *acetamido*-p-*hydroxybenzylacetone*, m. p. 135—136° (O-*acetyl* derivative, m. p. 123°; *semicarbazone*, m. p. 230—231°; *phenylhydrazone hydrochloride*, m. p. 195—197°; *picrate*, m. p. 125—126°; *benzylidene* derivative, m. p. 170—180° after sintering). Phenylaminoacetic acid gave *α-acetamido-α-phenylacetone*, m. p. 103—104°. Leucine gave *α-acetamido-α*-iso*butylacetone* (*amidoguanidine* derivative, m. p. 182—183°). Alanine yielded *α-acetamido-α-methylacetone* (*amidoguanidine* derivative, m. p. 183—184°); both glycine and hippuric acid yielded *acetamidoacetone*, identified by formation of methylglyoxalbisnitrophenylhydrazone on boiling with *p*-nitrophenylhydrazine in dilute sulphuric acid, and by formation of 2 : 5-dimethylpyrazine on acid hydrolysis followed by distillation with mercuric chloride and alkali.

C. R. HARINGTON.

Separation of the α-amino-acids resulting from the hydrolysis of proteins. G. W. MUHLEMAN (Diss., Geneva, 1927, No. 817, 5—31).—The amino-acids are benzoylated at a specified alkaline reaction; the by-products include the mixed anhydrides of benzoic and amino-acids, whether benzoylated or not, the anhydrides being readily hydrolysed by sodium ethoxide. Benzoic acid is removed by sublimation. The benzoylated amino-acids are esterified with diazomethane. Separation of the esters by fractional distillation is only approximate. The corresponding benzoylated acids, obtained by hydrolysis with sodium ethoxide, are more easily purified and identified. CHEMICAL ABSTRACTS.

Amino-acids. V. Synthesis of *N*-alkylglutamic acids. S. SUGASAWA (J. Pharm. Soc. Japan, 1927, [550], 1041—1043; cf. *ibid.*, 1927, [545], 359).—The semialdehyde of succinic acid or its ethyl ester reacts with potassium cyanide and alkylamines in alcoholic solution or their hydrochlorides in aqueous-alcoholic solution, yielding *N*-alkylglutamic acids or their esters. The following individuals are described: N-*methylglutamic acid*, m. p. 156—158° (*ethyl* ester, b. p. 108—109°/2 mm.; *hydrochloride*, m. p. 159—160°); N-*dimethylglutamic acid*, m. p. 155—156° (*ethyl* ester, b. p. 101—103°/0·5 mm.); N-*ethylglutamic acid*, m. p. 159—160 (*ethyl* ester, b. p. 109—110°/2 mm.).

Transformations of substances resembling peptides. XXV. So-called "arginylarginine" of E. Fischer, an αδ-diguanido-*n*-valeric anhydride. L. ZERVAS and M. BERGMANN (Ber., 1928, 61, [*B*], 1195—1203).—The uncertainties regarding the nature of "arginylarginine" are removed by the observation that it is optically inactive *αδ-diguanido*-n-*valeric anhydride*,

$NH_2\cdot C(:NH)\cdot NH\cdot[CH_2]_3\cdot CH<\begin{matrix}CO-NH\\ NH\cdot C:NH\end{matrix}$. The picrate, m. p. 218°, of Fischer and Suzuki (A., 1906, i, 73) is largely and the dinitrate entirely derived from this anhydride. This conception is founded on repeated elementary analysis of the nitrate and the picrate derived therefrom and the absence of nitrogen determinable by the formaldehyde or Van Slyke methods. Secondly, the condensation of *d*-arginine with *S*-ethyl*iso*thiocarbamide hydrobromide affords d-*αδ-diguanido*-n-*valeric anhydride dinitrate*, m. p. 189° (corr.), $[\alpha]_D^{10}$ —28·6° in water [corresponding *picrate*, m. p. 228° (corr.)], which readily suffers racemisation, with formation of a product identical with Fischer's "arginylarginine dinitrate." In the auto-condensation of arginine ester according to Fischer and Suzuki (*loc. cit.*), the liberation of the ester from its hydrochloride is immediately followed by interaction of the guanido-group of one molecule with the ester group of a second molecule, giving the methyl ester of an arginylarginine which is too unstable to permit isolation. In the second stage of the change, the peptide guanido-group reacts with the vicinal α-amino-group with ring closure, producing αδ-diguanido-*n*-valeric anhydride and ornithin methyl ester or a closely related product (separated from the mother-liquors of αδ-diguanido-*n*-valeric anhydride picrate as *d*-ornithuric acid). The observations of Kossel and Staudt (this vol., 81) and of Edlbacher and Bonem (A., 1925, i, 863) are based on experiments involving the use of a non-homogeneous picrate, m. p. 218°; when purified through the nitrate, the picrate has m. p. 228°. The unusually ready autoracemisation of *d*-αδ-diguanido-*n*-valeric anhydride is shared by *d*-phenylalanyl-*d*-arginine anhydride (Bergmann and Köster, unpublished work) and appears to be due to the presence of the asymmetric centre in a ring system and the basicity of the guanido-group.

Attempts to condense arginine ester with glycine

ester lead only to a greatly accelerated formation of glycine anhydride. H. WREN.

Characterisation of the $-OMgX$ group. H. GILMAN and F. SCHULZE (Rec. trav. chim., 1928, 47, 752—760).—To discover a general reagent capable of replacing the –MgX group in compounds of the type R·O·MgX and characterising the –OMgX group by giving a readily identifiable compound (cf. A., 1920, i, 483), a number of reactions of the R·O·MgX compounds have been examined. No general reagent has been discovered, the effectiveness of a given reagent depending also on the type of Grignard reagent used, the nature of the halogen atom, the size of the group R, and the temperature of replacement. The –OMgCl group is replaced more readily than –OMgBr, the latter than –OMgI, but the magnesium organochlorides are not always accessible. Media of higher b. p. than toluene should not be used and it is suggested than acyl halides or anhydrides or alkyl halides be tried first and then the phenylcarbimide, phenylcarbamine chloride, or phenylcarbamine bromide, which last are highly effective with certain types of –OMgX compounds. Cases in which replacement appears impossible may be due to the use of an insufficiently reactive reagent or the formation of a comparatively unstable product. In these cases the sulphur analogue may be used (cf. A., 1924, i, 382; 1926, 1132), or an organo-metallic compound containing a more positive element, *e.g.*, sodium alkyls or aryls, the reaction being almost certainly parallel to that with the Grignard reagent. Since, however, the –MgX group attached to carbon, nitrogen, and sulphur is readily replaced, failure to replace the –MgX group admits of the conclusion with some confidence that the –MgX group is attached to oxygen.

No appreciable replacement took place in the following cases: benzyl chloride with magnesium phenoxybromide; phenylcarbimide with bromomagnesium benzoate; phenylthiocarbimide with magnesium ethoxyiodide and *n*-butoxyiodide; diphenylcarbamine chloride with magnesium ethoxybromide; chloro- and bromo-acetophenone with magnesium phenoxy-chloride and -bromide; ammonia with magnesium phenoxyiodide; allyl iodide with magnesium *n*-butoxyiodide; ethylene oxide with magnesium *n*-butoxy- and phenoxy-iodide; zinc diethyl with magnesium diphenylmethoxybromide; ethyl sulphate with magnesium phenoxy- and triphenylmethoxy-bromides and with calcium or zinc diphenylmethoxy- and triphenylmethoxy-iodides.

With magnesium triphenylmethoxybromide and acetic anhydride, triphenylcarbinol is the only solid product, the acetate being easily hydrolysed. Benzoic anhydride is the only reagent of those tried which replaces the –MgBr group in magnesium diphenylmethoxybromide, affording 44—50% of benzhydryl benzoate. Benzyl bromide with magnesium diphenylmethoxybromide in cymene at 180° affords in small yield a substance, m. p. 176°, which is not benzyl benzhydryl ether; with the triphenylmethoxybromide in ether and toluene a 50% yield of triphenylmethane is obtained, a 70% yield resulting when the magnesium triphenylmethoxybromide is heated alone, together with a light brown viscous oil, probably in consequence of the reactions: $CPh_3{\cdot}O{\cdot}MgBr+Et_2O \longrightarrow CPh_3{\cdot}COEt+EtO{\cdot}MgBr$; $CPh_3{\cdot}COEt \longrightarrow CHPh_3+Me{\cdot}CHO$ (cf. Gomberg, A., 1913, i, 257; Norris and Young, A., 1925, i, 20). With magnesium phenoxy- or benzyloxy-bromides, benzyl bromide yields only a little distillate of high b. p. Magnesium phenoxybromide and triphenylmethyl chloride in benzene give some *p*-hydroxytetraphenylmethane.

Phenylcarbimide reacts smoothly with R·O·MgX compounds derived from a primary alcohol, but not from *sec.*- or *tert.*-alcohols of high mol. wt. Thus magnesium *n*-butoxybromide gives 80% of *n*-butylphenylcarbamate, magnesium phenoxyiodide, 70% of phenyl phenylcarbamate, and a small amount of a polymeride, m. p. 275° (probably triphenyl *iso*cyanurate), magnesium benzyloxybromide, 70% of benzyl phenylcarbamate, but magnesium diphenylmethoxybromide gives only carbanilide, triphenyl *iso*cyanurate, and unchanged benzhydrol, and the triphenylmethoxybromide only the original carbinol. Phenylthiocarbimide is unreactive.

Phenylcarbamine chloride and magnesium benzyloxybromide in ether give 70% of benzyl phenylcarbamate; magnesium diphenylmethoxybromide appears to react, but only carbanilide and benzhydrol could be isolated. With phenylcarbamine bromide in benzene the result was similar. Carbonyl chloride and magnesium benzyloxybromide in toluene yield a white precipitate, but no urethane on treatment with ammonia (cf. Yoder, A., 1923, i, 309).

Benzoyl bromoamide and magnesium phenoxy- or ethoxy-bromide in benzene react vigorously, but only benzamide and benzoylphenylcarbamide can be isolated.

Thionyl chloride and α-chloromethyl ether react with magnesium phenoxybromide in benzene, but no definite products were isolated; diazomethane reacts vigorously, giving anisole and insoluble material.

Bromomethyl ethyl ether and magnesium benzyloxybromide appear to give the benzylethylacetal. Keten and magnesium phenoxybromide in acetone yield about 15% of phenyl acetate and a little liquid of higher b. p. Phosphorus trichloride and magnesium diphenylmethoxybromide give some diphenylmethyl chloride, but mainly tetraphenylethylene.

Phenyl benzyl ether and magnesium *n*-butoxybromide in benzene or magnesium bromide in ether do not react; in benzene, magnesium bromide yields a little benzyl bromide and liquid of high b. p. The general order of reactivity of the R·O·MgX compounds is the reverse of the order of solubility, the iodides being the most, the chlorides the least soluble. Solubility decreases with increasing size of the alkyl group. Magnesium benzyloxy- and phenoxy-halides have practically the same solubility.

R. BRIGHTMAN.

Action of hypochlorous acid on benzene hydrocarbons. F. W. KLINGSTEDT [with G. WIESE and G. RUDBACK] (Acta Acad. Aboensis math. phys., 1927, 4, No. 2, 1—36; Chem. Zentr., 1928, i, 503—505).—Hypochlorous acid yields with benzene α- and β-benzene hexachloride, monochlorobenzene, and a *compound*, $C_6H_8OCl_4$; with naphthalene naphthalene dichloride and tetrachloride, 1-chloronaphthalene,

and 1 : 4-dichloronaphthalene; with toluene, *m*- and *p*-xylene, and *p*-*iso*propyltoluene only monosubstitution products were obtained. With dilute acid substitution is the chief reaction, and with more concentrated acid, addition; also only substitution derivatives are obtained in the dark. Modifications in the course of the reaction are observed when the acid reacts in presence of mercury oxide or oxychloride (cf. Carius and Neuhoff, Annalen, 1865, **136**, 323, 342). A. A. ELDRIDGE.

Action of niobium and tantalum pentachlorides on organic compounds. II. H. FUNK and K. NIEDERLÄNDER (Ber., 1928, **61**, [*B*], 1385—1388; cf. this vol., 408).—Under suitable conditions the pentachlorides of niobium and tantulum react with aromatic hydrocarbons evolving hydrogen chloride and leaving intensely coloured, non-crystalline residues which become carbonised when heated, and when decomposed with aqueous ammonia give coloured products in which the organic residue is attached to the metal. It is remarkable that substitution in the nucleus occurs, whereas this does not happen with the more active phenols (*loc. cit.*). Tantalum pentachloride and boiling benzene give the *compound* $TaCl_4·C_6H_5$, whereas with niobium pentachloride the *substance* $3NbCl_5,C_6H_6$ and, probably, $NbCl_5,C_6H_6$ and $2NbCl_5,C_6H_6$ are formed. According to the intensity of the reaction, tantalum pentachloride and naphthalene yield the *compounds* $TaCl_5,C_{10}H_8$, $TaCl_4·C_{10}H_7$, and $TaCl_3(C_{10}H_7)_2$, whereas from niobium pentachloride the *substances* $NbCl_4·C_{10}H_7$ and $NbCl_3(C_{10}H_7)_2$ are derived. Tetrahydronaphthalene gives the *compounds* $TaCl_4·C_{10}H_{11}$ and $TaCl_3(C_{10}H_{11})_2$. From anthracene the following *substances* are derived: $TaCl_5,C_{14}H_{10}$; $TaCl_4·C_{14}H_9$; $TaCl_3(C_{14}H_9)_2$; $NbCl_4·C_{14}H_9$. The additive compounds are completely decomposed by aqueous ammonia, giving colourless products. The compounds $NbCl_4·C_{14}H_9$ and $TaCl_3(C_{10}H_7)_2$ when similarly treated lose the expected quantity of chlorine and give a yellow, halogen-free product which, when evaporated with hydrogen chloride, leaves ammonium chloride in quantity corresponding with 1 mol. of NH_3 for one atom of niobium and two atoms of tantalum. H. WREN.

Laws of aromatic substitution. VIII. B. FLÜRSCHEIM and E. L. HOLMES (J.C.S., 1928, 1607—1616).—The nitration of toluene derivatives of the type $PhCX_3$, where $X_3 = H_2Cl$, $H_2(CO_2Et)$, HCl_2, $HCl(CO_2Et)$, $H(CO_2Et)_2$, Cl_3, $Cl_2(CO_2Et)$, $(CO_2Et)_3$, H_2Br, and $Br(CO_2Et)$, with nitric acid (*d* 1·52) at —10° or, in the case of compounds containing a mobile halogen atom, with a mixture of this acid and acetic anhydride at temperatures close to the ordinary, has been investigated. The ratio $m/(o+p)$, determined by oxidation to the corresponding mixture of nitrobenzoic acids which were analysed by the method previously described (this vol., 403), for the above derivatives is, respectively, 13·6 (Holleman, A., 1914, i, 511, found 4·4), 13·6 (Baker and Ingold, A., 1927, 558, found 9·9), 52·25 (Holleman, *loc. cit.*, 51·05), 43·35, 34·05 (Baker and Ingold, *loc. cit.*, 25), 160·1 (Holleman, *loc. cit.*, 181·7), 156·8, 132·6, 130·1, 7·45, and 65·05%. The nature of chemical polarity and polar effects is discussed from the point of view of the authors' theory of aromatic substitution. *Ethyl phenylmethanetricarboxylate*, b. p. 154—155°/1·5 mm., is obtained by the action of ethyl chloroformate on dry ethyl phenylsodiomalonate in dry ether for 7 hrs. It is very resistant to both hydrolysis and oxidation, and from the nitrated fraction most resistant to oxidation is isolated *ethyl* o-*nitrophenylmethanetricarboxylate*, m. p. 83—84°. *Ethyl phenylchloromalonate*, b. p. 143—144°/2—1·5 mm., is obtained by saturating a solution of ethyl phenylmalonate in carbon tetrachloride with dry chlorine at 0° and leaving the solution for 16 hrs. J. W. BAKER.

Nitration of *m*-acetamidobenzotrifluoride. H. ROUCHE (Bull. Acad. roy. Belge, 1927, [v], **13**, 346—357).—Nitration of *m*-acetamidobenzotrifluoride with a mixture of nitric and sulphuric acids at —5° and subsequent hydrolysis of the acetyl group with sodium hydroxide yields a mixture of (I) 6-*nitro*-, m. p. 129° (84%), and (II) 4-*nitro*-, m. p. 101° (6%), -m-*aminobenzotrifluoride*. The structure of (I) is proved by reduction with tin and hydrochloric acid to 3 : 6-*diaminobenzotrifluoride*, m. p. 58° (*sulphate*; *hydrochloride*). This is hydrolysed with 20% hydrochloric acid to 3 : 6-diaminobenzoic acid, converted by distillation into *m*-phenylenediamine. Deamination of (I) with ethyl nitrite and alcoholic sulphuric acid yields o-*nitrobenzotrifluoride*, b. p. 216·3°/765 mm., m. p. 32·5° (III), reduced with tin and hydrochloric acid to o-*aminobenzotrifluoride*, b. p. 73°/21 mm., m. p. —34·7° (*anilide*, m. p. 94°), which yields successively the corresponding o-*cyano*-derivative, m. p. 7·5°, and phthalic acid. Deamination of (II) yields p-*nitrobenzotrifluoride*, m. p. 41·5°. When nitration of the original substance is effected with acetyl nitrate at —5° the products obtained after hydrolysis are (II) (61%) and 2-*nitro*-m-*aminobenzotrifluoride*, m. p. 64° (24·7%), which by deamination is converted into (III). Thus the use of acetyl nitrate appears to favour the formation of the vicinal derivative. The results are compared with those of Wender (A., 1890, 884) on the nitration of *m*-nitroacetanilide, and of Kaiser (A., 1886, 149) on *m*-acetamidobenzoic acid. The carboxyl group exhibits a greater tendency to the formation of the vicinal derivative than does the trifluoromethyl group. J. W. BAKER.

Alkylation and acylation in the presence of titanium tetrachloride. G. STADNIKOV and L. KASCHTANOV (Ber., 1928, **61**, [*B*], 1389—1391).—The action of titanium tetrachloride on a solution of benzyl ethyl ether in boiling benzene yields primarily benzyl chloride which reacts with the benzene, giving diphenylmethane, and *p*- and *m*-dibenzylbenzene. Similar products are obtained when benzyl ethyl ether is replaced by benzyl chloride. *iso*Amyl acetate or benzoate does not react with benzene in presence of titanium tetrachloride, whilst di*iso*amyl ether is unaffected. Benzophenone could not be obtained from benzoyl chloride and benzene in presence of titanium tetrachloride, whereas the benzoyl group is readily introduced into thiophen. Benzene is unaffected by titanium tetrachloride. H. WREN.

Action of sulphur compounds on 1-chloro-2 : 4-dinitronaphthalene, 1-chloro-2 : 4 : 5-trinitronaphthalene, and 1-chloro-2 : 4-dinitrobenzene. H. W. Talen (Rec. trav. chim., 1928, **47**, 782—795; cf. this vol., 405).—1-Chloro-2 : 4-dinitronaphthalene and 1 mol. of sodium sulphide or disulphide in alcohol afford only 2 : 2′ : 4 : 4′-tetranitrodinaphthyl sulphide, m. p. 283° (decomp.) (cf. Zincke and Krollpfeiffer, A., 1913, i, 455); with excess of sulphide a small quantity of dark red substance, probably a reduction product, separates. If the sodium sulphide is added rapidly and, after dilution with water, iodine in aqueous potassium iodide is added to the red solution, 2 : 2′ : 4 : 4′-tetranitrodinaphthyl disulphide, decomp. 230° after darkening at 225°, is obtained; the 2 : 4-dinitro-α-thiolnaphthalene, m. p. 117—118°, may be isolated by acidifying the red solution. With 1 mol. and with 2 mols. of thiocarbamide in alcohol 1-chloro-2 : 4-dinitronaphthalene yields only 2 : 2′ : 4 : 4′-tetranitrodinaphthyl sulphide, the reaction with 1 mol. of sodium xanthate giving in addition a little sodium 2 : 4-dinitro-α-naphthalate and *ethyl* 2 : 4-*dinitronaphthyl disulphide*, m. p. 85°, the formation of the latter substance being in accordance with Weeldenburg's suggestion that in xanthate solutions there is an equilibrium between the isomeric *O*- and *S*-esters. The corresponding disulphide, decomp. 230°, was never produced.

Potassium thiocyanate also yields the monosulphide, m. p. 283° (decomp.), 2 : 4-*dinitronaphthyl thiocyanate*, m. p. 116° (decomp.), being obtained in a crude form only by the use of alcoholic ammonium thiocyanate. With alcoholic sodium sulphide or disulphide, 1-chloro-2 : 4 : 5-trinitronaphthalene yields only 2 : 4 : 5 : 2′ : 4′ : 5′-*hexanitrodinaphthyl sulphide*, decomp. 323°. These results are opposed to those obtained with 1-chloro-2 : 4-dinitrobenzene, the latter affording with 1 mol. of sodium xanthate mainly 2 : 4 : 2′ : 4′-tetranitrodiphenyl disulphide with some of the corresponding monosulphide, whilst with 0·5 mol. of sodium xanthate the monosulphide is practically the sole product. Similarly 1 mol. of thiocarbamide affords mainly disulphide and monosulphide in approximately equal amounts; with 0·5 mol. of thiocarbamide the disulphide is the principal product. Thiocarbanilide (1 mol.) and 1-chloro-2 : 4-dinitrobenzene (2 mols.) yield 2 : 4-dinitro-1-anilinobenzene and a little tetranitrodiphenyl sulphide, the formation of the sulphide being increased by addition of sodium ethoxide to the acid mother-liquors. With 2 mols. of thiocarbanilide and 1 mol. of 1-chloro-2 : 4-dinitrobenzene the proportion of sulphide formed is considerably increased. These results confirm the observations of Blanksma (A., 1902, i, 281) that the proportion in which the mono- and di-sulphides are formed from 1-chloro-2 : 4-dinitrobenzene depends on the proportions of sulphur compounds to the chlorodinitrobenzene present in the reaction mixture.

R. Brightman.

Reactivity of halogens in aromatic combination. H. Lindemann and A. Pabst (Annalen, 1928, **462**, 24—46).—A number of experiments have been carried out in order to test some of the theories of the cause of reactivity in halogeno-nitro-compounds of the benzene series. It is shown that the decomposition of the well-defined additive compound formed between α-naphthylamine and 1-chloro-2 : 4-dinitrobenzene is not a unimolecular reaction, from which it is concluded that this particular type of additive compound is not a necessary intermediary in the displacement of halogen by the arylamino-group.

Methyl groups have been introduced into the molecule of 1-chloro- or 1-bromo-2 : 4-dinitrobenzene, in order to test the reality or otherwise of a Flürscheim or Vorländer effect. Thus, 2-halogeno-3 : 5-dinitrotoluenes should, according to the Flürscheim or Vorländer theories, be less reactive than the corresponding 1-halogeno-2 : 4-dinitrobenzenes, which should be less reactive than the 5-halogeno-2 : 4-dinitrotoluenes or the 3-halogeno-2 : 6-dinitrotoluenes on the same theories. Actually, as is now shown, the 5-halogeno-derivatives (chloro- and bromo-) are less reactive than the corresponding simple halogenodinitrobenzenes, but considerably more reactive than the 2-halogeno-derivatives, whilst the 3-halogeno-derivatives have no reactivity at all when the reactivity is measured, as in the present work, using boiling alcoholic solutions of aniline. Even boiling aniline itself reacts only gradually with 3-halogeno-2 : 6-dinitrotoluenes. These results are regarded as disproving the validity of the Flürscheim or Vorländer explanations of reactivity causes.

The explanation of reactivity in terms of conjugation effects is considered, and it is concluded that the depressant effects of the methyl groups in the above compounds is due to the disturbance of conjugation by these groups, a conclusion reached as the result of measuring the optical exaltation of the substances concerned. The exaltation of the 5- and 2-chlorodinitrotoluenes is similar in magnitude to that of chlorodinitrobenzene, and much higher than that of the non-reactive 3-chlorodinitrotoluene. The difference in reactivity between *o*- and *p*-chloronitrobenzene can also be explained on the disturbance of conjugation theory.

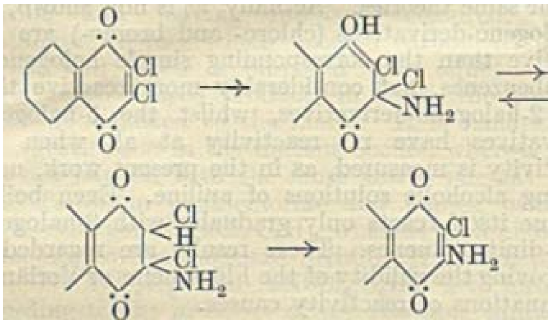
The fact that a methyl group depresses the activating effect of two nitro-groups when it is between the latter explains why 2-bromo-3 : 5-dinitro-*p*-xylene is non-reactive towards aniline and explains the now observed non-reactivity of 3-halogeno-2 : 6-dinitroaceto-*p*-toluidides (below). The non-reactivity of halogen in 3-halogeno-2 : 6-dinitro-*p*-toluidines (below) is to be expected merely in view of the known depressant effect of amino-groups.

5-*Bromo*-2 : 4-*dinitrotoluene*, m. p. 114°, is obtained by nitrating *m*-bromotoluene. Details are given for the preparation of 3-bromo-*p*-tolunitrile, m. p. 52° (lit., 47°), from 3-bromo-*p*-toluidine. Nitration of the nitrile affords 3-*bromo*-2 : 6-*dinitro*-p-*tolunitrile*, m. p. 165°. 3-*Bromo*-2 : 6-*dinitro*-p-*toluic acid*, m. p. 235°, is best obtained, not by the (difficult) hydrolysis of the above nitrile, but by nitrating 3-bromo-*p*-toluic acid. The acid *chloride*, m. p. 111°, is converted by sodium azide in aqueous acetone into the corresponding *azide*, m. p. 101°, which when heated in aqueous acetic acid at 100° passes into 3-*bromo*-2 : 6-*dinitro*-p-*toluidine*, m. p. 170° (*acetyl* derivative, m. p. 151°; *ethylurethane*, from the azide and boiling alcohol, m. p. 122°). Elimination of the amino-group

from the toluidine affords 3-*bromo*-2 : 6-*dinitrotoluene*, m. p. 86°.

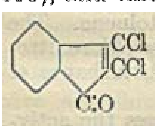
3-Chloro-2 : 6-dinitro-*p*-toluic acid, obtained by a method similar to that used for the 3-bromo-analogue, forms a *chloride*, m. p. 106°, convertible into an *azide*, m. p. 97° (decomp.), which when heated in dilute acetic acid at 100° is converted into 3-*chloro*-2 : 6-*dinitro*-p-*toluidine*, m. p. 173° (*acetyl* derivative, m. p. 154°). Deamination of the latter gives 3-*chloro*-2 : 6-*dinitrotoluene*, m. p. 77°.

The depressant action of the amino-group on the additive reactivity of conjugated systems is also shown in the case of 2-chloro-3-amino-α-naphthaquinone, which is readily prepared from 2 : 3-dichloro-α-naphthaquinone but is itself unaffected by ammonia. The annexed formulæ explain these facts :



In this case acetylation of the amino-group causes reappearance of reactivity on the part of the chlorine atome (Fries and Ochwat, A., 1923, i, 842).

Again, it is known that one chlorine atom in 2 : 3-dichloroindone is much more reactive than the other. If the present theory is correct, the 3-chlorine atom should be the reactive one (cf. Brass and Mosl, A., 1926, 838), and this is established by the fact that catalytic reduction of the chlorohydroxyindone obtained by the action of alkali on the dichloro-compound affords indane-1 : 3-dione (cf. annexed formula, showing the conjugation of only one chlorine atom in dichloroindone).



E. E. TURNER.

Preparation of dimethylaminodiaryl sulphones. E. GEBAUER-FÜLNEGG and P. SCHWARZ (Ber., 1928, **61**, [*B*], 1307—1308; cf. Bergel and Döring, this vol., 626).—p-*Dimethylaminophenyl* p-*tolyl sulphone*, m. p. 212°, and p-*dimethylaminodiphenyl sulphone*, m. p. 178°, are prepared by heating *p*-toluenesulphonyl chloride or benzenesulphonyl chloride dissolved in carbon disulphide with twice the molar quantity of dimethylaniline and the molar amount of aluminium chloride. H. WREN.

Aromatic compounds containing fluorine. II. 4 : 4′-Difluoro-3-aminodiphenyl and 3 : 4 : 4′-trifluorodiphenyl. G. SCHIEMANN and E. BOLSTAD (Ber., 1928, **61**, [*B*], 1403—1409; cf. Balz and Schiemann, A., 1927, 654).—Tetrazotisation of benzidine and treatment of the solution with borofluoric acid afford the bisdiazonium borofluoride, decomp. 137—138°, in 95% yield, which is converted by thermal decomposition into 4 : 4′-difluorodiphenyl, b. p. 115—116°/11 mm., in more than 80% yield. It is not readily nitrated by fuming nitric acid, nitric and acetic acids, potassium nitrate, or ethyl nitrate, but is converted by nitric acid of *d* 1·4 into 4 : 4′-*difluoro*-3-*nitrodiphenyl*, m. p. 94·6° (corr.), together with ill-defined products. Reduction of the nitro-compound with tin and concentrated hydrochloric acid affords 4 : 4′-*difluoro*-3-*aminodiphenyl*, b. p. 293°/766 mm., 159—160°/13 mm., m. p. 27·5° (corr.) [*acetyl* derivative, m. p. 96·2°; *benzoyl* compound, m. p. 122—123°], which is readily diazotised and then couples with β-naphthylamine, β-naphthol, Schaeffer's acid, *G* and *R* acids, *p*-toluidine, and benzidine. Conversely, the amine couples with tetrazotised benzidine. Treatment of diazotised 4 : 4′-difluoro-3-aminodiphenyl with borofluoric acid gives 4 : 4′-*difluorodiphenylyl*-3-*diazonium borofluoride*, decomp. 88°, which is transformed into 3 : 4 : -*trifluorodiphenyl*, m. p. 88·8°, d_4^{25} 1·43. H. WREN.

Thermal decomposition of nitrites ; nitrites of triphenylethylamine and diphenylethylamine. L. HELLERMAN, M. L. COHN, and R. E. HOEN (J. Amer. Chem. Soc., 1928, **50**, 1716—1729).—βββ-*Triphenylethylamine nitrite* (cf. A., 1927, 875) is stable at the ordinary temperature, but decomposes at 128° into triphenylethylene and a little β β-*triphenylethylamine nitrate*, decomp. 239°. In hot aqueous solution it gives mainly triphenylethylene. It is suggested that βββ-triphenyldiazoethane is first formed and then decomposed into nitrogen and the free radical, $CPh_3{\cdot}CH\colon$, which rearranges to triphenylethylene. A similar mechanism explains the anomalous behaviour of other primary amines with nitrous acid (cf. Freund and Lenze, A., 1891, 1172). Diphenylacetonitrile is obtained quantitatively from diphenylacetamide and thionyl chloride at 90—105°. A mixture of ββ-diphenylethylamine hydrochloride and sodium nitrite gives αβ-diphenylethylene when heated at 195° and phenylbenzylcarbinol in hot aqueous solution. In the latter case it is assumed that the radical, $CHPh_2{\cdot}CH\colon$, passes into an active form of stilbene, which then combines with water. Since ββ-*diphenyldiazoethane*, which may be prepared from the oily *nitroso*-derivative of ββ-diphenylethylurethane (cf. Sieglitz, A., 1922, i, 828) and sodium ethoxide, is probably an intermediate in this reaction, its thermal decomposition has been studied. In acid solution it gives αβ-diphenylethylene, but when heated alone or in alkaline or neutral solution it gives diphenylacetaldazine. Further evidence for the intermediate formation in the above reactions of free bivalent radicals is afforded by the oxidation of triphenylammonium nitrite by mercuric oxide at 135° to triphenylacetaldehyde. Similarly, benzoylphenyldiazomethane and moist mercuric oxide give benzil, but no diphenylketen (cf. Schroeter, A., 1909, i, 617). H. E. F. NOTTON.

Velocity measurements of intramolecular changes in arylacylhalogenoamines. (MISS) C. C. J. FONTEIN.—See this vol., 716.

Purification of 3 : 4-dichloroaniline. A. E. PARMELEE, ASSR. TO E. I. DU PONT DE NEMOURS & Co.—See B., 1928, 474.

Manufacture of water-soluble dinitroarylaminodiarylamines. I. G. FARBENIND. A.-G.—See B., 1928, 516.

Reduction of hydroxyazo-compounds to aminophenols by means of phenylhydrazine. II. 5-Aminosaligenin and its oxidation by phenylhydrazine. G. ODDO and A. GIACALONE (Gazzetta, 1928, **58**, 290—297; cf. A., 1905, i, 842).—Phenylhydrazine acts on benzeneazosaligenin, both on the azo-group as a reducing agent, giving 5-*aminosaligenin*, $C_7H_9O_2N$, m. p. 139° (*tribenzoyl* compound, m. p. 187°), and on the primary alcohol group as an oxidising agent, giving 5-aminosalicylaldehydephenylhydrazone (*benzoyl* derivative, m. p. 265°).

Benzeneazosaligenin, m. p. 145° (cf. Tummeley, A., 1889, 779), forms a *diacetyl* compound, m. p. 54°, and a *dibenzoyl* compound, m. p. 120°.

T. H. POPE.

Rearrangement of toluenediazoaminobenzene in aniline solution. M. FUKAMI and N. YOKOJIMA (J. Soc. Chem. Ind. Japan, 1928, **31**, 116—117).—The rearrangement of toluenediazoaminobenzene in aniline solution in the presence of aniline hydrochloride results in the formation of 70% of tolueneazoaniline and 30% of aminoazobenzene. Y. TOMODA.

Diaminotriphenylmethane and similar substances. H. WEIL, E. SAPPER, E. KRAMER, K. KLÖTER, and H. SELBERG (Ber., 1928, **61**, [*B*], 1294—1307).—The poor yields recorded previously for the preparation of diaminotriphenylmethane from aniline, benzaldehyde, and aniline hydrochloride are due to the use of too large a proportion of the latter reagent, which induces phenylation of the diamino-compound. The *aniline* compound of diaminotriphenylmethane, m. p. 126°, is remarkably stable, can be crystallised unchanged from alcohol, and loses aniline slowly and incompletely when distilled with steam. When the compound is crystallised from benzene, the aniline is replaced by 1 mol. of benzene; the reverse change can be similarly effected. With various solvents, diaminotriphenylmethane appears to form two types of additive compounds. Thus if the products containing benzene and aniline respectively are dissolved in cold glacial acetic acid and treated with cold acetic anhydride under similar conditions, the diacetyl derivative, m. p. 240—241°, separates quantitatively from the former within 4 hrs., whereas from the latter the production is approximately complete after about 24 hrs. Acetylation is not inhibited when the acetylating mixture is poured into water or dilute hydrochloric acid, but the periodic differences then disappear. Retardation of the activity of the amino-groups in the aniline complex is also observed towards formaldehyde and benzaldehyde, but the differences are less marked than with acetic anhydride. It is, therefore, not surprising that the aniline compound, although containing an additional basic group, is less basic than the aniline-free substance. It is assumed that the affinity of diaminotriphenylmethane towards benzene is due to the accumulation of phenyl groups and towards aniline to the multiplicity of aniline residues. It has not been possible to prepare a compound of *leuco*-malachite-green and dimethylaniline, although the two compounds are only incompletely separable by distillation with steam. Very distinct indications of the existence of a compound of dimethylaniline and hexamethyltriaminotriphenylmethane are, however, obtained.

Transitions are observed between the extremes, diaminotriphenylmethane–aniline and *leuco*-malachite-green–dimethylaniline. Thus 3-*chlorodiaminotriphenylmethane* ($+1C_6H_6$, m. p. 79°; $+1C_6H_5Me$, m. p. 73—75°) gives a crystalline additive *compound* with aniline, m. p. 92—93°, which loses the aniline when crystallised from alcohol; substitution of the third nucleus therefore affects the additive power of the other nuclei in marked degree. The following compounds are described: m-*nitrodiaminotriphenylmethane*, m. p. 157° (also $+1C_6H_6$, m. p. 76°, and $+1NH_2Ph$, m. p. 108°), of which the additive compound with benzene suffers slow acetylation and the *diacetyl* derivative, m. p. 204° (also +1AcOH, m. p. 166° with evolution of acetic acid), retains acetic acid so obstinately that it cannot be completely freed therefrom by crystallisation from alcohol; p-*chlorodiaminotriphenylmethane* ($+1NH_2Ph$, m. p. 109°; $+1C_6H_6$, m. p. 96—98°); o-*hydroxydiaminotriphenylmethane*, m. p. 150° ($+1NH_2Ph$, m. p. 125°; $+1C_6H_6$, m. p. 76°); m-*hydroxydiaminotriphenylmethane*, m. p. 172° (*sulphate*; $+1NH_2Ph$, m. p. 138°; $+1C_6H_6$, m. p. 106°; *diacetyl* derivative, m. p. 216°); p-*hydroxydiaminotriphenylmethane*, m. p. 178° [$+1NH_2Ph$, m. p. 153°; $+1C_6H_6$, m. p. 121°; *diacetyl* derivative, m. p. (indef.) 194°, and its *sodium* salt]; acetylation of the hydroxyl group in the foregoing compounds does not take place. Diaminotriphenylmethane forms compounds with aromatic bases which do not contain a substituent in the *para*-position. *Compounds* with the following bases are described: *o*-toluidine, m. p. 130°; *m*-toluidine; *p*-toluidine, m. p. 135—137°; *m*-chloroaniline, m. p. 92°; *m*-phenylenediamine, m. p. 46·5°; dimethylaniline, m. p. 142·5°; pyridine, m. p. 142°; piperidine, m. p. 112—116°, according to the rate of heating. *o*-Phenylenediamine, the three nitroanilines, aminobenzoic acid, the naphthylamines, diphenylamine, and benzylaniline do not unite with diaminotriphenylmethane. Similarly, benzene can be replaced by other non-basic substances, thus yielding *compounds* with the following: toluene, m. p. 100—101°; chlorobenzene, m. p. 108—109°; *o*-chlorotoluene, m. p. 108—112°, according to the rate of heating; thiophen, m. p. 110° (decomp.) after softening at 86° and second m. p. 139°; phenol, m. p. 110°; *o*-cresol, m. p. 97—98°. All *para*-disubstituted compounds, *m*-chlorotoluene, benzonitrile, diphenyl, benzenesulphonic acid, and nitrated hydrocarbons do not form compounds. H. WREN.

Chloroiodophenols obtained from 5-chloro- and 3 : 5-dichloro-salicylic acids. P. BRENANS and C. GIROD (Compt. rend., 1928, **186**, 1553—1555).—Iodine in the presence of sodium hydroxide reacts with 5-chlorosalicylic acid to afford 4-chloro-2 : 6-di-iodophenol, m. p. 108° (*ethyl ether*, m. p. 69°; *acetyl* derivative, m. p. 127·5°). In a similar way 3 : 5-dichlorosalicylic acid yields 2 : 4-dichloro-6-iodophenol, m. p. 63° (*ethyl ether*, b. p. 290—294°; *acetyl* derivative, m. p. 66°). G. A. C. GOUGH.

Tri-iodophenol from 5-iodo-, and 3 : 5-di-iodo-salicylic acid. P. BRENANS and C. GIROD

(Compt. rend., 1928, **186**, 1851—1852).—To 5-iodosalicylic acid (A., 1923, i, 797) in very dilute aqueous sodium hydroxide (sodium carbonate gives smaller yields) is added a solution of iodine in potassium iodide. The solution is partly decolorised and after 1 hr. excess of dilute sulphuric acid is added and excess of iodine is removed by sulphur dioxide. The white precipitate is purified through its soluble barium salt. Tri-iodophenol has m. p. 157° (cf. A., 1901, i, 322, 643). Excess of hydrochloric acid added to the barium salt yielded another *substance*, m. p. 140° and above. 3 : 5-Di-iodosalicylic acid is similarly converted by iodine (1 mol.) into 2 : 4 : 6-tri-iodophenol. Using 2 mols. of iodine and 4 mols. of sodium hydroxide a red *substance*, $C_6H_4OI_2$, was obtained.

J. D. FULTON.

Action of light on colouring matters containing the nitro-group. A. SEYEWETZ and D. MOUNIER (Bull. Soc. chim., 1928, [iv], **43**, 648—654).—See this vol., 167.

Reactions of activated magnesium. A. P. TERENTIEV and A. RUBINSTEIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 95—101).—*o*-Anisidine reacts with activated magnesium, analogously to other aromatic amines, forming the magnesium anisidide with liberation of hydrogen. the former substance giving with carbon dioxide the corresponding carbamate. This salt when heated at 250—270° decomposes with formation of the anisidide of 3-amino-2-methoxybenzoic acid, which on hydrolysis with alkalis gives 3-amino-2-methoxybenzoic acid. A. RATCLIFFE.

Mechanism of the reaction between pyrocatechol and phosphorus trichloride. L. ANSCHUTZ and W. BROEKER (Ber., 1928, **61**, [*B*], 1264—1267).—The initial product of the action of phosphorus trichloride on pyrocatechol is phosphorus pyrocatechyl monochloride, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}PCl$, b. p. 80°/10 mm., which yields successively *o-hydroxyphenyl o-phenylene phosphite*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}P{\cdot}O{\cdot}C_6H_4{\cdot}OH$, b. p. 155°/12 mm., m. p. 112—113°, and *o*-phenylene phosphite, $(C_6H_4)_3(PO_3)_2$, b. p. 242—248°/14 mm.; the three compounds can be isolated when reaction is effected in boiling benzene. *o*-Phenylene phosphite is obtained from *o*-hydroxyphenyl *o*-phenylene phosphite and phosphorus pyrocatechyl monochloride at 120°, whilst the latter compound results from *o*-phenylene phosphite and phosphorus trichloride at 160° in a sealed tube. The *thiochloride*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}PSCl$, b. p. 106°/1 mm., m. p. 49—50°, is obtained from the monochloride and sulphur at 195°. H. WREN.

Action of nitrosodimethylaniline on unsaturated compounds. A. QUILICO (Gazzetta, 1928, **50**, 317—325; cf. Bruni and Geiger, A., 1927, 1080).—When mixed in equimolecular proportions, safrole and nitrosodimethylaniline do not react in the cold, but at 120° violent reaction occurs, with formation of azodimethylaniline (cf. Lippmann and Lange, A., 1881, 161) and a highly stable Schiff's *base*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NMe_2$, m. p. 160°, which yields piperonylic acid and a small proportion of an unidentified acid when treated with alkaline permanganate; dissolves readily in mineral and acetic acids to deep red solutions; with dilute sulphuric acid gives a red *salt*, $C_{18}H_{18}O_2N_2,2H_2SO_4$; gives piperonylacraldehyde (cf. Ladenburg and Scholtz, A., 1895, i, 42) when boiled with sulphuric acid; yields a mixture of two isomeric oximes, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}OH$, and dimethyl-*p*-phenylenediamine when treated with hydroxylamine; and may be obtained also by the interaction of piperonylacraldehyde and dimethyl-*p*-phenylenediamine in alcoholic solution. The mechanism of the reaction is discussed. T. H. POPE.

Introduction of thiocyano-groups into organic compounds. I. G. FARBENIND. A.-G., ASSEES. OF H. P. KAUFMANN.—See B., 1928, 516.

Benzyl chloromethyl ether and dibenzylformal. P. CARRE (Compt. rend., 1928, **186**, 1629—1630).—When benzyl alcohol is treated with excess of formaldehyde in presence of hydrogen chloride (cf. Hill and Keach, A., 1926, 271), there are formed in addition to benzyl chloromethyl ether, some benzyl chloride and dibenzylformal, $CH_2(O{\cdot}CH_2Ph)_2$. This last compound is produced also by heating a mixture of benzyl alcohol and benzyl chloromethyl ether. When dibenzylformal is heated at 330° (cf. Delepine, A., 1900, i, 164), formaldehyde, toluene, and benzaldehyde are formed. H. BURTON.

Oxidation of alcohols by means of phenylhydrazine. G. ODDO and A. GIACALONE (Gazzetta, 1928, **58**, 298—300).—The formation of phenylosazones from phenylhydrazine and monosaccharides represents the only known instance of oxidation by means of phenylhydrazine, with partial conversion of the latter into aniline and ammonia. The results now described show that 5-aminosaligenin, saligenin, benzyl alcohol, and cinnamyl alcohol are readily oxidised by phenylhydrazine with formation of the phenylhydrazones of the corresponding aldehydes.

T. H. POPE.

Mobile anion tautomerism. II. Mechanism of anionotropic change, with special reference to the fate of the mobile anion. H. BURTON (J.C.S., 1928, 1650—1657; cf. Burton and Ingold, this vol., 634).—The possible fate of the mobile anion X (=Br, OAc, OH) in the anionotropic system $R{\cdot}CHX{\cdot}CH{:}CHR' \rightleftharpoons R{\cdot}CH{:}CH{\cdot}CHXR'$ is discussed. Two chief alternatives are proposed: (I) the simultaneous elimination of X at one end of the molecule and introduction of its equivalent, *e.g.*, from HX, at the other end, or (II) the elimination of $X^{\ominus}$ in combination with a catalyst and its subsequent return to an electromeric cation. In the latter case four possibilities are suggested, since $X^{\ominus}$ might take part in covalent interaction or molecular association with the catalyst and dissociation of the anion and cation might occur or not. The hypotheses were tested in the case of the conversion of α-phenylallyl *p*-nitrobenzoate into cinnamyl *p*-nitrobenzoate (cf. *loc. cit.*). Weak or strong acids did not catalyse the change. Isomerisation took place smoothly in acetic anhydride. The possibility of a mechanism in which *p*-nitrobenzoic-acetic anhydride reacted with cinnamyl acetate was excluded by an experiment in which use of the mixed anhydride yielded a mixture of esters, and by the absence of double decomposition between the acetate

and the mixed anhydride. Benzonitrile, of similar dielectric constant to acetic anhydride, but with less tendency to form covalent compounds, was an equally good catalyst. Isomerisation occurred smoothly in chlorobenzene (dielectric constant 11). In *p*-xylene slow isomerisation occurred, attributed to the effect of products of decomposition. In acetic anhydride with an equivalent of tetramethylammonium acetate, the product was a mixture of cinnamyl acetate and *p*-nitrobenzoate. It is concluded that $X^{\ominus}$ undergoes ionic dissociation dependent on the dielectric constant of the solvent, and probably combines electrostatically with it.

α-p-*Chlorophenylallyl alcohol*, b. p. 122—123°/10 mm., was prepared from *p*-chloroiodobenzene and acraldehyde by the Grignard reaction. The p-*nitrobenzoate*, m. p. 81—82°, was accompanied by a *substance*, m. p. 170°. The conversion of the alcohol into p-*chlorocinnamyl alcohol*, m. p. 56—58° (p-*nitrobenzoate*, m. p. 130—131°), by way of the *acetate*, b. p. about 155°/11 mm., by acetic anhydride, is described. p-*Chlorocinnamyl bromide*, m. p. 62—63°, was obtained from either alcohol with hydrobromic acid. α-m-*Tolylallyl alcohol*, b. p. 115—117°/11 mm. (p-*nitrobenzoate*, m. p. 53°), which yielded 3-*methylcinnamyl alcohol*, b. p. 137—140°/11 mm. (p-*nitrobenzoate*, m. p. 63—64°), by way of the *acetate*, b. p. about 145°/13 mm., is described, and the *bromide*, b. p. 138—140°/11 mm., derived from it. R. K. CALLOW.

Comparative stability of different isomerides according to their absorption spectra. Rearrangements in α-aryl-β-phenyl-β-ethylbutan-α-ols. (MME.) RAMART-LUCAS and ANAGNOSTOPOULOS (Compt. rend., 1928, **186**, 1626—1629).—When alcohols of the type $CPhEt_2\cdot CHAr\cdot OH$, are dehydrated by passing the vapour over kieselguhr at 300—350° under reduced pressure, unsaturated hydrocarbons of the form $CPhAr\colon CEt_2$, are obtained, whilst at 400—450°, the products have the general formula $CPhEt\colon CEtAr$. The absorption curves of the latter hydrocarbons are situated nearer the visible region than those of the former. The following compounds are described: p-*tolyl α-phenyl-α-ethylpropyl ketone*, m. p. 86°, b. p. 205°/15 mm. (*oxime*, m. p. 205°; *semicarbazone*, m. p. 169°); *anisyl α-phenyl-α-ethylpropyl ketone*, m. p. 56°, b. p. 222°/15 mm. (*oxime*, m. p. 180°); p-*tolyl α-phenylpropyl ketone*, m. p. 35°, b. p. 185°/11 mm. (*semicarbazone*, m. p. 161°); *anisyl α-phenylpropyl ketone*, m. p. 45°, b. p. 215—220°/20 mm. (*oxime*, m. p. 154°; *semicarbazone*, m. p. 118°); *αβ-diphenyl-β-ethylbutan-α-ol*, b. p. 209°/20 mm. (*phenylcarbimide* derivative, m. p. 166°); *β-phenyl-α-anisyl-β-ethylbutan-α-ol*, b. p. 234°/20 mm. (*phenylcarbimide* derivative, m. p. 122°); *αα-diphenyl-β-ethylbutan-α-ol*, b. p. 186°/15 mm.; *δ-phenyl-γ-p-tolylhexan-γ-ol*, b. p. 190°/15 mm.; *αα-diphenyl-β-ethyl-Δ^α-butylene*, b. p. 160°/11 mm.; *α-phenyl-α-p-tolyl-β-ethyl-Δ^α-butylene*, b. p. 172°/11 mm.; *α-phenyl-α-anisyl-β-ethyl-Δ^α-butylene*, b. p. 190°/11 mm.; *γδ-diphenyl-Δ^γ-hexene*, b. p. 168°/14 mm.; *δ-phenyl-γ-p-tolyl-Δ^γ-hexene*, b. p. 170°/11 mm., and *δ-phenyl-γ-anisylhexene*, b. p. 204°/12 mm. H. BURTON.

Degradation of high-molecular unsaturated acids. Degradation of chaulmoogric acid to homohydnocarpylamine. Modified Curtius reaction. C. NAEGELI and G. STEFANOVITSCH (Helv. Chim. Acta, 1928, **11**, 609—656).—Chaulmoogryl chloride reacts with excess of hydrazine hydrate to form the secondary *hydrazide*, $C_{36}H_{64}O_2N_2$, m. p. 127°, of chaulmoogric acid, although under regulated conditions the primary *hydrazide* (I), $C_{18}H_{34}ON_2$, m. p. 92°, in chloroform +28·34° (*hydrochloride*, decomp. 130° after previous sintering; *benzoyl* derivative, m. p. 114°; *benzylidene* derivative, m. p. 89·5—91°; *salicylidene* derivative, m. p. 109°), is obtained also. Ethyl chaulmoograte and hydrazine hydrate react under various conditions, yielding a mixture of (I) and 4-*amino*-3 : 5-*dihomohydnocarpyl*-1 : 2 : 4-*triazole*, m. p. 132—133°, $[\alpha]_D^{22}$ in chloroform +21·54°. This last compound is formed when (I) is heated at 160° for 5 hrs., and does not form condensation products with aldehydes. When (I) is converted into the *azide*, and this is treated with alcohol, *ethyl homohydnocarpylcarbamate* (II), m. p. 48·5°, in chloroform +47·62°, is obtained. This is hydrolysed by concentrated hydrochloric acid at 100° to *homohydnocarpylamine*, decomp. 90—120° (*hydrochloride*, decomp. 160°, $[\alpha]_D^{22}$ in alcohol +54·9°; *picrate*, m. p. 112°; *chloroplatinate*), also formed by the action of heat on a mixture of s-*dihomohydnocarpylcarbamide* (III), m. p. 113·5°, $[\alpha]^{22}$ in chloroform +54·96°, and moist calcium hydroxide. When chaulmoogryl chloride is treated with sodium azide in ether, and the product decomposed by boiling alcohol, (II) is the main product together with a small amount of (III). If the decomposition is carried out with water (III) is the sole product. Treatment of a methyl-alcoholic solution of chaulmoogramide with aqueous sodium hypochlorite (cf. Rinkes, A., 1927, 45) gives a *substance*, m. p. 81·5°, having the composition of methyl homohydnocarpylcarbamate, but showing an abnormally high mol. wt. in camphor. H. BURTON.

Action of sulphuric acid on aromatic acids: sulphonated aromatic acids. J. B. SENDERENS and J. ABOULENC (Compt. rend., 1928, **186**, 1497—1499).—*m*-Sulphobenzoic acid may be prepared by heating benzoic acid at 200—210° with sulphuric acid of *d* 1·84, which readily sulphonates the toluic acids at 150—160°, or better with fuming sulphuric acid (20% SO_3) at 200°. *p*-Sulphophthalic acid is best prepared from phthalic anhydride by sulphonation with excess of fuming sulphuric acid at 215°. Sulphuric acid of *d* 1·84 decomposes phenylacetic acid at 180° without effecting sulphonation. Similar decompositions occur together with partial sulphonation by treatment with the fuming acid in the cold. G. A. C. GOUGH.

Sodium salts of aromatic nitriles. I. M. M. RISING and T.-W. ZEE (J. Amer. Chem. Soc., 1928, **50**, 1699—1707).—Further evidence (cf. A., 1927, 359; this vol., 638) for the existence of the tautomeric forms, $CRPh\colon C\colon NNa$ (I), and $CRPh(CN)Na$ (II), of the sodio-derivatives of aromatic nitriles is discussed. These react in form (I) with acids, and in form (II) with acyl or alkyl halides. Thus yellow, amorphous *sodiophenylacetonitrile* gives with 50% sulphuric acid, 49% of the theoretical amount of hydrogen cyanide and 52% of benzyl alcohol. Sodio-α-phenylbutyronitrile gives, similarly, 100% of hydrogen cyanide and

69% of γδ-diphenyl-Δ^{γ}-hexene. These reactions are ascribed to the formation from (I) of the free radical, CRPh·, which then combines with itself or with water. These sodio-derivatives behave analogously to ethyl sodioacetoacetate and are probably present as intermediates in the aldol-type condensation of 2 mols. of a nitrile in presence of sodium (von Meyer, A., 1895, i, 582). H. E. F. NOTTON.

Oxidative degradation of carboxylic acids. S. SKRAUP and E. SCHWAMBERGER (Annalen, 1928, **462**, 135—158).—An investigation designed to discover whether oxidation of acids in an homologous series shows periodicity as regards type of degradation, periodicity being known to occur in other similar cases. A number of acids have been oxidised at 100° with alkaline permanganate, using the latter in amount corresponding with 3 atoms of oxygen per 1 mol. of acid (in some cases less permanganate).

Phenylacetic acid (1 mol.) gives 0·28 mol. of benzoic acid and, usually, some benzoylformic acid (permanganate added to acid) with 1O and 0·89 mol. of benzoic acid with 3O. Mandelic acid is not an intermediate stage in the oxidation, since it undergoes oxidation to benzoylformic acid, which is more stable towards permanganate than phenylacetic acid itself (slow oxidation, 1O giving benzoic acid, 0·74 mol.).

When permanganate is added slowly to benzoylacetic acid dissolved in potassium carbonate, steam being introduced at the same time, benzoic and oxalic acids are the main products, only traces of benzoylformic acid and acetophenone being formed. When the solution of the acid is slowly added to the permanganate, benzoic acid and benzoylformic acid are the chief products, together with traces of oxalic acid. The former oxidation is presumably that of the enolic form of benzoylacetic acid, the latter that of the keto-form. In the latter case carbon dioxide loss on the part of the keto-form produces acetophenone, which is then oxidised to benzoylformic acid (giving benzoic acid in turn). Since the oxidation of β-phenylpropionic acid gives benzoylformic, but no oxalic, acid, oxidation probably occurs in accordance with the scheme $CH_2Ph{\cdot}CH_2{\cdot}CO_2H \longrightarrow COPh{\cdot}CH_2{\cdot}CO_2H \longrightarrow COPh{\cdot}Me \longrightarrow COPh{\cdot}CO_2H \longrightarrow Ph{\cdot}CO_2H$. Accompanying this β-oxidation is almost certainly some α-oxidation: $CH_2Ph{\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_2Ph{\cdot}CO{\cdot}CO_2H \longrightarrow CH_2Ph{\cdot}CO_2H$. In any case, neither cinnamic acid nor phenylglyceric acid is formed during the oxidation of β-phenylpropionic acid, since both of these acids are oxidised to benzaldehyde and oxalic acid, neither of which is produced in the oxidation referred to.

The oxidation of γ-phenylbutyric acid to benzoic and benzoylformic acids and of δ-phenylvaleric acid to benzoic and oxalic acids is not readily interpretable. Investigation of the oxidation of β-benzoylpropionic and γ-benzoylpyruvic acids throws no light on the problem, since these acids do not give malonic and succinic acids, respectively, when oxidised, but benzoic, and benzoic and oxalic acids, respectively.

β-Phenylpropionic acid is only slowly oxidised; similarly, β-*p*-tolylpropionic acid is readily oxidisable only to β-*p*-carboxyphenylpropionic acid. On the other hand, γ-phenylbutyric acid (prepared by heating the *hydrazone-anhydride*, m. p. 153°, of β-benzoylpropionic acid with alcoholic sodium ethoxide at 160—170°) and δ-phenylvaleric acid (obtained by Skita reduction of cinnamylideneacetic acid; cf. Staudinger and Müller, A., 1923, i, 363) are readily oxidised.

Chlorobenzene and succinic anhydride condense in presence of aluminium chloride to give β-p-*chlorobenzoylpropionic acid*, m. p. 131°, the *hydrazone-anhydride*, m. p. 178°, of which may be converted into γ-p-*chlorophenylbutyric acid*, m. p. 62°, b. p. 185°/12 mm. Reduction of β-*p*-chlorobenzoylpropionic acid affords γ-p-*chlorophenylbutyrolactone*, b. p. 140—150°/1—2 mm. or 210°/15 mm.

n-Valeric, *n*-hexoic, *n*-heptoic, and *n*-octoic acids give only oxalic acid when oxidised under the present conditions. Suberic and azelaic acid show no appreciable difference in behaviour, such as might have been expected with two acids of even and odd carbon content, respectively. Both give oxalic acid as the only oxidation product. Neither fatty-aromatic nor fatty acids, therefore, exhibit periodicity as regards oxidation under the conditions now employed.

In extension of work done by Skraup and Nieten (A., 1924, i, 1185), *phenyl margarate*, m. p. 37°, b. p. 240—250°/11 mm. (decomp.), obtained from the acid by the thionyl chloride method, was heated for 72 hrs. at 328° in a sealed tube. The products are phenol and *n*-tetradecane, m. p. 5°, b. p. 130°/15 mm., some ester being recovered. Thus, since phenyl palmitate and stearate decompose, respectively, to give *n*-tridecane and *n*-pentadecane, no periodicity appears in such reactions either.

A general method is suggested for the preparation of straight-chain carboxylic acids, viz., by the oxidative degradation of the next higher homologue. Thus, methyl stearate is converted by magnesium phenyl bromide into diphenylheptadecylcarbinol, $C_{17}H_{35}{\cdot}CPh_2{\cdot}OH$, which without being purified is distilled under diminished pressure. The distillate (repeated distillation for pure product) contains a 75% yield of *αα-diphenyl-Δ^{α}-octadecene*, m. p. about −1°, b. p. 282—283°/18 mm., and this substance, when oxidised with chromic anhydride in dilute acetic acid, affords margaric acid (40 g. per 100 g. of stearic acid originally used).

Similarly, from methyl palmitate, *αα-diphenyl-Δ^{α}-hexadecene*, m. p. 17—18°, b. p. 265—270°/13 mm., and pentadecoic acid, b. p. 220—240°/15 mm., are obtained (25 g. of last-named acid from 100 g. of palmitic acid). Methyl oleate gives rise to *αα-diphenyl-$\Delta^{\alpha\kappa}$-octadecadiene*, $CH_2Me{\cdot}[CH_2]_6{\cdot}CH{:}CH{\cdot}[CH_2]_6{\cdot}CH{:}CPh_2$, b. p. 285—286°/15 mm., oxidised to *Δ^{η}-heptadecenoic acid*, m. p. −1°, b. p. 226—227°/20 mm. The latter acid is reduced (Skita method) to margaric acid, does not undergo the oleic–elaidic acid change (nitrous fumes) smoothly, and is oxidised by hydrogen peroxide in acetic acid (Hilditch, A., 1926, 938) to *ηθ-dihydroxymargaric acid*, m. p. 94°. *Methyl Δ^{η}-heptadecenoate*, b. p. 195°/15 mm., when oxidised by the method of Armstrong and Hilditch gives pelargonic and suberic acids (proof of constitution as a Δ^{η}-acid). The new degradative method affords a possible means of determining the constitution of an acid which is

otherwise difficult to deal with. Two examples are chosen: (1) *cyclo*Hexylacetic acid is converted into its methyl ester (b. p. 105°/20 mm.), and the latter by means of the Grignard reagent into *αα-diphenyl-β-*cyclo*hexylethylene*, $C_6H_{11}\cdot CH{:}CPh_2$, b. p. 210—215°/15 mm., which on oxidation gives *cyclo*hexanecarboxylic acid. (2) 4-Methyl*cyclo*hexanecarboxylic acid is esterified and then converted into 1-*methyl-4-diphenylmethylene*cyclo*hexane*, $C_7H_{13}{:}CPh_2$, b. p. 200°/12 mm., m. p. 65°, which is oxidised to 4-methyl*cyclo*hexanone. E. E. TURNER.

Isomeric 2-amino-α-arylcinnamic acids. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1928, 1478—1486).—2-*Amino*-3 : 4 : 2′ : 5′-*tetramethoxy-α-phenylcinnamic acid* is found to exist in two interconvertible isomeric forms similar to those of 2-amino-α-phenylcinnamic acid (Pschorr, A., 1896, i, 303; Stoermer and Prigge, A., 1915, i, 683). The form *A* ($+0{\cdot}5H_2O$), m. p. 219°, is colourless and sparingly soluble, whilst the form *B*, m. p. 167°, is yellow. In camphor solution, *A* is bimolecular and *B* unimolecular. Both are associated in azobenzene, but *A* has twice the mol. wt. of *B*. Both are unimolecular in acetic acid. In acid or alkaline solutions the form *B* predominates, and is precipitated by sodium acetate or acetic acid, respectively. The form *B* is converted into the form *A* fairly rapidly in azobenzene or benzene. The solid form *A* is produced also by sudden addition of the calculated amount of acetic acid to a solution in dilute ammonia of either form, and appears to be the stable form in neutral solution.

The acids were synthesised as follows: 2 : 5-dimethoxybenzaldehyde, prepared by introducing the aldehydo-group into *p*-dimethoxybenzene by the method of Adams and Levine (A., 1924, i, 860; cf. this vol., 654), was condensed with hippuric acid, yielding the azlactone, 5-*keto*-2-*phenyl*-4-(2′ : 5′-*dimethoxybenzylidene*)-4 : 5-*dihydro-oxazole*, m. p. 170—172°, which yielded on hydrolysis with dilute acid or alkali *α-benzamido*-2 : 5-*dimethoxycinnamic acid*, m. p. 195—196°, or, on prolonged alkaline hydrolysis, 2 : 5-*dimethoxyphenylpyruvic acid*, m. p. 166—170° (decomp.), which yielded with *o*-phenylenediamine 3-*hydroxy*-2′ : 5′-*dimethoxy*-2-*benzylquinoxaline*, m. p. 179—180° (+0·5EtOH). Oxidation of the pyruvic acid yielded 2 : 5-dimethoxyphenylacetic acid, the sodium salt of which, condensed with 2-nitroveratraldehyde, yielded trans-2-*nitro*-3 : 4 : 2′ : 5′-*tetramethoxy-α-phenylcinnamic acid*, m. p. 204°, accompanied by *trans*-2-nitro-3 : 4-dimethoxycinnamic acid. By reduction with ferrous sulphate and ammonia, the reaction product being just acidified with acetic acid, a mixture of the forms *A* and *B* of the amino-acid was obtained. The form *A* separated from the alcoholic solution of the mixture, and the form *B* was found in the mother-liquors, the proportion of *B* to *A* increasing with the amount of acetic acid used in the precipitation. Either form yielded, on boiling the methyl-alcoholic solution of the diazonium sulphate, 3 : 4 : 5 : 8-*tetramethoxyphenanthrene*-9-*carboxylic acid*, m. p. 190—198°, which yielded 3 : 4 : 5 : 8-*tetramethoxyphenanthrene*, m. p. 118—120° (*picrate*, m. p. 158°).

cis-2-*Nitro*-3 : 4 : 2′ : 5′-*tetramethoxy-α-phenylcinnamic acid*, m. p. 186°, was obtained by exposure of the sodium salt of the *trans*-acid to ultra-violet light, and on reduction yielded a solution from which acid precipitated 7 : 8 : 2′ : 5′-*tetramethoxy*-3-*phenylcarbostyril*, m. p. 189°. The same carbostyril was formed from the *trans*-amino-acids, either by exposing an alcoholic solution of form *B* to ultra-violet light, or by heating either *A* or *B* with acetic anhydride and a trace of sulphuric acid. R. K. CALLOW.

Amides of thio- and dithio-salicylic acid. A. REISSERT and E. MANUS (Ber., 1928, 61, [*B*], 1308—1316).—Dithiosalicylic acid is converted successively into the chloride, m. p. 153°, and amide, m. p. 239°; the anilide, m. p. 243°, and *methylamide*, m. p. 216·5°, are described. The amide is converted by 2*N*-sodium hydroxide into *benzo*iso*thiazolone*,

$C_6H_4<\begin{smallmatrix}CO\\S\end{smallmatrix}>NH$, m. p. 158° (*sodium* salt), dithiosalicylamide, and thiosalicylamide (*o*-thiobenzamide).

The primary action therefore yields the compounds $NH_2\cdot CO\cdot C_6H_4\cdot SNa$ and $NH_2\cdot CO\cdot C_6H_4\cdot S\cdot ONa$, the latter of which immediately loses water with closure of the ring. Dithiosalicylanilide and 33% sodium hydroxide afford thiosalicylanilide, m. p. 110°, and, probably, the corresponding sulphinic acid. Benzo*iso*thiazolone is most conveniently prepared by the successive action of bromine in carbon tetrachloride and boiling glacial acetic acid on dithiosalicylamide; 2-*phenylbenzo*iso*thiazolone*, m. p. 143—144°, and 2-*methylbenzo*iso*thiazolone*, m. p. 54° [*hydrochloride*, m. p. 130° (decomp.)], are analogously prepared. The *silver* salt of benzo*iso*thiazolone is converted by methyl iodide into a mixture of 3-*methoxybenzo*iso*thiazole* and 2-*methylbenzo*iso*thiazolone*, m. p. 54°, separated by taking advantage of the volatility of the former and non-volatility of the latter with steam. Oxidation of the benzo*iso*thiazolones with hydrogen peroxide affords the corresponding saccharins. Benzo*iso*thiazolone is transformed by benzoyl chloride into its N-*benzoyl* derivative, m. p. 167°, converted by treatment with sodium hydroxide in acetone followed by oxidation of the product with air into *di*-N-*benzoylbenzamide* oo′-*disulphide*, $[NHBz\cdot CO\cdot C_6H_4\cdot S\cdot]_2$, m. p. 191°, identical with that derived from dithiosalicylamide and 2 mols. of benzoyl chloride. *Thiosalicylamide* (*o*-thiolbenzamide), m. p. 140°, and *thiosalicylanilide*, m. p. 110°, are obtained by reduction of the corresponding dithio-compounds with zinc dust and dilute hydrochloric acid. S-*Benzoylthiosalicylamide*, $NH_2\cdot CO\cdot C_6H_4\cdot SBz$, m. p. 135°, is obtained when the dry *sodium* salt of thiosalicylamide is treated with benzoyl chloride in boiling benzene. Benzoylation of dithiosalicylamide by the Schotten–Baumann method affords a mixture of *N*-benzoylbenzo*iso*thiazolone and *N*-benzoylthiosalicylamide formed by isomerisation from the primary *S*-derivative; when 2 mols. of the chloride are used for 1 mol. of the amide the compound cannot be isolated, but its formation is established by the oxidative production of the corresponding disulphide, $[NHBz\cdot CO\cdot C_6H_4\cdot S\cdot]_2$. If benzoylation is effected by an excess of benzoyl chloride and sodium hydroxide, the *dibenzoyl* derivative,

$NHBz\cdot CO\cdot C_6H_4\cdot SBz$, m. p. 138°, and the *tribenzoyl* compound, $NBz_2\cdot CO\cdot C_6H_4\cdot SBz$, m. p. 220—222°, are obtained. The latter substance is converted into the former by boiling glacial acetic acid. Treatment of thiosalicylanilide with an excess of benzoyl chloride affords S-*benzoylthiosalicylanilide*, m. p. 140°, and NS-*dibenzoylthiosalicylanilide*, m. p. 164°.

H. WREN.

Synthesis of tropic acid. M. CHAMBON (Compt. rend., 1928, **186**, 1630—1631).—When ethyl phenylbromoacetate is treated with trioxymethylene and zinc filings in presence of benzene, and the resulting product hydrolysed with alcoholic barium hydroxide, tropic acid, m. p. 118°, is obtained in 50% yield.

H. BURTON.

Optical activity and polarity of substituent groups. IX. Menthyl esters of methoxynaphthoic and of diphenyl-2-carboxylic acids. E. BRETSCHER, H. G. RULE, and J. SPENCE (J.C.S., 1928, 1493—1504; cf. this vol., 765).—When their rotatory powers are compared with those of benzoates, there is found to be a lowering in the case of 1-naphthoates and a marked increase in the case of 2-naphthoates, consistent with the former being regarded as 2 : 3-substituted benzoates with an *o*-directive group in the 2-position and the latter as 3 : 4-substituted benzoates. The introduction of the methoxyl group has an effect on the naphthoates similar to that on the benzoates. Menthyl 1- and 3-methoxy-2-naphthoates show a depression in rotatory power, less marked in the former, possibly owing to a screening effect. Of the 1-naphthoates, menthyl 2-methoxy-1-naphthoate shows the maximum effect, the rotatory power being reversed in sign. A marked diminution is found in the 8-methoxy-1-naphthoate, suggesting that the effect of *o*-substituents is transmitted through space and not through the carbon chain. In the 4-position the rotatory power is raised; in the 5-position it is unaffected. In menthyl 2′-methoxydiphenyl-2-carboxylate the methoxyl group increases the rotation on account of its general polar effect, whilst in the unsubstituted ester the phenyl group has the usual depressant effect of an *o-p*-directive substituent.

2-*Methoxy*-1-*naphthoic acid*, m. p. 176°, was prepared from 1-bromo-2-methoxynaphthalene by reaction with magnesium and carbon dioxide. The *menthyl* ester, m. p. 122—123°, was prepared from the acid chloride and menthol in presence of pyridine. 4-Methoxy-1-naphthoic acid was obtained by oxidation of the aldehyde (from α-naphthyl methyl ether by Gattermann's reaction) and yielded a *chloride*, b. p. 210—215°/15 mm., and *menthyl* ester, m. p. 114—115°. Methylation of 1 : 8-naphtholactone yielded *methyl* 8-*methoxy*-1-*naphthoate*, m. p. 51—52°, and the *acid*, m. p. 162—163° (corr.). The *menthyl* ester, m. p. 96—96·5°, was obtained by esterification at 120° in the presence of hydrogen chloride. *Menthyl* 5-*methoxy*-1-*naphthoate*, m. p. 90·3°, *menthyl diphenyl-2-carboxylate*, b. p. 175°/0·4 mm., and *menthyl* 2′-*methoxydiphenyl-2-carboxylate*, b. p. 171—173°/0·3 mm., are also described. The values of $[M]^{20}$ for the menthyl esters at different wavelengths and in different solvents are tabulated.

R. K. CALLOW.

Constitution of phenolphthalein. I. Preparation of compounds of phthalein type. H. LUND (J.C.S., 1928, 1569—1575).—Condensation of phloroglucinol trimethyl ether with terephthalaldehydic acid under the influence of hydrogen chloride yielded 2′ : 4′ : 6′ : 2″ : 4″ : 6″-*hexamethoxytriphenylmethane*-4-*carboxylic acid*, m. p. 258—260° (corr.), which was converted by oxidation with lead tetra-acetate in acetic acid into 4-*carboxy*-2′ : 4′ : 6′ : 2″ : 4″ : 6″-*hexamethoxytriphenylcarbinyl acetate*, violet (*perchlorate*, decomp. on heating). The carbinol acid and its anhydride were unstable. Condensation of phloroglucinol trimethyl ether with *o*-phthalaldehydic acid yielded only 2′ : 4′ : 6′-*trimethoxyphenylphthalide*, m. p. 200° (corr.). Phthalyl chloride and phloroglucinol trimethyl ether in the presence of zinc chloride yielded *phloroglucinolphthalein hexamethyl ether*, m. p. 175—176° (corr.), colourless, but violet in dilute hydrochloric acid. This readily split off a molecule of phloroglucinol trimethyl ether on treatment with acid. Esterification and hydrolysis yielded 2′ : 4′ : 6′-*trimethoxybenzoyl*-o-*benzoic acid*, m. p. 184—185° (corr.). *Resorcinolphthalein tetramethyl ether*, m. p. 153° (corr.), colourless, reddish-violet in hydrochloric acid, was prepared by a new method of condensation, the action of sulphuric acid in anhydrous ether, from 2′ : 4′-dimethoxybenzoyl-*o*-benzoic acid and resorcinol dimethyl ether. Phenolphthalein monomethyl ether ($+0\cdot5C_7H_7$ from toluene) was obtained by the action of methyl sulphate on phenolphthalein and also by condensing 4′-methoxybenzoyl-*o*-benzoic acid with phenol in anhydrous ether and sulphuric acid. *Resorcinolphenolphthalein* 2′ : 4′-*dimethyl ether*, m. p. 220° (corr.), was prepared in the same way from 4′-hydroxybenzoyl-*o*-benzoic acid and resorcinol dimethyl ether. *Phloroglucinolphenolphthalein* 2′:4′:6′-*trimethyl ether*, m. p. 200° (corr.), was obtained similarly from phloroglucinol trimethyl ether.

The phenol group in the phthaleins $C_6H_4\cdot CO_2\cdot C\cdot CR\cdot C_6H_4\cdot OH$, where R is a methoxy-substituted phenyl group, displayed an increasing acidity with increasing substitution in R. The phthaleins of the type $C_6H_4\cdot CO_2\cdot C{:}R_2$ showed increasing basicity with increasing methoxy-substitution in the two groups R.

R. K. CALLOW.

Iodo-derivatives of phthaleins. F. R. GREENBAUM (Amer. J. Pharm., 1928, **100**, 374—384). Halogenated phthaleins used in choleocystography are found on intravenous injection to be highly toxic. A high iodine content is essential to render the drugs efficient. A number of new iodo-derivatives of various phthaleins, and xanthen derivatives, have been prepared. 1 : 2 : 3 : 4-*Tetraiodophenolphthalein*, prepared by heating tetraiodophthalic anhydride (1 mol.), phenol (2 mols.), and stannic chloride (2 mols.) at 200°, is amorphous, soluble in alkalis with a pink to red colour which disappears on further addition of alkali. It is iodinated by iodine in sodium hydroxide solution at the b. p. to *octaiodophenolphthalein*, yellow, and is readily soluble in dilute alkalis with a pale green colour. Dinitrophenolphthalein iodinated as above yielded *di-iododinitrophenol-*

phthalein, yellow, m. p. 249—250°, giving an orange colour in sodium hydroxide. Dinitrofluorescein yielded *di-iododinitrofluorescein*, orange-red, dissolving in sodium hydroxide with a blue colour. m-*Cresolphthalein* is yellowish-brown, and dissolves with a purple colour in dilute sodium hydroxide. On iodination in alkaline solution by iodine in potassium iodide followed by acidification with hydrochloric acid, *di-iodo*-m-*cresolphthalein*, brown, m. p. 214°, is obtained; it is only slightly soluble in dilute sodium hydroxide. Rhodamine-*B* from diethyl-*m*-aminophenol and phthalic anhydride, treated with iodine in potassium iodide gives a *monoiodo*-derivative and with iodine trichloride and hydrochloric acid a reddish-brown *di-iodo*-derivative, insoluble in dilute alkalis. Thymolphenolphthalein gave a *mono-iodo*-derivative soluble in dilute alkalis with a blue colour. J. D. FULTON.

Configuration of polymethylenedicarboxylic acids. III. *cis-cyclo*Butane-1 : 2-dicarboxylic acid. R. KUHN and A. WASSERMANN (Helv. Chim. Acta, 1928, **11**, 600—609).—Thermal decomposition of *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylic acid gives a mixture of *cis*- and *trans-cyclo*butane-1 : 2-dicarboxylic acids, having m. p. 97—98° and 130° (uncorr.), respectively (cf. Perkin, J.C.S., 1887, **51**, 25; 1894, **65**, 583). The mixture is separated by dissolution in concentrated hydrochloric acid, in which solvent the *cis*-acid is more soluble. When the *cis*-acid is heated with concentrated hydrochloric acid at 190°, it is converted into the *trans*-form. The two dissociation constants, K_1 and K_2, of the *cis*- and *trans*-acids have been determined in water and 50% methyl alcohol. The values for the ratio for the *cis*- and *trans*-acids in water are 98 and 66, and in 50% methyl alcohol 186 and 140, respectively. H. BURTON.

Condensation of ketones with ethyl acetoacetate. L. G. JUPP, G. A. R. KON, and E. H. LOCKTON (J.C.S., 1928, 1638—1644).—Condensation of *cyclo*hexanone with ethyl acetoacetate by the method of Merling and Welde (A., 1909, i, 479) yielded only *cyclo*hexenyl*cyclo*hexanone. With ethyl sodioacetoacetate the desired *ethyl* Δ^1-cyclo*hexenylacetoacetate*, b. p. 135°/20 mm. (*semicarbazone*, m. p. 141°), was obtained only in minute amount. The chief product was the *acid*, m. p. 121° (decomp.) (*semicarbazone*, m. p. 196°), accompanied by *cyclo*hexenyl*cyclo*hexanone and an equilibrium mixture of *cyclo*hexylideneacetone and Δ^1-*cyclo*hexenylacetone (cf. this vol., 887). Addition of water to the reaction mixture after 24 hrs. furnished a method of preparation of the last. The action of heat on Δ^1-*cyclo*hexenylacetoacetic acid yielded a mixture of *cyclo*hexylideneacetone and Δ^1-*cyclo*hexenylacetone containing the former in great excess of the equilibrium quantity. The acid could not be esterified. The silver salt and methyl iodide yielded a *substance*, $_{10}H_{14}O_3$, m. p. 177°. Methyl-alcoholic hydrogen chloride yielded an isomeric *substance*, m. p. 80°. An attempt to prepare the desired ester from ethyl sodio*cyclo*hexenylmalonate and acetyl chloride yielded *ethyl* Δ^1-cyclo*hexenylacetylmalonate*, b. p. 181°/ mm. (*semicarbazone*, m. p. 178°), and other methods (condensation of ethyl chloroformate with sodio*cyclo*hexenylacetone; conversion of ethyl *cyclo*hexenylmalonate into the acid-chloride-ester and reaction with zinc methyl iodide; condensation of *cyclo*hexenylacetone and sodium ethoxide) also failed.

Condensation of *cyclo*pentanone with ethyl sodioacetoacetate yielded *cyclo*pentylidene*cyclo*pentanone and a minute amount of cyclo*pentylideneacetoacetic acid*, m. p. 137° (decomp.). Pulegone and ethyl sodioacetoacetate yielded Δ^1-pulegenylacetone, b. p. 149—153°/21 mm. (cf. Barbier, A., 1899, i, 299) (*semicarbazone*, m. p. 187°), the structure of which was demonstrated by the formation of acetone and α-methylglutaric acid by ozonolysis. The ketone yielded with sodium and methyl iodide *α-methyl-α-*Δ^1-*pulegenylacetone*, b. p. 150°/21 mm., $d_4^{21\cdot2}$ 0·94694, 1·49347, $[R_L]_D$ 64·39 (*semicarbazone*, m. p. 191°), and with ethyl sodiomalonate a *dihydroresorcinol* derivative, m. p. 130°. Piperitone and ethyl sodioacetoacetate yielded a *ketone*, b. p. 155°/20 mm., $d_4^{21\cdot8}$ 0·95821, $n_D^{21\cdot8}$ 1·49610, $[R_L]_D$ 60·59 (*semicarbazone*, m. p. 217°), probably of analogous structure. Ethyl *iso*propylideneacetoacetate, b. p. 103°/18 mm., $d_4^{21\cdot0}$ 0·96308, $n_D^{21\cdot0}$ 1·45583, $[R_L]_D$ 46·52 (*semicarbazone*, m. p. 247°), could not be methylated with the aid of sodium powder, and the methylated ester decomposed in the presence of alcohol, giving ethyl trimethylacrylate, $d_4^{21\cdot0}$ 0·97812, $_D^{21\cdot0}$ 1·45802, $[R_L]_D$ 41·02, the structure of which was confirmed by ozonolysis, acetone being obtained. R. K. CALLOW.

Methyl phthalate and other esters of *o*-phthalic acid. J. A. HANDY and L. F. HOYT (J. Amer. Pharm. Assoc., 1928, **17**, 458—461).—The chemical, physical, and pharmacological properties of some commercial esters of *o*-phthalic acid, especially the methyl ester, are compared with those of ethyl phthalate.

E. H. SHARPLES.

Action of phosphorus pentachloride on homophthalic acid. W. DAVIES and H. G. POOLE (J.C.S., 1928, 1616—1620).—A method is described for preparing homophthalic acid in quantity by the oxidation of tetrahydronaphthalene with potassium permanganate (cf. von Braun, A., 1924, i, 48; Cornillot, A., 1927, 1069), and reduction of the phthalonic acid by hydriodic acid and red phosphorus. Homophthalyl chloride could not be prepared from the acid or the anhydride. When homophthalic anhydride was heated with phosphorus pentachloride (2·2 mols.) in excess of phosphoryl chloride, a smooth reaction occurred, yielding 3-*chloro*iso*coumarin*, m. p. 98·5—99°, b. p. 150°/5 mm. The anhydride reacts in the enolic form, the existence of which in solution is demonstrated by production of a coloration with ferric chloride under strictly specified conditions (cf. Dieckmann, A., 1914, i, 690). 3-Chloro*iso*coumarin is stable towards neutral or acid hydrolytic agents. From the product of reaction with ammonia in benzene *o*-carboxyphenylacetonitrile, m. p. 126°, was isolated. It reacts with aniline to yield *homophthalanilide*, m. p. 231·5°, and dissolves in sodium hydroxide to a yellow solution which reduces permanganate and yields homophthalic acid on acidification or boiling. When homophthalic acid is heated with phosphorus pentachloride and phosphoryl chloride, 3 : 3 : 4 : 4-*tetrachloro*-3 : 4-*dihydro*iso*coumarin*, m. p.

122°, is obtained, which reacts with aniline to produce a chlorine-free *anilide*, m. p. 225°. The chlorine atoms are remarkably inert, and hydrolysis in boiling aqueous-alcoholic sodium hydroxide, which yielded phthalonic acid (*compound*, m. p. 239°, with *p*-nitrophenylhydrazine), was very slow.

R. K. CALLOW.

Action of dibromotetracarboxylic esters on sodium derivatives of ethyl malonate, ethyl ethanetetracarboxylate, and analogous substances. J. J. LENNON and W. H. PERKIN, jun. (J.C.S., 1928, 1513—1526).—Compounds of the type of $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylic esters (Perkin and Prentice, J.C.S., 1891, **69**, 822; cf. Gregory and Perkin, *ibid.*, 1903, **83**, 782; 1905, **87**, 358) react with sodium derivatives intramolecularly rather than intermolecularly, yielding, in this case, with ethyl sodiomalonate, ethyl *cyclo*pentane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate. A number of reactions of this type have now been investigated. Ethyl dibromomalonate and ethyl disodioethanetetracarboxylate interact in alcoholic solution with formation of ethyl ethylenetetracarboxylate in good yield. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, m. p. 55°, and ethyl sodiomalonate yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate and ethyl disodioethanetetracarboxylate yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate, m. p. 83—85°, and ethyl sodiomalonate yield ethyl ethanetetracarboxylate and ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate, *cis-cyclo*butane-1 : 2-dicarboxylic anhydride, b. p. 165—170°/20 mm., m. p. 71—73° (acid, m. p. 136—138°), being isolated after hydrolysis. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate and ethyl disodioethanetetracarboxylate yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate and ethyl disodiobutane-$\alpha\alpha\delta\delta$-tetracarboxylate yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate alone.

The mechanism of these reactions is discussed. An intramolecular reaction, where possible, will always be favoured in comparison with an intermolecular reaction. In this case the substances are of the type of bromomalonic esters, $CRBr(CO_2Et)_2$, in which the bromine is "avid of electrons" and capable of substituting itself for hydrogen in suitably reactive molecules. The above reactions are considered to consist in rapid bromination of substituted sodiomalonic esters by substituted bromomalonic esters. There then follows, on the one hand, double decomposition of the normal type, and, on the other, intramolecular condensation.

Experiments were made to confirm these views. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate brominated boiling phenol, and the product, on hydrolysis, yielded *propane-$\alpha\alpha\gamma$-tricarboxylic acid*, m. p. 125°, which lost carbon dioxide at 150—160°, yielding glutaric acid. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate yielded similarly ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate, which gave adipic acid on hydrolysis. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate in alcohol with β-naphthol and sodium ethoxide yielded a product in large amount from which *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylic acid, m. p. 210—212° (effervescence), was obtained by hydrolysis.

The abnormal behaviour of ethyl $\alpha\epsilon$-disodiopentane-$\alpha\alpha\gamma\gamma\epsilon\epsilon$-hexacarboxylate previously noted (Bottomley and Perkin, J.C.S., 1900, **77**, 298) again occurs in reaction with ethyl $\alpha\beta$-dibromopropionate, when it yields ethyl *cyclo*pentanepentacarboxylate (identified by conversion into *trans-cyclo*pentane-1 : 2 : 4-tricarboxylic acid), and ethyl paramethylenemalonate. The first stage of this reaction is probably decomposition into ethyl paramethylenemalonate and ethyl disodiopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, and the latter then reacts with the ethyl $\alpha\beta$-dibromopropionate.

R. K. CALLOW.

2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-Dibromophenylhydrazines, *p*-bromophenylmethylhydrazine and their derivatives with aldehydes and ketones. E. VOTOČEK and R. LUKES (Chem. Listy, 1928, **22**, 217—225).—The following 2 : 5-*dibromophenylhydrazones* were prepared: acetone, m. p. 73°, benzaldehyde, m. p. 79°, furfuraldehyde, m. p. 104°, arabinose, m. p. 170—175°, rhamnose, m. p. 184°, galactose, m. p. 207°, and the corresponding *glucosazone*, m. p. 228—229°. The following 3 : 5-*dibromophenylhydrazones* were prepared: acetone, m. p. 85—86°, benzaldehyde, m. p. 106—107°, furfuraldehyde, m. p. 116°, and dextrose, m. p. 172°. 2 : 3-*Dibromophenylhydrazine*, m. p. 112° (*benzylidene* derivative, m. p. 106°), and 2 : 6-*dibromophenylhydrazine*, m. p. 110° (*benzylidene* derivative, m. p. 51—52°; *furfurylidene* derivative, m. p. 62°), were prepared. as-p-*Bromophenylmethylhydrazine*, m. p. 33°, was prepared by bromination of phenylmethylhydrazine, and also, in order to establish the position of the bromine atom, from *p*-bromoaniline, by way of p-*bromophenylmethylnitrosoamine*, m. p. 74 ; the corresponding *hydrazone* of benzaldehyde, m. p. 106—107°, and the *osazone* of lævulose, m. p. 153°, were prepared. The above bromohydrazones are in no way better for the identification of sugars than those commonly used.

R. TRUSZKOWSKI.

Behaviour of vanillin towards alkali sulphites and hydrogen sulphites. G. ROMEO and F. PIRRONE (Annali Chim. Appl., 1928, **18**, 189—193).—Vanillin behaves abnormally towards sulphites and hydrogen sulphites, and when the authors' method for determining aldehydes is applied to it (B., 1925, 970), the standard sulphite solution undergoes, not a diminution, but an increase in acidity corresponding with one equivalent per mol. of vanillin. Probably the aldehyde group first reacts with formation of a sulphonate, the sodium atom then migrating from the sulphonic group to the phenolic hydroxyl with formation of a readily hydrolysable hydrosulphonic acid. Thus, with sodium hydrogen sulphite, the reactions would be: $OH{\cdot}C_6H_3(OMe){\cdot}CHO+NaHSO_3 \longrightarrow$

$$OH{\cdot}C_6H_3(OMe){\cdot}CH(OH){\cdot}SO_3Na \longrightarrow$$
$$ONa{\cdot}C_6H_3(OMe){\cdot}CH(OH){\cdot}SO_3H \longrightarrow$$

$ONa{\cdot}C_6H_3(OMe){\cdot}CHO+H_2SO_3$, and with sodium sulphite, $OH{\cdot}C_6H_3(OMe){\cdot}CHO+Na_2SO_3+H_2O \longrightarrow$

$$OH{\cdot}C_6H_3(OMe){\cdot}CH(OH){\cdot}SO_3Na+NaOH \longrightarrow$$
$$ONa{\cdot}C_6H_3(OMe){\cdot}CHO+NaHSO_3+H_2O.$$

T. H. POPE.

Action of diazomethane on piperonal. E. Mosettig (Ber., 1928, **61**, [*B*], 1391—1395).—Piperonal is converted by diazomethane in presence of methyl alcohol into a mixture of piperonylacetone (semicarbazone, m. p. 163—165°), acetylpiperone, m. p. 87—88·5° (semicarbazone, m. p. 239—240°), and, mainly, a pleasant-smelling liquid, $C_{10}H_{10}O_3$, b. p. 140—143°/9 mm., possibly α-3 : 4-methylenedioxyphenylpropane αγ-oxide, which does not possess ketonic properties. If the reaction is effected in ethereal solution, the main product is acetylpiperone, whilst the substance $C_{10}H_{10}O_3$ is formed only in minimal amount. H. Wren.

Three-carbon system. XVII. *cyclo*Hexylideneacetone and *cyclo*hexylidenemethyl ethyl ketone. A. H. Dickins, W. E. Hugh, and G. A. R. Kon (J.C.S., 1928, 1630—1638).—The reaction of *cyclo*hexylideneacetyl chloride with zinc ethyl iodide and decomposition of the product with ice and carbon dioxide yielded cyclo*hexylidenemethyl ethyl ketone* (I), which was purified by distillation and conversion into the semicarbazone, m. p. 191° (cf. Kon and Narayanan, A., 1927, 878). The regenerated ketone had b. p. 112°/22 mm., $d_4^{18.1}$ 0·93810, 1·48945, $[R_L]_D$ 46·82. Occasionally a (possibly stereoisomeric) *semicarbazone*, m. p. 167°, yielding the same ketone, was produced. By the action of zinc ethyl iodide on Δ^1-*cyclo*hexenylacetyl chloride, Δ^1-cyclo*hexenylmethyl ethyl ketone*, (II), b. p. 107°/22 mm., $d_4^{17.5}$ 0·93020, $n_D^{17.5}$ 1·47320, $[R_L]_D$ 45·89, was prepared, being purified through its semicarbazone, m. p. 153° (Kon, A., 1926, 952). cyclo*Hexylideneacetone* (III), b. p. 89°/12·5 mm., $d_4^{19.0}$ 0·94931, $n_D^{19.0}$ 1·49128, $[R_L]_D$ 42·16 (*semicarbazone*, m. p. 180°), was prepared similarly to (I), using zinc methyl iodide. Δ^1-*cyclo*Hexenylacetone (IV) (cf. Wallach, A., 1913, i, 182; Kon, J.C.S., 1921, **119**, 816) was prepared from *cyclo*hexenylacetyl chloride in the same way. The compounds (I) and (II) were previously obtained as an equilibrium mixture (Kon and Nutland, A., 1927, 153). The equilibria of this pair of isomerides and of (III) and (IV) were studied quantitatively by the method of Linstead and May (A., 1927, 1167). It was found that (I) and (III), although sensitive to mineral acids at the moment of formation, were scarcely affected by them when purified. Equilibration proceeded very slowly in the presence of small amounts of barium hydroxide, piperidine, or sulphuric acid. With sodium ethoxide in excess, equilibrium was established in 24 hrs. The equilibrium mixture of (I) and (II) contained 69% of (II), whilst that of (III) and (IV) contained 71% of (IV). R. K. Callow.

Carbon rings. XI. Rings containing ten, eleven, twenty, and twenty-two carbon atoms, and formation of aliphatic together with cyclic ketones by decomposition of metal salts of polymethylenedicarboxylic acids. L. Ruzicka, M. Stoll, and H. Schinz (Helv. Chim. Acta, 1928, **11**, 670—686; cf. this vol., 642).—The action of heat on yttrium nonane-αι-dicarboxylate gives, in addition to *cyclo*decanone (A., 1926, 615), some cyclo*eicosane-1 : 11-dione* (I), m. p. 49—51°, d_4^{59} 0·9232, n_D^{59} 1·4662 (*dioxime*, m. p. 147—148°), and methyl nonyl ketone (*semicarbazone*, m. p. 115°). When (I) is treated with benzaldehyde in presence of sodium ethoxide, the resulting product heated with sodium hydrogen sulphate at 200°, ozonised, and then esterified with methyl alcohol, there is obtained *dimethyl-ι-keto-octadecane-ασ-dicarboxylate*, m. p. 59—60°. Reduction of the free acid by Clemmensen's method yields *octadecane-ασ-dicarboxylic acid*, m. p. 119—121°, whilst similar reduction of (I) affords cyclo*eicosanone*, m. p. 58—59° (*semicarbazone*, m. p. 179—180°). Fractionation of the acidic hydrolysis products of Japan wax gives japanic acid (cf. Schaal, A., 1908, i, 3), now shown to be *nonadecane-ατ-dicarboxylic acid*, m. p. 111—113° (*dimethyl* ester, m. p. 56—57°). This acid is also obtained by electrolysis of a mixture of the sodium salts of methyl hydrogen tetradecane-αξ-dicarboxylate and Δ^ζ-octenecarboxylic acid, and subsequent oxidation with ozone of the resulting Δ^ν-docosenecarboxylic acid. The thorium salt of japanic acid yields *cyclo*eicosanone, which when oxidised with chromic anhydride and acetic acid yields a dicarboxylic acid, m. p. 102—104° (dimethyl ester, m. p. 51—53°), probably a mixture of octadecane- and heptadecane-dicarboxylic acids. Yttrium decane-ακ-dicarboxylate gives in addition to *cyclo*undecanone, 1% of cyclo*docosane*-1 : 12-*dione*, m. p. 55—56°, d_4^{61} 0·9114, n_D^{61} 1·4633 (*disemicarbazone*, decomp. 228—230°; *dioxime*, m. p. 151—153°), and methyl decyl ketone (*semicarbazone*, m. p. 104—105°). Oxidation of the benzylidene derivative of the diketone yields after esterification *dimethyl λ-ketoeicosane-αυ-dicarboxylate*, b. p. 240°/0·5 mm., m. p. 68—70°. Reduction of the free acid by Clemmensen's method gives *eicosane-αυ-dicarboxylic acid*, m. p. 120—122°.

During the preparation of *cyclo*-do-, tri-, penta-, hexa-, hepta-, and octa-decanones (*loc. cit.*), there are formed small quantities of methyl undecyl (*semicarbazone*, m. p. 115—116°), methyl dodecyl (*semicarbazone*, m. p. 115—117°), methyl tetradecyl, m. p. 38° (lit. m. p. 43°; *semicarbazone*, m. p. 117—118°), prepared by hydrolysis of ethyl tridecylacetoacetate with barium hydroxide solution, methyl pentadecyl (*semicarbazone*, m. p. 116—118°), methyl hexadecyl (*semicarbazone*, m. p. 114—116°), and methyl heptadecyl (*semicarbazone*, m. p. 117—119°) ketones. H. Burton.

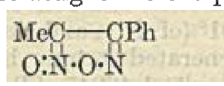
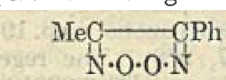
Carbon rings. XII. Preparation of methylated ketones containing fourteen, fifteen, and seventeen carbon atoms in the ring. L. Ruzicka, H. Schinz, and M. Pfeiffer (Helv. Chim. Acta, 1928, **11**, 686—700).—The action of heat on the thorium or yttrium salts of tetradecane-βν- and αν-, β-methyldodecane-αμ-, pentadecane-αξ-, hexadecane-βο-, β-methyltetradecane-αξ-, and βν-dimethyltetradecane-αξ-dicarboxylic acids does not furnish more than traces of cyclic ketones. Small amounts of methyl methyltetradecyl ketone (*semicarbazone*, m. p. 122°) and methyl βν-dimethyltetradecyl ketone (*semicarbazone*, m. p. 78—79°) were obtained from β-methyltetradecane-αξ- and βν-dimethyltetradecane-αξ-dicarboxylic acids, respectively. Yttrium γ-methyltridecane-αν-dicarboxylate furnishes 1-*methyl*cyclo*tetradecan-4-one*, b. p. 155°/12 mm., m. p. 28—29° (*semicarbazone*, m. p. 182—183°), together with a methyl methyltridecyl ketone, isolated as its *semicarbazone*, m. p. 118—119°. Methylation of *cyclo*-

pentadecanone with sodamide and methyl iodide yields 2-*methyl*cyclo*pentadecanone*, b. p. 171—173°/12 mm., d_4^{16} 0·9213, n_D^{16} 1·4812 (*semicarbazone*, m. p. 149—150°). Magnesium methyl iodide converts *cyclo*pentadecanone into 1-*methyl*cyclo*pentadecan*-1-*ol* (I), m. p. 85—86°, together with a *compound*, $C_{30}H_{56}O_2$ or $C_{30}H_{58}O_2$, m. p. 162°. Elimination of water from (I) by treatment with hot formic acid affords 1-*methyl*-Δ^1-cyclo*pentadecene*, b. p. 152—153°/12 mm., d_4^{20} 0·8697, n_D^{20} 1·4853, reduced by hydrogen in presence of platinum-black to *methyl*cyclo*pentadecane*, b. p. 147—148°/12 mm., d_4^{21} 0·8576, n_1^{21} 1·4735.

Thorium γ- and δ-methyltetradecane-αξ-dicarboxylates yield 1-*methyl*cyclo*pentadecan*-4-*one*, b. p. 125°/0·5 mm. (*semicarbazone*, m. p. 161—162°), and 1-*methyl*cyclo*pentadecan*-5-*one*, b. p. 125°/0·5 mm. (*semicarbazone*, m. p. 164°), respectively. From an optically active specimen of yttrium δ-methyltetradecane-αξ-dicarboxylate there was obtained *d*-1-methyl*cyclo*pentadecan-5-one, α_D in 30% alcohol +3·5°. Methylation of dihydrocivetone affords 2-*methyl*cyclo*heptadecanone*, b. p. 150°/0·5 mm. (*semicarbazone*, m. p. 142—143°). H. Burton.

Conversion of a C_6 into a C_5 ring by molecular transposition: isomerisation of the oxides of phenyl*cyclo*hexene and 1-phenyl-4-methyl-*cyclo*hexene. (Mlle.) J. Levy and J. Sfiras (Compt. rend., 1928, **187**, 45—47; cf. this vol., 410, 516).—When heated in presence of a trace of anhydrous zinc chloride 1-phenyl*cyclo*-Δ^1-hexene oxide affords 60% of 1-phenyl*cyclo*hexan-2-one (semicarbazone, m. p. 166°) and 9% of 1-*phenyl*cyclo*pentane*-1-*aldehyde*, b. p. 134°/15—16 mm. (*semicarbazone*, m. p. 196·5°), yielding on oxidation 1-*phenyl*cyclo*pentane*-1-*carboxylic acid*, m. p. 155—157° (*amide*, m. p. 108°). Similarly, 1-*phenyl*-4-*methyl*-$\Delta^{\sim}$-cyclo*hexene oxide*, m. p. 36°, b. p. 140—141°/15 mm. (obtained by the action of perbenzoic acid on 1-phenyl-4-methyl-Δ^2-*cyclo*hexene), is converted into 1-*phenyl*-4-*methyl*cyclo*hexan*-2-*one* (yield 55%) (*semicarbazone*, m. p. 217°), oxidised by permanganate to 1-benzoyl-3-methyl*cyclo*pentane-5-carboxylic acid, m. p. 56° (semicarbazone, m. p. 214°), and into 2% of 1-*phenyl*-3-*methyl*cyclo*pentane*-1-*aldehyde* (*semicarbazone*, m. p. 172°). 1-*Phenyl*-3-*methyl*cyclo*pentane*-1-*carboxylic acid* has m. p. 124°. Rupture of the oxide ring takes place always on the same side, the isomerisation being determined by the migration of an adjacent hydrogen or carbon atom to saturate the carbon atom previously linked with oxygen. R. Brightman.

Dioximes. L. G. Ponzio (Ber., 1928, **61**, [*B*], 1316—1328, and Gazzetta, 1928, **58**, 329—344).—A dioxime, m. p. 223°, isolated by the author must be added to the four isomeric dioximes of benzoyl *p*-methoxyphenyl ketone described by Meisenheimer, Lange, and Lamparter (A., 1925, i, 1073). It appears doubtful whether the α-form, m. p. 206—207°, is homogeneous, and the doubt extends also to the other compounds, so that the work cannot be regarded as an experimental verification of the Hantzsch–Werner theory. It is considered that this theory is not applicable to the dioximes of diketones, CH_3·CO·CO·Ar, which have been obtained in only two forms. Thus β-phenylmethylglyoxime, m. p. 238—239° (partial decomp.), has a higher m. p. than the α-compound, yields a complex nickel salt insoluble in dilute acetic acid, and can be obtained by heating the α-variety. It is converted by dehydrogenation into two *peroxides*, CH_3·[$C_2N_2O_2$]·Ar, m. p. 96° and 62°, respectively; the former is reduced exclusively to the α-glyoxime, whereas the latter is converted entirely into the *γ-glyoxime*, which passes into the β-compound at the atmospheric temperature. The peroxides are not isomorphous and differ widely from one another in chemical behaviour. That of higher m. p. is irreversibly transformed when heated into that of lower m. p.; it reacts vigorously with phosphorus pentachloride giving phenylmethylfuroxan; with sodium ethoxide it affords an isomeric *compound*, $C_9H_8O_2N_2$, m. p. 178—179° (decomp.), soluble in bases. The glyoxime of lower m. p. does not react with phosphorus pentachloride or sodium ethoxide and cannot be transformed into the isomeride of higher m. p. The constitutions (I) and (II) are assigned to the peroxides of higher and lower

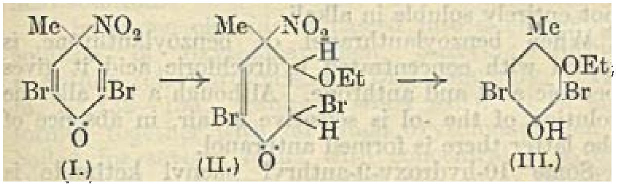
(I.)   (II.)

m. p., respectively. Since the β-glyoxime affords simultaneously the furoxan (I) and the peroxide (II) it must have both the *amphi*- and *syn*-configuration in the sense of the Hantzsch–Werner theory, whilst the α-glyoxime must have the *amphi*-configuration, since it yields exclusively the peroxide (II). These difficulties are avoided if one oximino-group is considered capable of behaving towards certain reagents in the nitron form. For the β-glyoxime the equilibrium MeC(:NH:O)·CPh:N·OH ⇌ MeC(:N·OH)·CPh:N·OH is assumed, whereas the α- and γ-glyoximes receive the constitutions MeC(:NH:O)·CPh:N·OH and MeC(:N·OH)·CPh:N·OH, respectively.

The following compounds are also described: β-anisylmethylglyoxime, m. p. 213—214° (partial decomp.); anisylmethylfuroxan, m. p. 99° (*bromo*-derivative, m. p. 109—110°; *nitro*-compound, m. p. 88—89°); *anisyl methyl peroxide*, m. p. 78—79°; *α-anisylmethylglyoxime*, m. p. 125° (*nickel* salt; *dibenzoyl* derivative, m. p. 157—158°); *bromoanisyl methyl peroxide*, m. p. 115—116°; *nitroanisyl methyl peroxide*, m. p. 112°; β-p-*bromophenylmethylglyoxime*, m. p. 223—224° (partial decomp.), by the successive action of amyl nitrite and hydroxylamine on *p*-bromophenyl ethyl ketone; p-*bromophenylmethylfuroxan*, m. p. 108—109°; p-*bromophenyl methyl peroxide*, m. p. 88—89°. H. Wren.

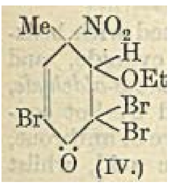
Quinonitroles and quinamines. K. Fries and G. Oehmke (Annalen, 1928, **462**, 1—24).—That quinonitroles are nitro-compounds and not, as suggested by von Auwers, the nitrous esters of the corresponding ψ-quinols is proved by the following experiments: When 3 : 5-dibromo-1 : 4-methylquinonitrole (I) is treated with alcoholic potassium hydroxide for 10 sec., the resulting solution then being acidified, there is produced 3 : 5-*dibromo*-1-*nitro*-2-*ethoxy*-4-*keto*-Δ^5-*tetrahydrotoluene* (II), m. p. 145° (elimination of nitrous fumes), the constitution of which follows (1) from its non-reactivity towards reagents for hydroxyl groups, and (2) from its reduc-

tion by zinc dust and hydrochloric and acetic acids, to 3-bromo-*p*-cresol. It is converted by hydrogen bromide in acetic acid into bromonitro-*p*-cresol. Treatment of (I) for 2 days with alcoholic alkali, or of (II) with boiling 2*N*-sodium hydroxide, gives 3 : 5-*dibromo-2-ethoxy-*p*-cresol* (*dibromocresorcinol ethyl ether*) (III), m. p. 91° (*acetyl* derivative, m. p. 67°), which is converted by hydrogen bromide in acetic acid into 3 : 5-dibromocresorcinol (*acetyl* derivative, m. p. 67°), and is evidently formed from (I) by the annexed scheme :



(I.) (II.) (III.)

When (II) is allowed to remain in cold pyridine solution for 1 day, there are formed ethyl alcohol, 3-bromo-5-nitro-*p*-cresol, and 3 : 3 : 5-*tribromo-1-nitro-2-ethoxy-4-keto-Δ^5-tetrahydrotoluene* (IV), m. p. 92°, reduced by zinc dust and hydrochloric acid to 3 : 5-dibromo-*p*-cresol, but not converted into a cresorcinol derivative by alkali, no doubt owing to its inability to undergo enolisation.



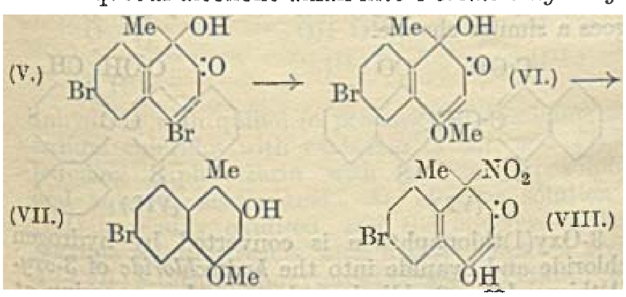
(IV.)

3 : 5-*Dibromo-1-nitro-2-methoxy-4-keto-Δ^5-tetrahydrotoluene* has m. p. 166° (elimination of nitrous fumes); 3 : 3 : 5-*tribromo-1-nitro-2-methoxy-4-keto-Δ^5-tetrahydrotoluene* has m. p. 105°; 3 : 5-*dibromo-2-methoxy-*p*-cresol* (*dibromocresorcinol methyl ether*) has m. p. 60° (*acetyl* derivative, m. p. 104°).

The above 3 : 5-dibromocresorcinol ethyl ether is transformed by dilute nitric acid or by sodium nitrite in acetic acid into 3-*bromo-5-nitro-2-ethoxy-*p*-cresol*, m. p. 73°, and by fuming nitric acid into 3 : 5-*dibromo-2-ethoxy*(?)-1 : 4-*methylquinonitrole*, m. p. 75° (elimination of nitrous fumes), which with water or alcohol gives the above nitro-derivative, m. p. 73°.

An improved method is given for the preparation of the 3 : 5-dibromo-1 : 4-methyl-ψ-quinol, which is converted by alcoholic alkali into tarry products.

When 4 : 6-dibromo-$\alpha\beta$-naphthamethyl-ψ-quinol (V) is treated with methyl-alcoholic sodium hydroxide there is formed 6-*bromo-4-methoxy-$\alpha\beta$-naphthamethyl-ψ-quinol* (VI), m. p. 155° (*acetyl* derivative, m. p. 168°; (corresponding 4-*ethoxy-ψ-quinol*, m. p. 144°); the methoxy- and ethoxy-ψ-quinols are converted by warm aqueous alcoholic alkali into 6-*bromo-4-hydroxy-*

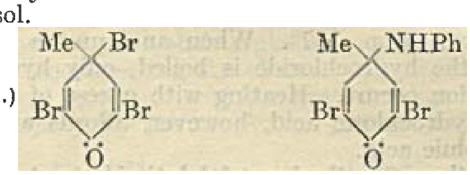


(V.) (VI.) (VII.) (VIII.)

$\alpha\beta$-naphthamethyl-ψ-quinol, m. p. 182° (*diacetyl* derivative, m. p. 147°), whilst reduction of the methoxy-quinole with zinc dust in boiling glacial acetic acid produces 6-*bromo-2-hydroxy-4-methoxy-α-methylnaphthalene* (VII), m. p. 143° (*acetyl* derivative, m. p. 125°). If the quinonitrole corresponding with (V) were the nitrous ester of (V), it should be converted by alcoholic alkali into (VI) and so on. Actually, however, it affords 6-*bromo-4-hydroxy-$\alpha\beta$-naphthamethylquinonitrole* (VIII), m. p. 195° (decomp.), which is converted by boiling alcoholic potassium hydroxide or by boiling glacial acetic acid into an *isomeride*, m. p. 275° (decomp.).

When 1 : 3 : 5-tribromo-4-keto-1 : 4-dihydrotoluene (IX) (improved preparation from *p*-cresol described) is kept, or more rapidly when it is heated to its m. p. (105°), it passes into 3 : 5-dibromo-*p*-cresol ψ-bromide (3 : 5-dibromo-4-hydroxybenzyl bromide), whilst when it is treated with alcoholic aniline it gives 3 : 5-*dibromo-1-anilino-4-keto-1 : 4-dihydrotoluene* (X), reduced by zinc dust and acetic acid to 3 : 5-dibromo-*p*-cresol.

(IX.)



(X.)

By similar processes, 3 : 5-*dichloro-1-bromo-4-keto-1 : 4-dihydrotoluene* is prepared from 3 : 5-dichloro-*p*-cresol. It has m. p. 106° and is convertible (1) into 3 : 5-*dichloro-*p*-cresol ψ-bromide* (3 : 5-*dichloro-4-hydroxybenzyl bromide*), m. p. 120°, (2) using zinc dust and hydrochloric and acetic acids, into 3 : 5-dichloro-*p*-cresol, and (3) into 3 : 5-*dichloro-1-anilino-4-keto-1 : 4-dihydrotoluene*, m. p. 148° (decomp.).

3 : 5-*Dibromo-1-o-toluidino-* and 3 : 5-*dibromo-1-p-toluidino-4-keto-1 : 4-dihydrotoluene* have m. p. 112° (decomp.) and 105° (decomp.), respectively.

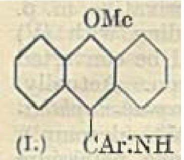
When the quinamine (X) is treated with hydrochloric–acetic acid it is converted into 2 : 6-*dibromo-4′-amino-4-methyldiphenyl ether*, $NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_2MeBr_2$, m. p. 120° (*acetyl* derivative, m. p. 180°). The similarly obtained 2 : 6-*dibromo-4′-amino-4 : 3′-dimethyldiphenyl ether*, m. p. 122·5° (*acetyl* derivative, m. p. 211°), and 2 : 6-*dichloro-4′-amino-4-methyldiphenyl ether*, m. p. 99° (*acetyl* derivative, m. p. 187°), are described. The last-named acetyl compound results when the dichlorophenylquinamine is treated with acetic anhydride and sulphuric acid.

Treatment of 5-bromo-4-*m*-xylenol in glacial acetic acid with bromine in presence of sodium acetate gives the unstable 1 : 5-*dibromo-4-keto-Δ^5-dihydro-*m*-xylene*, m. p. 63°, passing when heated at 100° into the *ψ-bromide* (3-*bromo-4-hydroxy-5-methylbenzyl bromide*), m. p. 104°, and converted by alcoholic aniline into 5-*bromo-1-anilino-4-keto-Δ^5-dihydro-*m*-xylene*, m. p. 107° (blackening). The last with acetic and hydrochloric acids affords 6-*bromo-4′-amino-2 : 4-dimethyldiphenyl ether*, m. p. 81° (*acetyl* derivative, m. p. 163°).

Similarly are obtained 5-*bromo-1-o-toluidino-4-keto-Δ^5-dihydro-*m*-xylene*, m. p. 103° (decomp.), and 6-*bromo-4′-amino-2 : 4 : 3′-trimethyldiphenyl ether*, m. p. 128° (*acetyl* derivative, m. p. 187°). E. E. TURNER.

Transformation products of anthranol and oxythionaphthen. F. KROLLPFEIFFER [with F. BRANSCHEID, F. THORN, and K. SCHNEIDER] (Annalen,

1928, **462**, 46—72).—The ease of formation of ketimides of the general formula (I) by the method previously employed (A., 1924, i, 184) is affected considerably by the nature of substituents in the radical Ar.



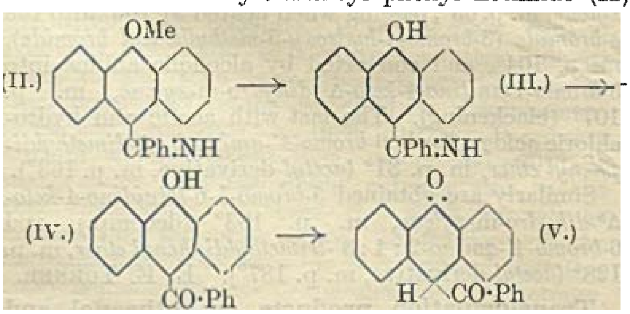
10-Methoxy-9-anthryl phenyl ketimide forms an additive *compound* with benzonitrile and hydrogen chloride, viz., $C_{22}H_{17}ON,HCl,PhCN$, but not with aceto-, phenylaceto-, or *p*-toluo-nitrile. When the ketimide is heated with acetic anhydride it gives an *acetyl* derivative, m. p. 204—205°, hydrolysed by hydrochloric acid to anthrone and benzoic acid. The corresponding *benzoyl* derivative has m. p. 206—207°.

10-*Methoxy*-9-*anthryl* p-*tolyl ketimide*, m. p. 150°, is produced in poor yield from *p*-toluonitrile (*o*-toluonitrile fails to give a ketimide): it forms a *hydrochloride*, an additive *compound* with benzonitrile (although not with *p*-toluonitrile), and gives an *acetyl* derivative, m. p. 147°. When an aqueous suspension of the hydrochloride is boiled, only hydrolytic dissociation occurs. Heating with excess of concentrated hydrochloric acid, however, affords anthrone and *p*-toluic acid.

10-*Methoxy*-9-*anthryl* m-*tolyl ketimide* (*acetyl* derivative, m. p. 199—200°), m. p. 127°, is formed in poor yield from *m*-toluonitrile, whilst 10-*methoxy*-9-*anthryl benzyl ketimide*, m. p. 202—203°, is somewhat unstable and is readily converted by warm hydrochloric acid into anthrone and phenylacetic acid. 10-*Methoxy*-9-*anthryl* p-*chlorophenyl ketimide*, readily formed, has m. p. 147—148°, gives a *hydrochloride*, an additive *compound* with benzonitrile (although none with p-*chlorobenzonitrile*), and forms an *acetyl* derivative, m. p. 176—177°. *p*-Methoxybenzonitrile fails to give a ketimide, but, from propionitrile, 10-*methoxy*-9-*anthryl ethyl ketimide* (*acetyl* derivative, m. p. 201—202°) is obtained as *hydrochloride*.

Careful study of the hydrolysis of 10-methoxy-9-anthryl *p*-chlorophenyl ketimide shows that cold concentrated sulphuric acid effects hydrolysis of ketimide to ketone without simultaneous removal of the *p*-chlorophenyl group. Thus, whilst boiling a solution of the hydrochloride in acetic acid gives anthrone and *p*-chlorobenzoic acid, products formed in other, similar, ways, cold sulphuric acid gives p-*chlorobenzoylanthrone*, m. p. 206—208°, acidification of the alkaline solution of which produces p-*chlorobenzoylanthranol*.

When 10-methoxy-9-anthryl phenyl ketimide (II)



is treated with cold sulphuric acid, the *sulphate* of 10-*hydroxy*-9-*anthryl phenyl ketimide* (III) (*diacetyl* derivative, m. p. 206—207°) is isolable if the product obtained by pouring on ice is at once collected, whilst if the latter is left in aqueous suspension for 2 days, benzoylanthranol (IV) results, together with some *benzoylanthrone* (V), m. p. 155—157°. When the last is melted, some benzoylanthranol is formed. Benzoylanthranol [*methyl ether*, m. p. 175—177° (decomp.); *acetyl* derivative, m. p. about 194° (impure)] has no definite m. p. It sinters at 125° and melts at 145° with slow heating; when heated rapidly it melts at about 140°, but the fused mass is not entirely soluble in alkali.

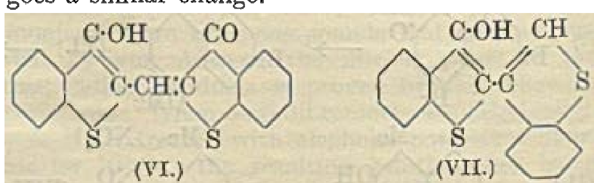
When benzoylanthranol or benzoylanthrone is boiled with concentrated hydrochloric acid it gives benzoic acid and anthrone. Although a hot alkaline solution of the -ol is sensitive to air, in absence of the latter there is formed anthranol.

Some 10-hydroxy-9-anthryl phenyl ketimide is formed during the preparation of the corresponding 10-methoxy-derivative, and a method for its isolation is given.

When anthranol methyl ether is treated with benzene, aluminium chloride, hydrogen cyanide, and hydrogen chloride, 10-*methoxyanthracene*-9-*aldehyde*, m. p. 165°, is formed. It is converted by hot concentrated hydrochloric acid into a mixture of anthrone, dianthrone, anthraquinone, and formic acid, whilst hydrochloric–acetic acid gives dianthrone after prolonged boiling, but a quantitative yield of anthranol after heating for 3 hrs. The aldehyde gives a *phenylhydrazone*, m. p. 138—139°, and an *oxime*, m. p. 142—143°. 10-*Ethoxyanthracene*-9-*aldehyde*, m. p. 93—94°, is formed similarly but in poorer yield.

Action of chloroform on a boiling alcoholic-alkaline solution of anthrone gives 9-(10′-*hydroxy*-9′-*anthrylmethylene*)*anthrone*, together with a *substance*, $C_{30}H_{18}O_2Cl_2$, m. p. 226—227°, for which two alternative formulæ are proposed (containing the radical $\cdot CHCl_2$). The same substance is obtained when the methylene compound is heated with alkaline-alcoholic chloroform.

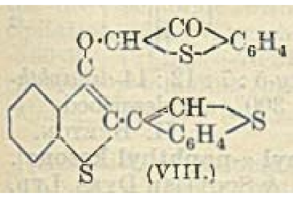
When a nitrobenzene solution of the methylene compound (*methyl ether*, m. p. 221—222°) is boiled, oxidation occurs, with formation of 9 : 9′-*dianthronylidenemethane*, m. p. 360°, reducible, if care is taken, to the substance from which it is prepared. The acetyl derivative of 9-(10′-hydroxy-9′-anthrylmethylene)anthrone is not oxidised in boiling nitrobenzene solution. Under similar conditions 3-oxy(1)thionaphthen-2-aldehydethioindogenide (VI) affords an oxidation *product* of type different from the above methane, and its *acetyl* derivative, m. p. 220°, undergoes a similar change.



3-Oxy(1)thionaphthen is converted by hydrogen chloride and cyanide into the *hydrochloride* of 3-*oxy*-(1)*thionaphthen*-2-*aldimine*, the free base passing at 135—155° into the above indogenide, and affording an *acetyl* derivative, m. p. 198°. When the aqueous

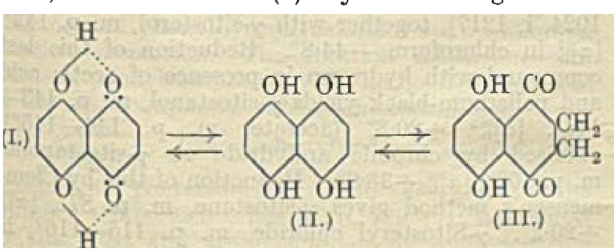
solution of the above hydrochloride is boiled, 3-oxy-(1)thionaphthen-2-aldehyde is formed (*methyl ether*, from 3-oxy(1)thionaphthen methyl ether, has m. p. 84—85°, b. p. 185°/14 mm., and gives a *phenylhydrazone*, m. p. 117—118°). When oxythionaphthen is heated with methyl iodide and alkali methoxide at 100°, the methyl ether is not formed, but, instead 3-*methoxy*(1)*thionaphthen-2-aldehyde-2'-indogenide*, m. p. 218—220°, also formed when (VI) is similarly methylated, and when 3-oxy(1)thionaphthen is condensed with its 2-aldehyde in alcoholic hydrochloric acid solution.

If hydrogen chloride is passed into a chloroform solution of oxythionaphthen, 3-oxy-2 : 3'-dithionaphthen (cf. Bartholomaus, Diss., Marburg, 1911), m. p. 132—133°, results (*sodium* salt). It is also formed together with tar when oxythionaphthen is boiled for several hours with concentrated hydrochloric acid, and forms a *methyl ether*, m. p. 96—97°.


(VIII.)

When bromine is added to a carbon disulphide solution of oxythionaphthen, the 3-*oxy*(1)*thionaphthenyl-2-ether* of 3-*oxy*-2 : 3'-*dithionaphthen* (VIII), m. p. 198—199°, is formed, through the intermediate formation of 2-bromo-3-oxy(1)thionaphthen, not isolated. E. E. Turner.

Constitution and mode of reaction of polynuclear polyhydroxyquinones. Naphthazarin and quinizarin. K. Zahn and P. Ochwat (Annalen, 1928, **462**, 72—97).—Maleic anhydride condenses with quinol in presence of aluminium and sodium chlorides at 200—220° to give naphthazarin, a fact which definitely establishes this substance as 5 : 8-dihydroxy-α-naphthaquinone (I) (cf. Wheeler and Edwards, A., 1916, i, 392; Dimroth and Ruck, A., 1926, 297). When naphthazarin is reduced with zinc dust and dilute sulphuric acid in presence of ether, 1 : 4 : 5 : 8-*tetrahydroxynaphthalene* (II), m. p. 190°, is formed, and when this substance is boiled in alcoholic hydrochloric acid solution, air being excluded, it passes into the *keto*-form (III), viz., 5 : 8-*dihydroxy*-1 : 4-*diketotetrahydronaphthalene*, m. p. 153—154°, also obtained (1) by condensing succinic

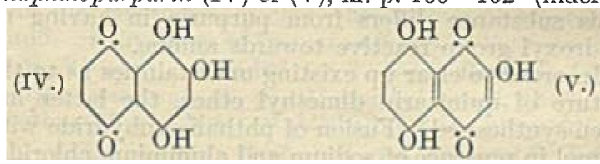

(I.) (II.) (III.)

anhydride with quinol in presence of aluminium and sodium chlorides with exclusion of air, and (2) by reducing naphthazarin with sodium hyposulphite and aqueous acetic acid. An alkaline solution of (III) is readily oxidised, and the aqueous-alcoholic alkaline solution reacts with methyl sulphate giving 1 : 4 : 5 : 8-tetramethoxynaphthalene (Perkin and Weizmann, J.C.S., 1906, **89**, 1659). The tetrahydroxynaphthalene described by Wheeler and Edwards (*loc. cit.*) must be an isomeride or a more fully hydroxylated naphthalene.

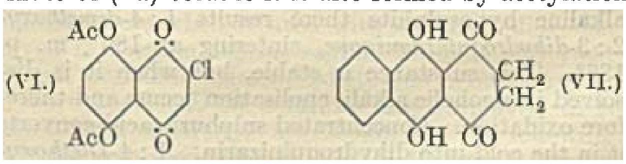
When the diketone is treated with acetic anhydride and a little concentrated sulphuric acid it gives 5 : 8-*diacetoxy*-1 : 4-*diketotetrahydronaphthalene*, readily converted into (III) by alkali. On the other hand, when naphthazarin diacetate is reduced, 1 : 4-dihydroxy-5 : 8-diacetoxynaphthalene is formed (cf. Wheeler and Edwards). Either acetyl compound or either dihydronaphthazarin passes into 1 : 4 : 5 : 8-tetra-acetoxynaphthalene when heated with acetic anhydride and sodium acetate.

Fusion of the diketone with phthalic anhydride and sodium and aluminium chlorides produces *tetrahydroxynaphthacenequinone*, m. p. above 300°, showing that di-enolisation precedes condensation.

When naphthazarin, for which formula (I) is suggested, is oxidised with nitric acid it gives oxalic acid, whilst in glacial acetic acid solution with lead tetra-acetate, 1 : 4 : 5 : 8-*naphthadiquinone*, decomp. 220°, results. The latter passes into naphthazarin when heated in alcohol or glacial acetic acid, reducing agents also effecting the change very rapidly. Concentrated sulphuric acid converts the diquinone into *naphthopurpurin* (IV) or (V), m. p. 160—162° (indef.),


(IV.) (V.)

also produced when naphthazarin is oxidised with manganese dioxide and sulphuric acid. *Naphthopurpurin triacetate* is formed by the action of acetic anhydride and sulphuric acid on the diquinone, which with hydrogen chloride in acetic acid gives chloronaphthazarin, m. p. 178—179°. Addition of chlorine in glacial acetic acid to naphthazarin diacetate, or acetylation of naphthazarin dichloride, affords *diacetoxynaphthaquinone dichloride*, m. p. 136—137°, decomposed by boiling alcohol to give *chloronaphthazarin diacetate*, m. p. 193—194°, which must be (VI) because it is also formed by acetylation


(VI.) (VII.)

of the above chloronaphthazarin. When 1 : 4 : 5 : 8-naphthadiquinone is treated with chlorine in chloroform solution, the *dichloride*, decomp. 252—254°, is formed, and this substance is converted by potassium iodide or by sulphur dioxide into naphthazarin.

Fusion of 1 : 4-dihydroxynaphthalene with maleic anhydride and sodium and aluminium chlorides at 220° affords quinizarin, which is therefore 9 : 10-dihydroxy-1 : 4-anthraquinone. Reduction of quinizarin, followed by acetylation, produces 1 : 4-*diacetoxy*-2 : 3-*dihydroanthraquinone*, m. p. 215°, also obtained by reducing quinizarin with zinc dust and acetic acid. Excess of acetyl chloride and pyridine in the former process gives rise to 1 : 4 : 9 : 10-*tetra-acetoxyanthracene*, m. p. 240—242°. On the other hand, if dihydroquinizarin or the above diacetyl derivative is heated

(b. p.) with acetic anhydride and sodium acetate, the chief product is 1 : 4 : 9-*triacetoxyanthracene*, m. p. 210—211°.

Both chlorine atoms in 5 : 8-dichloroquinizarin are labile, so that when the latter substance is heated with aniline in presence of sodium acetate, 5 : 8-*dianilino*-1 : 4-*dihydroxyanthraquinone*, m. p. 258—260°, is formed. Reduction of dichloroquinizarin with tin and acetic–hydrochloric acid affords the *dichlorodihydroquinizarin*, reacting with aniline in presence of boric acid to give 5 : 8-*dichloro*-1 : 4-*dianilinoanthraquinone*, m. p. 234—235°. Reduction of this substance with stannous chloride in acetic acid affords dihydroquinizarin (VII).

Reduction of 2-methylquinizarin with tin and hydrochloric acid gives 2-*methyldihydroquinizarin*, m. p. 114—115°, converted by *p*-toluidine in presence of boric acid at 125°, followed by air oxidation, into 4-p-*toluidino*-1-*hydroxy*-2-*methylanthraquinone*, m. p. 178°. Oxidation of 2-methylquinizarin with lead tetra-acetate gives 2-*methyl*-1 : 4 : 9 : 10-*anthradiquinone*, from which by the acetic anhydride–sulphuric acid method 2-*methylpurpurin* (*acetyl* derivative, m. p. 204—206°; *triacetate*, m. p. 207—208°) is obtained (cf. Eder and Manoukian, A., 1926, 407). This substance differs from purpurin in having no hydroxyl group reactive towards aniline.

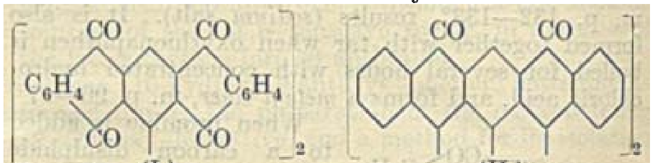
In order to clear up existing uncertainties as to the nature of quinizarin dimethyl ether, the latter has been synthesised. Fusion of phthalic anhydride with quinol in presence of sodium and aluminium chlorides at 120—125° (higher temperatures give quinizarin) produces 2 : 5-*dihydroxybenzophenone*-2′-*carboxylic acid*, m. p. 189—190°. The *dimethyl ether* (m. p. 161—162°) of the latter, prepared using methyl sulphate and alkali, passes into quinizarin dimethyl ether, *i.e.*, 1 : 4-dimethoxyanthraquinone, when dissolved in warm concentrated sulphuric acid. Alkylation of quinizarin is readily effected using the alkyl *p*-toluenesulphonate in trichlorobenzene solution in presence of sodium carbonate at 160—170°. The *diethyl ether* so obtained has m. p. 170—171°.

When quinizarin dimethyl ether is reduced with alkaline hyposulphite there results 1 : 4-*dimethoxy*-2 : 3-*dihydroanthraquinone*, sintering at 180°, m. p. 186°. This substance is stable, but when it is dissolved in alcoholic alkali, enolisation occurs and therefore oxidation. Concentrated sulphuric acid converts it in the cold into dihydroquinizarin. 1 : 4-*Diethoxy*-2 : 3-*dihydroanthraquinone* has m. p. 174—176°.

Acetic anhydride in presence of a little concentrated sulphuric acid converts dihydroquinizarin dimethyl and diethyl ethers, respectively, into 1 : 4-*dimethoxy*- (m. p. 225°) and 1 : 4-*diethoxy*-9 : 10-*diacetoxyanthracene*, m. p. 203—205°.

E. E. TURNER.

Dibenzoylxylenes and dinaphthanthradiquinones. IV. H. DE DIESBACH and T. JANZEN (Helv. Chim. Acta, 1928, **11**, 724—730).—2-*Amino*-4 : 6-*dibenzoyl*-m-*xylene*, m. p. 188·5° (*acetyl* derivative, m. p. 190·5°), obtained by reducing the corresponding nitro-derivative (A., 1924, i, 1082) with iron powder and acetic acid, is converted by the Sandmeyer reaction into 2-*chloro*-4 : 6-*dibenzoyl*-m-*xylene*, m. p. 92·5° (2-*bromo*-derivative, m. p. 121—122°). Consecutive oxidation of this with nitric acid (*d* 1·15) at 170° in a sealed tube, and alkaline potassium permanganate affords 2-*chloro*-4 : 6-*dibenzoyl*iso*phthalic acid*, m. p. 155—157° (2-*bromo*-derivative, m. p. 206°), which when heated with concentrated sulphuric acid at 160—200° yields 6-*chloro*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, sublimes at 320° (6-*bromo*-derivative). When this chloro-compound is treated with copper powder in boiling nitrobenzene 2 : 3 : 2′ : 3′-*diphthalyl*-1 : 1′-*dianthraquinonyl* (I), m. p. above 360°, is obtained, which is converted by the action of copper powder and concentrated sulphuric acid into the *tetraketo*-compound (II). This compound, which is a pyrene derivative, is reducible only with difficulty, and is therefore useless as a vat dye.



(I.) (II.)

6-*Amino*- and 6-*hydroxy*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, sublimes at 300°, are described.

H. BURTON.

Dye intermediates [phenyl α-naphthyl ketone]. H. A. DRESCHER, J. THOMAS, & SCOTTISH DYES, LTD. —See B., 1928, 474.

Ketones of the anthracene series. I. G. FARBENIND. A.-G.—See B., 1928, 516.

Plant sterols. K. BONSTEDT (Z. physiol. Chem., 1928, **176**, 269—281).—When sitosterol, m. p. 137—138° (all m. p. are corr.), $[\alpha]_D^{19.5}$ in chloroform $-33·9°$, from soya-bean oil, is heated with finely-divided nickel (cf. Windaus, A., 1916, i, 813; 1927, 557), sitostanone, m. p. 156°, is produced. Prolonged treatment of a chloroform solution of sitostene with hydrogen chloride affords *sitostene hydrochloride*, m. p. 132—133°, which when heated with potassium acetate and alcohol gives *ψ-sitostene*, $C_{27}H_{46}$, m. p. 69°. *Sitosterol hydrochloride* has m. p. 155° (decomp.) and decomposes in warm chloroform solution. Fractional crystallisation of crude soya-bean sitosterol from alcohol gives a small amount of dihydrositosterol, m. p. 144°, $[\alpha]_D^{18}$ $+28·0°$ (cf. Anderson, A., 1924, i, 1217), together with γ-sitosterol, m. p. 142°, $[\alpha]_D^{17}$ in chloroform $-44·8°$. Reduction of this last compound with hydrogen in presence of acetic acid and palladium-black yields γ-sitostanol, m. p. 143—144°, $[\alpha]_D^{16.5}$ $+20·8°$ (acetate, m. p. 144—145°), oxidised by chromic anhydride to γ-sitostanone, m. p. 163°, $[\alpha]^{15}$ $+38·0°$. Reduction of this by Clemmensen's method gives γ-sitostane, m. p. 87°, $[\alpha]_D^{15}$ $+20·2°$. γ-Sitosteryl chloride, m. p. 115—116°, is reduced by sodium and amyl alcohol to γ-sitostene, m. p. 73°, $[\alpha]_D^{19}$ $-59·3°$.

The sterols of rape oil (Windaus and Welsch, A., 1909, i, 228) do not appear to contain any γ-sitosterol.

H. BURTON.

Constituents of *Phellodendron amurense*, Rupr. I. Y. YAMAMURA and J. TAKATA (J. Pharm. Soc. Japan, 1927, [550], 1035—1040).—One of the non-basic components of *Phellodendron* (a drug

widely used in Japan), which the authors name "obakunine," has the composition $C_{27}H_{33}O_7,6H_2O$ or $C_{28}H_{35}O_7,6H_2O$, m. p. 229—230° (*semicarbazone*, m. p. 224—225°; *oxime*, m. p. 275°). The mother-liquor of obakunine contains a phytosterol, $C_{26}H_{44}O,H_2O$ or $C_{27}H_{46}O,H_2O$, m. p. 142°, $[\alpha]_D^{19}$ −28·86° (Liebermann's colour reaction, positive; *acetyl* derivative, m. p. 135—137°), and some palmitic and linolenic acids. The drug contains about 1·6% of berberine as hydrochloride. Tetrahydroberberine, obtained from it by reduction with zinc dust, after being repeatedly crystallised from alcohol-chloroform, has m. p. 173° (lit. 167°).

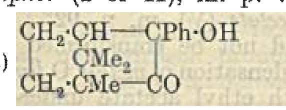
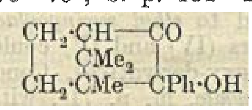
Higher-boiling constituents of essential oil of hops. A. C. CHAPMAN.—See B., 1928, 501.

Carene. M. LAGACHE (Bull. Inst. Pin, 1927, 255—256; Chem. Zentr., 1928, i, 904).—*Carene-nitrolaniline*, $C_{10}H_{15}\cdot NO,NH_2Ph$, obtained by heating the nitrosochloride with alcoholic aniline and precipitation with water, has m. p. 143—144°, $[\alpha]_{yellow}$ +60·50°, $[\alpha]_{green}$ +76·81° (in benzene); the corresponding *p*-toluidine *compound* has m. p. 148—149°, $[\alpha]_{yellow}$ +165·66°, $[\alpha]_{green}$ +203·31° (in benzene).

A. A. ELDRIDGE.

[Addition of chlorine and bromine to pinene.] O. ASCHAN (Ber., 1928, **61**, [*B*], 1342—1343).—A reply to Kondakov (this vol., 526). H. WREN.

Phenylcamphor. H. RUPE [with A. WIRZ] (Verh. Naturforsch. Ges. Basel, 1927, **38**, 164—187; Chem. Zentr., 1928, i, 907—908).—By the action of magnesium phenyl bromide on camphorquinone, only one keto-group is attacked, yielding *phenylhydroxycamphor* (I or II), m. p. 78—79°, b. p. 184—187°/

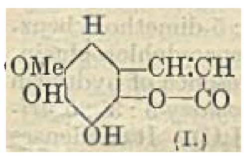
(I.)   (II.)

10 mm., $[\alpha]_D^{20}$ +7·96° in benzene (*methyl ether*, b. p. 161—163°/10 mm.; *ethyl ether*, b. p. 165—166°/10 mm., d_4^{20} 1·0600, n_D^{20} 1·5284). The possibility of formulation as $C_8H_{14}<\begin{smallmatrix}C\cdot OH\\ \|\\ C\cdot OPh\end{smallmatrix}$ or $C_8H_{14}<\begin{smallmatrix}CO\\ |\\ CH\cdot OPh\end{smallmatrix}$ considered and rejected. The *cyclo*acetal formulation for hydroxycamphor is not approved. Camphorquinone and phenylhydroxycamphor show abnormal rotation dispersion. The rotation dispersion constants of phenylcamphor deviate markedly from those of the alkylcamphors. Phenylchlorocamphor, $C_8H_{14}<\begin{smallmatrix}CO\\ |\\ CClPh\end{smallmatrix}$ from phenylhydroxycamphor and phosphorus pentachloride in 36—48 hrs. at the ordinary temperature, has m. p. 129°; it is reduced by zinc dust and acetic acid, or by hydrogenation in a mixture of alcohol, ethyl acetate, and water in presence of a nickel catalyst, to *phenylcamphor*, b. p. 172—174°/10 mm., m. p. 45—46°, $[\alpha]_D^{20}$ +184·42° or +180·45° in benzene. *Phenylborneol*, $C_8H_{14}<\begin{smallmatrix}CH\cdot OH\\ |\\ CHPh\end{smallmatrix}$, obtained from phenylhydroxycamphor, sodium, and boiling alcohol, has m. p. 139—140°, $[\alpha]^{20}$ −76·19° in benzene (*isomeride* from petroleum, b. p. 179—182°/10 mm., d_4^{20} 1·0897, $[\alpha]_D^{20}$ +20·43°). Treatment of this with formic acid or phosphoric acid affords *phenylbornylene*, $C_{18}H_{14}<\begin{smallmatrix}CH\\ \|\\ CPh\end{smallmatrix}$, b. p. 135—141°/11 mm., d_4^{20} 0·9767, n_D^{20} 1·54167, $[\alpha]_D^{20}$ +40·56°, or d_4^{20} 0·9865, n_D^{20} 1·54445, $[\alpha]_D^{0}$ +8·33°, respectively.

A. A. ELDRIDGE.

Essential oil from timber of rosewood (*Dysoxylon Fraseranum*). A. R. PENFOLD.—See B., 1928, 502.

Constitution of fraxetin. F. WESSELY and E. DEMMER (Ber., 1928, **61**, [*B*], 1279—1284).—Fraxetin, m. p. 227—228° (slight decomp.) after darkening at 150°, is known to be the monomethyl ether of a trihydroxycoumarin. When treated with diazomethane it affords dimethylfraxetin, m. p. 103—104°, which is converted by successive treatment with sodium methoxide and methyl iodide into methyl tetramethoxycinnamate, transformed by hydrolysis followed by oxidation into 2 : 3 : 4 : 5-*tetramethoxybenzoic acid*, m. p. 87·5°. Synthesis of this acid is effected from 2 : 5-dimethoxy-3 : 4-methylenedioxybenzoic acid, which is transformed by resorcinol and concentrated sulphuric acid into 3 : 4-dihydroxy-2 : 5-dimethoxybenzoic acid, which, with diazomethane, yields the tetramethoxy-compound. Ethylation of fraxetin affords *diethylfraxetin*, m. p. 81—82°, degraded to 2 : 5-*dimethoxy*-3 : 4-*diethoxybenzoic acid*, m. p. 83° (*methyl* ester), the constitution of which is established by its preparation



from 3 : 4-dihydroxy-2 : 5-dimethoxybenzoic acid. The constitution (I) is therefore assigned to fraxetin, whereas fraxin contains the dextrose residue in place of one of the two hydroxyl hydrogen atoms. H. WREN.

Alkali periodide salts with organic neutral components. H. SCHMIDT (Ber., 1928, **61**, [*B*], 1347—1353; cf. Lowenbein and Schmidt, A., 1927, 1072).—A solution of iodine and sodium iodide in acetone when concentrated in a vacuum yields the crystalline *salt*, $(COMe_2)_6I(NaI)_3$. 3-Bromo-3-arylcoumaranones when treated with sodium iodide dissolved in acetone deposit sodium bromide and yield sodium periodide salts of 2-keto-3-arylcoumaranyls; if more concentrated solutions are employed di-2-keto-3-arylcoumaranyls also separate. The following *salts* are described: $(C_{14}H_9O_2I)_3(NaI)_2$ from 3-bromo-3-phenylcoumaranone; $(C_{15}H_{11}O_2I)_2(NaI)_3$ from 3-bromo-3-phenyl-5-methylcoumaranone; $(C_{16}H_{13}O_3I)(NaI)_2$ from 3-bromo-3-*p*-anisyl-5-methylcoumaranone; $(C_{18}H_{11}O_2I)(NaI)_3$ and $(C_{18}H_{11}O_2I)(NaI)_2$ from 3-bromo-3-phenyl-4 : 5-benzocoumaranone; $(C_{19}H_{13}O_3I)_2(NaI)_3$ and $(C_{19}H_{13}O_3I)(NaI)_2$ from 3-bromo-3-*p*-anisyl-4 : 5-benzocoumaranone. The salts yield the di-2-keto-3-arylcoumaranyls when their solutions in benzene are titrated with aqueous thiosulphate or shaken with copper-bronze or molecular silver or mercury or when their solutions in acetone are boiled with zinc wool.

H. WREN.

Synthesis of pyrylium salts of anthocyanidin type. XV. Synthesis of cyanidin chloride by means of *O*-benzoylphloroglucinaldehyde. A.

ROBERTSON and R. ROBINSON (J.C.S., 1928, 1526—1532).—Condensation of ω : 3 : 4-triacetoxyacetophenone and O-benzoylphloroglucinaldehyde in ethyl acetate–alcohol solution under the influence of hydrogen chloride yields 5-O-*benzoylcyanidin chloride* ($+1\cdot5H_2O$). Hydrolysis by means of 8% cold aqueous-alcoholic sodium hydroxide involves, in addition, rupture of the pyrylium ring. Cyanidin chloride, identical with the natural product, is obtained on acidification of the solution. The constitution of cyanidin chloride is therefore fully established as 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride (cf. Malkin and Nierenstein, this vol., 646).

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVI. Synthesis of pelargonidin chloride by means of O-benzoylphloroglucinaldehyde. A. ROBERTSON, R. ROBINSON, and J. SUGIURA (J.C.S., 1928, 1533—1537).—Condensation of O-benzoylphloroglucinaldehyde and ω-4-diacetoxyacetophenone in ethyl acetate solution in presence of hydrogen chloride yields 3 : 7 : 4′-*trihydroxy*-5-*benzoyloxyflavylium chloride* (5-O-*benzoylpelargonidin chloride*) (I) ($+1\cdot5H_2O$). Debenzoylation gives pelargonidin chloride. The reactions of (I) resemble those of pelargonenin and pelargonin, thus confirming the view that pelargonenin is a pelargonidin 5- or 7-glucoside.

ω : 3 : 5-*Trimethoxyacetophenone*, m. p. 42° (*semicarbazone*, m. p. 149—149·5°), obtained from ethyl αγ-dimethoxyacetoacetate and 3 : 5-dimethoxybenzoyl chloride, condenses with O-benzoylphloroglucinaldehyde in ethereal solution in presence of hydrogen chloride, giving 7-*hydroxy*-5-*benzoyloxy*-3 : 3′ : 5′-*trimethoxyflavylium chloride* (II) ($+2H_2O$). It condenses with O-triacetylphloroglucinaldehyde in presence of formic acid and hydrogen chloride, giving 5 : 7-*dihydroxy*-3 : 3′ : 5′-*trimethoxyflavylium chloride* (III), ($+0\cdot5H_2O$), alternatively obtained by hydrolysis of (II). The salt (III) decomposed on attempted demethylation by means of hydriodic acid in presence of phenol, although indications of the production of 3 : 5 : 7 : 3′ : 5′-pentahydroxyflavylium chloride were obtained.

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVII. Synthesis of peonidin chloride by means of O-benzoylphloroglucinaldehyde. S. MURAKAMI and R. ROBINSON (J.C.S., 1928, 1537—1541; cf. A., 1926, 1043).—Condensation of O-benzoylphloroglucinaldehyde and ω : 4-diacetoxy-3-methoxyacetophenone in ethyl acetate solution in presence of hydrogen chloride yields 5-O-*benzoylpeonidin chloride* ($+0\cdot5H_2O$; $+3H_2O$). The alkali colour-reaction of this salt closely resembles that of peonin chloride. Debenzoylation yields peonidin chloride [$+H_2O$; $+1\cdot5H_2O$ (2 modifications)] identical in reactions with peonidin chloride of natural origin. The crystal habit and solubility relations could be equated, however, only after drastic purification of the anthocyanidin from peonin. A small trace of persistent impurity, probably malvidin, was still present in the natural product.

M. CLARK.

Synthesis of pyrylium salts of anthocyanidin type. XVIII. Synthesis of malvidin chloride. W. BRADLEY and R. ROBINSON (J.C.S., 1928, 1541—1569; cf. A., 1926, 1043).—When *ethyl benzoylbenzoyloxyacetate*, m. p. 61°, obtained by interaction of ethyl sodiobenzoyl acetate and benzoyl peroxide, is heated with water in a sealed tube at 200°, it yields ω-benzoyloxyacetophenone. Further degradation by means of boiling aqueous-alcoholic sulphuric acid gives only a poor yield of benzoylcarbinol. Interaction of the potassium derivative of ethyl 3 : 4 : 5-trimethoxybenzoylacetate (I) and benzoyl peroxide affords *ethyl* 3 : 4 : 5-*trimethoxybenzoylbenzoyloxyacetate*, m. p. 107°. Long-continued heating of this substance with water in a sealed tube at 200° gives ω-*benzoyloxy*-3 : 4 : 5-*trimethoxyacetophenone*, m. p. 98—100°, which cannot be condensed with O-benzoylphloroglucinaldehyde to a flavylium salt nor hydrolysed to trimethoxybenzoylcarbinol. Interaction of (I) with acetyl peroxide gives *ethyl* 3 : 4 : 5-*trimethoxybenzoylacetoxyacetate*, m. p. 88°, which is converted by direct hydrolysis with hot dilute sulphuric acid into 3 : 4 : 5-*trimethoxybenzoylcarbinol* (II), m. p. 87—88° (the *diphenylhydrazone* of 3 : 4 : 5-*trimethoxyphenylglyoxal* has m. p. 137—138°). The ketone (II) condenses with O-benzoylphloroglucinaldehyde giving 3 : 7-*dihydroxy*-5-*benzoyloxy*-3′ : 4′ : 5′-*trimethoxyflavylium chloride*, converted by the successive action of cold aqueous sodium hydroxide and hydrochloric acid into delphinidin chloride 3′ : 4′ : 5′-trimethyl ether (III). Malvidin, contaminated with delphinidin or, more probably, delphinidin 3′-methyl ether, was obtained by hydrolysis of (III) with hydrogen bromide in acetic acid solution at 45—50°.

Condensation of O-*acetylsyringoyl chloride*, m. p. 126°, and ethyl sodioacetoacetate gives *ethyl* O-*acetylsyringoylacetoacetate* (IV), m. p. 114°, which is hydrolysed to *ethyl syringoylacetate* (V), m. p. 92°. The esters (IV) and (V) could not be transformed into acyloxy-derivatives. Condensation of *methyl* O-*benzylsyringate*, m. p. 71°, with ethyl acetate under the influence of sodium could not be effected. The acid *chloride*, m. p. 45°, of O-*benzylsyringic acid*, m. p. 157° (*amide*, m. p. 152°), condenses with ethyl sodioacetoacetate, giving *ethyl* O-*benzylsyringoylacetoacetate*, m. p. 97—102°, which yields on hydrolysis *ethyl* O-*benzylsyringoylacetate* (VI), m. p. 67° (*copper* derivative, m. p. 212°). Oxidation of (VI) with benzoyl peroxide gave a product converted by heating with water in a sealed tube at 160—170° into ω-*benzoyloxy*-4-*benzyloxy*-3 : 5-*dimethoxyacetophenone* (VII), m. p. 105°, together with a small quantity of ω-*hydroxy*-4-*benzyloxy*-3 : 5-*dimethoxyacetophenone* (VIII), m. p. 87—89°. Whilst the compound (VII) did not condense readily with O-benzoylphloroglucinaldehyde to form a flavylium salt, the compound (VIII) yielded a substance regarded as benzoylmalvidin chloride. Reaction of acetyl peroxide in ethereal solution with the potassio-derivative of ethyl benzylsyringoylacetate gave a product yielding, on hydrolysis with dilute sulphuric acid, a crude benzoylcarbinol derivative together with a small quantity of a *substance*, m. p. 85—87°. Condensation of the benzoylcarbinol with O-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of hydrogen chloride gave a flavylium salt converted by debenzoylation and debenzylation into a malvidin derivative

contaminated with salts and not containing a free hydroxyl group in position 3. Oxidation of ethyl benzylsyringoylacetate in acetic acid solution by lead tetra-acetate gives *ethyl di(benzylsyringoyl)succinate*(?), m. p. 173—176°, alternatively prepared by the action of iodine on the potassium derivative of ethyl benzylsyringoylacetate. Interaction of diazomethane and benzylsyringoyl chloride in ethereal solution affords *ω-diazo-4-benzyloxy-3 : 5-dimethoxyacetophenone*, m. p. 122—123° (decomp.). The diazo-ketone decomposes in a vacuum, giving a *substance*, m. p. 58—59°. It is converted by the action of boiling dilute aqueous-alcoholic sulphuric acid into *O-benzylsyringoylcarbinol* (?), m. p. 85—86° (*diphenylhydrazone* of related phenylglyoxal derivative has m. p. 131° after sintering at 110°), and by warming with acetic acid into *ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone* (IX), m. p. 60·5—61°. Condensation of *O*-benzoylphloroglucinaldehyde with (IX) in cold ethyl acetate solution under the influence of hydrogen chloride yields 5-benzoylmalvidin chloride ($+2\cdot5H_2O$), the acetoxy- and benzyloxy-groups being hydrolysed. The alkali colour-reaction of this 5-benzoylmalvidin chloride closely resembles that of malvin chloride. Debenzoylation by treatment with cold aqueous sodium hydroxide and subsequent acidification gives malvidin chloride ($+H_2O$), showing all the characteristic properties and reactions described by Willstatter and Mieg (A., 1915, i, 287) and identical with a specimen obtained by hydrolysis of natural malvin chloride. When ethyl *O*-benzylsyringoylacetate is heated with water in a sealed tube at 178—180°, *4-benzyloxy-3 : 5-dimethoxyacetophenone* (X), m. p. 60—61° [*semicarbazone*, m. p. 166°; *2 : 4-dinitrophenylhydrazone*, m. p. 192—193°; iso*nitroso*-derivative, m. p. 107—108° (*oxime*, m. p. 141—142°)], is obtained. Debenzylation by hydrogen bromide in acetic acid solution yields *4-hydroxy-3 : 5-dimethoxyacetophenone*, m. p. 117°. Attempts to prepare this substance by condensation of pyrogallol 1 : 3-dimethyl ether and acetyl chloride in carbon disulphide in presence of anhydrous ferric chloride resulted in formation of 3-acetoxy-2 : 4-dimethoxyacetophenone. Condensation of (X) with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of dry hydrogen chloride gives a mixture of the anticipated flavylium salt with a debenzylated derivative. On complete debenzoylation and debenzylation *5 : 7 : 4′-trihydroxy-3′ : 5′-dimethoxyflavylium chloride* ($+H_2O$), m. p. 280°, is obtained. *O*-Acetylsyringoyl chloride reacts with ethyl sodio-αγ-dimethoxyacetoacetate, giving a product which on hydrolysis affords *4-hydroxy-ω : 3 : 5-trimethoxyacetophenone* (XI), m. p. 90°. Condensation of (XI) with *O*-benzoylphloroglucinaldehyde and hydrogen chloride gives *7 : 4′-dihydroxy-5-benzoyloxy-3 : 3′ : 5′-trimethoxyflavylium chloride*, converted by debenzoylation into *5 : 7 : 4′-trihydroxy-3 : 3′ : 5′-trimethoxyflavylium chloride* ($+0\cdot5H_2O$) (*malvidin chloride 3-methyl ether*). This substance gives alkali colour-reactions divergent from those of malvin, malvidin, and 5-benzoylmalvidin. It is concluded that a free hydroxyl group not only in position 4′, but also in position 3 is essential for the exhibition of a pure greenish-blue alkali colour-reaction in the malvidin series and that malvin is therefore a malvidin 5- or 7-diglucoside. The experiments of Karrer (A., 1927, 1197), who considers it to be malvidin 3-diglucoside, are, however, consistent with the hypothesis that malvin may be a 3- or 5-diglucoside. The 7-diglucoside configuration is thus excluded and malvin should be the 5-diglucoside of malvidin.

M. Clark.

Synthesis of anthocyanins. V. Synthesis of 3-β-glucosidylpelargonidin chloride, believed to be identical with callistephin chloride. A. Robertson and R. Robinson (J.C.S., 1928, 1460—1472).—ω-Chloro-4-hydroxyacetophenone is converted into ω-acetoxy-4-hydroxyacetophenone, m. p. 133° (lit. 127°), and then by means of aqueous sodium hydroxide into the sodium salt of ω-4-dihydroxyacetophenone (I) (*4-carbomethoxy*-derivative, m. p. 84°; *4-benzoyl* derivative, m. p. 140—141°; *ω : 4-dibenzoyl* derivative, m. p. 180—182°). Partial acetylation of (I) yields *ω-hydroxy-4-acetoxyacetophenone*, m. p. 95—96°, which condenses with *O*-tetra-acetyl-α-glucosidyl bromide in presence of silver carbonate in benzene solution at 35°, giving *ω-O-tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone* (II), m. p. 132°. Condensation of *O*-benzoylphloroglucinaldehyde with (II) in a mixture of ether and chloroform under the influence of dry hydrogen chloride yields *3-O-tetra-acetyl-β-glucosidoxy-7-hydroxy-5-benzoyloxy-4′-acetoxyflavylium chloride* (III). Hydrolysis of (III) with 8% cold aqueous sodium hydroxide gives a solution of the debenzoylated and deacetylated glucoside in a form in which the pyran ring is probably open. Acidification regenerates the pyrylium salt, giving, after a difficult purification, *3-β-glucosidylpelargonidin chloride* ($+2H_2O$) (*picrate*). This substance, which gave, on hydrolysis with 15% hydrochloric acid, pelargonidin chloride, was identical in properties with naturally-occurring callistephin chloride (A., 1917, i, 44). The distribution number between amyl alcohol and 0·5% hydrochloric acid is 32.

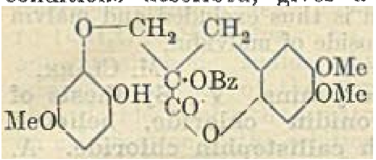
ω-O-Tetra-acetyl-β-glucosidoxy-4-benzoyloxyacetophenone, m. p. 147°, fails to condense with *O*-benzoylphloroglucinaldehyde to give a derivative of callistephin. *ω-O-Tetra-acetyl-β-glucosidoxy-4-methoxyacetophenone* has m. p. 133°.

Recognition of the 3-glucosidyl structure of callistephin and consideration of its properties and those of pelargonenin and pelargonin leads to the conclusion that the two last-named compounds are 5- or 7-saccharides; Karrer's experiments (A., 1927, 1197) are consistent only with the hypothesis that these anthocyanins are 3- or 5-saccharides. The 5-saccharide configuration is thus most probable.

M. Clark.

Synthesis of brazilin and hæmatoxylin and their derivatives. III. W. H. Perkin, jun., J. N. Ray, and R. Robinson (J.C.S., 1928, 1504—1513).—Reduction of trimethylbrazilone by phenylhydrazine in acetic acid solution yields deoxytrimethylbrazilone (I), together with a by-product, $C_{25}H_{22}O_4N_2$, m. p. described by Herzig and Pollak (A., 1905, i, 605) as the main product of this reaction. Possible constitutions for the by-product are suggested. Attempts to add the elements of water or of an acid, HX, to (I) were unsuccessful owing to the ease with which the substance under-

goes oxidation or conversion, in presence of acids, into the *iso*brazilein salt. Oxidation of (I) with perbenzoic acid in chloroform solution, under the conditions described, gives a *substance*, $C_{26}H_{24}O_9$, m. p. 152°, to which the annexed formula is ascribed, by analogy with the products derived from brazilein derivatives by oxidation with hydrogen peroxide.

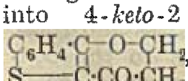


Deoxytrimethylbrazilone yields a deep crimson *dibromide* (which gives up bromine to form *iso*brazilein hydrobromide trimethyl ether), and a *perbromide*, $C_{19}H_{18}O_4Br_6$. Reduction of (I) with hydrogen and a palladium catalyst yields a *dehydro*-derivative, m. p. 109°, converted into trimethylbrazilone (II) on oxidation with chromic acid in acetic acid solution. Reduction of (II) by aluminium amalgam yields a *compound*, $C_{19}H_{20}O_6,0{\cdot}5H_2O$ (?), m. p. 129° (decomp.), converted by the action of acetic anhydride into a *derivative*, m. p. 116°. Reduction of (II) by zinc dust in alcoholic acetic acid solution yields an intramolecular *pinacol*, $C_{19}H_{20}O_6$, m. p. 167—168°, resembling in its behaviour tetramethyldihydrobrazileinol. The pinacol yields a *formate*, *anhydro-sulphate*, and *anhydro-hydrochloride*. O-*Triacetyl-brazilone* ($+0{\cdot}5H_2O$) has m. p. 187° (decomp.). O-*Tribenzoylbrazilone* has m. p. 205° (decomp.).

The nature of deoxytrimethylbrazilone dibromide and of the brazilein salts is discussed and a scheme for the synthesis of brazilein is indicated. M. CLARK.

4-Keto-2 : 3-thionaphthen-5 : 6-dihydro-γ-pyran. F. KROLLPFEIFFER and K. SCHNEIDER (Ber., 1928, **61**, [*B*], 1284—1291).—β-3-*Hydroxythio-naphthenylpropionic acid*,

$S{<}^{C_6H_4}_{CH}{\gg}C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, m. p. 164—165°, is prepared by the action of β-chloropropionic acid on 3-hydroxythionaphthen in presence of potassium hydroxide. Ring closure does not occur when it is distilled in a vacuum over phosphoric oxide or treated with concentrated sulphuric acid. It is converted through the chloride by means of aluminium chloride into 4-*keto*-2 : 3-*thionaphthen*-5 : 6-*dihydro-γ-pyran*,



m. p. 144—145° (*semicarbazone*), converted by warm alkali hydroxide into 2-β-*hydroxy-propionyl*-3-*hydroxythionaphthen*, m. p. 129—130° (*phenylcarbamate*, m. p. 148—150°), obtained also from 2-β-chloropropionyl-3-hydroxythionaphthen and sodium hydroxide. The following compounds are obtained by treating the methyl ether of 3-hydroxythionaphthen with the requisite acid chloride and aluminium chloride in presence of carbon disulphide: 2-*acetyl*-3-*hydroxythionaphthen*, m. p. 82°; 2-*propionyl*-3-*hydroxythionaphthen*, b. p. 183°/15 mm., m. p. 73—74° (*semicarbazone*, m. p. 188—189°); 2-β-*chloro-propionyl*-3-*hydroxythionaphthen*, m. p. 121—122°, reduced by zinc dust and acetic acid to 2-propionyl-3-hydroxythionaphthen and converted by sodium carbonate into 4-keto-2 : 3-thionaphthen-5 : 6-dihydro-γ-pyran; 2-benzoyl-3-hydroxythionaphthen, m. p. 118—119° (phenylhydrazone, m. p. 167—168°). 4-Keto-2 : 3-thionaphthen-5 : 6-dihydro-γ-pyran is not affected by bromine in carbon disulphide, but is transformed by free bromine into the *monobromo*-derivative, $C_{11}H_7O_2BrS$, m. p. 189—190°, which is not affected by boiling dimethylaniline, but is converted by 2*N*-sodium hydroxide into the *compound* $C_{11}H_9O_3BrS$, m. p. 135—136°. 2-Acetyl-4-methylthioltoluene is converted by bromine in carbon disulphide into the ω-*bromoacetyl* derivative, m. p. 77—78° (in glacial acetic acid a *compound*, m. p. 226—227°, is produced), which in boiling glacial acetic acid affords a mixture of 5 : 5′-dimethylindigotin and 3-hydroxy-5-methylthionaphthen; the latter compound is also obtained when the bromo-substance is distilled with steam or heated above its m. p. or, similarly, from the corresponding ω-*iodo*-compound, m. p. 86—87° (from the bromo-derivative and potassium iodide in acetone). 2-*Propionyl*-4-*methylthiol-toluene*, b. p. 176—177°/10 mm., m. p. 42—43°, and the corresponding α-*bromo*-compound, m. p. 98°, are described. The latter compound loses methyl bromide when distilled with steam, yielding products, m. p. 199° and b. p. 165°/10 mm., m. p. 126—127°. 2-*Bromoacetyl*-4-*methoxytoluene* has m. p. 74—75°.

H. WREN.

[Derivatives of] diphenylene sulphide. C. COURTOT, L. NICOLAS, and T. H. LIANG (Compt. rend., 1928, **186**, 1624—1626).—*Chlorodiphenylene sulphide*, m. p. 113—114°, is obtained from the corresponding amino-derivative (A., 1926, 605) by the Sandmeyer reaction, or by the action of cold thionyl chloride on nitrodiphenylene sulphide, m. p. 184° (*loc. cit.*). *Bromodiphenylene sulphide*, m. p. 125—126°, is prepared similarly, and also by direct bromination of diphenylene sulphide in chloroform solution. *Iodo-diphenylene sulphide*, m. p. 87—88°, is obtained by the Sandmeyer reaction. *Dichloro*-, m. p. 205—206°, *dibromo*-, m. p. 229°, and *di-iodo-diphenylene sulphides*, m. p. 219—220°, have been prepared from the corresponding diamino-derivative (A., 1926, 620). The same dibromo-derivative results when diphenylene sulphide is brominated. The above mono- and dibromo-compounds undergo the Grignard reaction, and *monocarboxy*-, m. p. 255°, and *dicarboxy*-, m. p. 320°, derivatives of diphenylene sulphide have been prepared. Nitration of bromodiphenylene sulphide affords a *bromonitro*-derivative, m. p. 264—265°, together with *bromodiphenylene sulphinone*, m. p. 171—172°. Reduction of the nitro-derivative gives *bromoaminodiphenylene sulphide*, m. p. 150—151°, from which the above dibromo-compound is obtained. The orientation of the bromonitro-derivative is therefore the same as that of the diamino-compound.

The ultra-violet absorption spectra of the above derivatives have been examined. Introduction of one halogen atom into the diphenylene sulphide molecule induces bathochromic and hyperchromic effects, which are least marked for iodine. A second halogen atom causes an increase in the bathochromic effect, the di-iodo-derivative being the most powerful, although not so pronounced as hydroxy-, amino-, or nitro-derivatives. H. BURTON.

Organic compounds of sulphur. IX. Preparation of aromatic thioketones by the action

of thioacetic acid on keto-chlorides. Action of copper bronze on thiobenzophenone and its derivatives. A. SCHONBERG, O. SCHUTZ, and S. NICKEL [with H. KRULL, W. MARSCHNER, and F. KAPLAN] (Ber., 1928, **61**, [*B*], 1375—1385; cf. this vol., 72).—A general method for the preparation of aromatic thioketones consists in the treatment of the corresponding keto-chlorides with thioacetic acid: $CAr_2Cl_2 \xrightarrow{AcSH} CAr_2Cl\cdot SH \longrightarrow CAr_2{:}S$. *Thiobenzophenone*, b. p. 126—129°/0·05 mm., m. p. 51°, forms blue needles which are converted by exposure to air into a colourless, crystalline *compound* (decomp. above 100°) containing sulphur. 4 : 4′-*Diphenylthiobenzophenone* has m. p. 228—229°. 4-*Methoxy*-4′-*ethoxybenzophenone*, m. p. 112°, prepared from anisyl chloride and phenetole in the presence of aluminium chloride and carbon disulphide, is transformed by the successive action of oxalyl chloride and thioacetic acid into 4-*methoxy*-4′-*ethoxythiobenzophenone*, m. p. 94—96°. 2 : 2′-*Dimethoxythiobenzophenone*, m. p. 121°, and 4 : 4′-*dimethoxythiobenzophenone*, m. p. 114—115°, are described. The action of oxalyl chloride and thioacetic acid on xanthone affords *xanthione*, $C_{13}H_8OS$, m. p. 156°, converted by repetition of the treatment into *thioxanthione*, $C_6H_4{<}^{CS}_{S}{>}C_6H_4$, m. p. 168°. N-*Phenylthioacridone*, m. p. 227—228°, is prepared by the action of phosphorus pentasulphide on *N*-phenylacridone in boiling benzene.

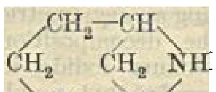
Treatment of thiobenzophenone with copper bronze in boiling xylene in an atmosphere of nitrogen yields tetraphenylethylene. Tetra-anisylethylene, m. p. 183°, tetraphenetylethylene, and tetra-4-ethoxy-*m*-tolylethylene are similarly prepared. Xanthione and thioxanthione afford *dixanthylene* and *dithioxanthylene*, m. p. not below 340°, respectively, whereas *N*-phenylthioacridone remains unchanged. H. WREN.

Action of aromatic Grignard reagent on methylsuccinimide. Synthesis of 2 : 5-diphenyl-1-methylpyrrole. R. LUKES and V. PRELOG (Chem. Listy, 1928, **22**, 244—251).—*N*-Methylsuccinimide reacts with magnesium phenyl bromide to yield 2-*hydroxy*-2-*phenyl*-1-*methylpyrrolid*-2-*one*, m. p. 139—141° (*phenylhydrazone*, m. p. 186°), and 2 : 5 *diphenyl*-1-*methylpyrrole*, m. p. 204°, b. p. 225—235°/12 mm. Where the Grignard reagent is not present in excess and the time of reaction is short, the former product predominates; otherwise the latter is the main product. The former substance on acid hydrolysis yields methylamine and β-benzoylpropionic acid, and on distillation under reduced pressure gives water and 5-*phenyl*-1-*methylpyrrolone*, m. p. 59°, b. p. 150—165°/9 mm. R. TRUSZKOWSKI.

The dicyclic 2 : 6-methylenepiperidine. J. VON BRAUN, W. HAENSEL, and F. ZOBEL (Annalen, 1928, **462**, 283—300).—In continuation of previous work (A., 1927, 266) an attempt has been made to prepare and investigate β-3-chloro*cyclo*hexylethylmethylamine.

*Resorcinol mono*iso*amyl ether*, b. p. 165°/12 mm. (*benzoate*, m. p. 31—32°), from resorcinol, sodium ethoxide, and *iso*amyl bromide in alcoholic solution, is reduced by Sabatier's method to 3-*hydroxy*cyclo*hexyl* iso*amyl ether*, b. p. 140°/16 mm. Oxidation of the latter substance gives 3-iso*amyloxy*cyclo*hexanone*, m. p. 128—130°/16 mm., d_4^{18} 0·9421, 1·4518 (*semicarbazone*, m. p. 146°; *oxime*, b. p. 162°/12 mm.), readily converted by alkali into a *ketone*, C_6H_8O, b. p. 170—172°. The *cyclo*hexanone reacts with a mixture of magnesium and ethyl bromoacetate in ether to give *ethyl* β-*hydroxy*-β-3-iso*amyloxy*cyclo*hexylpropionate*, b. p. 175°/12 mm. (?), which, when heated with potassium hydrogen sulphate at 150°, is converted into *ethyl* 3-iso*amyloxy*cyclo*hexenylacetate*, b. p. about 170°/12 mm. (?), d_4^{23} 0·9740, 1·4670. Reduction of this ester with sodium and alcohol produces the corresponding *acid* (b.p. 190°/11 mm.), together with β-3-iso*amyloxy*cyclo*hexenylethyl alcohol*, b. p. 162°/11 mm., d_4^{24} 0·951, n_D^{24} 1·474. Reduction of the same ester with platinum or palladium in methyl alcohol produces 3-*ethyl*cyclo*hexyl* iso*amyl ether*, b. p. 110—120°/12 mm., together with β-3-iso*amyloxy*cyclo*hexylethyl alcohol*, b. p. 160°/12 mm., d_4^{21} 0·941, n_D^{21} 1·468 (7 g. from 500 g. of resorcinol). Treatment of the latter alcohol with phosphorus pentabromide in chloroform solution gives β-3-iso*amyloxy*cyclo*hexylethyl bromide*, b. p. 155°/16 mm., which is converted by methylamine in benzene solution at 100° into β-3-iso*amyloxy*cyclo*hexylethylmethylamine*, b. p. 140°/14 mm., and the latter, with concentrated hydrochloric acid at 125°, affords the hydrochloride and thence the *chloroplatinate* of β-3-*chloro*cyclo*hexylethylmethylamine*, m. p. 171—173° (previous sintering), obtained only in minute quantities.

Sodium and alcohol reduction of 3-*iso*amyloxy*cyclo*hexanone oxime (above) gives 3-iso*amyloxy*cyclo*hexylamine*, b. p. 120°/13 mm., d_4^{17} 0·898 (*hydrochloride*, m. p. 134—136°; *chloroplatinate*, decomp. 240—243°; *acetyl* derivative, b. p. 190—192°/12 mm.; *benzoyl* derivative, m. p. 61—64°). When the base is heated with fuming hydrobromic acid at 100° it is converted into 3-*bromo*cyclo*hexylamine, hydrobromide*, m. p. 206—208° (corresponding *picrate*, m. p. 175—177°). Cold alkali, or warm alkali for only a short time, liberates the free base, but prolonged action of warm alkali gives a mixture of the following substances: (1) tetrahydroaniline, giving a p-*toluenesulphonyl* derivative, m. p. 75°; (2) 2 : 6-*methylenepiperidine* (annexed formula) (*hydrochloride*, m. p. 258°; *picrate*, m. p. 158—162°; N-p-*toluenesulphonyl* derivative, m. p. 123°), reduced by hydrogen and palladised animal charcoal to *cyclo*hexylamine;



(3) N-cyclo*hexenyl*-1 : 3-*diamino*cyclo*hexane*, $C_6H_9\cdot NH\cdot C_6H_{10}\cdot NH_2$, b. p. 112—115°/14 mm. (*dibenzoyl* derivative, m. p. 188—189°), giving when exhaustively methylated (one stage) a salt from which a *chloroplatinate*, $C_{17}H_{34}N_2Cl_6Pt$, m. p. 185—186°, is isolable; and (4) a *base* regarded, on account of its b. p. (140—145°/14 mm.), as $(C_6H_{11}N)_3$. In the actual identification of (1) and (2) (mixed together after preliminary separation of the whole mixture by distillation), exhaustive methylation was carried out. This gave two *methiodides*: (1) that, $C_9H_{18}NI$, m. p. 241—242°, derived from tetrahydroaniline, and (2) that, $C_8H_{16}NI$, m. p. 206—208°, derived from methylenepiperidine.

When the above *iso*amyloxy*cyclo*hexanone is treated with phenylhydrazine etc. in the course of a dihydrocarbazole synthesis, amyl alcohol is eliminated. Such removal is much less ready in the case of 2-iso*amyloxy*cyclo*hexanone*, b. p. 116°/12 mm., d_4^{21} 0·9377 (*semicarbazone*, m. p. 166°; *oxime*, b. p. 155°/14 mm.), which may be obtained by oxidising *hexahydropyrocatechol mono*iso*amyl ether* (2-*hydroxy*cyclo*hexyl* iso*amyl ether*), b. p. 122°/12 mm. E. E. TURNER.

Asymmetric nitrogen atom. LV. True autoracemisation with optically active ammonium salts. E. WEDEKIND and G. L. MAISER (Ber., 1928, 61, [*B*], 1364—1375; cf. this vol., 74).—1-Methyl-1-allyltetrahydroquinolinium iodide is resolved into its optical components by treatment with silver *d*-bromocamphorsulphonate in a mixture of acetone and ethyl acetate, removal of silver iodide, and concentration of the filtrate. The highest observed molecular rotations for the cation are +202° and −157°. Conversion into the active iodides by the action of potassium iodide in water or sodium iodide in acetone on the camphorsulphonates requires great caution to avoid racemisation. The highest observed values for $[M]_D$ for the active iodides are +28° and −27°, these figures being notably lower than those calculated. Water and methyl and ethyl alcohols cause a relatively rapid diminution of activity, whereas acetone and chloroform are without action. The effect of water accounts for the difference between the observed and calculated values for the optical activity of the iodides. In water at 20° the reaction coefficient for a unimolecular change is found to be k=0·00543, whereas in alcoholic solution k=0·00643. In chloroform at 25° k=0·00131 to 0·00198, whereas optical constancy is observed in solutions in acetone. In water or alcohol the rate of reaction remains constant throughout the change, whereas in chloroform the values of k increase progressively. This latter phenomenon is characteristic of inactivation due to the decomposition of the molecule. In water and alcohol, on the other hand, the electrical conductivity remains unchanged throughout the reaction and hence inactivation is a truly stereochemical transformation such as was observed previously with compounds containing an asymmetric carbon atom. The course of the decomposition of 1-methyl-1-allyltetrahydroquinolinium iodide in chloroform resembles that of phenylmethylpropylallylammonium iodide, so that ring formation appears to have no influence on this property. The absence of decomposition in alcoholic solution is further established by the almost quantitative recovery of the iodide by precipitation with ether after such period as would suffice for complete racemisation and by the observation that the temperature coefficient in the interval of 10° (20—30°) is 2·06, whereas for a decomposing salt the value is 3·6—4·1. True autoracemisation is observed only with salts containing ionisable halogen attached to nitrogen. Aqueous solution of 1-methyl-1-allyltetrahydroquinolinium bromocamphorsulphonate are optically stable after addition of alkali nitrate or sulphate, whereas the activity falls after addition of potassium chloride, bromide, or iodide.

1-*Methyl*-1-*ethyltetrahydroquinolinium iodide*, m. p. 174°, and 1-*ethyl*-1-*allyltetrahydroquinolinium iodide* (two forms, decomp. 136° and 118°) are incidentally described. H. WREN.

Stereoisomerism of 8-hydroxydecahydroquinoline and its derivatives. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 161—171).—The hydrogenation of 8-hydroxyquinoline in acetic acid at 40—45° in presence of platinum-black yielded decahydroquinoline (10%), b. p. 89—93°/20 mm., and two isomeric 8-*hydroxydecahydroquinolines*, b. p. 136—146°/20 mm., (*A*), m. p. 111—112° (50—60%), obtained by recrystallisation from light petroleum, and (*B*), m. p. 92—93° (30—40%), separated by recrystallisation of its *hydrobromide*, m. p. 251°. A third isomeride (*C*), m. p. 101—102°, was obtained from (*A*) or (*B*) by heating the sodium derivatives. (*A*) yielded a *hydrochloride*, m. p. 201—202°, *hydrobromide*, m. p. 202—203°, *chloroaurate*, m. p. 191—192°, O-*benzoyl* derivative, m. p. 89—91° (+H_2O) and 130—131° (anhydrous) [*hydrochloride*, m. p. 255—256° (decomp.)], NO-*dibenzoyl* derivative, m. p. 81—83° (by the action of benzoyl chloride in pyridine), and d-*bromocamphorsulphonate*, m. p. 189—192°. (*B*) yielded a *hydrochloride*, m. p. 247—248°, *chloroaurate*, m. p. 188—189°, and O-*benzoyl* derivative, m. p. 93—95° (+H_2O) and 135—136° (anhydrous) [*hydrochloride*, m. p. 251° (decomp.)]. (*C*) yielded a *hydrochloride*, m. p. 245—246°, *chloroaurate*, m. p. 152—153°, O-*benzoyl* derivative (anhydrous), m. p. 99—100°, and NO-*dibenzoyl* derivative, m. p. 92—93°, stable to permanganate. Heating the hydrochloride of (*C*) with formaldehyde yielded the N-*methyl* derivative, b. p. 125—126°/8 mm. [double salts not crystallisable with exception of the *picrate*, m. p. 123—124°, and *methiodide*, m. p. 285—286° (decomp.)], from which was obtained the O-*benzoyl*-N-*methyl* derivative, m. p. 91—92° (*chloroplatinate*, m. p. 231°; *picrate*, m. p. 193—195°). The hydroxyl group in (*C*) was not methylated by methyl sulphate and alkali, only the above *N*-methyl methiodide being isolated after treatment with potassium iodide. This methiodide gave on decomposition a small quantity of a *base*, isolated as the *picrate*, $C_{17}H_{24}O_7N_4$, m. p. 173—174°. d-8-*Hydroxydecahydroquinoline* (*C*) d-*bromocamphorsulphonate*, m. p. 294—295°, $[\alpha]^{25}$ +84·9°, separated from water, and yielded the d-*base*, $[\alpha]_D^{25}$ +47·6° (*hydrobromide*, m. p. 213—214°, $[\alpha]_D^{25}$ +29·6°). The *salt* of the l-*base* (from the mother-liquors), m. p. 262—263°, $[\alpha]_D^{25}$ +41·8°, yielded the l-*base*, $[\alpha]_D^{22}$ −53·1° (*hydrobromide*, m. p. 211—213°, $[\alpha]_D^{25}$ −31·6°).

Hydrogenation of quinoline in presence of platinum-black (cf. Huckel and Stepf, A., 1927, 572) yielded decahydroquinoline, m. p. 48—48·5° [*hydrobromide*, m. p. 277—279°; chloroaurate, m. p. 124—125°; chloroplatinate, m. p. 228° (decomp.); benzoyl derivative, m. p. 53—54° (yielding on oxidation β-2-benzamido*cyclo*hexylpropionic acid, m. p. 199—200°)], and a liquid isomeride, b. p. 205—206° and 89—91°/19—21 mm., d_4^{20} 0·9426, n_D^{20} 1·4926 [*hydrobromide*, m. p. 232°; *hydrochloride*, m. p. 223—224°; *chloroaurate*, m. p. 157—158°; *picrate*, m. p. 135—136°; *benzoyl* derivative, m. p. 96—97° (yielding on oxidation β-2-benz-

amido*cyclo*hexylpropionic acid, m. p. 156—157°)}. The liquid isomeride was also obtained in 10% yield on reduction by Sabatier's method (A., 1914, i, 323).

R. K. CALLOW.

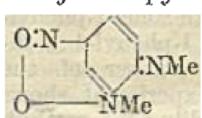
Reactions of bromo-derivatives of 2-amino-pyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (Ber., 1928, **61**, [*B*], 1236—1244; cf. following abstract).—The interaction of methyl iodide with 3 : 5-dibromo-2-aminopyridine resembles that with 2-aminopyridine, yielding mainly 3 : 5-*dibromo*-1-*methyl*-2-*pyridoneimide*, m. p. 99—100° [*hydriodide* (+0·5H_2O), m. p. 218—219° (decomp.) after darkening at 200°], with a small proportion of 3 : 5-*dibromo*-2-*methylaminopyridine*, m. p. 56·5—57°. The constitution of the latter compound follows from its formation by the action of methyl sulphate on the sodium derivative of 3 : 5-dibromo-2-aminopyridine and by the direct bromination of 2-methylaminopyridine, whereby 5-*bromo*-2-*methylaminopyridine*, m. p. 70—71°, is isolated as an intermediate product. With nitrous acid it gives the corresponding *nitroso*-derivative, m. p. 56—57°, whereas 3 : 5-dibromo-1-methyl-2-pyridoneimide gives 3 : 5-dibromo-1-methyl-2-pyridone. Dibromomethylaminopyridine with sulphuric and nitric acids yields 3 : 5-*dibromo*-2-*nitromethylaminopyridine*, m. p. 100—101°. Under similar conditions, 3 : 5-dibromo-2-aminopyridine affords a mixture of 3 : 5 - dibromo-2-nitroamino-pyridine, m. p. 123° (decomp.) after darkening at 121°, and 3-bromo-5-nitro-2-aminopyridine, m. p. 216—217°. Methylation of 3 : 5-dibromo-2-nitroamino-pyridine with methyl sulphate affords 3 : 5-dibromo-2-methylnitroaminopyridine, m. p. 100—101°, and 3 : 5-dibromo-1-methyl-2-pyridonenitroimide, m. p. 186—187°. The latter compound is also obtained by the nitration of 3 : 5-dibromo-1-methyl-2-pyridoneimide; it is transformed by boiling water into 3 : 5-dibromo-1 - methyl - 2-pyridone, m. p. 182°. Nitrous acid converts the dibromomethylpyridoneimide into 3 : 5-dibromo-1-methyl-2-pyridone. The action of concentrated sulphuric acid on 3 : 5-dibromo-2-nitroaminopyridine and 3 : 5-dibromo-2-methylnitro-aminopyridine affords 3 : 5 - dibromo - 2-hydroxy-pyridine, m. p. 208°, and 3 : 5-dibromo-2-methyl-nitrosoaminopyridine, m. p. 56—57°. Replacement of bromine by the nitro-group or wandering of the methyl radical does not occur with 3 : 5-dibromo-1-methyl-2-pyridonenitroimide under similar conditions.

H. WREN.

Nitro-derivatives of methylated forms of 2-aminopyridine. II. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (Ber., 1928, **61**, [*B*], 1223—1235; cf. A., 1925, i, 1328).—Repetition and extension of previous work on the methylation of nitro-aminopyridines shows that the methyl group wanders from the ring nitrogen atom of the pyridine nucleus to the amino-group. The presence of nitro-groups in one of the 3 or 5 positions impedes the addition of methyl iodide to the ring nitrogen atom; if a methyl group is already attached to this atom, the union is loosened.

5-Nitro-2-aminopyridine is converted by methyl iodide at 120° almost quantitatively into 5-*nitro*-2-*methylaminopyridine*, m. p. 181° (regarded previously as 5-nitro-1-methylpyridoneimide). 3-Nitro-2-amino-pyridine is transformed similarly into 3-*nitro*-2-*methyl-aminopyridine*, m. p. 63—64°, b. p. 262—262·5°/740 mm. 1-Methyl-2-pyridonenitroimide is isomerised by cold, concentrated sulphuric acid to a mixture of the nitromethylaminopyridines described above. 2-Methylaminopyridine is converted by a mixture of concentrated sulphuric acid and nitric acid (*d* 1·5) into 2-*nitromethylaminopyridine*, $C_5H_4N\cdot NMe\cdot NO_2$, m. p. 30—31°, which is converted by concentrated sulphuric acid into 2-*nitrosomethylaminopyridine*, m. p. 111—112°, 5-nitro-2-methylaminopyridine, m. p. 181°, and 3-nitro-2-methylaminopyridine, m. p. 63—64°. Boiling, dilute alkali hydroxide converts 5-nitro-2-methylaminopyridine into 5-nitro-2-hydroxypyridine, m. p. 190—191°, and methylamine, a similar change occurring with the isomeride. More concentrated alkali hydroxide decomposes the methyl-amino-compounds completely, whereas 5-nitro-2-aminopyridine is smoothly transformed into 5-nitro-2-hydroxypyridine and ammonia under these conditions. The preparation of 5-*nitro*-2-*nitrosomethyl-aminopyridine*, m. p. 112—113°, and 3-*nitro*-2-*nitroso-methylaminopyridine*, m. p. 102—103°, is recorded. 3-*Bromo*-5-*nitro*-2-*methylaminopyridine*, m. p. 163—164°, and 5-*bromo*-3-*nitro*-2-*methylaminopyridine*, m. p. 149—150°, are described. 3-Nitro-2-methylamino-pyridine is converted by concentrated sulphuric acid and nitric acid (*d* 1·5) into 3-*nitro*-2-*methylnitroamino-pyridine*, m. p. 89°. Methylation of 5-nitro-2-nitro-aminopyridine with methyl sulphate affords 5-nitro-2-nitroaminomethylpyridine, m. p. 59—60°, and 5-nitro-1-methyl-2-pyridonenitroimide. The following isomerisations of methyl derivatives of nitro-nitroaminopyridines by sulphuric acid are recorded: 3-nitro-2-nitromethylaminopyridine to 3 : 5-*dinitro*-2-*methylaminopyridine*, m. p. 147—148°, also obtained (in addition to other compounds) from 5-nitro-2-nitroaminomethylpyridine; 5-nitro-1-methyl-2-pyr-idonenitroimide chiefly to 3 : 5-dinitro-2-methyl-aminopyridine or 5-nitro-2-methylaminopyridine, mainly according to temperature. 3-Nitro-2-nitro-aminopyridine is isomerised to dinitro-2-amino-pyridine.

5-Nitro-2-methylaminopyridine is converted by methyl iodide at 125° into a mixture of 5-*nitro*-2-*methylaminopyridonium iodide*, m. p. 225° (decomp.), and 5 - nitro - 2 - dimethylaminopyridine, m. p. 152—153°. The methiodide is converted by ammonia into the compound (I), m. p. 149·5—150·5°, obtained also by nitration of 1 - methyl - 2 - pyridonemethyl-imide; it is transformed by boiling water into 5-nitro-1-methyl-2-pyridone, m. p. 171—172°, 5-nitro-2-methylaminopyridine, m. p. 181°, methyl alcohol, and methylamine.



(I.)

5-Nitro-2-dimethylaminopyridine is transformed by boiling 5% sodium hydroxide into 5-nitro-2-hydroxy-pyridine and dimethylamine. Acetic anhydride at 100° converts 5-nitro-2-methylaminopyridine into its *acetyl* derivative, m. p. 99°; 3-nitro-2-methylamino-pyridine is unchanged under these conditions.

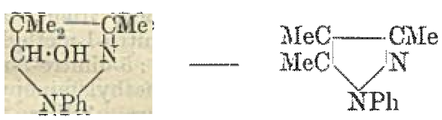
H. WREN.

Molecular compounds in the veronal series. P. PFEIFFER and R. SEYDEL (Z. physiol. Chem., 1928,

176, 1—16).—Veronal but not dimethylveronal forms additive compounds with pyramidone, antipyrine, and sarcosine anhydride (cf. Pfeiffer and Angern, A., 1926, 739); monosubstituted veronals, *N*-methylveronal, and *N*-phenylveronal form no true chemical compounds of this type, as determined by the mixed m.-p. curve method. Substitution of the two ethyl groups of veronal by hydrogen (barbituric acid) or one only by phenyl (luminal) does not destroy the power to form additive compounds. Luminal gives molecular *compounds* with antipyrine, with pyramidone, m. p. 132°, and with sarcosine anhydride (mol. ratio 2 : 1), m. p. 127°; barbituric acid forms *compounds* with antipyrine and with sarcosine anhydride, but these compounds have not been isolated. *N*-Methylbarbituric acid, like methylveronal, does not give additive compounds. Veramone solutions precipitated with ammonium sulphate yield precipitates which contain veronal and pyramidone in the mol. ratio 1 : 1, and not 1 : 2 as suggested by Mareeuw (Pharm. Weekblad, 1927, **30**, 753).

A. Wormall.

Ease of wandering and strength of attachment of organic radicals in transformations of alkylated hydroxypyrazolines. K. von Auwers and F. Dersch (Annalen, 1928, **462**, 104—134).—As stated by Knorr and Jochheim (A., 1903, i, 528), 5-hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline (I) is converted by concentrated sulphuric acid into 1-phenyl-3 : 4 : 5-trimethylpyrazole (II). This type of change has now been extensively studied in order to obtain further evidence as to the strengths of attachment, *i.e.*, valency requirements, of different radicals. Some striking dissimilarities are discovered. The 4 : 4-diethylpyrazoline changes like (I), but does so much more readily, whilst the 4 : 4-dipropyl deriv-

(I)  (II.)

ative eliminates propyl alcohol and not water, giving 1-phenyl-3-methyl-4-propylpyrazole. (The diallyl member gave tars, whilst the dibenzyl and diphenyl compounds could not be prepared.) The 4-methyl-4-ethyl compound gives mainly 1-phenyl-3 : 4-dimethyl-5-ethylpyrazole, together with some 1-phenyl-3 : 5-dimethyl-4-ethylpyrazole or 1-phenyl-4 : 5-dimethyl-3-ethylpyrazole. Although neither of the latter can be isolated pure, the experiment shows that ethyl migrates much more readily than methyl. The 4-ethyl-4-*n*-propyl compound (as I) gives doubtful results when treated with sulphuric acid, but an examination of the less complex case of 5-hydroxy-1-phenyl-3 : 4-diethyl-4-*n*-propylpyrazoline shows that the propyl group retains its position, whilst the ethyl group wanders. 5-Hydroxy-1-phenyl-3 : 4-dimethyl-4-*n*-propylpyrazoline is converted by sulphuric acid into 1-phenyl-3 : 4-dimethylpyrazole, with total elimination of propyl, and a similar result is obtained with the corresponding pyrazolines containing *iso*propyl, *n*-butyl, allyl, and benzyl radicals together with methyl in position 4. In every case 1-phenyl-3 : 4-dimethylpyrazole is formed, although the precise proportions of other products are difficult to establish.

The work enables certain definite conclusions to be reached. Measurement of the speed of disappearance of the different pyrazolines shows firstly that the nature of the substituent in position 3 is of no great consequence. Secondly, assuming in the cases in which water alone is eliminated that the intermediate at once changes to a pyrazole, it is clear that elimination of water is aided by substitution of methyl (in position 4) once or twice by ethyl. This again shows the smaller valency requirement of ethyl as against methyl. The loosely-attached allyl group confers a very high transformation rate on the pyrazolines studied, as would be anticipated, yet the benzyl group unexpectedly produces the converse effect. Other anomalies are that the 4 : 4-methylpropyl- and -dipropyl-pyrazoline derivatives undergo rapid conversion, whilst the intermediate ethylpropyl compound is particularly slow in changing. The results do show, however, that a methyl group is most firmly held, and that *n*-butyl, allyl, and benzyl groups are loosely held. Intermediately come ethyl, *n*-propyl, and *iso*propyl. Further, it is by no means certain that a radical (*e.g.*, phenyl) possessing large valency requirements is necessarily firmly held.

The pyrazolines required are prepared by reducing the appropriate pyrazolones using sodium and boiling amyl alcohol. The pyrazolones are obtained by converting a β-ketonic ester into the phenylhydrazone (at 100°), and then heating the latter, as a rule, at 180° until a test portion heated with acid no longer gives phenylhydrazine.

1-*Phenyl*-3-*methyl*-4-*propyl*-5-*pyrazolone*, from ethyl *n*-propylacetoacetate, has m. p. 101—102°; the *iso*-*propyl* analogue has m. p. 116—117° and b. p. 186—190°/15 mm.; the n-*butyl* analogue has m. p. 93·5—94·5° and b. p. 210°/16 mm. 1-*Phenyl*-3 : 4 : 4-*trimethyl*-5-*pyrazolone* has b. p. 300—303°/750 mm. and 158—160°/12 mm. 1-*Phenyl*-3 : 4-*dimethyl*-4-*ethyl*-5-*pyrazolone*, from ethyl methylethylacetoacetate, has m. p. 25·5—27·5°, b. p. 301°/760 mm. and 163—165°/12 mm. The 4-n-*propyl* analogue has b. p. 185—189°/13 mm.; the iso*propyl* analogue (intermediate *phenylhydrazone* has m. p. 111—113°) has m. p. 66—75° (indef.); the 4-n-*butyl* analogue has b. p. 205°/20 mm., d_4^{20} 1·039, and n_{He} 1·54023; the 4-*allyl* analogue has b. p. 189°/12 mm., d_4^{20} 1·0684, and 1·55564; the 4-*benzyl* analogue has m. p. 81—82°. 1-*Phenyl*-3-*methyl*-4 : 4-*diethyl*-5-*pyrazolone* has m. p. 51—52°, b. p. 170°/11 mm., 1-*phenyl*-3-*methyl*-4-*ethyl*-4-n-*propyl*-5-*pyrazolone*, b. p. 181°/12 mm., 1-*phenyl*-3-*methyl*-4 : 4-*di*-n-*propyl*-5-*pyrazolone*, b. p. 184°/12 mm., and 1-*phenyl*-3-*methyl*-4 : 4-*diallyl*-5-*pyrazolone*, b. p. 192°/11 mm. Ethyl propiopropionate, from ethyl propioacetate and methyl iodide etc., has b. p. 199° or 83°/15 mm., and is convertible into *ethyl* αα-*dimethylpropioacetate*, b. p. 83°/15 mm., from which 1-*phenyl*-3-*ethyl*-4 : 4-*dimethyl*-5-*pyrazolone*, b. p. 310° or 177°/11 mm., is obtained. 1-*Phenyl*-3 : 4-*diethyl*-4-n-*propyl*-5-*pyrazolone*, b. p. 203—208°/30 mm., d_4^{20} 1·035, n_{He} 1·54634, is obtained from *ethyl* α-*ethyl*-α-n-*propylpropioacetate*, b. p. 138—142°/40 mm., synthesised from *ethyl* α-n-*propylpropioacetate*, b. p. 127°/30 mm. 1-*Phenyl*-4 : 4-*dimethyl*-3-n-*propyl*-5-*pyrazolone*, b. p. 305°/30 mm., is obtained from *ethyl* αα-*dimethyl*-n-*butyroacetate*, b. p. 99—104°/15

mm., itself obtained from ethyl α-methyl-*n*-butyroacetate, which has b. p. 115—121°/38 mm.

Whilst ethyl dibenzylacetoacetate may be converted into the *hydrazone*, m. p. 112—113° (cf. Giua, A., 1916, i, 608), the latter does not pass normally into the expected 1-phenyl-4 : 4-dibenzyl-3-methyl-5-pyrazolone, which, however, may be the *product*, m. p. 139—140°, of the action of benzyl chloride on 1-phenyl-4-benzyl-3-methyl-5-pyrazolone in alcoholic sodium ethoxide solution.

The following 5-hydroxy-1-phenyl-3 : 4-dimethyl-4-alkyl-pyrazolines are described: 4-*ethyl*-, m. p. 97—98°; 4-n-*propyl*-, m. p. 98°; 4-n-*butyl*-, m. p. 104·5—106°; 4-*allyl*-, m. p. 95·5—97·5°; and 4-*benzyl*-, m. p. 121°.

5-Hydroxy 1-phenyl-3-methyl-4 : 4-diethylpyrazoline has m. p. 94—95°; *5-hydroxy-1-phenyl-3-methyl-4 : 4-di*-n-*propylpyrazoline*, m. p. 87—89·5°; *5-hydroxy-1-phenyl-4 : 4-dimethyl-3-ethylpyrazoline*, m. p. 78·5—79·5°; and *5-hydroxy-1-phenyl-4 : 4-dimethyl-3*-n-*propylpyrazoline*, m. p. 85—86°.

The following pyrazoles, prepared largely as reference compounds, were made either from αγ-diketones and phenylhydrazine or from the corresponding pyrazolones and phosphorus tribromide and yellow phosphorus at 200°. *1-Phenyl-3-methyl-4*-n-*propylpyrazole* has b. p. 155—164°/15 mm. [*picrate*, m. p. 111—112·5°; *mercuric chloride additive* compound, m. p. 180° (indef.); *hydrochloride*, m. p. 84—91°; *hydrobromide*]. *1-Phenyl-3-methyl-4*-iso*propylpyrazole* has b. p. 160—165°/15 mm. (*picrate*, m. p. 100·5—101·5°; *hydrobromide*, m. p. 144°). *1-Phenyl-3-methyl-4*-n-*butylpyrazole*, b. p. 170°/16 mm., forms a *picrate*, m. p. 90—93°. 1-Phenyl-3 : 4-dimethyl-5-ethylpyrazole has b. p. 283° or 150°/12 mm. (not 150°/75 mm. as lit.) (picrate formation suggests presence of the other possible isomeride, since two *picrates*, m. p. 112° and 87—94°, result) (*mercuric chloride* compound, m. p. 108—110°). *1-Phenyl-3 : 5-dimethyl-4-ethylpyrazole* has m. p. 79—80°, b. p. 159°/15 mm. (*picrate*, m. p. 114·5—115°; *mercuric chloride* compound, m. p. 135—139°). *1-Phenyl-3-methyl-4 : 5-diethylpyrazole*, b. p. 170°/17 mm., gives a *picrate*, m. p. 89·5—90·5°, and a *mercuric chloride* compound, m. p. 142·5—143·5°. *1-Phenyl-3-methyl-4-ethyl-5*-n-*propylpyrazole*, b. p. 175°/12 mm., forms two interconvertible *picrates*, m. p. 53—65° and 84—85°, and a *mercuric chloride* compound, m. p. 126—127°. *1-Phenyl-3 : 5-dimethyl-4*-n-*propylpyrazole* has b. p. 166°/11 mm. (*picrate*, m. p. 99—100°; *mercuric chloride* compound, m. p. 127·5—128·5°). *1-Phenyl-3 : 4-dimethyl-5*-n-*propylpyrazole* has b. p. 190—192°/33 mm. and 160°/11 mm. (*picrate*, m. p. 75—76°; *mercuric chloride* compound, m. p. 102—104°). *1-Phenyl-3-methyl-5-ethyl-4*-n-*propylpyrazole*, b. p. 172°/12 mm., forms a *picrate*, m. p. 85—87°, and a *mercuric chloride* compound, m. p. 136—137°. *1-Phenyl-3 : 5-dimethyl-4*-iso*propylpyrazole* has m. p. 36—37°, b. p. 194°/40 mm., d_4^{20} 1·024, and n_{He} 1·55810 (*picrate*, m. p. 92·5—93·5°; *mercuric chloride* compound, m. p. 128—130°). *1-Phenyl-3 : 5-dimethyl-4*-n-*butylpyrazole* has b. p. 180—184°/14 mm., *1-phenyl-3 : 5-dimethyl-4-allylpyrazole*, b. p. 205°/40 mm., $_4$ 1·028, and n_{He} 1·56932 (*picrate*, m. p. 87—89·5°). *αα-Dipropionylbutane*, b. p. 100°/15 mm. (*copper* salt, m. p. 160—161°), is converted by phenylhydrazine into *1-phenyl-3 : 5-diethyl-4*-n-*propylpyrazole*, b. p. 180—185°, d_4^{20} 0·996, n_{He} 1·54474 (*picrate*, m. p. 103·5—105·5°; *mercuric chloride* compound, m. p. 102—105°).

The conversions of pyrazolines into pyrazoles are in general effected by means of concentrated sulphuric acid at 100°. The following data are recorded: The 3 : 4 : 4-trimethylpyrazoline is completely transformed in 1 hr. into 1-phenyl-3 : 4 : 5-trimethylpyrazole, the mercuric chloride compound of which has m. p. 167·5° (not 131—132° as Jochheim, Diss., Jena, 1896). The 3-methyl-4 : 4-diethylpyrazoline takes 2—5 min. for transformation into 1-phenyl-3-methyl-4 : 5-diethylpyrazole, b. p. 284° or 141°/15 mm. The 3-methyl-4 : 4-di-*n*-propylpyrazoline rapidly affords a mixture of mono- and di-propylpyrazoles. The 3 : 4-dimethyl-4-ethyl compound (2 min.) gives 1-phenyl-3 : 4-dimethyl-5-ethylpyrazole, b. p. 154°/15 mm., from which the picrate, m. p. 112°, is obtained (see above). The 4 : 4-dimethyl-3-ethylpyrazoline (¾—1 hr.) affords *1-phenyl-4 : 5-dimethyl-3-ethylpyrazole*, b. p. 282° or 156°/12 mm. (*picrate*, m. p. 110—111°; *mercuric chloride* compound, m. p. 130—130·5°). The 3-methyl-4-ethyl-4-propylpyrazoline (1½ hrs.) affords some 1-phenyl-3-methyl-4-ethylpyrazole (*mercuric chloride* compound, m. p. 123—125°), but mainly a *phenylmethylethylpropylpyrazole*, b. p. 295—297° or 173—175°/17 mm., which forms a *mercuric chloride* compound, m. p. 132—133°, and may or may not be identical with the above 1-phenyl-3-methyl-5-ethyl-4-propylpyrazole. The 3 : 4-diethyl-4-propylpyrazoline gives 1-phenyl-3 : 5-diethyl-4-propylpyrazole, b. p. 175—180°/16 mm. or 170—175°/10 mm. The 4 : 4-dimethyl-3-*n*-propylpyrazoline readily passes into *1-phenyl-4 : 5-dimethyl-3-propylpyrazole*, b. p. 180—185°/35 mm., d_4^{20} 1·014, n_{He} 1·55435 (*picrate*, m. p. 72—74°; *mercuric chloride* compound, m. p. 110—111°). The 3 : 4-dimethyl-4-propylpyrazoline gives a mixture of products, containing 1-phenyl-3 : 4-dimethylpyrazole.

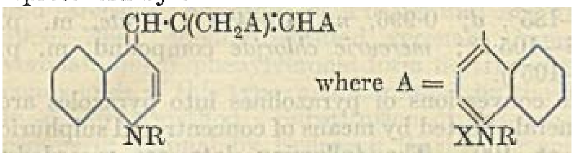
E. E. Turner.

Preparation of 2 : 2′-dipyridyl. J. P. Wibaut and J. Overhoff (Rec. trav. chim., 1928, 47, 761—763).—2 : 2′-Dipyridyl, m. p. 70·1°, b. p. 273—275° (picrate, m. p. 157—158·5°), is obtained in 60% of the theoretical yield by boiling a solution of 2-bromopyridine in cymene with copper powder for 1½ hrs. Some pyridine is also formed. With 2-iodopyridine the yield of 2 : 2′-dipyridyl is only 20%; 2-chloropyridine does not react.

R. Brightman.

Neocyanine. F. M. Hamer (J.C.S., 1928, 1472—1478).—The formation of neocyanine (B., 1927, 566) as a by-product in the preparation of 1 : 1′-diethyl-4 : 4′-carbocyanine iodide by the action of ethyl orthoformate on lepidine ethiodide in presence of pyridine (this vol., 76) has been described. This method is now applied to the preparation of *neocyanine ethiodide*, m. p. about 284° (decomp.), *ethobromide*, m. p. about 291° (decomp.), and *methobromide*, m. p. about 288° (decomp.); the best yield of neocyanine obtained was 41% of theory. By increasing the amount of pyridine, the yield of the 4 : 4′-carbocyanine is increased at the expense of that of the

neocyanine. It is suggested that neocyanine is represented by the formula



This hypothesis is based on analytical evidence, a consideration of the method of formation and of the properties of the neocyanines, and on analogy.

M. CLARK.

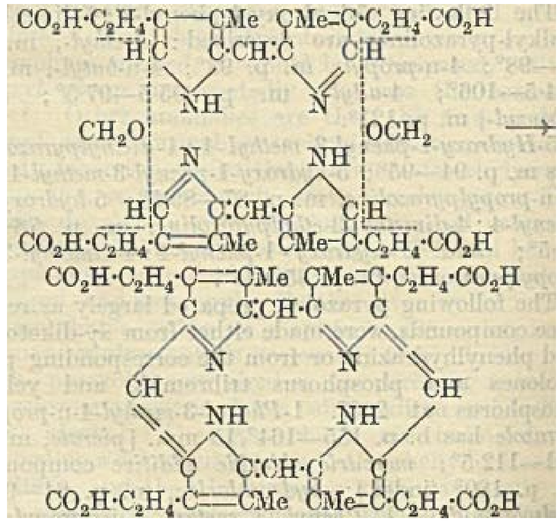
Porphyrin syntheses. XVII. Syntheses of opso- and hæmo-pyrrolecarboxylic acids. Synthesis of coproporphyrin. II. H. FISCHER and W. LAMATSCH (Annalen, 1928, 462, 240—250).—The methods (A., 1926, 1261) by which opsopyrrolecarboxylic acid (4-methylpyrrole-3-propionic acid) was obtained are unsuitable for preparative purposes and other methods have been sought. Reduction of bis-(5-carbethoxy-4-methyl-3-β-carboxyethylpyrryl)-methane with hydriodic and acetic acids gives a 40—48% yield of opsopyrrolecarboxylic acid, but, in addition, 80—84% of the theoretical yield of cryptopyrrolecarboxylic acid, so that this method is also unsuitable.

The readily obtained 5-carbethoxy-2 : 4-dimethylpyrrole-3-aldehyde is convertible without difficulty into the -3-acrylic and thence into the -3-propionic acid, viz., 5-carbethoxycryptopyrrolecarboxylic acid. The bromination of the latter is now under investigation; the resulting bromo-compound (readily characterised by heating it with alcohol, which converts it into *5-carbethoxy-4-methyl-2-ethoxymethylpyrrole-5-propionic acid*, m. p. 152°) reacts with 3 mols. of sulphuryl chloride (cf. this vol., 776) in cold ethereal solution to give *5-carbethoxy-4-methyl-3-β-carboxyethylpyrrole-2-carboxylic acid*, m. p. 243°, hydrolysed by alkali to *4-methyl-3-β-carboxyethylpyrrole-2 : 5-dicarboxylic acid*, m. p. 220° [or (?)224—226°]. The latter, when heated in a vacuum at 220°, passes into opsopyrrolecarboxylic acid, which is, however, better prepared by heating the carbethoxy-acid, m. p. 243°, with alkali at 175—180°, under pressure. Opsopyrrolecarboxylic acid resists all attempts at esterification, and when treated with sodium nitrite gives, not the oxime of cryptopyrrolecarboxylic acid, but a 50% yield of hæmatic acid.

When heated with formic and hydrobromic acids, opsopyrrolecarboxylic acid is converted into *(3-methyl-4-β-carboxyethylpyrryl)-(3-methyl-4-β-carboxyethylpyrrolenyl)methene hydrobromide*, m. p. 194—195° (decomp.), which, with glacial acetic and hydriodic acids at 100°, undergoes scission into opso- and hæmopyrrolecarboxylic acids. Opsopyrrolecarboxylic acid, when dissolved in chloroform and ether, reacts with hydrogen cyanide and chloride to give the expected imine (not isolated), which, when reduced by the Kishner–Wolff method at 160°, gives a good yield of hæmopyrrolecarboxylic acid.

Bromination of the last-named methene (hydrobromide?) affords *(5-bromo-3-methyl-4-β-carboxyethylpyrryl)-(5-bromo-3-methyl-4-β-carboxyethylpyrrolenyl)-methene hydrobromide*, which, when heated with cryptopyrrolecarboxylic acid and succinic acid at 180°, is converted into the tetramethyl ester, m. p. 288°, of coproporphyrin II.

When opsopyrrolecarboxylic acid methene hydrobromide is heated at 120° with formic and hydrobromic acids, only traces of porphyrin are produced, but the ester, m. p. 288°, results when the methene hydrobromide is heated with formaldehyde and hydrobromic acid at 120—125°, the constitution of coproporphyrin II thus being definitely established (annexed scheme):



Opsopyrrolecarboxylic acid 2-aldehyde, when heated with hydrobromic acid or with formic and hydrochloric acids, gives a methene identical with that obtained from opsopyrrolecarboxylic acid (when the methene so formed is heated with hydrobromic acid and formaldehyde, coproporphyrin II is formed and may be identified as the tetramethyl ester).

E. E. TURNER.

Hæmin syntheses. I. H. FISCHER and K. ZEILE (Annalen, 1928, 462, 210—230).—Addition of bromine (vapour) in light petroleum solution to ethyl 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate produces *ethyl 2 : 4-dimethyl-3-αβ-dibromoethylpyrrole-5-carboxylate*, m. p. 133°, whilst use of 3 mols. of bromine in glacial acetic acid gives ethyl 3-bromo-2 : 4-dimethylpyrrole-5-carboxylate, identical with the product of brominating ethyl 2 : 4-dimethylpyrrole-5-carboxylate. When a carbon disulphide or light petroleum solution of the vinylpyrrole is treated with hydrogen chloride, *ethyl 2 : 4-dimethyl-3-α-chloroethylpyrrole-5-carboxylate*, m. p. 95°, is formed, and this reacts with methyl-alcoholic potassium methoxide to give *ethyl 2 : 4-dimethyl-3-α-methoxyethylpyrrole-5-carboxylate*, m. p. 115°, also produced when the vinylpyrrole is treated with methyl-alcoholic hydrogen chloride, followed by basification. On the other hand, when the vinylpyrrole is heated with methyl-alcoholic sulphuric acid, it is apparently converted into *methyl 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate*, m. p. 123°.

Oxidation of the methoxyethyl derivative with chromic anhydride in acetic acid gives a mixture of ethyl 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate and 5-carbethoxy-2 : 4-dimethylpyrrole-3-carboxylic acid, the latter being formed by the similar oxidation of the vinyl derivative. Bromine converts ethyl 2 : 4-

dimethyl-3-α-methoxyethylpyrrole-5-carboxylate into ethyl 3-bromo-2 : 4-dimethylpyrrole-5-carboxylate.

When ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate is treated with magnesium methyl iodide, there is formed *ethyl* 2 : 4-*dimethyl*-3-α-*hydroxyethylpyrrole*-5-*carboxylate*, m. p. 100·5°, converted by phosphorus pentachloride in carbon disulphide into a chloro-compound which with potassium methoxide affords a methoxy-derivative identical with that (m. p. 115°) described above, the constitution of which is thus established.

If ethyl 2 : 4-dimethyl-3-α-hydroxyethylpyrrole-5-carboxylate is heated in a vacuum at 150°, there is formed a *dimeride*, m. p. 187°, also produced by boiling a light petroleum solution of ethyl 2 : 4-dimethyl-3-α-chloroethylpyrrole-5-carboxylate.

A well-defined *potassium* salt of ethyl 2 : 4-dimethyl-3-β-nitrovinylpyrrole-5-carboxylate is obtained by treating the latter with methyl-alcoholic potassium methoxide. The nitrovinyl ester brominates abnormally in acetic acid solution, the *monobromo*-derivative (m. p. 177°) formed not containing a 2-bromomethyl group, since instead of being converted by boiling water into a methene, it gives ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate. Similarly, 2 : 4-dimethylpyrrole-3-aldehyde is readily brominated, but apparently to give 5-*bromo*-2 : 4-*dimethylpyrrole*-3-*aldehyde*, m. p. 149° (decomp.). A methene of the type desired is, however, obtained as follows : 2 : 4-dimethylpyrrole-3-aldehyde is converted by formaldehyde in boiling aqueous alcoholic solution into *bis*-(3-*aldehydo*-2 : 4-*dimethylpyrryl*)*methane*, m. p. 286° (condensation *product* with aniline, $C_{21}H_{21}N_3$, has m. p. 165°; condensation *product* with Wurster's base, $C_{23}H_{26}N_4$, has m. p. 145°), which passes into the corresponding *methene hydrobromide* when treated with bromine in acetic acid (*methene* base sinters at 207°, decomp. 255—260°).

2 : 4-Dimethylpyrrole-3-aldehyde condenses with nitromethane in alcoholic solution, in presence of a little methylamine hydrochloride and sodium carbonate, to give 2 : 4-*dimethyl*-3-β-*nitrovinylpyrrole*, m. p. 149°, converted by hot formaldehyde solution into *bis*-(2 : 4-*dimethyl*-3-β-*nitrovinylpyrryl*)*methane*. 2 : 4-Dimethylpyrrole-3-aldehyde and malononitrile condense in presence of alcoholic methylamine (as above) giving 2 : 4-*dimethyl*-3-ββ-*dicyanovinylpyrrole*, m. p. 148° (the similarly prepared 2 : 4-*dimethyl*-5-ββ-*dicyanovinylpyrrole* has the same m. p.), which is converted by formaldehyde into *bis*-(2 : 4-*dimethyl*-3-ββ-*dicyanovinylpyrryl*)*methane*. The latter, when boiled with alkali, gives bis-(3-aldehydo-2 : 4-dimethylpyrryl)methane, as does the last-named nitrovinylmethane.

2 : 4-Dimethyl-3-ββ-dicyanovinylpyrrole is converted by hydrogen cyanide in chloroform and ether in presence of hydrogen chloride into the imino hydrochloride, which with ice-water passes into 2 : 4-*dimethyl*-3-ββ-*dicyanovinylpyrrole*-5-*aldehyde*, m. p. and this when heated with alkali gives 2 : 4-dimethylpyrrole-3 : ω-dialdehyde, m. p. 165° (Wasenegger, Diss., Techn. Hochsch., München, 1927).

Ethyl 2 : 4-dimethylpyrrole-5-carboxylate is converted by β-chloropropionyl chloride and aluminium chloride in carbon disulphide solution into ethyl 3-β-*chloropropionyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 138°, reacting with dimethylamine to give *ethyl* 3-β-*dimethylaminopropionyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 78° (sintering) (*hydrochloride*, m. p. 184°). The similarly prepared *ethyl* 3-*dimethylaminoacetyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate* has m. p. 87—88° (*hydrochloride*, m. p. 214°). 3-*Hydroxyacetyl*-2 : 4-*dimethylpyrrole*-5-*carboxylic acid*, m. p. 231°, is formed when ethyl 3-chloroacetyl-2 : 4-dimethylpyrrole-5-carboxylate is heated with alkali, and, when heated at 210—230°, passes into 3-*hydroxyacetylpyrrole*-2 : 4-*dimethylpyrrole*, m. p. 143°. The last with formaldehyde affords *bis*-(3-*hydroxyacetyl*-2 : 4-*dimethylpyrryl*)*methane*, m. p. 252° (previously sintering).

3-Methoxyacetyl-2 : 4-dimethylpyrrole-5-carboxylic acid at 170° gives 3-*methoxyacetyl*-2 : 4-*dimethylpyrrole*, m. p. 127°. *Ethyl* 3-*ethoxyacetyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate* has m. p. 113—114°.

E. E. TURNER.

Determination of active hydrogen in hæmin, in certain of its derivatives, and in pyrroles. III. H. FISCHER and P. ROTHEMUND (Ber., 1928, **61**, [*B*], 1268—1276; cf. A., 1926, 630; 1927, 1099).—In consequence of the very varying results obtained by the application of Zerevitinov's method to hæmins and pyrroles, the reaction itself has been subjected to critical examination. Zerevitinov's postulate that experiments are valid only when the blank value zero is obtained can be fulfilled by suitable treatment of pyridine, but very slight exposure of the solvent to moist air frequently suffices to destroy this ideal condition so that it is not practicable to fulfil this desideratum invariably. Further, comparable data are obtained only when analyses are completed within approximately equal times and the minimum gas evolution is adopted for calculation, thus introducing a somewhat arbitrary factor. It is essential that the compound under investigation should be completely dissolved throughout the whole reaction. Under these conditions, bis-2-carbethoxy-2 : 4-dimethylpyrrylmethene gives 1—1·5 active hydrogen atoms, whereas for its hydrobromide the value 2·6—2·97 is obtained (about 1 atom more than required by theory). High results are obtained with (2-bromo-3-carbethoxy-4-methylpyrryl)-(3'-carbethoxy-2' : 4'-dimethylpyrryl)methene, whereas almost identical values are obtained with the aldazine of 5-aldehydo-2 : 4-dicarbethoxy-3-methylpyrrole and its copper derivative.

It appears therefore that the methene as well as the imino-group of pyrroles is active toward the Grignard reagent. The Zerevitinov method is thus not applicable to the hæmins and porphyrins which contain four methene groups of which the behaviour cannot be predicted. Confirmation of this view is found in the observation that (4-hydroxy-3-carbethoxy-2-methylpyrryl)-(3'-carbethoxy-2' : 4'-dimethylpyrrolenyl)methane gives only two active hydrogen atoms and the compound,

$$\begin{array}{l}\mathrm{C(CO_2Et)\cdot CMe}\\ \mathrm{CH_2R}\qquad\mathrm{NH}\end{array}\!\!>\mathrm{C\cdot CH{:}C}<\!\!\begin{array}{l}\mathrm{CMe{:}C\cdot CO_2Et}\\ \mathrm{N{-\!\!-}CH_2R}\end{array}$$

$$\left[\mathrm{R = CH_2}<\begin{array}{l}\mathrm{C(CO_2Et)\cdot CMe}\\ \mathrm{NH{-\!\!-\!\!-}CH}\end{array}\right]$$

contains only 2·6. Determination of active hydrogen in a series of hæmins and porphyrins with exclusion of all possible errors fails to give concordant results. With hæmin the variation is between two and three at the atmospheric temperature. Hæmin dimethyl ester and the iron salt of tetramethylhæmatoporphyrin contain exactly one active hydrogen atom. As a mean, hæmin has three active hydrogen atoms, but certain data must be disregarded without apparent reason. Uro- and *iso*uro-porphyrin esters, octaethylporphin, and acetonepyrrole give varying results from which definite conclusions cannot be reached. With xanthoporphinogens paradoxical values are obtained. Contrary to the literature, azobenzene does not contain active hydrogen.

It is concluded that unavoidable catalysts greatly influence the evolution of gas during the Zerevitinov reaction and that this effect is also produced by complex pyrrole derivatives. H. WREN.

Thiazole derivatives. II. H. W. STEPHEN and F. J. WILSON (J.C.S., 1928, 1415—1422; cf. A., 1926, 1262).—Diacetophenonethiocarbohydrazone reacts in alcoholic solution in presence of sodium ethoxide with ethyl α-bromopropionate (I), ethyl α-bromo-*n*-butyrate (II) and ethyl phenylbromoacetate, yielding 3-*phenylmethylmethyleneamino*-2 : 4-*diketo*-5-*methyl* (*ethyl* or *phenyl*)*tetrahydrothiazole*-2-*phenylmethylmethylenehydrazone*, m. p. 150°, 110°, and 165°. Thiocarbohydrazide and ethyl chloroacetate (III) yield 3-*amino*-2 : 4-*diketo-5-tetrahydrothiazole-2-hydrazone* (?), m. p. 119—120°. 3-*Amino*-2 : 4-*diketo*-5-*methyltetrahydrothiazole-2-hydrazone*, m. p. 100—101° (*dibenzylidene* derivative, m. p. 114°), and 3-*amino*-2 : 4-*diketo*-5-*ethyltetrahydrothiazole*-2-*hydrazone* (?), m. p. 92—93° (*dibenzylidene* derivative, m. p. 106°), were prepared similarly from (I) and (II), respectively. *o*-Phenylenethiocarbamide with sodium ethoxide and (I) or (II) yields respectively *ethyl benziminazolyl*-2-α-*thiolpropionate* (IV), m. p. 100° (dimorphous), and *ethyl benziminazolyl*-2-α-*thiol*-n-*butyrate* (V), m. p. 108—109° (dimorphous). Hydrolysis of (V) with hydrochloric acid affords *benziminazolyl*-2-α-*thiol*-n-*butyric acid*, m. p. 176° (decomp.). When (IV) is heated in dry benzene solution with sodium and the solid thereby deposited is treated in alcoholic solution with concentrated aqueous hydrochloric acid, no compound of dicyclic structure can be isolated, but *benziminazolyl*-2-α-*thiolpropionic acid*, m. p. 179° (decomp.), is formed. When dry gaseous hydrogen chloride is substituted for aqueous hydrochloric acid in the above procedure, a *compound*, m. p. 118—119°, is produced. When (V) undergoes similar treatment, a *compound*, m. p. 120°, results. *Benziminazole*-2-*thioglycollic acid*, m. p. 215°, is obtained by heating together *o*-phenylenethiocarbamide and aqueous chloroacetic acid. *Ethyl* 1 : 4 : 5 : 6-*tetrahydropyrimidine-2-thioglycollate*, m. p. 256° (decomp. from 200°), is prepared by heating trimethylenethiocarbamide and (III) in pyridine solution, whilst benzoylenethiocarbamide and (III) yield an oil from which *ethyl* 4-*keto*-3 : 4-*dihydroquinazoline*-2-*thioglycollate*, m. p. 149°, is obtained by fractional distillation. 2 : 4-*Diketotetrahydrothiazole-2-semicarbazone*, m. p. 221—222° (decomp.), is obtained by condensation of hydrazothiodicarbonamide with chloroacetic acid, and yields 2 : 4-diketotetrahydrothiazole and semicarbazide on hydrolysis with hydrochloric acid. Hydrazodithiodicarbonamide and (III) in alcoholic sodium ethoxide solution yield a substance regarded as 2 : 4-diketotetrahydrothiazole-2-ketazine, since it is hydrolysed by hydrochloric acid to 2 : 4-diketotetrahydrothiazole and hydrazine. This substance was previously regarded by Frerichs and Holler (A., 1913, i, 909) as 3 : 3-bis-ψ-thiohydantoin. *Acetophenone*-δ-*phenylthiosemicarbazone* has m. p. 195°. M. CLARK.

Aminothiophenol [benzthiazole] derivatives. J. POLLAK, E. RIESZ, and Z. KAHANE (Monatsh., 1928, 49, 213—228).—4 : 4′-Dichloro-2 : 2′-dinitrodiphenyl disulphide (Blanksma, A., 1901, i, 461) on treatment with an alkaline sodium sulphide solution yields the sodium salt of chloronitrothiophenol, which without being isolated is treated with chloroacetic acid; on acidification, 4-*chloro-2-nitrophenylthioglycollic acid*, m. p. 209—210°, separates. This when treated with concentrated sulphuric acid at 100° yields 5 : 5′-dichloro-7 : 7′-dinitrobisthionaphthenindigo; it is oxidised by peracetic acid to 4-*chloro*-2-*nitrophenylsulphonacetic acid*, m. p. 158°, and reduced by zinc and acetic acid to 6-*chlorobenzo*-3-*ketodihydro*-1 : 4-*thiazine*, $C_6H_3Cl<\begin{matrix}NH\cdot CO\\ S—CH_2\end{matrix}$, m. p. 204°.

Dichlorodinitrodiphenyl disulphide is reduced by zinc and acetic acid to a product which, filtered from zinc and zinc mercaptide and recrystallised from hydrochloric acid, is 4-*chloro-2-aminothiophenol hydrochloride*, m. p. 207°. This when heated with nitrous acid yields 5-chlorobenzthiodiazole.

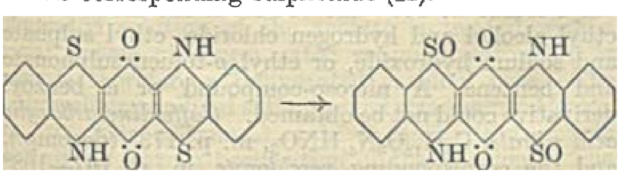
$C_6H_3Cl<\begin{matrix}N\\S\end{matrix}>N$, m. p. 107° (cf. Beilstein and Kurbatow, A., 1879, 231). When the chloroaminothiophenol in alcoholic solution is treated with picryl chloride, a *picryl* derivative, $C_{12}H_7O_6N_4ClS$, is obtained, decomp. on heating; when, however, a solution of the hydrochloride in alcohol is treated with picryl chloride and sodium acetate, and the mixture is heated, the product is 6-*chloro*-2 : 4-*dinitrophenthiazine* (cf. Kehrmann, A., 1900, i, 62), m. p. 280° (charring). When the reduction of the dichlorodinitrodiphenyl disulphide is effected by zinc in a mixture of acetic acid, acetic anhydride, and sodium acetate, the product is 4-chloro-1-methylbenzthiazole, $C_6H_3Cl<\begin{matrix}N\\S\end{matrix}>CMe$.

The reagent chloronitrophenylsulphur chloride condenses with dichlorodiaminodiphenyl disulphide in ether to give the *hydrochloride*, m. p. 182°, of a base, 4″-*chloro*-2″-*nitrophenylthiol*-2 : 2′-*diamino*-4 : 4′-*dichlorodiphenyl disulphide*, m. p. 164—165°, which further condenses in benzene with the reagent, to give *bis*-[4-*chloro*-2-(p-*chloro*-o-*nitrophenylthiolamino*)-*phenyl*] *disulphide*, $(NO_2\cdot C_6H_3Cl\cdot S\cdot NH\cdot C_6H_3Cl\cdot S\cdot)_2$, m. p. 159°. No reaction is observed between chloroaminothiophenol and the reagent. Aminothiophenol in ether condenses with the reagent to give the *hydrochloride*, m. p. 205°, of the base 4′-*chloro*-2-*nitro*-4-*aminodiphenyl disulphide*, m. p. 130—131°; the latter condenses with a further quantity of the reagent to give chloronitroaminodiphenyl disulphide

hydrochloride and 4-*chloro*-2-*nitro*-4′-(p-*chloro*-o-*nitrophenylthiolamino*)*diphenyl disulphide*, $NO_2\cdot C_6H_3Cl\cdot S_2\cdot C_6H_4\cdot NH\cdot S\cdot C_6H_3Cl\cdot NO_2$, m. p. 187°. It is suggested that the failure of *p*-chloro-*o*-aminothiophenol to react with the reagent is due to its existence as an internal salt, thus : $C_6H_3Cl{<}{\overset{NH_3}{\underset{S}{|}}}$.

When anilinetrisulphonyl chloride (Lustig and Katscher, A., 1927, 867) is reduced in acetone by zinc and hydrochloric acid, and filtered immediately a cloudiness or precipitate appears, dilution with water followed by ether extraction gives the unstable 2 : 4 : 6-*trithiolaniline*. This with picryl chloride yields a *tripicryl* derivative, which on treatment with alcoholic potassium hydroxide gives 2 : 4-*dinitro*-7 : 9-*di*(*picrylthiol*)*phenthiazine*, soluble in nitrobenzene only. Reduction of anilinetrisulphonyl chloride by zinc, acetic acid and anhydride, and sodium acetate yields in the ethereal extract 3 : 5-*di*(*acetylthiol*)-1-*methylbenzthiazole*, m. p. 127°, and in the residue a product extracted by hydrochloric acid, and also obtained by the action of alcohol and hydrochloric acid on the above product, viz., 3 : 5-*dithiol*-1-*methylbenzthiazole*, m. p. 180—181°. This and the corresponding *disulphide* obtained by oxidation are only faintly yellow, and are not dyes, for the production of which a second fused benzene ring or series of rings is required. E. W. WIGNALL.

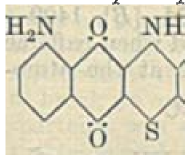
Dibenzodithiazinoquinone, a class of vat dyes. II. Reaction between nitric acid and dibenzodithiazinequinone. R. SHIBATA (J. Soc. Chem. Ind. Japan, 1928, **31**, 73—75).—When dibenzodithiazinequinone was treated with a cold mixture of fuming nitric acid and glacial acetic acid, a substance was obtained which resembles orange-II in colour, is soluble in dilute alkali, and forms crystalline *compounds* with alkali hydroxides which are soluble in water. From the hyposulphite vat containing sodium hydroxide, it gives the same shade on fibres as dibenzodithiazinoquinone (I). Analysis shows that the action of the mixed acid is one of oxidation, not of nitration, resulting in the formation of the corresponding sulphoxide (II).



(I.) (II.)

Y. TOMODA.

lin-Benzo-p-thiazinoquinones. K. FRIES, W. PENSE, and O. PEETERS (Ber., 1928, **61**, [*B*], 1395—1402; cf. A., 1922, i, 577; 1924, i, 525).—2 : 5-Dianilino-3 : 6-dimethylthiol-*p*-benzoquinone, m. p. 260°, is unexpectedly converted by hydrogen peroxide in glacial acetic acid into 2 : 5-dianilino-*p*-benzoquinone. Dibenzothiazinoquinone (formula I, preceding abstract), which does not melt below 360°, is obtained by treating dichlorodianilino-*p*-benzoquinone with sodium disulphide in boiling alcohol. With alkali hydroxide and sodium hyposulphite it gives a golden-yellow vat from which cotton is dyed feebly, wool readily. The *diacetyl* compound is described. The quinone is reduced to the corresponding *quinol*, m. p. above 360° (*tetra-acetyl* derivative, m. p. 305°). Oxidation of the dye with hydrogen peroxide in concentrated sulphuric acid affords the *disulphone*, $C_{18}H_{10}O_6N_2S_2$, m. p. above 360°. Chloranil and *p*-anisidine yield 2 : 5-*dichloro*-3 : 6-*di*-p′-*methoxyanilino*-p-*benzoquinone*, m. p. 291°, transformed into *dimethoxybenzothiazinoquinone*, m. p. above 300°. 2 : 2 : 3 : 3 : 4-*Pentachloro*-5-*nitro*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 159° (decomp.), is obtained by prolonged treatment of a solution of 5-nitro-α-naphthylamine in hydrochloric and acetic acids with chlorine. It is converted by treatment with aqueous sodium hydrogen sulphite into 2 : 3 : 4-*trichloro*-5-*nitro*-α-*naphthol*, m. p. 208° (*acetate*, m. p. 150°), which is transformed by nitric acid in glacial acetic acid into 2 : 3 : 4-*trichloro*-4 : 5-*dinitro*-1-*keto*-1 : 4-*dihydronaphthalene*, m. p. 85° (decomp.). When warmed with concentrated sulphuric acid the ketone is converted into 2 : 3-*dichloro*-5-*nitro*-1 : 4-*naphthaquinone*, m. p. 176°. The latter compound is also obtained by the nitration of 2 : 3-dichloro-1 : 4-naphthaquinone. 3-*Chloro*-5(8)-*nitro*-2-*anilinonaphthaquinone*, m. p. 273°, and sodium sulphide in aqueous alcohol afford 5(8)-*amino*-2-*anilino*-3-*thiol*-1 : 4-*naphthaquinone*, which is further converted into 9-*amino*-lin-*benzonaphtho*-p-*thiazinoquinone* (I), m. p. 300° (*monoacetyl* derivative, m. p. 300°).



(I.)

2 : 3-Dichloro-5-nitro-1 : 4-naphthaquinone is reduced by stannous chloride and hydrochloric acid in glacial acetic acid to 2 : 3-*dichloro*-5-*amino*-1 : 4-*dihydroxynaphthalene hydrochloride*, oxidised by ferric chloride to 2 : 3-*dichloro*-5-*amino*-1 : 4-*naphthaquinone*, m. p. 220°. 3-*Chloro*-5(8)-*amino*-2-*anilino*-1 : 4-*naphthaquinone* has m. p. 210°. H. WREN.

Stereochemistry of the saturated tervalent nitrogen atom. VIII. Methyl*iso*pelletierine. J. MEISENHEIMER and E. MAHLER (Annalen, 1928, **462**, 301—316).—Methylconhydrinone and methyl*iso*pelletierine, regarded by Hess and Grau as stereoisomerides (A., 1925, i, 425), are shown to be structural isomerides. The former substance is, as these authors suppose, α-2-*N*-methylpiperidylpropan-α-one [2-propionyl-1-methylpiperidine], but methyl*iso*pelletierine is now shown to be α-2-*N*-methylpiperidylpropan-β-one [2-acetonyl-1-methylpiperidine].

If Hess and Grau's contention were correct, the supposed stereoisomerides should give one and the same methiodide, but two distinct methiodides are obtained. Further, methyl*iso*pelletierine and methylconhydrinone differ greatly in their reactions as ketones. The former is readily reduced to an alcohol, the latter is not, and so on.

Hess' supposed α-2-*N*-methylpiperidylpropan-β-one is shown to be a mixture (cf. A., 1917, i, 350, 352; 1918, i, 34). The pure ketone has been synthesised as follows : 2-β-hydroxy-*n*-propylpyridine (preparative details for this are given) is converted into the methosulphate, which is reduced catalytically in presence of platinum–platinum oxide to 1-methyl-

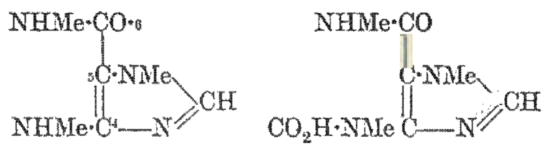
2-β-hydroxy-*n*-propylpiperidine, b. p. 110—120°/22 mm. Oxidation of the latter with chromic anhydride in glacial acetic acid at the b. p. gives methyl*iso*pelletierine, identified by conversion into the picrate, hydrochloride, hydrobromide, chloroaurate, methiodide, semicarbazone, and semicarbazone hydrochloride.

Catalytic reduction of 2-β-hydroxy-*n*-propylpyridine affords 2-β-hydroxy-*n*-propylpiperidine, m. p. 69—70° (the low m. p. 45—47° given by Ladenburg is accounted for by the hygroscopic nature of the substance). Oxidation of the latter with chromic anhydride in acetic acid produces *iso*pelletierine [α-2-piperidylpropan-β-one], the picrate of which melts at 147—148°, not at 113—115° as stated by Hess and Eichel (A., 1918, i, 34).

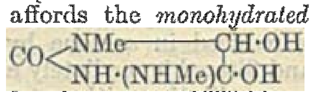
Methylation of 2-β-hydroxy-*n*-propylpiperidine by Hess' method (A., 1916, i, 67; 1917, i, 351) gives 1-methyl-2-β-hydroxy-*n*-propylpiperidine, identical with the above product. Its picrate melts at 145°, not at 136—137° as stated by Hess, whose product was evidently a mixture; the semicarbazone hydrochloride has decomp. 210°, not 183° (Hess).

E. E. TURNER.

Caffeidine and caffeidinecarboxylic acid. H. BILTZ and H. RAKETT (Ber., 1928, **61**, [*B*], 1409—1422).—Caffeidine (I) is readily formed when caffeine is shaken with 2*N*-sodium hydroxide at the atmo-



(I.) (II.)

spheric temperature and is separated from the resulting solution as the *nitrate*, m. p. 215° (decomp.). The filtrate from the salt is treated with sodium acetate and copper acetate, whereby copper caffeidinecarboxylate is precipitated. Caffeidine, m. p. 93°, is isolated from the nitrate by dissolution in sodium carbonate and extraction with chloroform. When moist, it is very sensitive to air, but can be preserved unchanged when dry if protected from light. It behaves as a monoacid base; the *perchlorate*, $C_7H_{12}ON_4,HClO_4$, m. p. 220—221° (decomp.), *hydrochloride*, m. p. 215° (decomp.), and the *vanadylmalonate*, $(C_7H_{12}ON_4)_2,H_2[VO(C_3H_2O_4)_2],2H_2O$, are described. With silver nitrate and a little ammonia it affords *silver dicaffeidine nitrate*, $Ag(C_7H_{12}ON_4)_2NO_3$. The basic nature of caffeidine appears to be due to the nitrogen atom 3; the methylamino-residue attached to carbon atom 4 appears incapable of adding acid, probably owing to the immediate presence of the double linking. *Benzoylcaffeidine* has m. p. 174°. The action of nitrous acid gives *nitrosocaffeidine*, m. p. 155° (decomp.), in which the imino-group 8 suffers change, the methylamino-residue 7 remaining unaffected, since *allo*caffuric acid and caffeidinecarboxylic acid do not react with nitrous acid. Methyl sulphate and potassium hydroxide transform caffeidine into *methylcaffeidine*, m. p. 86° (*perchlorate*, m. p. 173°), whereas it is not affected by diazomethane. 1:3-Dimethylparabanic acid is readily formed by oxidation of caffeidine, probably according to the scheme: (I)⟶NHMe·CO·CO·NMe·CO_2H⟶ $\begin{matrix}CO\cdot NMe\\ CO\cdot NMe\end{matrix}\!\!>\!CO$. The double linking between carbon atoms 4 and 5 is readily established by the action of methyl alcohol and chlorine, whereby the *dimethyl ether* of *caffeidine*-4:5-*glycol*, m. p. 164° (*hydrochloride*), is produced. The action of chlorine water on caffeidine affords the *monohydrated hydrochloride* of the *base*,  m. p. 112°, from which the free *base*, m. p. 163° (decomp.), is derived by means of potassium cyanate.

Caffeidine is readily converted into caffeine by treatment with ethyl chloroformate or potassium cyanate. Carbamide and caffeidine when treated with hydrogen chloride afford *caffeidine-8-carboxylamide*, m. p. 244—245°, which is transformed by boiling, dilute mineral acids into theobromine and methylamine, thus establishing the constitution of the amide; analogous reactions could not be effected with thiocarbamide or guanidine. With thiocarbonyl chloride caffeidine affords 2-*thiocaffeine*, m. p. 205° after softening at 203° [*perchlorate*, m. p. 239—240° (decomp.)], which is readily chlorinated in chloroform to 8-*chloro-2-thiocaffeine*, m. p. 186—187°. Treatment of the latter compound with sodium methoxide affords 8-*methoxy-2-thiocaffeine*, m. p. 174°, from which 2-*thiotetramethyluric acid*, m. p. 297—298°, and 2-*thio*-1:3:7-*trimethyluric acid*, m. p. 343° (apparent decomp.), are derived by the action of methyl alcohol at 200° and warm dilute hydrochloric acid, respectively. 8-Chloro-2-thiocaffeine and potassium hydrogen sulphide afford 2:8-*dithio*-1:3:7-*trimethyluric acid*, $C_8H_{10}ON_4S_2$, m. p. 285° (decomp.) (*monosodium* and *monopotassium* salts). Treatment of the dithio-acid with alkali hydroxide and the requisite alkyl sulphate or bromide yields the *methyl*, m. p. 183°, *ethyl*, m. p. 156°, and *allyl*, m. p. 98°, *ethers* of 2-thio-8-thiolcaffeine.

Caffeidinecarboxylic acid, m. p. 159° (decomp.), with acetic acid of crystallisation, m. p. 127—129°, is obtained from the copper salt (see above). An ester could not be obtained by treating the copper salt with ethyl iodide at 105—110° or from the free acid by ethyl alcohol and hydrogen chloride, ethyl sulphate and sodium hydroxide, or ethyl *p*-toluenesulphonate and benzene. A nitroso-compound or a benzoyl derivative could not be obtained. *Caffeidinecarboxylic acid nitrate*, $C_8H_{12}O_3N_4,HNO_3$, m. p. 173° (decomp.), and the corresponding *perchlorate*, m. p. 167—168° (decomp.), and *hydrochloride*, m. p. 179° (decomp.), are described.

H. WREN.

Sparteine. I. K. WINTERFELD (Arch. Pharm., 1928, **266**, 299—325).—Sparteine is not readily attacked by many reagents: it is recovered unchanged after being treated with ethyl chloroformate, or hydrogen iodide in glacial acetic acid at the b. p. or even at 180°. When oxidised it tends to break down completely, but Gadamer's reagent, viz. mercuric acetate in dilute acetic acid, is now found to effect a stepwise dehydrogenation. In the cold two hydrogen atoms are removed and, when the three acetatomercuric groups introduced are eliminated, there remains in the solution the acetate of *dehydrosparteine*,

$C_{15}H_{24}N_2$. Dehydrosparteine is isomeric with Willstatter's spartyrine (A., 1905, i, 544), but differs completely from the dehydro-compound of Wolffenstein and Reitmann (A., 1927, 887). It is a viscous oil, unsaturated and unstable when exposed to air. It has $[\alpha]_D$ −142·10° (in chloroform) and so presumably a double linking has been formed in proximity to an asymmetric carbon atom. It is not displaced from its salts except by alkali hydroxide and so appears to be the anhydride of the carbinol form of a quaternary ammonium base. Moureu and Valeur's formula for sparteine (A., 1913, i, 89) allows of various possibilities, but, as will be seen, the main result of the present work is to throw doubt on the validity of this formula. *Dehydrosparteine chloroplatinate*, m. p. 255° (decomp.), *chloroaurate*, m. p. 155—158°, and *mercuric chloride double salt*, m. p. 256—257° (decomp.), are described. When the base is reduced with zinc and hydrochloric acid sparteine is apparently not regenerated, for the *product* has $[\alpha]_D$ about −18·5° and yields an amorphous *chloroaurate*, m. p. 166—167°. Dehydrosparteine is oxidised by potassium permanganate in cold acetone solution, the equivalent of five oxygen atoms being consumed. The *acid* so obtained is a syrup which is converted with difficulty into the *methyl* or *ethyl* ester. The methyl ester, $C_{15}H_{26}O_2N_2$, yielded once a solid *chloroplatinate*, m. p. 256—257° (decomp.), but other solid derivatives were not obtained. Efforts to prepare a chloride or an amide, or to reduce the ethyl ester to the corresponding alcohol were likewise fruitless, and on distillation the esters decomposed completely. The methyl ester yields an oily *monoacetyl* and an oily *mononitroso*-derivative, so that it is evident that in the oxidation one nitrogen atom has become secondary in function. A *hydrazide* (*benzylidene* derivative, m. p. 207°) is also obtained; this yields a *nitrosoazide* which is normally converted by way of the *nitrosourethane* into the *amine* (*picrate*, m. p. 187°), but all these derivatives are either gummy or viscous oils. When the oxidation of sparteine with mercuric acetate is carried out in hot solution, four hydrogen atoms are lost. The product, *didehydrosparteine*, $C_{15}H_{22}N_2$, is extracted only by using an ether–chloroform mixture, when a concentrated solution of the acetate is treated with a great excess of concentrated sodium hydroxide; it also is therefore a dehydrated carbinol base. The only well-crystallised salt obtained was the *perchlorate*, m. p. 256° (decomp.), $[\alpha]_D$ +44·87° (the optical activity is lost on basification of the solution). The *chloroplatinate*, m. p. 273° (decomp.), *chloroaurate*, m. p. 147° (decomp.), *picrate*, m. p. 178° (decomp.), and *mercuric chloride double salt*, m. p. 196—198° (decomp.), are also described. This stepwise oxidation of sparteine is evidence that there are two independent nitrogen ring systems in the compound, but suggests that they are either not, as Moureu and Valeur's formula (*loc. cit.*) would indicate, symmetrically arranged about a central carbon atom or not built on a similar plan. Didehydrosparteine is oxidised by potassium permanganate in cold dilute sodium carbonate solution, the equivalent of ten oxygen atoms being consumed, to a dibasic *acid*, the *methyl* ester, $C_{15}H_{26}O_4N_2$, and *ethyl* ester, $C_{17}H_{30}O_4N_2$, of which are syrups. The methyl ester yields *diacetyl*, and *dinitroso*-derivatives, and so it is proved that both nitrogen atoms are now secondary in function. The acetyl derivative of the ester was reduced by Karrer's modification of Bouveault and Blanc's method to the corresponding amino-alcohol, which was obtained in passable yield; it was converted directly by treatment first with phosphorus pentachloride in chloroform solution, and then with amalgamated zinc and hydrochloric acid into a *base*, $C_{13}H_{24}N_2$(?), the *chloroaurate* of which had m. p. 145° (decomp.). The methyl ester gave a *dihydrazide*, a resinous mass [*benzylidene* derivative, m. p. 175° (decomp.)], which was successively converted into an oily *dinitrosodiazide*, a syrupy *dinitrosourethane*, and so into a *diamino-compound*, which, as was to be expected from its possessing two primary and two secondary amino-groups, yielded a *tetrabenzoyl* derivative; this was an oil, but gave a crystalline *chloroaurate*, m. p. 98° (decomp.).

[With W. Ipsen.]—A preliminary account is given of attempts to carry out the Hofmann exhaustive methylation, which was the main theme of Moureu and Valeur's work (*loc. cit.*), with particular attention to the following points: (i) the products of each destructive distillation to be hydrogenated so as to leave no unsaturated linkings; (ii) after each methylation the isomerides to be separated; (iii) in forming methiodides the action to be if possible stepwise, *i.e.*, to break up one N-ring at once. The α-methiodide of sparteine was separated and converted into methylsparteine as described by Moureu and Valeur. It was not found possible to hydrogenate this directly by catalytic methods. The substance is a mixture of α- and β-methylsparteines, and the α-compound was separated in a pure condition as the sparingly soluble monohydriodide. It was then successfully hydrogenated, in glacial acetic acid solution and using platinum oxide as catalyst, to *dihydro-α-methylsparteine*, which is converted, with difficulty, into a *dimethiodide*, m. p. 125°. The formation of this dimethiodide rendered it impossible to carry out proposal (iii).

W. A. Silvester.

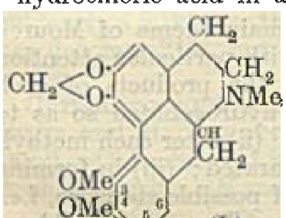
Solutions of quinine in ethylurethane. M. Giordani (Annali Chim. Appl., 1928, **18**, 239—244).—When heated at 100° or exposed to ultra-violet rays in presence of various substances, solutions of quinine undergo transformation into the toxic isomeride, quinotoxin. Among the accelerators of this change are urethane and glycerol, which are largely used in the preparation of doses for endomuscular or endovenous injection. Alcohol, chloroform, and hydrochloric acid are inactive in this respect. The abnormal effects sometimes observed when quinine is administered orally may arise from the ingestion of foods, such as milk, fruit, etc., giving rise to the formation of malic, citric, or lactic acid, which may effect partial conversion of the quinine into quinotoxin.

T. H. Pope.

Double salts of alkaloids with zinc iodide. R. Danet (J. Pharm. Chim., 1928, **7**, [viii], 548—550).—Crystalline compounds of quinine and codeine, containing 1 mol. of zinc iodide to 1 mol. of quinine dihydriodide and 2 mols. of codeine hydriodide, respectively, are obtained by mixing warm solutions

of the appropriate salts acidified with hydriodic acid, and cooling slowly. B. FULLMAN.

Alkaloid of *Corydalis cava*. XII. Synthesis of *d*-bulbocapnine methyl ether. E. SPÄTH and O. HROMATKA (Ber., 1928, **61**, [*B*], 1334—1342; cf. Gadamer, A., 1911, i, 1012; Späth and others, this vol., 432).—*Nitrohomoveratroylhomopiperonylamide*, $CH_2O_2{:}C_6H_3{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_2(OMe)_2{\cdot}NO_2$, m. p. 158°, is obtained in 94·6% yield by the action of *nitrohomoveratroyl chloride*, m. p. 54—56°, on homopiperonylamine in benzene, sodium hydroxide being added to complete the reaction. It is transformed by the relatively prolonged action of phosphoric oxide on small quantities of the material into 6 : 7-*methylenedioxy*-1 : 2′-*nitro*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydroisoquinoline*, m. p. 167·5—168° [*hydrochloride*, decomp. 217—218°; *methiodide*, m. p. 192—193° (decomp.)]. The methiodide is converted into the more freely soluble *methochloride*, which is reduced by tin and hydrochloric acid in alcoholic solution to the non-



(I.)

crystalline *amino*-derivative. Diazotisation of the latter followed by treatment with copper powder and reduction with zinc dust and concentrated hydrochloric acid affords bulbocapnine methyl ether (I), with bases of the type of dilaudanosine, phenolic bases, and other impurities. Purification of bulbocapnine methyl ether is exceptionally difficult and is largely effected by distillation in a high vacuum, whereby a fraction of b. p. 170—190°/0·0005 mm. is obtained closely analogous to the methyl ether of natural bulbocapnine. A small portion, soluble in light petroleum, is undoubtedly *dl*-bulbocapnine methyl ether. Resolution of the crude product with *l*-tartaric acid yields *d*-bulbocapnine methyl ether, identical with the natural product. H. WREN.

Constitution of ψ-scopine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1928, [iv], **43**, 590—603).—Mainly an account of work already published (this vol., 310). In the conditions described by Gadamer (A., 1921, i, 588) chlorosulphonation of ψ-scopine affords a sulphuric *ester*,

$$O\Big\langle\begin{array}{l}CH{-}CH{-}CH_2\\ \quad\;|\;\; NMe\; CH{\cdot}O{\cdot}SO_3H\\ CH{-}CH{-}CH_2\end{array}$$ m. p. above 300°,

regenerating ψ-scopine on hydrolysis. ψ-Scopine is unattacked by sodium in xylene, whereas scopoline is partly converted into a sparingly soluble sodium compound which readily dissociates. These results, the formation of *nor*-ψ-scopine by alkaline oxidation with barium permanganate, the formation of the same degradation products in approximately the same yield with chromic and sulphuric acid as are afforded by scopinium salts, and the difference in properties between the phenylurethanes of ψ-scopine and scopoline confirm the structure,

$$O\Big\langle\begin{array}{l}CH{-}CH{-}CH_2\\ \quad\;|\;\; NMe\; CH{\cdot}OH\\ CH{-}CH{-}CH_2\end{array}$$ previously advanced (*loc. cit.*)

for ψ-scopine, the ψ-scopine and scopine derivatives differing structurally, not being simply *cis-trans*-isomerides. R. BRIGHTMAN.

Organic derivatives of silicon. XXXVI. Highly complex condensation products of diphenyl- and di-*p*-tolyl-silicanediol. Fission of the Si–Ph linking. F. S. KIPPING and A. G. MURRAY (J.C.S., 1928, 1427—1431).—Three open-chain and two closed-chain condensation products formed from 2, 3, or 4 mols. of diphenylsilicanediol have been described (J.C.S., 1912, **101**, 2108; J.C.S., 1914, **105**, 484) and also 2 (or 3) closely related derivatives of di-*p*-tolylsilicanediol (J.C.S., 1923, **123**, 2833). By the action of alkalis at 100°, each of these diols is converted into a mixture of much more complex *condensation products*, which with the aid of boiling benzene can be separated into an insoluble (*A*) and a soluble portion (*B*); all these four substances seem to be amorphous and melt indefinitely or decompose at high temperatures. The mol. wts. of the two (*B*) compounds determined in camphor indicate molecules of the order of $(SiR_2O)_{20}$, but it has not been possible to decide whether any of the four products is an open- or a closed-chain compound; if of the former type the silicanediols may be compared with methylene glycol in their capacity for forming a whole series of anhydro-derivatives; if of the latter type, it would seem that compounds containing closed chains of 20 or more $-SiR_2O-$ groups are formed even more readily than the C_{10}—C_{16} cyclic ketones investigated by Ruzicka.

Diphenylsilicanediol is very slowly decomposed by 20% sodium hydroxide solution at 95—100° with formation of benzene and sodium silicate.

M. CLARK.

Organic derivatives of silicon. XXXVII. Production of tetrabenzylsilicane, tribenzylsilicyl oxide, and other products by the action of sodium on dibenzylsilicon dichloride. A. R. STEELE and F. S. KIPPING (J.C.S., 1928, 1431—1439).—Complex changes occur when dibenzylsilicon dichloride is heated with sodium (or potassium) in toluene solution in absence of oxygen, and no silicohydrocarbon corresponding with one or other of the four compounds $(SiPh_2)_n$ produced from diphenylsilicon dichloride (this vol., 79) has been obtained. The soluble product contains a very small proportion of tribenzylsilicyl oxide and about 15% of tetrabenzylsilicane, the rest consisting of a resinous substance which seems to be an oxide $[Si(CH_2Ph)_2]_4O$; some insoluble material which contains less than one benzyl group to each silicon atom is also formed. The apparent migration of benzyl groups from silicon to silicon seems to be due to the fission of the $Si—CH_2Ph$ binding by the alkali metal with formation of sodium benzyl, which then reacts with the unchanged dichloride; there is ample evidence that organic sodium compounds are produced at some stage of the interaction although their nature is unknown. The fact that the main product is an oxide (as proved by determinations of its hydrogen value), in spite of all precautions having been taken to exclude oxygen and moisture, is ascribed to the presence of a very small proportion of oxides in the alkali metals. The properties of this oxide rendered its investigation a matter of considerable difficulty and no crystalline

derivative, except dibenzylsilicanediol, has been obtained from it. During its examination, it was found that certain benzyl derivatives of silicon are readily attacked by alkalis, with fission of the carbon–silicon binding; dibenzylsilicol, for example, is decomposed into toluene and silica or benzylsiliconic acid at temperatures below 100°.

M. CLARK.

Behaviour of polypeptides and their derivatives towards alkalis and acids. VI. Experiments with polypeptides substituted in the amino-group. E. ABDERHALDEN and P. MOLLER (Z. physiol. Chem., 1928, **174**, 196—213).—The previous findings (cf. this vol., 81), that the velocity of hydrolysis of polypeptides by dilute alkalis is influenced by substitution in the free amino-group and that the benzoyl group accelerates whilst the β-naphthalenesulphonyl group retards this hydrolysis, have been confirmed with other di- and tri-peptides. Thus benzoyl-*dl*-leucylglycine is hydrolysed by *N*-sodium hydroxide at 38° more quickly than *dl*-leucylglycine, whilst the β-naphthalenesulphonyl derivative undergoes no significant hydrolysis. Similar results have been obtained with *dl*-leucyl-*dl*-leucine (with 3*N*-sodium hydroxide at 100°), glycyl-*dl*-leucylglycine and glycyl-*dl*-leucyl-*dl*-leucine and their derivatives. With glycyl-*dl*-leucyl-*dl*-leucine, cleavage of the glycine occurs first with the formation of leucyl-leucine, which is hydrolysed very slowly. The following groups have an accelerating influence similar to that of benzoyl, whereas the oleoyl group retards: propionyl, butyryl, and *iso*valeryl. The following compounds have been prepared: *chloroacetyl*-dl-*leucylglycine*, m. p. 145°, *glycyl*-dl-*leucylglycine*, decomp. at 232°, *chloroacetyl*-dl-*leucyl*-dl-*leucine*, m. p. 138° (sinters at 136°), *glycyl*-dl-*leucyl*-dl-*leucine*, decomp. at 227°, *benzoyl*-dl-*leucyl*-dl-*leucine*, m. p. 185° (sinters at 183°), *benzoylglycyl*-dl-*leucylglycine*, m. p. 177°, *benzoylglycyl*-dl-*leucyl*-dl-*leucine*, m. p. 117—118°, p-*nitrobenzoyl*-dl-*leucylglycine*, m. p. 184°, β-*naphthalenesulphonyl*-dl-*leucyl*-dl-*leucine*, m. p. 158° (sinters at 156°), β-*naphthalenesulphonylglycyl*-dl-*leucylglycine*, m. p. 158°, β-*naphthalenesulphonylglycyl*-dl-*leucyl*-dl-*leucine*, m. p. 140°, *propionyl*-dl-*leucylglycine*, m. p. 140°, *butyryl*-dl-*leucylglycine*, m. p. 150°, iso*valeryl*-dl-*leucylglycine*, m. p. 180—181°, *benzenesulphonyl*-dl-*leucylglycine*, an oil, and *oleoyl*-dl-*leucylglycine*, m. p. 129°.

A. WORMALL.

Chromoproteins. Acid-combining properties of globin. N. ISHIYAMA (Z. physiol. Chem., 1928, **176**, 294—300).—When a solution of globin in a large excess of 0·1*N*-hydrochloric acid is treated with alcohol and ether, a *hydrochloride* is precipitated. Similarly salts containing phosphoric acid, eosin, and taurine, have been obtained. Maximum combination occurs with strong inorganic acids.

H. BURTON.

Preparation of electrolyte-free gelatin. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1928, **11**, 477—479).—Powdered gelatin is treated with acetic acid (*M*/128) to remove cations, and then with dilute sodium hydroxide solution to remove anions. The gelatin is brought back to its isoelectric point with dilute acetic acid and washed well to remove electrolyte.

W. O. KERMACK.

Determination of organic carbon in soil and in pure organic compounds by means of permanganic anhydride. L. U. DE NARDO (Giorn. Chim. Ind. Appl., 1928, **10**, 253—255).—Durand's method (A., 1924, ii, 500, 546) may be modified to make it of general applicability. With a soil, 0·2—4 g. of the powdered sample and 5 c.c. of 30% sulphuric acid solution are introduced into a carbon dioxide flask which, if the soil is calcareous, is heated for a few moments and freed from the liberated carbon dioxide by a current of air and then cooled. The flask is fitted with means for introducing reagent, and connected with suitable absorption vessels etc. Permanganic anhydride (prepared by dissolving 1 g. of potassium permanganate in 10 c.c. of cold, concentrated sulphuric acid) is drawn gradually into the flask, the reaction with the soil occupying only a few seconds. The flask is then heated to boiling in 5 min. and the heating discontinued, a stream of air being drawn through the apparatus for 10—15 min., and the absorption apparatus detached, cooled, and weighed.

With a pure organic compound, 0·1—0·2 g. is added to or, better, dissolved in 5 c.c. of sulphuric acid, 10 c.c. of the permanganic anhydride are added, and the heating is carried out carefully, the liquid being finally kept boiling for 2—3 min. The subsequent procedure is as with soil. The whole operation occupies 20—30 min.

With pure compounds, the results obtained are practically of theoretical accuracy, and with soils, values virtually identical with those given by ordinary elementary analysis are found.

T. H. POPE.

Elementary organic analysis. A. WAHL and J. P. SISLEY (Compt. rend., 1928, **186**, 1555—1558).—The rapidity of the combustion method of Heslinga (A., 1925, ii, 65) is due to the small amounts of material used and not to the replacement of the copper oxide by manganese dioxide. Operating with 0·08—0·1 g. of the substance and a shortened tube (55—60 cm.) of the usual construction, accurate determinations may be made in $\frac{1}{2}$—1 hr.

G. A. C. GOUGH.

Biochemistry.

Determination of the respiratory elimination of acetone in man. R. COQUOIN (Compt. rend., 1928, **186**, 1581—1582).—Acetone is eliminated by respiration after oral administration in approximately constant amounts during the first period and then in smaller amounts. The acetone in the breath is absorbed by passage through an aqueous solution of sodium sulphite and hydrogen sulphite, liberated by distillation with sodium hydroxide, and collected in water. The distillate is basified with sodium hydroxide and a known excess of iodine added. The amount of acetone present is determined by titration of the excess iodine with sodium thiosulphate.

G. A. C. GOUGH.

Minimum oxygen pressure necessary for life. BEHAGUE, GARSAUX, and C. RICHET, jun. (Compt. rend., 1928, **186**, 1573—1575).—The minimum partial pressure of oxygen necessary for life in a non-toxic gas mixture (critical physiological oxygen pressure) is found to be lower in mixtures containing a smaller proportion of oxygen. It is concluded that the absolute pressure of the oxygen is not the only factor affecting respiration and that consequently, in aviation, life should become impossible at lower altitudes than those indicated by the theory of Bert. G. A. C. GOUGH.

Respiration of nerve in oxygen and in nitrogen. R. W. GERARD (Amer. J. Physiol., 1927, **82**, 381—404).—The oxygen consumption of the resting frog's sciatic nerve, the oxygen consumption and carbon dioxide production of the stimulated nerve and of the nerve after being kept in nitrogen have been determined manometrically. The resting oxygen consumption after the first hour is constant for 20 hrs. Small amounts of dextrose and sodium lactate are without effect Potassium cyanide diminishes but does not abolish the oxygen consumption even in 0·01*M*-concentration. The temperature coefficient is 2·2 between 15° and 25°. The respiratory quotient is 0·77. The quantitative and time relations between the character of the stimulus and the extra metabolism of the stimulated nerve are reported and good agreement is found between the extra oxygen consumption and the extra heat produced. The temperature coefficient of extra oxygen consumption is 2·1 and the respiratory quotient of excess metabolism is 0·97. The question of the rate of diffusion of oxygen into isolated nerves is considered mathematically. A nerve kept in nitrogen develops an "oxygen debt." It is considered that nerve does not rely on a lactic acid mechanism as a source of anaerobic energy for activity, but that some oxidising reserve is present. R. K. CANNAN.

Union of carbon dioxide and hæmoglobin. B. GROÁK (Biochem. Z., 1928, **196**, 478—487).—The results of Straub and Meier (A., 1918, ii, 467; 1919, i, 53; 1920, i, 200) are critically discussed and their conclusions are tested. Hæmoglobin unites with carbon dioxide both as an acid and in virtue of the ampholytic character of hæmoglobin, the union being therefore affected by the presence of neutral salts. P. W. CLUTTERBUCK.

Determination of hæmoglobin by means of the silver iodide photogalvanic cell. K. UCHIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 173—184).—The coincidence of the principal absorption bands of hæmoglobin with the region of maximum sensitivity of the silver iodide photogalvanic cell has been utilised for the determination of hæmoglobin in blood, the amount of absorption as measured by the silver iodide cell being made an index for the concentration of hæmoglobin in the absorbing layer. E. A. LUNT.

Oxidation of sodium lactate by red blood cells. G. B. RAY (Amer. J. Physiol., 1927, **82**, 405—414).—The consumption of oxygen and production of carbon dioxide have been demonstrated in suspensions of blood cells in isotonic buffered solutions of sodium lactate. In the absence of oxygen the product is acetaldehyde. In the presence of oxygen methæmoglobin is formed. R. K. CANNAN.

Effect of carbon monoxide and oxygen at high pressure on the oxidation of guaiacum by animal tissue. A. L. MEYER (Amer. J. Physiol., 1927, **82**, 370—375).—The ability of blood to oxidise guaiacum in the presence of hydrogen peroxide depends on the ratio of peroxide to blood. In the presence of carbon monoxide, the proportion of hydrogen peroxide required is increased. Carbon dioxide, on the other hand, does not inhibit the peroxidase reaction of muscle tissue. Brain tissue that has been exposed to oxygen under pressure gives a weaker test than does untreated brain tissue. R. K. CANNAN.

Fall of osmotic pressure and of hydrogen-ion concentration in the arterial blood and the blood of the portal and hepatic veins. C. HABLER and K. WEBER (Biochem. Z., 1928, **195**, 364—375).—The osmotic pressure of arterial blood and blood of the hepatic and portal veins is determined cryoscopically before and after removal of carbon dioxide. In fasting animals, when the tension of carbon dioxide is not taken into account, the osmotic pressure of the blood of the portal vein is not higher than that of the arterial vein and that of the hepatic vein is only slightly higher, whilst if the tension of carbon dioxide is taken into consideration, the osmotic pressure of the blood of the portal vein is definitely higher than that of the arterial, but that of the blood of the hepatic vein is not higher than that of the portal vein blood. A method is described for obtaining the "actual" reaction of blood, the blood of the portal vein being found usually to be more acid than the arterial, and of the hepatic vein, more alkaline than that of the portal vein. P. W. CLUTTERBUCK.

Regulation of the hydrogen-ion concentration of blood. IV. Chemical properties of quinone, quinol, and quinhydrone and their relation to the reduction and oxidation systems of blood. V. Influence of salts, acids, and bases and of temperature on the course of the potential of quinone, quinol, and quinhydrone. VI. Thermodynamic action of different standard solutions on the quinhydrone electrode. VII. Relationship of buffering to the chemical reactions of quinone, quinol, and quinhydrone. Buffer regulation of the chemical reactions of blood and tissue fluids. VIII. Influence of temperature on the development of potential by serum, plasma, blood, blood-corpuscle suspensions, and hæmoglobin solutions during the use of the quinhydrone electrode. S. K. LIU (Biochem. Z., 1928, **195**, 248—273, 274—300, 301—308, 309—335 336—363; cf. A., 1927, 786).—IV. The course of the potential during dissolution of quinone, quinol, and quinhydrone is irregular, rising, during thorough stirring, for the first 5—10 min. and then gradually falling. A saturated solution of quinone shows a smaller, of quinol a larger, and of quinhydrone an intermediate *P.D.* The potential, in an oxidation-reduction system, is directly proportional to the reduction and inversely to the oxidation of quinhydrone. Reduction and oxidation of quinhydrone change not

only the hydrogen-ion concentration, but also the number of charges absorbed in these reactions. The reactions between quinone and quinol and between oxy- and met-hæmoglobin are theoretically discussed and relationships deduced between concentration of hydrogen ions and of other materials and between the reaction velocity coefficients. Quinone, quinol, and quinhydrone can convert oxyhæmoglobin and possibly reduced hæmoglobin into methæmoglobin, the reduction with quinone and quinhydrone being very rapid.

V. The potential developed during dissolution of quinone, quinol, and quinhydrone is increased by rise in temperature, but is not doubled by a rise of 10°. The course of the potential is not affected by dilute, but is inhibited by saturated, salt solutions and also by strongly acid or alkaline solutions, but is increased in neutral and faintly alkaline dilute solution. Oxidation of quinol takes place very rapidly and the rate is greatly influenced by temperature.

VI. The quinhydrone *P.D.* for the three standard solutions most frequently used in the electrode, viz., standard acetate, Veibel's, and electrode solution, after thorough stirring for 30—60 sec., shows no real variation. The potential of these three solutions is lowered by rise of temperature, the change of potential being almost a linear function of change of temperature. By change of temperature of the opposed positive and negative electrodes, it can be shown that the *P.D.* of standard acetate and electrode fluids is almost a linear function of temperature, whereas the curve for Veibel's solution and standard electrode fluid shows considerable deviation. For the determination of p_H by the quinhydrone electrode, absolute equality of temperature of the two electrodes is essential.

VII. The relationships between change of potential and displacement of hydrogen-ion concentration, between potential changes and buffering, between the oxidation–reduction system of quinhydrone and hæmoglobin, and between reaction velocity and buffering are formulated, discussed theoretically, and experimentally investigated. Buffering, apart from regulating acid–base equilibrium, appears also to inhibit many chemical reactions such as reduction and oxidation of quinhydrone and the reductions and oxidations of blood and tissue fluids. An investigation of the influence of temperature on the chemical reactions between different buffer mixtures and saturated quinhydrone shows that a rise of 10° does not double the reaction velocity.

VIII. The reaction velocity or rate of fall of potential of dilute (1 in 4) blood or serum is about doubled for each rise of 10° from 10° to 40°. For whole blood, the rate of change of potential does not run parallel with temperature. The thermodynamic relationship between oxy- or met-hæmoglobin, total buffering, and quinhydrone is theoretically discussed. The determination of the initial potential of serum, plasma, diluted blood, and hæmoglobin solutions is best carried out at lower temperatures when the velocity is much smaller. The chief disadvantage of the quinhydrone electrode for the determination of the p_H of blood lies in the reduction processes between quinhydrone and the hydrogen ions or the hæmoglobin. The reduction process with quinhydrone and oxyhæmoglobin is more sensitive to change of temperature and occurs more quickly than the oxidation process.

P. W. CLUTTERBUCK.

Colorimetric determination of p_H of urine and of blood. V. C. MYERS and E. MUNTWYLER (J. Biol. Chem., 1928, **78**, 225—242, 243—255).—The p_H of urine diluted 1 : 5 with 0·9% sodium chloride and kept under oil during the experiment, is determined colorimetrically by the use of the appropriate indicator of the phthalein series and a bicolorimeter; subtraction of 0·2 from the figure so observed at 25° gives the true (electrometric) p_H of the undiluted urine at 38°. The salt errors of the various indicators employed have been investigated. Application of the bicolorimeter to the method of Cullen (A., 1922, ii, 672) for the determination of the p_H of blood-plasma gives good results, the observed value at 25° being, for human blood, 0·22 p_H greater than the true value at 38°; the difference between the observed and the true value is chiefly due to the difference of temperature.

C. R. HARINGTON.

Determination of catalase in blood. P. I. GOLTZOV and V. D. JANKOVSKI (Russ. J. Physiol., 1928, **11**, 33—42).—The method of Bach and Zubkova (A., 1922, i, 392) is not suitable for the determination of catalase in blood, but satisfactory results are obtained if the amount of hydrogen peroxide used is doubled. If the blood solution has been kept at the ordinary temperature for some time before extracting the catalase it is necessary to add traces of ethyl alcohol (1 : 5000) in order to reactivate the catalase.

W. O. KERMACK.

Fate of acetylcholine in blood. I and II. O. GALEHR and F. PLATTNER (Pfluger's Archiv, 1927, **218**, 488—505, 506—513; Chem. Zentr., 1928, i, 1056).—"Vagus substance" and acetylcholine are apparently identical. Acetylcholine is deacetylated very rapidly by human blood, the reaction being complete in 24 sec. at 20°, or 15 sec. at 40°; the effect appears to be due to the albumin fraction, and not the globulin fraction, and is less rapid with animal blood than with human blood.

A. A. ELDRIDGE.

Adsorption of phenol-red by the blood of animals. L. BRAUN (Pfluger's Archiv, 1927, **218**, 523—527; Chem. Zentr., 1928, i, 1054).—Differences in the absorption of phenol-red by blood and sera do not support the supposed connexion between adsorptive power and fission of acetylcholine.

A. A. ELDRIDGE.

Adsorption of quinine by blood cells. O. S. GIBBS (J. Pharm. Exp. Ther., 1928, **33**, 185—190; cf. Acton and King, A., 1921, i, 474).—In the method of Ramsden and Lipkin (Brit. Med. J., 1918, i, 580) for determining quinine in small amounts of blood ten separate extractions of 10 c.c. were substituted for the repeated process. By extracting for several minutes with 0·6% acid, followed by saturation of the extract with solid ammonium sulphate in known amounts, crystallisation during filtration was avoided. The importance of adsorption errors is emphasised. The results of Acton and King were confirmed. It was found that under the conditions of experiment (defibrinated rabbit's blood was used) about 75% of

the quinine added to blood can be recovered and that the quinine is distributed approximately equally between cells and serum. W. McCartney.

Bilirubin content of blood following injections of chlorophyll. J. L. Bollman, C. Sheard, and F. C. Mann (Amer. J. Physiol., 1927, **82**, 239—240).—No increase occurred in the rate of bilirubin formation in dogs following intravenous injection of chlorophyll. R. K. Cannan.

Detection of menstrual blood. II. Menotoxin and yeast fermentation. K. Bohmer (Deut. Z. ges. gerichtl. Med., 1927, **10**, 448—456; Chem. Zentr., 1928, i, 1055).—Dried menstrual blood of the first and second days in 6·6—10% solution arrests the fermentation of dextrose; inhibition by blood of the umbilical cord or of cadavers is less marked. Inhibition is particularly marked with premenstrual and menstrual saliva. Umbilical cord blood-serum appears to contain an inhibitive agent which is paralysed by the blood-corpuscles. A. A. Eldridge.

Properties of serum-proteins. M. Piettre (Compt. rend., 1928, **186**, 1657—1659).—When serum-globulin is precipitated by hydrochloric acid the protein is halogen-free. Determinations of the p_H values of $0·01M$-hydrochloric acid and sodium hydroxide solutions, and of similar solutions to which various amounts of globulin have been added, show that there is no appreciable difference in the two sets of values, even after 72 hrs. Similarly, serum-albumin in $0·01—0·001N$-hydrochloric acid gives only small variations in the p_H values. The amino- and ammoniacal nitrogen in serum-albumin and globulin is small, and it is concluded that the nitrogen in these proteins is combined in peptide form. H. Burton.

Micro-determination of the residual nitrogen of blood by means of sodium hypobromite. R. Iwatsuru (Biochem. Z., 1928, **195**, 442—448).—The tungstate blood filtrate is ashed and the nitrogen determined by treating with standard hypobromite and determining the iodine liberated on adding potassium iodide and acid. The error of the method when the values were compared with a Kjeldahl determination was, for the residual nitrogen of human serum −3%, of guinea-pig's blood −1·8%, for total nitrogen of human urine −1·1%, for total nitrogen of human blood 0, for uric acid −0·1%, for carbamide +3·2%, and for glycine −0·2%. P. W. Clutterbuck.

Determination of sugar in blood. J. P. Bose (Indian Med. Gaz., 1928, **63**, 72—76).—After removal of the protein with sodium tungstate and sulphuric acid, the filtrate and a standard dextrose solution are both warmed with alkaline copper solution, treated with phosphomolybdic acid, and the colours adjusted by dilution. Chemical Abstracts.

Distribution of sugar in normal human blood. M. Somogyi (J. Biol. Chem., 1928, **78**, 117—127).—The ratio corpuscle-sugar : serum-sugar in normal human blood is, on the average, 1·1 for apparent sugar (*i.e.*, total reducing substances), but 0·77 for true (*i.e.*, yeast-fermentable) sugar. C. R. Harington.

Distribution of sugar between blood corpuscles and plasma in various species, in normal human beings, and in diabetics. R. E. Shope (J. Biol. Chem., 1928, **78**, 107—110, 111—115).—Figures are given for the distribution of sugar in the blood of various animals. In normal human beings and in diabetic patients with and without insulin treatment, approximately 50% of the total blood-sugar is contained in the corpuscles. There must therefore be free interchange of sugar between corpuscles and plasma. C. R. Harington.

Relation between blood-sugar and coagulation time. A. Paros and F. Svec (Pflüger's Archiv, 1927, **218**, 209—215; Chem. Zentr., 1928, i, 1057).—The rapidity of coagulation runs parallel with the blood-sugar content for rabbit's blood. A. A. Eldridge.

Blood-sugar. IX. Effect of the Hofmeister series on glycolysis in blood. H. K. Barrenscheen and K. Hübner (Biochem. Z., 1928, **196**, 488—494).—Addition of sulphate to suspensions of red blood-corpuscles accelerates glycolysis in the same way as do phosphate ions. The other anions and cations of the series are without effect. P. W. Clutterbuck.

Hydrolysis of blood-plasma and sugar combined with protein. H. Bierry (Compt. rend. Soc. Biol., 1927, **97**, 1456—1458; Chem. Zentr., 1928, i, 936).—Hydrolysis of horse's blood-plasma with dilute sulphuric acid in an autoclave at 130° for 30 min. increases the reduction value (as dextrose) from 0·5 to 2·1 g. per litre. Values for dog's and rabbit's blood are 1·15, 2·20, and 1·20, 2·50, respectively. A. A. Eldridge.

Calcium, inorganic phosphorus, and alkaline reserve of the blood of horses which have undergone various endurance tests. N. A. Fedorov (J. med.-biol., 1928, **4**, 84—92).—The blood-calcium of horses during fatigue (after trotting, galloping, or doing hard work) is subnormal but independent of the alkaline reserve. The variations in calcium and phosphorus show an inverse relationship. W. O. Kermack.

Equalisation of the chloride concentration between blood-corpuscles and sodium chloride solutions and its relation to "osmotic resistance." E. Skujin (Pflüger's Archiv, 1927, **218**, 343—353; Chem. Zentr., 1928, i, 1057).—Equalisation of the chloride concentration of sodium chloride solution and of erythrocytes suspended therein is not reached in 24 hrs.; the deviation is maximal for 0·60% sodium chloride solution, and is diminished by treatment with carbon dioxide, keeping the blood-corpuscles, or by narcosis. A. A. Eldridge.

Potassium content of the blood of normal men. Kramer–Tisdall method for the determination of potassium. H. Tómasson (Biochem. Z., 1928, **195**, 475—485).—Kramer and Tisdall's method (A., 1921, ii, 412) for the determination of potassium was tested with a pure solution of potassium chloride, a mixture of potassium and sodium chlorides, a mixture of potassium chloride and ammonia, and also with sera with and without added potassium chloride. Trustworthy results were obtained with potassium

chloride and with the mixture of potassium and sodium chlorides, but the presence of large amounts of ammonia made the method unusable. Determinations of potassium added to serum gave low results. The small amount of ammonia in serum causes slightly high results, but the method is usable with care. In 13 normal persons, the mean potassium content of 100 c.c. of serum was 20·30 mg., the lowest value being 17·7 and the highest 22·1 mg.-%. At the beginning of menstruation an increase in serum-potassium was found. Excessive bodily work does not change the serum-potassium value. P. W. CLUTTERBUCK.

Iron, copper, and manganese content of blood-serum. E. ABDERHALDEN and P. MOLLER (Z. physiol. Chem., 1928, **176**, 95—100).—The differences between the total iron present in horse blood-serum and that present as hæmoglobin are so small that it is doubtful if non-hæmoglobin iron is present in the serum. The amount of copper present in horse serum is of the same order as that found by Warburg for human serum (cf. A., 1927, 985; Warburg and Krebs, this vol., 192), whilst the serum contains 1·15 mg. of manganese per litre. Only very small amounts of the copper and iron of serum are dialysable and it appears probable that both elements are present in organic combination, although the non-dialysability may be due to adsorption on the proteins.
A. WORMALL.

Action of arsenic and related elements. VII. Arsine hæmolysis and effect of colloidal arsenic. R. LABES (Arch. exp. Path. Pharm., 1928, **131**, 322—334).—An arsenic sol, free from protective colloid, the preparation and properties of which are described, is able to effect hæmolysis of red blood-cells in Ringer solution, but this action is inhibited if small quantities of serum are present or if the arsenic sol has been heated or kept for some time. The effects of various other factors, *e.g.*, hydrogen-ion concentration, certain inorganic salts, and the concentration of the red blood-cells, have also been investigated. It is considered probable that hæmolysis by arsine (cf. this vol., 317) is dependent on its oxidisability to arsenic.
W. O. KERMACK.

Inhibitory effect of sugars on hæmolysis by sodium taurocholate. E. PONDER and J. F. YEAGER (Biochem. J., 1928, **22**, 703—710).—The inhibitory action of sucrose, dextrose, and lactose on sodium taurocholate hæmolysis was studied quantitatively. The inhibition is due to a double effect of the added sugar. One effect increases the resistance of the cells, the other depresses the activity of the lysin. The activity of the lysin is most depressed in those concentrations in which it is commonly found to be most unstable. S. S. ZILVA.

Imitation of organic forms by means of albumin. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], **7**, 544—547).—Descriptions and illustrations are given of the forms produced by egg-albumin with hydrochloric and sulphuric acids.

Permeability of surviving animal membranes. R. AMMON (Biochem. Z., 1928, **196**, 441—464).—The diffusion constants to dextrose of a variety of surviving and dead mouse, frog, and guinea-pig membranes are determined and compared with the diffusion of dextrose in water. The individual membranes differ considerably in their permeability and the diffusion constants are very small compared with the diffusion constant in water. The permeability of the dead membranes is 3—5·5 times that of the surviving. Apparent changes in permeability due to insulin are more probably explained in terms of increased oxidation of sugar in its presence.
P. W. CLUTTERBUCK.

Calcium content of bone cartilage. A. POLICARD (Compt. rend., 1928, **186**, 1380—1382).—Descriptions are given of the ash obtained by micro-incineration of the various layers of cartilage during the ossification of certain regions of the tibia. The probable sequence of the modifications which take place is discussed. E. A. LUNT.

Quantitative analysis of skin. I and II. Sugar content of normal skin. E. URBACH and P. FANTL (Biochem. Z., 1928, **196**, 471—473, 474—477).—The sugar of normal rabbit's skin, carefully separated from subcutaneous fat, was determined by the Hagedorn–Jensen method and varied in a large number of determinations from 89 to 144 mg. per 100 g. of tissue, the blood-sugar by the same method varying from 89 to 125 mg.-%. P. W. CLUTTERBUCK.

Acid covering of the skin. H. SCHADE and A. MARCHIONINI (Klin. Woch., 1928, **7**, 12—14; Chem. Zentr., 1928, i, 1061).—Electrometric observations on the thin film of acid left by evaporation on the skin were made. A. A. ELDRIDGE.

Iodine compounds in fish products. G. LUNDE and K. CLOSS (Tidsskr. Kjem. Berg., 1928, **8**, 33—34).—Sea fishes contain a relatively large amount of iodine (3·2—4·2 mg. per kg.) and most of this remains in the dried and salted product. A portion of the total iodine can be extracted by shaking an acidified aqueous extract of the fish with chloroform (lipoid iodine) and a little is present in the form of protein substances (protein iodine), but the greater portion is in the form of unknown organic iodine compounds, insoluble in water. Deep-sea fishes contain more iodine than those living near the surface: dried haddock contains six times as much iodine as coalfish, and twenty times as much as herring. In the deep-sea prawn the iodine appears to be mainly concentrated in the skin and internal organs, the muscles being relatively poor in this constituent.
H. F. HARWOOD.

Pepsin content of gastric juice. F. DELHOUGNE (Deut. Arch. klin. Med., 1927, **157**, 299—308; Chem. Zentr., 1928, i, 948—949).—The pepsin concentration varies during a period of secretion between fairly wide limits. Histamine stimulates the secretion of pepsin. The clinical significance of determinations in pathological conditions is considered.
A. A. ELDRIDGE.

Clinical significance of cholesterol in bile and blood-serum. IV. Experimental alteration of cholesterol concentration and p_H in fistula bile. R. STERN (Arch. exp. Path. Pharm., 1928, **131**, 221—232).—Cholesterol in the bile of a dog is not necessarily increased when the blood-cholesterol is increased, *e.g.*, after the intravenous administration of cholesterol. It was not possible experimentally

to decrease the p_H of bile sufficiently to account for the coagulation of cholesterol which results in the formation of gallstones (cf. A., 1927, 1025).

W. O. KERMACK.

Lange's ring-test for acetone in urine. GABRIELSEN (Pharm. Ztg., 1928, **73**, 792).—The Kraft–Kissingen modification is described.

E. H. SHARPLES.

Excretion of fat in the urine after cutaneous absorption. H. MOSER and A. WERNLI (Pharm. Zentr., 1928, **69**, 401—405).—The influence of cutaneous absorption of fat on the fat content of the urine has been examined. Moderate quantities of fat applied to the skin cause increased fat content of the urines. Cutaneous absorption leads to no allergic phenomena as is the case with protein absorption. The relationship between the quantities of fat injected and fat excreted is discussed graphically. Ingestion of large quantities of fat in some cases could not be detected in the urine and in others only a very small quantity could be detected.

E. H. SHARPLES.

Colorimetric micro-determination of phosphate [in urine]. K. HINSBERG and K. LANG (Biochem. Z., 1928, **196**, 465—470).—A method is described for the determination of phosphate in 0·2 c.c. of urine, the error of which is less than 1%. The urine is diluted, the phosphate precipitated with a standard solution of uranium acetate, and the excess of uranium in the filtrate determined colorimetrically with ferrocyanide.

P. W. CLUTTERBUCK.

Amino-acid determination in urine by Folin's colorimetric method. E. SCHMITZ and H. SCHOLTYSSEK (Z. physiol. Chem., 1928, **176**, 89—94). —Technical permutite may be used instead of Folin's purified permutite for the removal of ammonia from urine prior to the determination of amino-nitrogen by Folin's β-naphthaquinonesulphonic acid method (A., 1922, ii, 540) when the phenolphthalein modification used for the determination with blood is introduced.

A. WORMALL.

Determination of dextrose in normal urine. R. H. HAMILTON, jun. (J. Biol. Chem., 1928, **78**, 63—65).—Successive extraction of Lloyd's reagent with hydrochloric and nitric acids yields a product which can be successfully employed in the method of Folin (A., 1926, 648) without necessitating the use of permutite.

C. R. HARINGTON.

Reducing power of urine. AUFRECHT (Pharm. Ztg., 1928, **73**, 729; cf. this vol., 542, 789).—The reducing properties of urine are not due to the presence of indican, which can act as a reducing agent only after hydrolysis with mineral acid. The strongest reducing activity of urine (sugar- and protein-free) is due to purine substances, especially uric acid and urates, uric acid alone being responsible for about one third of the reducing power. Smaller importance is attached to creatinine, which reduces metallic oxides only after long boiling. The fermentation test for the presence of sugar in urine is advisable in doubtful cases.

E. H. SHARPLES.

Indican in urine investigations. G. MAUE (Pharm. Ztg., 1928, **73**, 791—792).—Glycuronic acid, which, according to Schlecht, is in combination with indican in the urine, and reduces Fehling's and Nylander's solutions when it is liberated by hydrolysis, occurs also in the urine combined with certain products such as phenol, terpenes and their derivatives, and pyrazolone derivatives when these compounds are administered medicinally. Indican in urine is not present as plant indican, as stated by Aufrecht (see preceding abstract), but as potassium indoxylsulphonate, and the simplest representation of the formation of indigotin is by oxidation of the free indoxylsulphonic acid, with liberation of sulphuric acid.

E. H. SHARPLES.

Reducing power of urine. C. OTTO (Pharm. Ztg., 1928, **73**, 792).—In reply to Aufrecht (cf. preceding abstracts), uric acid and its salts reduce Fehling's but not Nylander's solution.

E. H. SHARPLES.

Ammonia in sweat. G. A. TALBERT, R. FINKLE, and D. KATSUKI (Amer. J. Physiol., 1927, **82**, 639—643).—The ammonia-nitrogen in the sweat varied between 0·05 and 0·35 mg. per c.c. (73 determinations. An increase of ammonia in the urine as a result of sweating is indicated.

R. K. CANNAN.

Amino-acids in sweat. C. O. HAUGEN and G. A. TALBERT (Amer. J. Physiol., 1928, **85**, 224—228).— The amino-acid nitrogen of the sweat varied from 1·57 to 4·76 mg. per 100 c.c. in 23 subjects. No relationship was evident between the amino-acid nitrogen of the blood, urine, and sweat.

R. K. CANNAN.

Blood as a physico-chemical system. VII. Composition and respiratory exchanges of human blood during recovery from pernicious anæmia. D. B. DILL, A. V. BOCK, C. VAN CAULAERT, A. FOLLING, L. M. HURXTHAL, and L. J. HENDERSON (J. Biol. Chem., 1928, **78**, 191—214).—Nomographic representations are given of the condition of the blood of a patient suffering from severe pernicious anæmia and of the blood of the same patient after recovery under treatment with liver.

C. R. HARINGTON.

Ultra-violet chemiluminescence of cells in relation to the problem of carcinoma. A. and L. GURWITSCH (Biochem. Z., 1928, **196**, 257—275).— Rays of short wave-length ("primary" radiation) emanate from many growing plant and animal cells and may be detected by the increase in the number of mitoses which they cause in tissues exposed to them. The immediate effect of this mitogenetic induction is the breakdown of a carbohydrate substance stored in the cell, thus providing energy for cell division. If this reaction proceeds far enough the cell reacts by mitosis, but if it does not, the energy liberated is radiated as a "secondary" radiation. Transplantable adenocarcinoma of mouse, transplantable carcinoma of rat, and a very malignant melanosarcoma of man all showed a mitogenetic induction power which was primary, *i.e.*, it appeared without irradiation with ultra-violet light.

P. W. CLUTTERBUCK.

A. Phosphate excretion by surviving tumour sections. B. Action of potassium cyanide on phosphate excretion of surviving tumour section.

C. Action of narcotics on the phosphate excretion of surviving tumour sections. D. Further researches on surviving tumour sections. H. Lange and N. Henning (Arch. exp. Path. Pharm., 1928, **131**, 70—74, 75—79, 115—118, 119—126).—*A*. Thin sections of rat's sarcoma, suspended immediately after excision in dextrose–Ringer solution saturated with oxygen, produce phosphoric acid at first comparatively rapidly, then less quickly, and after a short time at a constant rate.

B. If during this last period the section is treated with potassium cyanide a marked increase occurs in the rate of excretion of phosphoric acid, which returns to normal again after the cyanide has been removed, provided that the concentration of cyanide is sufficiently low and its period of action not too prolonged.

C. The increase in the phosphate excretion of surviving tumour sections which occurs when they are treated with potassium cyanide (see above) is also observed when they are treated with other narcotics, *e.g.*, phenylurethane.

D. The influence of various factors (*e.g.*, keeping) on the phosphate excretion of tumour sections and on the effect of the application of phenylurethane is described. W. O. Kermack.

Effect of insulin on nitrogen metabolism in diabetes. Labbe, F. Nepveux, and Hiernaux (Compt. rend., 1928, **186**, 1384—1386).—The effect of insulin on the decreased capacity for nitrogen retention occurring in severe diabetes has been studied in 15 cases; the effect varies from zero to complete restoration to normality. In the majority of cases the ratio amino-nitrogen/total-nitrogen in the serum was restored to normal by insulin administration.

E. A. Lunt.

Variations of the different forms of phosphorus under the influence of diabetes and hypoglycæmic agents. G. Florence, J. Enselme, and T. Zola (Bull. Soc. Chim. biol., 1928, **10**, 675—683).—In the blood-plasma of diabetics, the inorganic phosphorus is diminished, whilst the esterified phosphorus is increased about seven times and the other organic phosphorus is doubled. Injection of insulin or synthalin tends to the adjustment of the values to the normal. In the muscle, the amounts of inorganic and organic phosphorus are respectively reduced and increased, whilst the lipoid-phosphorus values remain unchanged. G. A. C. Gough.

Blood and cerebrospinal fluid in epilepsy. M. Osanto, J. A. Killian, T. Garcia, and M. R. Mattice (Brain, 1927, **50**, 581—600).—In epilepsy the following results were obtained: blood serum-calcium 9·5—12·1 (average 10·94) mg. per 100 c.c.; inorganic phosphorus 2·7—4·5 (3·51); blood total phenols (1·8 mg.); cerebrospinal fluid, calcium 5·0—6·3 (5·68), inorganic phosphorus 1·2—1·9 (1·59), total phenols (0·69). The blood-cholesterol was usually 0·125—0·171 (average 0·140) %; the cerebrospinal fluid contained only traces. Most of the cerebrospinal fluid protein values were above 50 mg. per 100 c.c. The blood-sugar is normal, but the dextrose content of both blood and fluid rises after seizures. The cerebrospinal fluid sugar value was about 74% of the blood-sugar value. The p_H of the blood and fluid was normal. Chemical Abstracts.

Nitrogen content of the bile in diagnosis. A. J. Boekelman (Klin. Woch., 1928, **7**, 65—67; Chem. Zentr., 1928, i, 1075).—The gall-bladder bile contains less than 200 mg.-% N; the nitrogen content in disease of the gall bladder is recorded.

A. A. Eldridge.

Insulin sensitiveness of man. K. Csepai and Z. Ernst (Wien. klin. Woch., 1928, **41**, 25—26; Chem. Zentr., 1928, i, 1055).—In exophthalmic goitre and hyperthyreosis sensitiveness to insulin is markedly increased in man, the minimal blood-sugar value being reached in 1 hr. or more instead of 39 min., and the normal value being still not reached after 2 hrs. A. A. Eldridge.

Elimination of amino-acids in hepatic disease. E. Derra (Z. ges. exp. Med., 1927, **57**, 657—671; Chem. Zentr., 1928, i, 1060—1061)—The urinary amino-acid is increased in fever, but scarcely in pernicious anæmia; in hepatic disease it is variable.

A. A. Eldridge.

Carbohydrate metabolism in hyperthyroidism. H. J. John (Endocrinology, 1927, **11**, 497—581).—There is no typical dextrose tolerance curve for hyperthyroidism. The association of diabetes with hyperthyroidism is discussed. Depletion of glycogen is due to a toxic condition or to rapid consumption of the available carbohydrate on account of the high basal metabolism. Chemical Abstracts.

Rickets in rats. IV. Effect of varying acid–base content of diet. A. T. Shohl, H. B. Bennett, and K. L. Weed (J. Biol. Chem., 1928, **78**, 181—190).—Rickets was produced in rats by means of a diet deficient in vitamin-*D* and with a Ca : P ratio of 0·45; phosphate was added to the diet to bring the Ca : P ratio to 0·95, but with different amounts of base or acid, so that the final diets varied in reaction. Cure of the rickets ensued in all cases; the best retention of calcium and phosphorus and ash-deposition in the bones occurred in rats on the neutral diets, and the poorest in those on acid diets; the animals on neutral diets, however, and sometimes those on alkaline diets, showed symptoms of tetany. C. R. Harington.

Mode of action of irradiated ergosterol in rickets. A. Hottinger (Naturwiss., 1928, **16**, 484—491).—An account is given of clinical experience with irradiated ergosterol. The *D*-factor appears to render innocuous some material which can hinder the assimilation of calcium. This substance may possibly be an enzyme capable of decomposing calcium glycero- and hexose-phosphates. R. A. Morton.

Hypoglycæmia in scleroderma. W. T. Longcope (J. Amer. Med. Assoc., 1928, **90**, 1—7).

Role of fat in the human organism (during starvation and in tuberculosis). W. H. Stefko (Biochem. Z., 1928, **195**, 396—402).—During starvation the Hubl iodine value of tissue fat decreases and approximates to that of the peripheral fat. The decrease of fat in the organism, especially of oleic acid (as measured by iodine value), may be regarded as indicating a decrease of resistance to tuberculosis.

P. W. Clutterbuck.

Hydrogen sulphide in blood in uræmia; hydrogen sulphide-decomposing power of blood and other body fluids. E. Becher (Munch. med. Woch., 1927, **74**, 1950—1951; Chem. Zentr., 1928, i, 1056).—In severe renal insufficiency and true uræmia hydrogen sulphide could not be detected in the blood; that obtained on acidification and distillation probably arose from thiocyano-compounds. All body fluids can oxidise hydrogen sulphide to thiosulphuric acid. The disappearance of hydrogen sulphide added to blood does not depend on the formation of sulphhæmoglobin. A. A. Eldridge.

Metabolism of stationary and growing tissues. O. Rosenthal and A. Lasnitzki (Biochem. Z., 1928, **196**, 340—425).—The metabolism of resting and growing tissues of warm-blooded animals is investigated *in vitro*. Since the morphological character of tissues of mesenchymatous origin (connective tissue, smooth muscle, lymphadenoid tissue) changes greatly during growth, it is not possible strictly from measurements of metabolism to reach conclusions on the changes of cellular metabolism, but it is possible to say that the anaerobic fermentation of the whole tissue attains its highest value with the strongest growth. On the other hand, the fermentative power of three human sarcomata was smaller than that of the Jensen rat sarcoma. Of the stationary epithelial tissues, mucous membrane has a greater fermentative power than epithelial glands. The rather small fermentative power of liver and kidney in the stationary condition is considerably increased in fœtal and post-fœtal growth. Fermentative power progressively decreases with development, but respiration increases. Pathologically growing epithelial tissue possesses considerable fermentative power. In normally growing thyroid gland tissue and with greater colloid content, fermentation appeared to be greater than in the stationary condition. The excess fermentation $U=Q_M'$ is positive in abnormally growing tissue except in human sarcoma, but in most normal tissues its mean value is negative. The Warburg quotient $Q_M^{O_2}/Q_{O_2}$ for stationary and normally growing tissue is $\leqq 0{\cdot}3$, for regulated pathological growth 0·5—1·3 and for unregulated pathological growth >2. For human sarcoma the coefficient is, however, about 1. In a number of experiments the metabolism was measured both in Ringer's solution and in serum. The small aerobic fermentation of the mucous membrane of the rabbit's large intestine, always obtained in Ringer's solution, disappears in its own serum (active or inactivated), but inactivated foreign serum had no effect. The aerobic fermentation of liver tissue of fœtal and grown rats and of rat tumours does not change in horse serum. On the other hand, the respiration of rat's kidney in inactivated horse serum is about 50% and of smooth muscle of rabbit's large intestine 50—100% greater than in Ringer's solution. P. W. Clutterbuck.

Physico-chemical phenomena during regeneration. I. Determination of the hydrogen-ion concentration of the regenerating extremities of the axolotl. N. Okuneff (Biochem. Z., 1928, **195**, 421—427).—On the first day after amputation, the p_H of the extremity of the axolotl decreases from 7·178 to 6·818, during the second and third days it increases to 6·963—6·980, but does not attain normal, on the fifth and sixth days it shows a fresh decrease to 6·638, and finally the p_H gradually rises to normal by about the fifteenth day. The meaning of these changes is discussed. P. W. Clutterbuck.

Physical chemistry of resorption. I. P. J. Jurisič (Biochem. Z., 1928, **196**, 223—245).—An examination of the phenomena associated with the Reid experiment (movement of liquid through frog skin etc. in a direction contrary to the laws of osmotic pressure). Experiments are recorded with frog skin and also with artificial membranes of gelatinised collodion; on the basis of the latter a tentative explanation of the phenomenon is advanced. J. H. Birkinshaw.

Carbon dioxide dissociation curve of nerve and muscle. W. O. Fenn (Amer. J. Physiol., 1928, **85**, 207—223).—Variations in the carbon dioxide-combining capacity of nerves and muscles have been measured in fatigue, death, rigor, and anoxæmia. From the data, inferences are drawn concerning the p_H inside the tissues in different conditions. The carbon dioxide-combining capacity is less in winter than in summer frogs and is only one third to one half that of blood. About half the lactic acid formed in muscle is neutralised by liberation and escape of carbon dioxide. The rate at which carbon dioxide diffuses into nerves agrees with that predicted from Fick's law of diffusion. The diffusion coefficient is $7{\cdot}1\times10^{-5}$ cm.²/min. in nerves and $11{\cdot}7\times10^{-5}$ cm.²/min. in muscles. R. K. Cannan.

Relation between lactic acid formation and oxygen consumption in muscle contraction. O. Meyerhof and W. Schulz (Pflüger's Archiv, 1927, **217**, 547—573; Chem. Zentr., 1928, i, 821).—From the difference of the increase of lactic acid in oxygen and in nitrogen, for equal work, divided by the respired oxygen, the oxidation quotient of the lactic acid (lactic acid disappeared/lactic acid equivalent oxidised) was determined for frog's gastrocnemius. The mean value was 4·7 (cf. Embden, Lehnartz, and Henschel, A., 1927, 589). The significance of the value is discussed. A. A. Eldridge.

Role of magnesium and calcium in the acidification or fatigue of muscle. (Behaviour of alkaline-earth phosphates of muscle in acid and alkaline rigor.) L. Wacker (Biochem. Z., 1928, **196**, 426—440).—The ash content of muscles left *in situ* declines with the onset of rigor, the loss being greater in acid than in alkaline rigor. In spite of the decrease of total ash content, the soluble mineral constituents of muscle increase during post-mortem acid formation at the cost of the insoluble mineral matter, magnesium and calcium phosphates being chiefly concerned in these changes. The curare-like action of magnesium administered parenterally, the sedative influence in muscular convulsions, and the increase of magnesium ions in the muscle during activity and other evidence are cited in favour of the view that the condition known as fatigue is due to the effect of the increase of magnesium ions in the muscle during the increase in acidity.

P. W. Clutterbuck.

Anaerobic resynthesis of phosphocreatine after stimulation of isolated frog's muscle. H. GORODISSKY (Z. physiol. Chem., 1928, **175**, 261—291).—After tetanic stimulation for short periods of the isolated frog gastrocnemius, there is a decrease in the phosphocreatine (phosphagen), and in the subsequent recovery in oxygen resynthesis of this compound occurs, results which confirm those of Eggleton and Eggleton (A., 1927, 271, 990). If the stimulation is not too prolonged, resynthesis of phosphocreatine in the recovery process can take place either anaerobically or aerobically, whereas Eggleton and Eggleton found that resynthesis occurred only under aerobic conditions; after more severe stimulation (for 25 sec., compared with 12 sec. previously) the resynthesis occurs only in the presence of oxygen. The resynthesis of phosphocreatine, like that of lactacidogen (cf. Embden and Hentschel, A., 1926, 427), takes place more readily in the presence of oxygen, although it is not an oxidative process. A. WORMALL.

Natural guanidinophosphoric acids (phosphagens) in striped muscle. I. Physiological behaviour of phosphagens. II. Physicochemical properties of guanidinophosphoric acids. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1928, **196**, 22—48, 49—72).—I. The hydrolysis of creatine-phosphoric acid by muscle enzyme is adversely influenced by carbohydrate and fluoride. The velocity of reaction is strongly influenced by p_H. Below p_H 8 synthesis occurs in fresh muscle extract; this can be increased by addition of creatine.

The general behaviour of arginine-phosphoric acid (present in crustacean muscle) is similar to that of creatine-phosphoric acid. It is split on muscle contraction and re-formed when oxygen is supplied. In muscle extract, the tendency to synthesis predominates at the neutral point and is a maximum at p_H 8. For comparison the enzymic hydrolysis of aminophosphoric acid is also studied.

II. The isolation of arginine-phosphoric acid from crab muscle and the identification of the fission products are described. The purification of the phosphagen depends on the fractional precipitation, by means of alcohol, of the barium salt, and later of the sulphate of the free acid complex. The barium salt has $[\alpha]_D +2°$ and the free acid $[\alpha]_D^{18} +5°$. The α-amino-group of the complex is free. Measurements of the heat of hydrolysis of creatine-phosphoric acid, arginine-phosphoric acid, and aminophosphoric acid were made at acid reaction (h_a) and at neutral reaction (h_n); the respective values obtained for the three acids were: h_a 12,000—13,000, 11,000—12,000, 16,000 g.-cal. per mol.; h_n 10,000—11,000, 8000—10,000, 15,000 g.-cal. per mol. The dissociation curves of the three acids were also studied. The hydrolysis of the compounds in muscle at about the neutral point has practically no effect on p_H, but the hydrolysate has a strong buffering action.

J. H. BIRKINSHAW.

Decomposition of creatine-phosphoric acid in relation to the activity of muscle. I. D. NACHMANSOHN (Biochem. Z., 1928, **196**, 73—97).—The amount of creatine-phosphoric acid (phosphagen) hydrolysed is compared with the lactic acid formed and with the tonus under varied conditions. Phosphagen decomposition is the same for direct as for indirect stimulation, but much less with curarised muscle. There is an anaerobic resynthesis closely connected with relaxation which is complete in 20 sec.; about 30% of the phosphagen is reconstituted. During anaerobic reconstitution no lactic acid is formed and no ammonia disappears. J. H. BIRKINSHAW.

Effect of feeding creatinine on growth and on its distribution in the liver and muscles of normal mice. A. CHANUTIN and H. H. BEARD (J. Biol. Chem., 1928, **78**, 167—180).—Addition of creatine to a normal diet has no effect on the growth of young mice. Administration of creatine causes a rapid but slight increase in the creatine of the muscles, and a slower and more irregular but greater increase in that of the liver. The creatine of the muscles attained a maximum which was independent of the amount of creatine fed and of the duration of the experiment. Cessation of the administration of creatine is followed by a rapid disappearance of the excess from the liver, whilst the creatine content of the muscles remains high for some time.

C. R. HARINGTON.

Behaviour of creatinol in the animal body. F. PETERS (Z. physiol. Chem., 1928, **174**, 177—178).—Following the subcutaneous injection of 7 g. of creatinol [α-methyl-α-(β-hydroxyethyl)guanidine] into a dog kept on a nitrogen-deficient diet, the increase in the total nitrogen of the urine for the same day accounts for practically all the nitrogen of the creatinol. Very small amounts only of unchanged creatinol are excreted and the creatinine and the nitrogenous bases of the urine precipitated by phosphotungstic acid increase to a very slight extent.

A. WORMALL.

Metabolism of amino-acids. I. Changes in nitrogenous constituents of the blood following administration of amino-acids. M. W. JOHNSTON and H. B. LEWIS (J. Biol. Chem., 1928, **78**, 67—82).—The changes in the non-protein nitrogenous constituents of the blood of rabbits following oral administration of various amino-acids vary with the nature of the amino-acid. Glycine and alanine produce a marked rise in the amino-nitrogen of the blood, which, in the case of glycine especially, is prolonged, indicating that these amino-acids are rapidly absorbed but slowly deaminated. Glutamic and aspartic acids on the other hand cause very little increase in the amino-nitrogen, but a steady rise in the carbamide-nitrogen of the blood, so that, in these cases, absorption is slow and deamination rapid. The residual nitrogen of the blood is considerably increased after glycine, possibly owing to synthesis of peptides.

C. R. HARINGTON.

Variations in the amino-acid content of some Lepidoptera while in chrysalis. A. COURTOIS (Compt. rend., 1928, **186**, 1575—1576).—The amino-acid content of many chrysalides falls to a constant minimum during this stage of metamorphosis. It is suggested that the amino-acids are utilised in the formation of the imago. G. A. C. GOUGH.

Uric acid formation. G. NAITO and T. NISHIOKA (J. Biochem. Japan, 1927, **8**, 225—233).—Oral

administration of urea causes in man an accelerated synthesis and increased excretion of uric acid.

CHEMICAL ABSTRACTS.

Fate of *o*-nitrocinnamic acid in the dog. A. A. CHRISTOMANOS (Z. physiol. Chem., 1928, **176**, 74—75).—Administration of *o*-nitrocinnamic acid to a dog *per os* does not lead to an increased excretion of kynurenic acid as expected, but a small percentage of the administered substance and traces of *o*-nitrohippuric acid are excreted in the urine. After the administration of 3·5 and 4·0 g. of the substance, 0·33 and 0·62 g. respectively of *o*-nitrocinnamic acid and 0·12 and 0·14 g. of *o*-nitrohippuric acid were isolated from the urine. Intravenous injection of *o*-nitrocinnamic acid causes a transient lowering of the blood pressure, whereas cinnamic acid has no similar effect.

A. WORMALL.

Water and fat metabolism. I. L. ELEK and E. ROTH (Arch. exp. Path. Pharm., 1928, **132**, 246—252).—Serum containing a large amount of fat when compared with a normal serum shows an increased tendency to bind water. Experiments in which the serum was dialysed against distilled water, sodium chloride, or calcium chloride solutions indicate abnormal behaviour of the calcium ions in the case of the serum containing much fat.

W. O. KERMACK.

Influence of unphysiological nutrition on the composition of the organs and on metabolism. I. Unbalanced fat diet. W. BICKENBACH and P. JUNKERSDORF (Arch. exp. Path. Pharm., 1928, **132**, 129—144).—Administration of much fat to dogs following a period of starvation results in a fall of the blood-sugar followed by a steep rise to a hyperglycæmic level. This result is attributed to a disturbance of the blood-sugar-regulating mechanism of the liver following fat infiltration.

W. O. KERMACK.

Effect of closing the hepatic veins on the sugar and cholesterol content of blood. J. J. ROUZAUD and L. C. SOULA (Compt. rend., 1928, **186**, 1378—1380).—A steadily increasing hyperglycæmia and a transitory hypocholesterolæmia result in experiments on the dog. At the end of 1 hr. the blood-sugar content is increased 100%, and at the end of 30 min. the hypocholesterolæmia begins to decrease.

E. A. LUNT.

Changes in metabolism during irradiation. III. Changes of carbohydrate metabolism. L. PINCUSSEN and D. JACOBY (Biochem. Z., 1928, **195**, 449—456).—The lactic acid content of the whole blood decreases by 20—30% during irradiation, but this is detected only when the animal is examined shortly after irradiation. The lactic acid content of serum, however, increases, and it is suggested that during irradiation the permeability of the corpuscles increases and a considerable part of the lactic acid they contain passes into the serum. The glycogen values for heart and muscle, if changing at all, show a slight decrease, but the total carbohydrate increases considerably. It appears, therefore, that irradiation causes a sparing of sugar, but it is not certain whether this is due to decreased breakdown of sugar or to increased formation of sugar from lactic acid.

P. W. CLUTTERBUCK.

Decomposition of sugar in the human placenta and the effect of hormones thereon. S. HAYASHI (Biochem. Z., 1928, **196**, 323—332).—Anaerobic decomposition of sugar in the human placenta is optimal at p_H 10. Of the hexoses, lævulose yields lactic acid most readily, then dextrose, whilst galactose is almost without effect. Of disaccharides, sucrose gives most, and sodium sucrosephosphate and lactose give less lactic acid. Of the polysaccharides, glycogen is most readily attacked. The following hormones accelerate the anaerobic decomposition of sugar by the placenta, the extent of their activity being in the order given: insulin, folliculin, thyroxine, adrenaline, thymoglandol, and hypophysin. The human placenta is able to convert methylglyoxal into lactic acid.

P. W. CLUTTERBUCK.

Metabolism of the placenta. I. E. ISHIKAWA (Biochem. Z., 1928, **195**, 469—474).—Incubation under aseptic conditions of rabbit's placenta or placenta extracts causes both aerobically and anaerobically an increase of reducing substances (glycogenolysis). Addition of dextrose has no effect on, and of lævulose and dihydroxyacetone causes an acceleration of glycogenolysis. Placenta pulp and extract do not attack either lævulose or dihydroxyacetone under aseptic conditions in experiments lasting a short time. Under aerobic conditions the lactic acid content is usually initially decreased and then increases, whereas under anaerobic conditions, the initial decrease is not obtained. Addition of dextrose and lævulose has no influence on the amount and course of lactic acid formation.

P. W. CLUTTERBUCK.

Calcium deposition in animal tissues. I. Form of calcium in tissues and tissue fluids. H. KLEINMANN. **II. Acidity of tissue in dystrophic calcification.** H. KLEINMANN and I. REMESOW. **III. Experimental calcification by administration of calcium salts.** H. KLEINMANN (Biochem. Z., 1928, **196**, 98—145, 146—160, 161—176).—I. Experiments by means of cataphoresis show that cartilage has a more strongly acid nature and therefore greater binding power for calcium than other tissues. The hydrogen carbonate and phosphate ions of serum are completely dialysable and therefore non-colloidal. Gassmann's theory of a calcium phosphate-carbonate complex in bone is contested.

The effect of the solid phase on the deposition of serum-calcium was studied under varied conditions, by shaking both serum and Ringer solution with various substances. Inoculation of serum with tertiary calcium phosphate leads to a marked decrease in serum-calcium and in the carbon dioxide content. Other solid phases such as glass and calcium carbonate have no action. The phenomenon appears to be mainly due to the crystallisation effect from a supersaturated liquid on addition of a crystal of the solute—namely, calcium phosphate. A secondary effect is present depending on the exchange of the phosphate in the solid phase for the carbonate ion in solution. This leads to a further precipitation of serum-calcium.

II. In an attempt to account for the appearance of the first crystal nuclei of calcium phosphate in calci-

fication, the acidity of dead tissue was compared with that of living tissue. One kidney of a rabbit was ligatured and the p_H of the expressed fluid and ground-up organ from the two kidneys was compared after varying intervals of time. In all cases the dystrophic organ had the more alkaline reaction.

III. Artificial calcification in the tissues of mice was produced by feeding and by subcutaneous injection of calcium salts with the addition of acid- or alkali-forming substances. Calcium was deposited with "acid" and with alternately "acid and alkaline" phosphate diet, but not with "alkaline" phosphate diet. The subcutaneous injection of calcium and phosphoric acid showed even more clearly the influence of alkali or acid on calcium deposition. Calcium and phosphoric acid metabolism experiments were carried out on rabbits to which acid and alkali were administered. Acid produced a calcium and phosphoric acid excretion in excess of the intake, alkali rather the reverse. Poisoning with mercuric chloride seems to hinder the calcium and phosphate excretion. The deposition of calcium produced by metabolic disturbances is thus closely related to dystrophic calcification.

J. H. Birkinshaw.

Iron content of plant and animal foods. W. H. Peterson and C. A. Elvehjem (J. Biol. Chem., 1928, **78**, 215—223).—Figures are given for the iron content of 150 different animal and vegetable foodstuffs.

C. R. Harington.

Importance of manganese to animals. G. Bertrand and H. Nakamura (Compt. rend., 1928, **186**, 1480—1483; cf. A., 1924, i, 1151).—The period of survival of mice fed on a vitamin-deficient diet is increased by the presence of manganese salts. Considerable quantities of the metal are retained in the body.

G. A. C. Gough.

Is sea-water a physiologically equilibrated solution for the isolated organs of warm-blooded animals? S. W. Ziganow (Biochem. Z., 1928, **196**, 333—339).—Sea-water, diluted until isotonic and heated to body temperature, can be introduced into the circulation of mammals without adverse results, can replace part of the blood (up to 40 c.c. per kg. body-weight) in cases of hæmorrhage etc., and can be used as a physiologically equilibrated medium for the isolated intestine and heart, but in the last case the normal work is not maintained, the sympathetic innervation being depressed.

P. W. Clutterbuck.

Action of various gases on the hen's egg. Absorption of carbon monoxide as an inert gas. S. Ancel (Compt. rend., 1928, **186**, 1579—1580).—The germs of the eggs, which do not develop after short exposure of the egg to a toxic gas such as hydrogen sulphide, ammonia, acetylene, or carbon dioxide, develop normally after exposure for several days to hydrogen, nitrogen, or carbon monoxide. It is concluded that carbon monoxide has no toxic action on living cells and that it is toxic for highly differentiated organisms only in the sense that it deprives them of their proper supply of oxygen.

G. A. C. Gough.

Comparison of the pharmacological action of diacetone alcohol and acetone. D. C. Walton, E. F. Kehr, and A. S. Loevenhart (J. Pharm. Exp. Ther., 1928, **33**, 175—183).—2 : 4-Dinitrophenylhydrazine gives a red precipitate with diacetone alcohol (acetonyldimethylcarbinol) and a yellow precipitate with acetone, and the attempt is being made to utilise this reaction in the analysis of mixtures of the two substances. Experiments on rats, rabbits, and dogs showed that the carbinol is somewhat more toxic than acetone. Both substances produce a fall in blood pressure. The soporific action of the alcohol develops more rapidly and it has a more constant depressant effect on the respiration.

W. McCartney.

Influence of alcohols on the bile-stimulating action of salts of bile acids. E. Prokop (Z. ges. exp. Med., 1927, **58**, 330—339; Chem. Zentr., 1928, i, 1062).—Ethyl alcohol and amylene hydrate inhibit the action of parenterally administered *apo*cholic, bilianic, cholic, or deoxycholic, but not dehydrocholic, acids.

A. A. Eldridge.

Biochemical study of thiocarbamide. E. Nicolas and J. Lebduska (Compt. rend., 1928, **186**, 1441—1443).—Solutions of thiocarbamide which up to a strength of 3% have no coagulating action on blood possess hæmolytic action at all concentrations, including that of the isotonic solution. Duodenal administration of 1 g. per kg. of body-weight produces, in the case of dogs, only a slow and transient rise in the blood pressure with no respiratory effects. Intravenous doses of 10 and 11 g. per kg. for dogs and rabbits respectively cause death primarily through the hæmolysis of the blood; thiocarbamide is less toxic than carbamide.

G. A. C. Gough.

Parenteral action of irritants. I. Intravital decomposition of protein in the liver of sensitised animals. II. Biological action of parenterally injected amino-acids. III. Histological findings in liver. R. Wigand (Arch. exp. Path. Pharm., 1928, **132**, 1—17, 18—27, 28—30).—I. The method of Hashimoto and Pick (*ibid.*, 1914, **1**, 76), according to which the toxicity of parenterally injected substances is measured by determining after a certain time the ratio of the uncoagulable nitrogen to the total nitrogen in the liver of the injected animal, has not been found satisfactory.

II. Aliphatic amino-acids parenterally injected into guinea-pigs increase the number of leucocytes in the blood. Aspartic acid induces diuresis. Of various aliphatic and aromatic amino-acids tyrosine is peculiar in producing symptoms of profound collapse.

III. Histological findings observed in the liver of guinea-pigs injected parenterally 1—48 hrs. previously with horse-serum are described.

W. O. Kermack.

Pharmacology of certain pyridylpyrroles and derivatives of 2-aminopyridine. E. Dingemanse and J. P. Wibaut (Arch. exp. Path. Pharm., 1928, **132**, 365—381).—By observing the general effect following subcutaneous injection in frogs, the anæsthetic effect on decapitated frogs, on isolated nerve-muscle preparations, and on the rabbit's cornea, and also the effect on the blood pressure of spinal cats, the pharmacology of 2-aminopyridine and its derivatives and of certain pyridylpyrroles has been inves-

tigated. 2-Aminopyridine has a strong toxic effect, produces convulsions, and raises the blood pressure. Its derivatives show on the whole similar, but weaker properties. The pyridylpyrroles have a powerful anæsthetic action (stronger than cocaine), and produce convulsions in certain cases. The effect on the blood pressure is variable. H. D. KAY.

Purine diuresis in the dog. A. M. PREOBRASCHENSKI (Arch. exp. Path. Pharm., 1928, **132**, 330—348).—If insufficient fluid is given to the animals, the diuretic effect of caffeine is inconstant. Theobromine, on the other hand, always produces some diuresis. If distilled water is given previously by the mouth, caffeine increases the urinary volume and also the amount of chloride excreted, whilst the blood-chloride is raised. In the same circumstances theobromine also increases the urinary volume, the excretion of chloride is raised, though to a smaller extent than with caffeine, but the blood-chloride is not increased.

Following the administration of 0·9% sodium chloride solution by mouth both caffeine and theobromine increase the urinary volume and chloride excretion; the effect of caffeine is, however, greater than that of theobromine. Subcutaneous injection of caffeine results in an earlier occurrence of the diuresis and a higher urinary concentration of chloride.

H. D. KAY.

Pharmacology of narcosis. "Narcotic range." L. LENDLE (Arch. exp. Path. Pharm., 1928, **132**, 214—245).—The "narcotic range" (which lies between the minimum dose producing narcosis and the minimum lethal dose) has been determined for a number of homologous alcohols and the relations between their narcotic action and their chemical constitution are discussed. W. O. KERMACK.

Pharmacology of hydrogen cyanide in cold-blooded animals. I. Role of lung and skin respiration in the lightening of the colour of venous blood during poisoning by hydrogen cyanide. II. Effect of certain factors on oxidation in hydrogen cyanide poisoning. W. M. KARASSIK (Arch. exp. Path. Pharm., 1928, **132**, 193—204, 205—213).—I. The lightening of the colour of the venous blood of the frog under the action of hydrogen cyanide occurs less quickly and only with much larger doses when the lung respiration is inhibited.

II. Rise of temperature tends to bring about darkening of the blood of animals poisoned by cyanide. W. O. KERMACK.

Utilisation of carbohydrate in mammals. H. HANDOVSKY (Klin. Woch., 1927, **6**, 2464—2466; Chem. Zentr., 1928, i, 1059—1060).—In an atmosphere of very dilute hydrogen cyanide rabbits showed, besides inhibition of oxidation, (*a*) a disturbance of the skeletal muscular carbohydrate, (*b*) an increase of lower carbohydrates, (*c*) a diminution of glycogen—the ratio glycogen/lactic acid becomes 1·5 instead of 3·5, (*d*) an increase of the extractable muscular thiolic substances, (*e*) a decrease of cholesterol in muscle, but not in the liver. Injection of guanidine reduced the muscle-glycogen, values for the lower carbohydrates being fairly high. The ratio carbohydrate/lactic acid was 2·0. Thiolic substances soluble in water were increased. Oral administration of synthalin (highly toxic) did not lead to significant change in the muscular carbohydrate or the blood-sugar, although the muscular water-soluble thiolic substances were increased. The effect of administration of insulin, cysteine, and dithioglycollic acid was also investigated. A. A. ELDRIDGE.

Fatal case of poisoning by scopolamine *per os* and by injected potassium cyanide. Location of the injected cyanide etc. A. SCHIRM and D. H. WESTER (Arch. Pharm., 1928, **266**, 283—289).

W. A. SILVESTER.

Glycolysis in blood rendered non-coagulable by means of morphine. G. LO MONACO (Arch. Farm. sperim., 1928, **45**, 1—5).—After injection of morphine into the mesenteric vein of dogs, the blood, which is rendered non-coagulable, exhibits marked hyperglycæmia. Under such conditions the glycolytic power of the blood is more pronounced than that of the normal blood of the same animal prior to the injection, regard being had to the dextrose content. T. H. POPE.

Hyperglycæmia in dogs after intravenous injection of pilocarpine nitrate. A. LE GRAND and G. BIERENT (Compt. rend. Soc. Biol., 1927, **97**, 1483—1484; Chem. Zentr., 1928, i, 936).—Injection of pilocarpine (1 mg.) increases the blood-sugar by 80%, after removal of the suprarenals, 10%, and after removal of the thyroid, 40%. After removal of suprarenals and thyroid, pilocarpine (1 mg.) is without influence on the blood-sugar. A. A. ELDRIDGE.

Comparative study of synthetic and natural ephedrines. K. K. CHEN (J. Pharm. Exp. Ther., 1928, **33**, 237—258).—The hydrochloride of the synthetic material (Merck's "ephetonine") has m. p. 187° and with cupric hydroxide it gives an ether-extractable purple colour which is indistinguishable from that given by the same amount of the natural product. Qualitatively synthetic ephedrine possesses all the properties of the natural substance, but quantitatively the former is in some respects less powerful.

W. MCCARTNEY.

Ultra-violet absorption spectra of alkaloids of the tropane group and of some biological and pharmaceutical products. A. CASTILLE and E. RUPPOL (Bull. Soc. Chim. biol., 1928, **10**, 623—668).—Ultra-violet absorption spectra have been determined for many alkaloids and other organic compounds of biological interest. The proportions of the tautomerides in acid and alkaline solutions of cyanuric acid, barbituric acid, and veronal may be determined from their spectra. The characteristic absorption spectra of alkaloids such as cocaine permit their determination in extracts of viscera containing large amounts of foreign substances.

G. A. C. GOUGH.

A case of hydrofluosilicic acid poisoning. J. DROST (Pharm. Zentr., 1928, **69**, 385—386).

E. A. LUNT.

Action of arsenic and related elements. VI. Conditions of action of salts of hydrogen sulphide and hydrogen iodide on the nerve-muscle preparation of the frog. R. LABES (Arch. exp. Path.

Pharm., 1928, **131**, 305—321).—The harmful action of hydrogen sulphide on a nerve-muscle preparation is increased by the presence of oxidising agents (methylene-blue and hydrogen peroxide) and it is concluded that its toxic action is due in part at least to the formation of sulphur in the tissue (cf. this vol. 548). Similarly, hydrogen iodide or alkali iodides exert a toxic action when conditions are favourable to the formation of free iodine, *e.g.*, in presence of hydrogen peroxide. W. O. KERMACK.

Is glutathione the arsenic receptor in insects ? D. E. FINK (J. Econ. Entomol., 1927, **20**, 794—801).—The normal glutathione content of insects is variable; the determination is described. Injection of arsenious or arsenic acid reduces the glutathione by 41% and 32%, respectively. CHEMICAL ABSTRACTS.

Chemical and enzymic processes in the light of stereochemical research. C. NEUBERG and M. KOBEL (Naturwiss., 1928, **16**, 392—396).—The work of Neuberg and colleagues is reviewed. When an ethereal solution of acetobromo-*d*-glucose and *dl*-borneol is shaken with silver carbonate and the solution subjected to steam distillation, *l*-borneol is carried over. A partial resolution of racemic menthol can also be achieved in this way. The interaction of *dl*-menthol, quinoline, and acetobromo-*d*-glucose results in the formation of glucosides. The residue after steam distillation gives *l*-menthol on hydrolysis. Enzyme chemistry permits these purely chemical processes to be checked, since *l*-menthol-α-glucoside is practically completely decomposed by α-glucosidase (maltase), but is unattacked by β-glucosidase (emulsin). On the other hand, *d*-menthol-β-glucoside is hydrolysed to the extent of 93% by emulsin, but is perfectly stable towards maltase.

Methyl-*n*-propylcarbinol can be separated into *d*- and *l*-compounds after forming the glucoside, followed by fractional crystallisation. d-*Amyl*-β-d-*glucoside* can be obtained in this way, whilst *l*-amyl-β-*d*-glucoside remains in the mother-liquors.

The new methods of fractional fermentative hydrolysis of the glucosides of racemic alcohols, for the preparation of optical isomerides, and the asymmetric action of vegetable phosphatase on the potassium salts of racemic monoborneolorthophosphate (cf. this vol., 88) are described. By the action of glyoxalase on methylglyoxal, an excess of *l*-lactic acid is obtained, and on phenylglyoxal an almost quantitative yield of *l*-mandelic acid is obtained. In the presence of lactic acid bacteria, *d*-mandelic acid is obtained. R. A. MORTON.

Enzymic processes in mammalian skeletal muscle. M. K. BEATTIE, J. BELL, and T. H. MILROY (J. Physiol., 1928, **65**, 109—145).—When extracts of muscle are incubated at 22—45° in hydrogen carbonate solution there is, approximately, an equimolar production of phosphoric and lactic acids from the breakdown of the hexosediphosphoric ester present. When glycogen is added, formation of lactic acid and esterification of phosphoric acid occur in roughly equimolar proportions. The rates of these changes are less at 37° than at 22°. At 45° esterification is suppressed, but hydrolysis of glycogen and of phosphoric esters continues, whilst at 50° diastatic action alone survives. In the presence of inorganic phosphate the amount of esterification exceeds the amount of lactic acid produced—most notably at the lower temperatures. In the presence of fluoride, esterification alone occurs and is greater than in the absence of the fluoride. Electrometric studies of the increased acidity and changes in buffer capacity accompanying esterification of phosphoric acid indicate that there are produced not only esters having dissociation constants about 10^{-6} but also others having lower values. R. K. CANNAN.

Mechanism of fluoride action. F. LIPMANN (Biochem. Z., 1928, **196**, 3—21).—Sodium fluoride has a specific inhibitory action on the hydrolysis of hexose- and glycero-phosphoric esters by tissue and yeast enzymes. The formation of lactic acid in chopped muscle is also inhibited; this is a factor in the decrease of respiration. The oxidation quotient of lactic acid is diminished; in the presence of sufficient fluoride it approaches unity, when the whole of the lactic acid disappearing undergoes oxidation. The oxidation of glycerophosphoric acid is almost unchanged by fluoride, but the hydrolysis is depressed. Hydrocyanic acid has the opposite effect. J. H. BIRKINSHAW.

Mechanism of oxidative processes. XIII. Oxidases and peroxidases. H. WIELAND and H. SUTTER (Ber., 1928, **61**, [*B*], 1060—1068).—Attempts to repeat the isolation from *Lactarius vellereus* of the material which accelerates the auto-oxidation of quinol with production of hydrogen peroxide (Wieland and Fischer, A., 1926, 806) have unexpectedly led to the isolation of Bach and Sbarsky's enzyme (A., 1911, i, 824). The fungus is subjected to pressure and the expressed juice is treated with a small quantity of alcohol, whereby inert matter is precipitated, and then with more alcohol, which causes separation of the crude enzyme; after dialysis, the latter is 630 times as active as the fungus paste. Its activity is measured by observation of the rate of absorption of oxygen by buffered solutions of quinol in water; hydrogen peroxide is not thereby formed, although its presence is readily detected if Wieland and Fischer's preparation (*loc. cit.*) is added to the enzyme mixture. The activity of the enzyme is completely destroyed if its aqueous solution is heated for 3 min. at 100°, and is greatly restricted by hydrocyanic acid. The optimal p_H is 4·6. The rate of reaction is almost independent of the concentration of the quinol. It scarcely accelerates auto-oxidation of the iodine ion.

The peroxidase of horseradish, after purification by adsorption with aluminium hydroxide, does not accelerate the oxidation of quinol by molecular oxygen. Its catalytic activity is irreversibly restricted by hydrogen cyanide even at very great dilution, and even more markedly by hydrogen sulphide. Hydrazine and hydroxylamine are somewhat less restrictive, whereas ammonium sulphate, aniline hydrochloride, arsenious acid, hydrogen, oxygen, and nitrogen are inactive. H. WREN.

Interferometric and chemical detection of Abderhalden's serum enzymes. E. KUSTER and K. KOULEN (Fermentforsch., 1928, **9**, 265—299).—

During aseptic autolysis of serum at 37°, the amino-nitrogen value increases, but not sufficiently to cause any measurable increase in interferometric value. Addition of kaolin does not accelerate autolysis. The dialysate of serum, when dialysed against distilled water, has a stronger ninhydrin reaction than when dialysed against physiological saline, but this is not accompanied by increase of amino-nitrogen. Addition of placenta substrate to serum frequently causes an increase in residual nitrogen which bears no relationship to changes in interferometric value, even when errors due to swelling are avoided. The same organ substrate may show different behaviour with serum of different individuals, and the substrates of different organs may behave differently with the same serum; the largest change of interferometric value is only of the order of experimental error. No results of diagnostic value could be obtained.

P. W. CLUTTERBUCK.

Peptic hydrolysis. S. P. L. SØRENSEN and L. KATSCHIONI-WALTHER [with a note on **Indicators** by K. LINDERSTRØM-LANG] (Compt. rend. Trav. Carlsberg, 1928, **17**, No. 7, 24 pp.).—See this vol., 551.

Purification of pepsin. H. PENAU and J. PLE (J. Pharm. Chim., 1928, [viii], 7, 601—606).—The addition of acetone to pepsin solutions does not appreciably diminish the activity of this enzyme even after 48 hrs., if the p_H of the mixture is kept at 2·5 (isoelectric point of pepsin). Acetone is therefore a more suitable protein precipitant in the purification of pepsin than alcohol. E. A. LUNT.

[Specificity and mode of action of erepsin, trypsin, and trypsin-kinase. Specificity of peptidases. II. Comparison of peptide-sugar condensation with the mode of action of erepsin.] K. JOSEPHSON (Ber., 1928, **61**, [*B*], 1276—1279).—The author does not concur with the observation of Waldschmidt-Leitz and Rauchalles (this vol., 672, 673) that the condensation of dextrose and peptides differs greatly from that of dextrose and amino-acids in its dependence on the p_H of the solution, since a well-defined maximal p_H exists for the initial rate of condensation in the latter case. H. WREN.

Specificity of animal proteases. XIV. Comparison of activating power of enterokinase from different sources. E. WALDSCHMIDT-LEITZ and O. SHINODA (Z. physiol. Chem., 1928, **176**, 301—313).—Investigation has been made, by the caseinogen method (A., 1927, 174), of the hydrolytic action of erepsin-free trypsin from three animal sources, activated by erepsin-free enterokinase from eleven animal sources. With trypsin from the pancreas of the pig and the cat, it is found that activation is of the same value in all the cases examined. Differences are found in the hydrolytic action of sea-lion trypsin with pig and ox enterokinase, but the action is of the same order when enterokinase from the dog, rabbit, or the monkey *Cercopithecus sabaeus* is employed as the activator. H. BURTON.

Mode of action of enzymes attacking proteins and their constituent materials (polypeptides). E. ABDERHALDEN (Naturwiss., 1928, **16**, 396—399).—Dipeptides are hydrolysed by means of erepsin but not by trypsin. Some decomposition occurs, however, by the action of trypsin-kinase on polypeptides, *e.g.*, leucyltriglycyl-*l*-tyrosine. If a naphthalene-2-sulphonyl group is attached at the amino-group of polypeptides the action of trypsin-kinase is more marked than on the unsubstituted compound. It is possible that the points of attack in the polypeptide molecule are the amino-group for erepsin and the carboxyl group for trypsin. Some polypeptides are attacked only by erepsin, others only by trypsin. Some, however, are hydrolysed (at different rates) by both enzymes. The complications arising from this latter result are possibly due to different "trypsins," since the enzyme may be complex.

N-Alkali has a greater effect on polypeptides than *N*-acid. Glycyl chains are easily detached by alkali, and the longer chains more readily than the shorter. If substitution has occurred in the amino-group, hydrolysis by means of alkali is definitely hindered or assisted, depending on the substituent. The naphthalene-2-sulphonyl group decreases the action, whilst the benzoyl group causes an increase. The phenylcarbimido-group is responsible for a greatly increased hydrolysis for a given concentration of alkali. Each substituent brings about a change in the optimal concentration of hydroxyl ions. Erepsin is regarded as attaching itself to the amino-group, the complex requiring such a p_H value that the process of hydrolysis occurs very easily. This idea makes the mechanism of enzymic hydrolysis a catalytic one in the Ostwald sense of an acceleration of a reaction already proceeding slowly. The erepsin-polypeptide then resembles the phenylcarbimido- rather than the β-naphthalenesulphonyl-polypeptide by the test of the action of dilute alkali. It seems clear that erepsin attacks the amino-group.

The work has implications for the investigation of the structure of proteins. R. A. MORTON.

Influence of various amino-acids on yeast peptidase. A. FODOR and R. COHN (Z. physiol. Chem., 1928, **176**, 17—28).—The effect of the following amino-acids on the action of yeast peptidase has been determined; glycine, *dl*-leucine, *l*-leucine, *d*-leucine, *d*-alanine, *l*-tyrosine, *l*-cystine, *d*-arginine, *l*-histidine, *d*-lysine, and *d*-glutamic acid, the first four being prepared synthetically and the rest used as natural products. With the exception of tyrosine, which has a slight inhibiting influence, all these amino-acids activate the hydrolysis of silk peptone by yeast maceration juice at p_H 8, and the influence of equimolecular quantities of the amino-acids is of the same order. This action appears to be due to a larger grouping, perhaps $\cdot CH(NH_2)\cdot CO_2H$, rather than to the amino- or carboxyl groups alone. The peptidase activity of a yeast macerate increases up to a maximum on being kept under sterile conditions, and this increase is attributed to autolytic processes which lead to an increase in the "zymolabile" form with a decrease in the "zymostable" system; in the "zymolabile" form the active group or "zymohaptic" substance is attached to amino-acids, whilst in the "zymostable" form it is associated with the natural proteins. Thus the stimulating action of leucine on the peptidase activity of yeast juice

decreases as the latter is kept. *d*-Leucine has a slightly greater activating influence than *dl*- or *l*-leucine and the last two have approximately equal effects. Cystine has an activating influence, whereas an inhibitory effect was previously recorded (Fodor and Schoenfeld, A., 1927, 76). A. WORMALL.

Enzymic proteolysis. VII. Influence of ions on the stability of trypsin. P. RONA and H. KLEINMANN (Biochem. Z., 1928, **196**, 177—196).—The influence of electrolytes in stabilising aqueous trypsin solution at p_H 5—6 was examined. The action is due to the cation; the higher its valency, the lower is the concentration necessary for stabilisation. The optimum for sodium chloride and sulphate is about 2*N*, for magnesium chloride and sulphate about 0·02—0·1*N*, and for aluminium sulphate about 0·01*N*. The addition of salts has thus a stabilising effect similar to the action of hydrogen ions. Addition of cations at the optimum p_H (1·7) has a harmful effect; the stability of unpurified trypsin solution thus depends on the total cation content. The harmful action of boiled gastric juice of normal acidity (p_H 1·5—2) on trypsin solution is due to its electrolytes. J. H. BIRKINSHAW.

Enzymic proteolysis. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, **196**, 197—222).—Caseinogen solutions after a short hydrolysis by trypsin were subjected to dialysis at a collodion membrane. Although caseinogen itself is not adsorbed by the membrane, the fission products are strongly adsorbed, as shown by the loss of nitrogen from the liquid. The increase in amino-nitrogen is, on the other hand, very small. It therefore appears that the caseinogen is first broken down into large fragments without hydrolysis of the ·CO·NH· linking. J. H. BIRKINSHAW.

Evaluation of the power of enzymic mordants by their action on elastin. J. SCHNEIDER, jun., and A. HAJEK (Biochem. Z., 1928, **195**, 403—414).—A method for the preparation of elastin from the ligamentum nuchæ is outlined and the influence of the following factors on its degradation by trypsin is investigated and the results are tabulated: p_H, time of disintegration, fineness of the elastin threads, temperature, variation of relative amounts of elastin and enzyme. P. W. CLUTTERBUCK.

Inactivation of urease. E. G. SCHMIDT (J. Biol. Chem., 1928, **78**, 53—61).—Figures are given for the concentration of various salts which inhibit the action of urease. In the case of mercuric chloride a direct proportionality was observed between the amount of the salt present and the amount of enzyme inactivated; solutions of carbamide containing varying amounts of mercuric chloride may therefore be used for the standardisation of solutions of urease. The mercury in the blood of patients suffering from poisoning with mercuric chloride was not sufficient to affect the action of urease. C. R. HARINGTON.

Alcoholic fermentation. XIV. Zymin fermentation. S. KOSTYTSCHEV and V. FAERMANN. **Fermentation by yeast macerate.** S. KOSTYTSCHEV and A. CHOMITSCH (Z. physiol. Chem., 1928, **176**, 46—54, 55—73).—XIV. Fermentation by zymin (prepared by the acetone method) differs from that by dried yeast, which is attributed to the presence of living yeast cells (cf. Kostytschev and others, A., 1927, 902), in having no "induction" period, whilst zymin, unlike dried yeast, does not stimulate the growth of yeast cells. The second difference, however, is due to the inability of the stimulating substances to diffuse out of the cells of the zymin, and heated zymin has this stimulating action. Under special conditions, *e.g.*, by adding zymin to 10% sucrose solution and keeping at 30° for 14 hrs. and then diluting gradually over 7 hrs. to a 2% sugar concentration and inoculating on plates, good growth can be obtained from zymin. The conclusion is reached that zymatic cells are present in zymin and that zymin does not effect a cell-free fermentation.

XV. Fermentation by yeast maceration juice is essentially due to bacteria and there is no evidence of cell-free fermentation by this juice. Rapid filtration of the juice through a filter candle yields a solution which can ferment, but this is due to the passage of bacteria through the filter, and slow filtration gives an inactive solution. A. WORMALL.

Alcoholic fermentation. XVII. Pyruvic acid as an intermediate product of alcoholic fermentation. S. KOSTYTSCHEV and S. SOLDATENKOV (Z. physiol. Chem., 1928, **176**, 287—291).—During the fermentation of a 10% sucrose solution by pure yeast, semicarbazide acetate was added at intervals. Examination of the product after 3 weeks demonstrated the presence of pyruvic acid semicarbazone. H. BURTON.

Methylglyoxalase and co-zymase. A. GOTTSCHALK (Z. physiol. Chem., 1928, **176**, 314—316).—Co-zymase-free, dry bottom yeast has no appreciable action on solutions of methylglyoxal, whilst a yeast with a low co-zymase content effects about 20% transformation (cf. Neuberg and Kobel, A., 1927, 592). Thus, the activity of methylglyoxalase is related to the presence of co-zymase. H. BURTON.

Production of glycerol by fermentation. V. Effects of sulphites on the yeast cell and on fermentation. Y. TOMODA (J. Soc. Chem. Ind. Japan, 1928, **31**, 9—20).—The effects of sulphites on the yeast cell and on fermentation have been studied by staining the cell with methylene-blue and determining the decrease of sugar in the fermenting medium respectively. Sodium hydrogen sulphite is very injurious to both the cell and fermentation. The inhibiting action of sodium hydrogen sulphite is reversible to some extent. The activity of the yeast cell which has been injured by this salt can be restored if sodium carbonate or sodium hydrogen carbonate is added within 20 hrs. In a synthetic medium, which contains sodium sulphite, the velocity coefficient of the fermentation is a linear function of the number of yeast cells in unit volume. In a natural medium, however, such as molasses solution, the velocity coefficient becomes a linear function of the logarithm of the number of yeast cells. The inhibiting action of sodium hydrogen sulphite can be eliminated by adding acetaldehyde, but not by adding co-zymase. Y. NAGAI.

Aldehyde-mutation of acetic bacteria. K. Myrback, H. von Euler, and E. Sandberg (Z. physiol. Chem., 1928, **175**, 316—320).—Acetic bacteria, which can effect the dismutation of acetaldehyde, contain the co-enzyme (co-zymase) which is necessary for yeast and animal mutases, but the amount of co-zymase present in a heated suspension of the bacteria is not very large. A. Wormall.

Metabolism of the anaerobes. I. Proteolysis by *Clostridium putrefaciens* compared with that of other anaerobes. II. Relation between the volatile acid and ammonia production during metabolism of *C. putrefaciens*. III. Volatile acids produced by *C. putrefaciens* in cooked-meat medium. L. B. Parsons and W. S. Sturges (J. Bact., 1927, **14**, 181—215).—At all ages there is molar equivalence between the ammonia and volatile acids produced. There appears to be a high degree of specificity in the deamination of amino-acids by *C. putrefaciens*. The volatile acids are acetic (85 mol.-%), butyric (6%), and valeric (9%).

Chemical Abstracts.

Action of *Bacillus diphtheriæ* and some related organisms on glucosamine. W. C. Noble, jun., and (Miss) F. E. D. Knacke (J. Bact., 1928, **15**, 55—65).—Glucosamine is not a source of nitrogen for *B. diphtheriæ*, *B. xerosis*, or *B. Hofmanni*; it is not as easily fermented as dextrose. Ability to ferment glucosamine is not related to ability to produce toxin. Chemical Abstracts.

Light-activated hæmolysin produced by *Bacillus influenzæ*. H. K. Ward (J. Bact., 1928, **15**, 51—54).—*B. influenzæ* grown on blood-agar plates containing hæmatin in light shows hæmolysis after a time depending on the intensity of the light.

Chemical Abstracts.

Toxic substances produced by the *Salmonella* group of organisms. E. E. Ecker and C. Rimington (J. Hyg., 1927, **27**, 44—48).—The toxin in the dialysate of the filtered and concentrated medium was precipitated by neutral lead acetate. Ammonium sulphate decomposed the lead precipitate without impairing its toxicity. The concentrated preparations contained 0·3—0·4% N; carbohydrates were present. Chemical Abstracts.

Fermentative metabolism of bacteria. V. Staphylococcus. H. W. Nicolai and N. Kageura (Biochem. Z., 1928, **196**, 246—256).—Under anaerobic conditions staphylococci ferment dextrose and lævulose producing two molecules of fixed acid. Maltose and sucrose give four molecules of acid. The velocity of fermentation and the rate of respiration are proportional to the cell concentration. The optimum p_H is that of blood; the temperature coefficients of respiration and of glycolysis (anaerobic) are 2·27 and 2·6, respectively. Glycolysis and respiration are sensitive to elevation of osmotic pressure; calcium and especially magnesium chlorides have a detrimental effect, whilst potassium is less harmful than sodium chloride. J. H. Birkinshaw.

Antigenic complex of *Streptococcus hæmolyticus*. II. Chemical and immunological properties of the protein fractions. III. Species-specific substance. R. C. Lancefield (J. Exp. Med., 1928, **47**, 469—480, 481—491).—The type-specific substance is precipitated by the usual protein reagents, is progressively destroyed by removal of the amino-group with nitrous acid, and is readily digested by trypsin and pepsin. After considerable purification it contains 14% N. The species-specific substance resists tryptic and peptic digestion, but gives Molisch's reaction; a purified sample, however, contained 4·2% N and only 28% of reducing sugars.

Chemical Abstracts.

Is diacetyl a product of [bacterial] metabolism? H. Schmalfuss and H. Barthmeyer (Z. physiol. Chem., 1928, **176**, 282—286).—When fumaric, succinic, or malic acid is heated under the conditions previously described (A., 1927, 648), no diacetyl is produced. When a culture of *Streptococcus acidi lacti*, Grotenfeldt, + *S. cremoris* is grown on sterilised milk, an odour of diacetyl is perceptible, and distillation of the culture yields a very small amount of diacetyl, identifiable by the nickel test (*loc. cit.*). The diacetyl does not arise from the lactic acid formed during the growth of the culture nor is it produced by atmospheric oxidation of acetylmethylcarbinol. H. Burton.

Precipitation of the lethal principle of tuberculin by ammonium sulphate. R. R. Henley, M. Dorset, and H. E. Moskey (J. Amer. Vet. Med. Assoc., 1928, **72**, 363—366).—Ammonium sulphate precipitates the lethal principle from young, alkaline cultures. With old, acid cultures there is an increase in soluble carbohydrates, a decrease in the material precipitable by acetic acid, and a change in the character and amount of the ammonium sulphate precipitate. Chemical Abstracts.

Soil bacteria which decompose aromatic compounds. P. H. H. Gray and H. G. Thornton (Zentr. Bakt. Par., 1928, II, **73**, 74—96; Chem. Zentr., 1928, i, 1052).—Bacteria (25 kinds) from English soil which decompose phenol, cresols, naphthalene, phloroglucinol, resorcinol, and toluene have been isolated. A. A. Eldridge.

Do bacteria reduce phosphate? F. Liebert (Zentr. Bakt. Par., 1927, II, **72**, 369—374; Chem. Zentr., 1928, i, 1052—1053).—Rudakov's observation (this vol., 447) could not be repeated.

A. A. Eldridge.

Effect of carbamide and of thiocarbamide on the development and vitality of bacteria. E. Nicolas and J. Lebduska (Compt. rend., 1928, **186**, 1767—1769).—Thiocarbamide inhibits the development and vitality of bacteria grown in a beef broth-peptone medium of p_H 7·4 to a greater extent than carbamide. No hydrogen sulphide was evolved, and the amount of ammonia liberated was not influenced. The effect is similar to but less marked than that obtained with the higher plants (A., 1925, i, 757). On the other hand, the toxicity of carbamide towards animals is greater than that of thiocarbamide (this vol., 919). J. Grant.

Relative importance of additive and antagonistic effects of cations on bacterial viability. C. E. A. Winslow and A. F. Dolloff (J. Bact., 1928, **15**, 67—92).—The stimulating effect of sodium,

potassium, calcium, magnesium, barium, lead, and mercury ions in low concentrations on bacterial growth, and their inhibitory effect in high concentrations, are investigated quantitatively.

CHEMICAL ABSTRACTS.

Bactericidal action of dyes. A. PHILIBERT and J. RISLER (Compt. rend., 1928, **186**, 1583—1584).—Cultures of various pathological bacteria on defibrinated human blood-serum are almost unaffected by the light of a neon lamp (the growth of staphylococci is slightly retarded). In the presence of methyl-violet (1 in 10,000), almost immediate sterilisation takes place. G. A. C. GOUGH.

Hormones and adsorption. A. ZONDEK and H. W. BANSI (Biochem. Z., 1928, **195**, 376—386).—Adsorption of adrenaline by animal charcoal follows the Freundlich adsorption isotherm, and is considerably inhibited by narcotics, the action of which is according to the Richardson law of homologous series. Calcium ions in high and caffeine in small concentration accelerate, whilst calcium ions in small concentration inhibit, the adsorption.

P. W. CLUTTERBUCK.

Radiation substance in the heart. H. ZWAARDEMAKER (Pflüger's Archiv, 1927, **218**, 354—373; Chem. Zentr., 1928, i, 1053).—Skeletal muscle contains a substance ("automatinogen"), dialysable and adsorbed by talc, which can be activated by irradiation to automatin. Automatin is probably identical with Demoor's "substances actives" and Haberlandt's heart hormone. Although there is only one automatinogen, natural β-automatin and artificial α-automatin are very similar but not identical.

A. A. ELDRIDGE.

Effect of insulin on acetonuria. J. H. BURN and H. W. LING (J. Physiol., 1928, **65**, 191—203).—The excretion of "acetone substances" by rats on a fat diet is greater in summer than in winter. In winter there is a steady rise in the glycogen content of the liver which is not compensated by a fall in the muscle-glycogen or by an increased excretion of nitrogen. Injections of insulin delay this rise for about 2 days, during which period the ketonuria is increased and then disappears. R. K. CANNAN.

Production of alcohol in the animal body. III. Influence of insulin on the amount of physiological alcohol in the blood of animals. M. AOKI (J. Biochem. Japan, 1927, **7**, 333—344).—In birds, injection of insulin leads to a reduction of blood-alcohol in 90 min. CHEMICAL ABSTRACTS.

Effect of insulin on faulty lipoid metabolism in acute diabetes. M. LABBE, F. NEPVEUX, and HIERNAUX (Compt. rend., 1928, **186**, 1445—1446).—The blood of diabetics is characterised by the low alkaline reserve, the large amounts of cholesterol and lecithin, and by the appearance of acetone derivatives which are not normally present. On the administration of insulin the latter disappear from the blood and the alkaline reserve becomes normal. In most cases the cholesterol and lecithin contents fall to the normal values. Since these symptoms are partly due to faulty lipoid metabolism, insulin is probably concerned in some way in the assimilation of lipoids.

G. A. C. GOUGH.

Influence of insulin and synthalin on purine metabolism. G. TAUBMANN (Arch. exp. Path. Pharm., 1928, **132**, 124—128).—Moderate doses of insulin administered to a dog do not cause a significant increase in the excretion of total nitrogen, but do cause an increase in the excretion of purine. Administration of synthalin markedly increases the excretion of allantoin in the urine. W. O. KERMACK.

Effect of insulin and of pancreatectomy on distribution of potassium and phosphorus in blood. S. E. KERR (J. Biol. Chem., 1928, **78**, 35—52).—The potassium content of the blood-serum of dogs is decreased by administration of insulin, whilst that of the corpuscles is not affected. The lipin phosphorus of the blood is not affected by excess or absence of insulin; the organic acid-soluble phosphorus of the blood corpuscles is slightly increased after pancreatectomy, but is not affected by excess of insulin. The conclusion of Kay and Robison (A., 1924, i, 1368) that insulin favours the synthesis of hexosephosphoric esters in the blood is therefore not supported. C. R. HARINGTON.

Regulation of the production of insulin. II. Action of carbohydrates (except dextrose) on the production of insulin. E. GRAFE and F. MEYTHALER (Arch. exp. Path. Pharm., 1928, **131**, 80—91; cf. A., 1927, 1115).—By the use of the technique previously described (*loc. cit.*) it is shown that the production of insulin is stimulated not only by dextrose, but also by any reducing sugar or any carbohydrate which may give rise to reducing sugars on hydrolysis by the animal body.

W. O. KERMACK.

Detection of vitamin-*A*. H. STEUDEL and E. PEISER (Z. physiol. Chem., 1928, **174**, 191—195).—Comparative experiments show that there is no agreement between the antimony trichloride test for vitamin-*A* (Carr and Price, A., 1926, 870) and feeding tests with young rats. Whale oil diluted with chloroform gives the colour reaction in concentrations of 2% and 0·2%, but not 0·02%, whereas similar dilutions of the oil (with vegetable oils) do not prevent avitaminosis when fed to rats kept on a diet deficient in vitamin-*A*. Doubt is expressed as to whether the colour reaction is due to vitamin-*A*. Crude cholesterol prepared from the oil gives an intense colour reaction, but on recrystallisation this property is lost and the material responsible for the reaction is found in the mother-liquor.

A. WORMALL.

Water-soluble vitamins of group *B*. Probable existence of a thermostable and alkali-stable factor essential to life. (MLLE.) L. RANDOIN and R. LECOQ (Compt. rend., 1928, **187**, 60—62).—By using a fuller's earth of low adsorptive power to adsorb the antineuritic factor from extract of brewer's yeast two products have been obtained: (1) an extract deprived of antineuritic factor but containing the "nutrition" factor, and (2) an earth in which the antineuritic factor is concentrated. Neither this activated earth nor extract of yeast autoclaved in alkaline medium is capable of lengthening appreciably the lives of pigeons on a diet deficient in vitamin-*B*, but with mixtures of these two products or with

extract (1) the period of survival is considerably extended. The autoclaved extract appears to contain a water-soluble factor which is stable to heat and to alkali and is indispensable to the life of the pigeon, probably functioning in the digestion processes, and the extract obtained on removal of the antineuritic factor with fuller's earth appears to contain the same nutritive, thermostable factor. R. BRIGHTMAN.

Complex nature of vitamin-*B* as found in wheat and maize. C. H. HUNT (J. Biol. Chem., 1928, **78**, 83 90).—Better growth was obtained in rats receiving a mixture of wheat or maize with autoclaved yeast as a source of vitamin-*B* than in those receiving wheat or maize alone. These cereals are therefore relatively rich in vitamin-B_1 and poor in vitamin-B_2. C. R. HARINGTON.

Comparative influence of fats and sugar in the course of avitaminosis-*B*. (MLLE.) L. RANDOIN (Compt. rend., 1928, **186**, 1438—1441).—Two groups of rats were fed on two separate diets deficient in vitamin-*B*. The first contained lard but no sugars and in the second the lard was replaced by an amount of dextrose equivalent to it in energy value. Whilst young rats eat the dextrose-containing diet more readily, in all experiments survival was longest where dextrose was withheld.
G. A. C. GOUGH.

Avitaminosis-*B* and the suprarenal gland. II. Behaviour of pigeons deprived of vitamin-*B* towards adrenaline and choline. E. SCHMITZ and H. J. POLLACK (Biochem. Z., 1928, **195**, 428—441).—The protective action of an extract of the whole suprarenal gland against avitaminosis-*B* is not due either to the adrenaline or to the choline which it contains, but to some unknown substance.
P. W. CLUTTERBUCK.

Human milk. V. Comparison of vitamin-*D* in human and cow's milk. J. OUTHOUSE, I. G. MACY, and V. BREKKE (J. Biol. Chem., 1928, **78**, 129—144).—Addition of human milk in amounts up to 40 c.c. daily to a diet otherwise deficient in vitamin-*D* failed to prevent development of rickets in rats; addition of 30 c.c. daily of cow's milk to the same diet produced healing of rickets in 7 days.
C. R. HARINGTON.

Reactions of irradiated ergosterol (vitamin-*D*). A. STEIGMANN (Kolloid-Z., 1928, **45**, 165—166).—Reactions of ergosterol before and after irradiation suggest that vitamin-*D* is an unsaturated ketone. The irradiated material gives a violet coloration with fuchsin, the colour of which has been discharged by a slight excess of sodium hydrogen sulphite. Neither ergosterol before irradiation nor ergosterol peroxide gives this reaction. The irradiated material reduces ammoniacal silver nitrate, forming a yellowish-brown colloidal sol of silver. It is considered that the silver is protected by a polymerisation product of ergosterol formed simultaneously. E. S. HEDGES.

Activation of the antirachitic factor in dried yeast. W. KIRSCH (Biochem. Z., 1928, **196**, 294—300).—Dried yeast, on account of its ergosterol content, develops on irradiation with ultra-violet light a powerful antirachitic action, but this is considerably reduced by storing for seven months. The antirachitic action of dried yeast is equally good also after irradiation with direct sunlight and in animals fed with it when they are irradiated. Rats which were irradiated daily for 1 min. for a considerable length of time were protected against rickets, but showed an inhibition of development when compared with non-irradiated animals.
P. W. CLUTTERBUCK.

Photosynthesis of the antirachitic vitamin by ultra-violet radiation of short wave-length. H. D. GRIFFITH and K. C. SPENCE (Brit. J. Actinother., 1928, **3**, 69—72).—Ergosterol has been irradiated by light from a mercury-vapour lamp passed through a quartz prism to separate the waves. The sample irradiated by light of wave-length 366—313 $\mu\mu$ did not become antirachitic when tested on rats, whilst those treated with light of 313—265 $\mu\mu$ and of less than 265 $\mu\mu$ were activated, the latter apparently less than the former. W. O. KERMACK.

Factor *H* in the nutrition of trout. C. M. McCAY, F. C. BING, and W. E. DILLEY (Science, 1928, **67**, 249—250).—Raw liver contains a factor *H*, not identical with vitamin-*A*, *B*, *C*, *D*, or *E*, which is essential for the growth of trout.
CHEMICAL ABSTRACTS.

Orthophosphoric acid as a stimulator of the germinating power of seeds. M. GRACANIN (Biochem. Z., 1928, **195**, 457—468).—Treatment of the seeds of *Beta vulgaris*, *Secale cereale*, *Vicia sativa*, *Helianthus annuus*, *Lolium perenne*, *Festuca arundinacea*, *Trisetum flavescens*, and *Dactylis glomerata* with orthophosphoric acid accelerates the process of germination considerably, the optimal conditions consisting of treatment for 15 hrs. with an amount of acid equivalent to 0·05—1% P_2O_5 for the various seeds. The optimal concentration for the germination process is not, however, optimal for the plant embryos. Whereas only 2% of the seeds of *Hordeum vulgare* germinate after 10 days, treatment with 1% orthophosphoric acid causes the germination of 61% after 72 hrs. P. W. CLUTTERBUCK.

Enzyme formation in ripening seeds. A. OPARIN and N. DJATSCHKOV (Biochem. Z., 1928, **196**, 289—293).—The amylase content of ripening seeds increases only while they are attached to the mother plant, whereas the peroxidase and catalase contents increase even after separation therefrom.
P. W. CLUTTERBUCK.

Maintenance of semi-permeability in the plant-cell during leaching experiments. F. C. STEWARD (Proc. Leeds Phil. Soc., 1928, **1**, 258—270).—Protracted leaching experiments have shown that leaching does not necessarily result in loss of semi-permeability.
W. E. DOWNEY.

Passage of boric acid and certain salts into fruits and vegetables. L. KAHLENBERG and R. TRAXLER (Plant Physiol., 1927, **2**, 39—54).—A study of the permeability, under various conditions, of the outer membranes of cherries, tomatoes, plums, grapes, apples, gooseberries, peaches, cucumbers, and carrots to 0·1*M*-solutions of lithium chloride, nitrate, sulphate, and borate, boric acid, borax, potassium iodide, barium chloride, and strontium chloride.
CHEMICAL ABSTRACTS.

Plant colloids. XX. Behaviour of starch sols in the dark field. XXI. Distribution of phosphorus and nitrogen in starch grains. M. SAMEC (Biochem. Z., 1928, **195**, 40—71, 72—78).—XX. During ageing of starch sols, Brownian movement of the ultramicroscopic particles first stops and is followed by a period of vibration and finally all movement ceases. The particles aggregate either in spherical masses, which give a blue colour with iodine, or in chains, which give a red colour with iodine. The ultrafiltrate of starch sols contains a smaller number of smaller particles than the original sol. Only quantitative differences were observed between wheat and potato starch. By heating starch sols, the number of visible particles decreases, the movement is lost, but the typical aggregation is retained. Traces of phosphorus in the starch sol appear to have a stabilising effect. Ultramicroscopic observation reveals only a small fraction of the total substance dissolved.

XXI. The outermost part of starch grains contains the greatest amount of phosphorus and nitrogen. Amylocellulose of wheat and maize starch is especially rich in these elements and also contains silica, whilst that of potato starch may be obtained free from nitrogen. P. W. CLUTTERBUCK.

Alkaloids of Chinese *Corydalis ambigua*, Cham. et Sch. I. T. Q. CHOU (Chinese J. Physiol., 1928, **2**, 203—218).—From the tubers of this plant five alkaloids have been separated. (1) Corydalis *A*, $C_{22}H_{27}O_4N$, m. p. 135° $[\alpha]_D^{25}+295°$ (ethosulphate, m. p. 162°; hydrochloride, m. p. 214°; nitrate, m. p. 197°; chloroplatinate, m. p. 227°; methiodide, m. p. 228°). It is identical with corydaline. (2) *Corydalis* B, $C_{20}H_{23}O_4N$, m. p. 148—149°, optically inactive (*hydrochloride*, m. p. about 218°; *hydrogen oxalate*, m. p. 208°). (3) *Corydalis C*, $C_{20}H_{19}O_5N$, m. p. 201°, optically inactive (*hydrochloride*, m. p. 248°; *hydrogen oxalate*, m. p. 237°; *chloroaurate*, m. p. 195°; *hydrobromide*, m. p. 250°). It is possibly identical with protopine. (4) *Corydalis* D, $C_{19}H_{16}O_4N$ or $C_{19}H_{17}O_4N$, m. p. 204°, $[\alpha]_D^{25}-295°$; (*hydrochloride*; m. p. about 250°; *hydrobromide*, m. p. about 260°). (5) *Corydalis* E, m. p. 219° (*hydrochloride*, m. p. 246°). Corydalis *B* has narcotic and local anæsthetic properties. Corydalis *C* appears to be a cerebral stimulant. H. D. KAY.

Constant alkaloidal content of *Datura Stramonium*, L. var. *inermis*. W. PLOSKI (Bull. Acad. Polonaise, 1927, *A*, 397—401).—The roots, stems, leaves, and fruit of *D. Stramonium* grown with various manures have been analysed in respect of total nitrogen and alkaloid content. In spite of the marked variation in total nitrogen, the various parts show a remarkably constant alkaloid content.

W. O. KERMACK.

Constitution of the anthochlorin of the yellow dahlia. L. SCHMID and A. WASCHKAU (Monatsh., 1928, **49**, 83—91).—The yellow pigment "anthochlorin" (Prantl, Bot. Ztg., 1871, **29**, 425) of the yellow dahlia has been isolated in quantity in a crystalline condition by extraction with 50% aqueous alcohol, evaporation of the alcohol in a vacuum, repeated (20 times) precipitation from an alcoholic solution by addition of water, hydrolysis with 2% alcoholic hydrogen chloride, acetylation, and subsequent hydrolysis of the acetyl derivative. By a comparison of the triacetate and the dimethyl ether, the products of fusion with potassium hydroxide (*p*-hydroxyacetophenone and *p*-hydroxybenzoic acid), and by oxidation of the dimethyl ether with potassium permanganate to anisic acid, it is proved to be identical with apigenin. J. W. BAKER.

Micro-chemistry of plants. XVII. Chromogen of a red colouring matter obtained from cacti. H. MOLISCH (Ber. deut. bot. Ges., 1928, **46**, 205—211).—The occurrence of a red colouring matter, to which the name *cactorubin* has been given, is reported on the cut surfaces of cactus stem kept moist and in contact with air. It is suggested that the formation is due to the action in the dying cells of an oxidase on the chromogen of the substance. Of the 29 varieties of cactus examined 28 contained cactorubin. Cactorubin is slightly soluble in water, insoluble in alcohol, ether, and benzene, and has not yet been obtained crystalline. E. A. LUNT.

Occurrence of a red pigment in the root of the plane tree. R. SCHAEDE (Ber. deut. bot. Ges., 1928, **46**, 298—300).—The pigment, observed in a tree felled in December, was only slightly soluble in water, soluble but unstable in alkalis, soluble in methyl and ethyl alcohols, and insoluble in ether, benzene, carbon disulphide, or chloroform. It is concluded that it is a phlobaphen the function of which in the root is that of a reserve food material, since a second tree of the same age and species felled in the spring showed only traces of the substance. E. A. LUNT.

Enzymes of oil-bearing seeds. X. Glycerophosphatases. O. FERNANDEZ and A. PIZARROSO (Anal. Fís. Quím., 1928, **26**, 118—121).—Comparative measurements were made of the activity of glycerophosphatases in the seeds of *Amygdalus communis* (var. *dulcis*), *Corylus avellana*, *Arachis hypogea*, *Cannabis sativa*, *Sinapis nigra*, *Pinus pinea*, and *Juglans regia*, using the method of Nemec (A., 1923, i, 882). The increase of activity with slight acidity found by Nemec was confirmed, but no definite regularity could be found in the effect of added glycerol. R. K. CALLOW.

Ergosterol from the mushroom *Cortinellus Shiitake*. M. SUMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 116—119).—Ergosterol has been isolated from this mushroom by the usual methods and identified by its chemical and physical properties and its physiological effect after irradiation. J. STEWART.

Biochemistry of sulphur. II. Ergothioneine from ergot of rye. B. A. EAGLES (J. Amer. Chem. Soc., 1928, **50**, 1386—1387).—The isolation of the mercurichloride by the method of Tanret (A., 1909, i, 671) and its conversion into the pure base (A., 1927, 477) (0·065% of the wt. of ergot) are detailed.

H. E. F. NOTTON.

Chemical constituents of the spores of *Aspergillus oryzæ*. M. SUMI (Biochem. Z., 1928, **195**, 161—174).—The spores of *A. oryzae*, grown on damp soya bean, contain the following: a small amount of soluble reducing sugar and pentosan and a large

amount of mannitol; glycogen (not starch); lecithins and organic and inorganic phosphates; considerable amounts of betaine and a little stachydrine; histamine; considerable amounts of chitin; a sterol, $C_{16}H_{28}O$, m. p. 160°; uric acid (0·6% of the air-dried material); invertase, amylase, peptase, chymase, urease, glucosidase, peroxidase, nuclease, esterase, phytase, and catalase, the first three being especially active. The following enzymes were not detected: lipase, tyrosinase, maltase, inulase, trehalase, deamidase, and oxidase. P. W. CLUTTERBUCK.

Biochemical differences between sexes in Mucors. V. Quantitative determination of sugars in (+) and (−) races. S. SATINA and A. F. BLAKESLEE (Proc. Nat. Acad. Sci., 1928, **14**, 308—316; cf. this vol., 563).—The amounts of total soluble, of reducing, and of non-reducing sugars were determined for various Mucor species. In order to compare the amounts of sugar present in the two sexes, the determinations were made in pairs, each containing a (+) and a (−) race of a given species. In the majority of cases more sugar was found in (+) than in (−) races. The amount of reducing sugars present was not high, and was insufficient to be chiefly responsible for the reduction reaction which takes place between the alcoholic extracts of the two sexes and potassium permanganate. It is probable that the difference in reduction capacity of (+) and (−) races is mainly due to other substances possibly related to the tannins. Gravimetric tests were made for fat content in the same mycelia in which sugar was determined. The amount of fat present is relatively large, but shows no relationship to sex. A. J. MEE.

Physiology of *Rhizopus* species. T. TAKAHASHI and K. SAKAGUCHI (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 35—45).—In the surface growth acid production predominates, and the ratio of carbon dioxide to alcohol is greater than in yeast fermentation; in the submerged growth the fungus behaves like yeast. Formation of alcohol from dextrose occurs when subnormal amounts of potassium and phosphoric acid are present. A decrease in potassium causes a decrease in acid formation. The fungus produces succinic acid from glycerol. CHEMICAL ABSTRACTS.

Inhibition of enzymic action as a possible factor in the resistance of plants to disease. L. J. KLOTZ (Science, 1927, **66**, 631—632).—The hydrolytic action of the diastase and invertase of the dried mycelium of *Pythiacystis citrophthora* and *Phomopsis californica* is inhibited by the bark of sour orange or tangelo more than by that of lemon; urease, however, was not so inhibited. A. A. ELDRIDGE.

Pentathionic acid, the fungicidal factor of sulphur. H. C. YOUNG and R. WILLIAMS (Science, 1928, **67**, 19—20).—Sulphur contains adsorbed pentathionic acid, to which its fungicidal action is due. After destruction of the pentathionic acid with ammonia a suspension of sulphur in water soon regains its toxicity, equilibrium being reached in presence of oxygen. CHEMICAL ABSTRACTS.

Calibration of Barcroft's manometer. M. JOWETT (Biochem. J., 1928, **22**, 717—719).—A simple method, accurate to about 1%, of calibrating the Barcroft constant-volume manometer is described. S. S. ZILVA.

Titrimetric quinhydrone electrodes; comparison with the hydrogen electrode for p_H determinations in whole blood, plasma, and other biological fluids. G. H. MEEKER and J. G. REINHOLD (J. Biol. Chem., 1928, **77**, 505—518).—For the blood-plasma and serum of man and the horse, and for biological fluids such as cerebrospinal fluid and urine, results obtained with the quinhydrone electrode, employing the authors' titrimetric technique (A., 1926, 442), agreed with those obtained with the hydrogen electrode (cf. Cullen and Earle, this vol., 438); the quinhydrone electrode is not applicable to whole blood or to the blood-serum of the dog. C. R. HARINGTON.

Determination of chlorides in body fluids. J. PATTERSON (Biochem. J., 1928, **22**, 758—761).—The effect of the presence of protein on the determination of chloride in various body fluids by the Volhard titration can be readily overcome by use of a high concentration of nitric acid together with selected proportions and sequence of the reagents normally employed. S. S. ZILVA.

Rapid determination of organic iodine. G. PFEIFFER (Biochem. Z., 1928, **195**, 128—133).—A method is described for the determination of iodine of organic material (thyroid etc.) in which, by rapid decomposition of the tissue with concentrated sulphuric acid and hydrogen peroxide, the time of a determination is reduced to 40 min., the results being comparable with those of older methods. P. W. CLUTTERBUCK.

Determination of uric acid in biological fluids. R. VLADESCO (Bull. Soc. Chim. biol., 1928, **10**, 602—605).—The phosphotungstic acid colorimetric method for determining uric acid in biological fluids from which the proteins have been removed is unsatisfactory owing to the rapid fading of the sample and the standards, and the titration of the coloured complex with aqueous chlorine is recommended. Since the titre is not strictly proportional to the uric acid content, two titrations are made in the presence of two different volumes of standard uric acid solution. G. A. C. GOUGH.

Dialysis with stirring. M. KUNITZ and H. S. SIMMS (J. Gen. Physiol., 1928, **11**, 641—644).—The solution to be dialysed is contained in a stoppered collodion sac along with a marble or a bubble of air. The sac is placed within a test-tube which is in a rocking machine, and distilled water is led into the test-tube outside the collodion sac. The movement of the marble or bubble of air agitates the solution and accelerates dialysis. W. O. KERMACK.

BRITISH CHEMICAL ABSTRACTS

PURE CHEMISTRY

SEPTEMBER, 1928.

General, Physical, and Inorganic Chemistry.

Absorption spectrum of thallium vapour between 7000 and 1850 Å. R. G. Loyarte and A. T. Williams (J. Phys. Radium, 1928, [vi], 9, 121—126).—Observations on the absorption spectrum of thallium vapour between 700° and 900° show, in agreement with Grotrian (A., 1923, ii, 106) and others, the lowest level to be $^2P_1$ and all the corresponding lines of the series $^2P_1-{}^2S_1$ and $^2P_1-{}^2D_2$ have been observed. At 700° and below, some lines corresponding with the level $^2P_2$ appear, but they are fewer than in the case of aluminium, gallium, or indium. No trace of the green line 5350·46 Å. could be detected. Sharp, fine lines between 2210 and 2105 Å., previously recorded as band or diffuse lines by earlier workers, have been observed. L. S. Theobald.

Filtration of arc and spark lines in a magnetic field by using disruptive discharge in a vacuum. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1928, 4, 195—197).—The method of separating arc and spark lines in a spectrum by using the disruptive discharge in a strong magnetic field (cf. this vol., 339) gives ambiguous lines in some cases, due to the resistance of the air to the motion of the ions. This can be prevented by using the discharge in a vacuum. An apparatus is described by means of which this can be studied. A. J. Mee.

Influence of energy factors on the structure of spectra. T. Negresco (J. Chim. phys., 1928, 25, 308—319).—The influence of temperature on flame spectra and of the nature of the electrodes, the surrounding atmosphere, the potential gradient between the electrodes, and the nature of the current on arc and spark spectra is discussed, and also the effect of self-induction on the spark discharge and its spectrum. The emission of radiation of low potential is not due solely to the hot envelope of metallic vapour, but is primarily an electrical effect. The effect of self-induction is due to the lowering of the potential gradient in the initial discharge, which causes an increase in the intensity of the radiations due to the subsequent oscillations W. A. Richardson.

Series in the spark spectra of germanium. K. R. Rao and A. L. Narayan (Proc. Roy. Soc., 1928, A, 119, 607—627).—The spark spectrum of germanium has been investigated over the range 6484·32—2099·98 Å. A small quantity of germanium was fused to the tips of pure tin rods, which were used as electrodes between which the spark took place. The spark was studied in an atmosphere of hydrogen under varying conditions, the spectra being photographed by a 5-foot concave grating and a large Hilger quartz spectrograph. The region below 2400 Å. was photographed on Schumann plates. Detailed descriptions and analyses are given of the spectra of singly-ionised (Ge II), doubly-ionised (Ge III), and trebly-ionised (Ge IV) germanium, and the results are in complete agreement with the Pauli–Heisenberg–Hund theory. The second ionisation potential is computed to be about 15·88 volts, and the third about 33·17 volts. A characteristic group of lines has been observed which appears more intensely under weaker stimuli. When the excitation is a maximum the lines disappear, but the inclusion of self-induction brings them out clearly. As such, their behaviour is similar to that of arc lines, but their presence has not been recorded by any previous investigator of the arc spectrum of germanium. A table is given of all the lines of germanium which have been classified. L. L. Bircumshaw.

Intensity ratio of the doublets of the principal series of the alkali metals. H. Jacob (Ann. Physik, 1928, [iv], 86, 449—493).—The intensity ratio of the components of the second doublet of the principal series of potassium, rubidium, and cæsium has been measured by means of Merton's method. The lines were produced at the highest possible temperature (2600°) by the use of an oxy-hydrogen flame. The values of K, the intensity ratio, were found to vary between 1·80 and 2·02. In the case of rubidium and of cæsium the method of Gouy was used in addition for the purpose of obtaining the "true" intensity ratio. The "true" intensity ratio for the cæsium lines approximates to 4·0. For rubidium the ratio is evidently greater than 2·3, but the value of the "true" intensity ratio was not reached. W. E. Downey.

Intensity of spectral lines. A. Kupper (Ann. Physik, 1928, [iv], 86, 511—529).—Mathematical. Calculations based on Schrödinger's wave equation lead to values for the intensities of the lines of the Balmer, Paschen, Brackett, and 5th series. W. E. Downey.

Intensity ratio of the ortho- and para-series in relation to the structure of the helium atom. J. Stark (Ann. Physik, 1928, [iv], 86, 530—540).—A helium line arising from the $1s$ state cannot be detected. The ratio of the intensity of the para-series of helium to that of the corresponding ortho-series decreases with increasing gas pressure. The ratio is greater, for a given pressure, when the excitation is due to fast cathode rays than when slow cathode rays are used. The para-series correspond with the singlet series of the alkaline-earth metals,

the ortho-series to the triplet ones. The spectral and structural similarity of helium and the alkaline-earth metals leads to the view that a para-state is less stable and, therefore, less frequent than the corresponding ortho-state. W. E. DOWNEY.

Spectrum of ionised sodium. F. H. NEWMAN (Nature, 1928, **122**, 97).—The author's pairs of wave-number differences in the Na II spectrum do not appear to be accidental (cf. Laporte, this vol., 680). A. A. ELDRIDGE.

Spark spectrum of palladium (Pd II). A. G. SHENSTONE (Physical Rev., 1928, [ii], **32**, 30—38).—The analysis of the spectrum of Pd II differs from that of McLennan and Smith (A., 1926, 875). The terms include $4d^2D(4d^9)$; $5s^{4\,\&\,2}F$, $^{4\,\&\,2}P$, $-D$, $^2G(4d^85s)$; all the related triads from the structure $4d^85p$; $6s^{4\,\&\,2}F$, $^4P_3$, $^2G_5(4d^86s)$; and fragments of terms due to $4d^85d$. Zeeman effects for most of the lines have been measured. The ionisation potential is calculated as 19·8 volts from $4d^9$ to $4d^8$. A. A. ELDRIDGE.

Structure of the resonance line, 6708 Å., of the lithium arc spectrum; isotope effect with lithium. H. SCHÜLER and K. WURM (Naturwiss., 1927, **15**, 971—972; Chem. Zentr., 1928, i, 644).—A weak third component, situated towards the red, of the lithium resonance line 6708 Å. is recorded, and is considered to be a component of the Li^6 doublet. A. A. ELDRIDGE.

Polarisation of resonance radiation of cadmium. P. SOLEILLET (Compt. rend., 1928, **187**, 212—214).—The effect of a magnetic field on the lines 3261 and 2288 Å. in the resonance spectrum of cadmium has been investigated, the exciting radiation being unpolarised. In a zero field, or one in the same direction as the incident light, the maximum polarisation is 85% for 3261 Å. and 60% for 2288 Å. The two orbits of the $2'P_1$ level have different stabilities, and durations of about 2×10^{-6} sec. and 10^{-9} sec., respectively. C. W. GIBBY.

Optically excited iodine bands with alternate missing lines. R. W. WOOD and F. W. LOOMIS (Phil. Mag., 1928, [vii], **6**, 231—238).—The fluorescence spectrum of iodine enhanced by the presence of helium at 0·5 mm. pressure has been examined and the fluorescence lines have been found to correspond exactly with the absorption lines with even initial rotational quantum numbers, and the alternate lines to be missing in the fluorescence bands. It then follows that, since the original excited iodine molecules after absorbing light and immediately before colliding with helium atoms had the rotational quantum number 34, during collisions in which the electronic quantum number is unchanged the rotational quantum number of an iodine molecule can change only by an even number. This conclusion is not in accordance with the selection principle, but is in agreement with the theory of Hund (A., 1927, 809) that the rotational states of symmetrical molecules are divided into two classes, characterised by eigen-functions symmetrical and unsymmetrical, respectively, in the position co-ordinates of the nuclei, between which transitions do not occur. A. E. MITCHELL.

Afterglow in mixtures of nitrogen and oxygen. B. LEWIS (Nature, 1928, **122**, 241).—Using an electrodeless discharge with a spark gap, at 1·8—0·01 mm., there is for a given mixture, *e.g.*, air, a sharp minimal afterglow at 0·53 mm. separating the yellowish-green oxygen afterglow (at higher pressures) from the orange-yellow nitrogen afterglow (at lower pressures). In a certain pressure region near this minimum a long discharge gives a blue afterglow; the nitrogen bands also appear at a suitable pressure. With a very short discharge only the yellowish-green afterglow is visible. Thus, different types of afterglows may be excited in the same gas mixture at the same pressure merely by altering the period of discharging. A. A. ELDRIDGE.

Spectrum of trebly-ionised antimony, Sb IV. J. B. GREEN and R. J. LANG (Nature, 1928, **122**, 242).—A $^3P^3S$ multiplet between 805 and 861 Å., a very strong $^3P^3D$ multiplet between 873 and 940 Å., a $^3D^3F$ multiplet between 2077 and 2113 Å., and a possible $^3P^3P'$ group between 1051 and 1193 Å. have been identified. The ionisation potential is computed as 42 volts. A. A. ELDRIDGE.

Analysis of the first spark spectrum of sulphur (S^+). D. K. BHATTACHARYYA (Nature, 1928, **122**, 241—242).

Influence of magnetic fields on the bands of the third positive group in nitrogen. B. POGANY and R. SCHMID (Z. Physik, 1928, **49**, 162—166).—Data are given for the broadening of the lines of the (0,1) and (0,2) bands of the third positive group of nitrogen in a field of 26 kilogauss. R. W. LUNT.

Classification of the band spectra associated with the neutral oxygen molecule. W. OSSENBRUGEN (Z. Physik, 1928, **49**, 617—216).—The classification of the oscillation and rotational terms in the Schumann bands of the neutral oxygen molecule is discussed in detail; by adopting the value $6{\cdot}54\times10^{-27}$ for h, the following values are derived for the moment of inertia in a motionless unexcited state and for the effective atomic radius respectively, $19{\cdot}20\times10^{-40}$ g. cm.^{2}, $0{\cdot}6005\times10^{-8}$ cm. R. W. LUNT.

Variation of the intensity of the lines of the mercury spectrum excited by different types of discharge. T. HORI (Z. Physik, **49**, 259—268).—Qualitative data are given for the intensity of mercury lines excited by arc discharges with and without the presence of hydrogen, by low-velocity electrons from an oxide-coated cathode, and by a Geissler tube discharge. These results, which are preliminary to a quantitative investigation, indicate that the observed variations cannot be traced solely to variations in absorption; it is thought that the emission of HgH bands in the presence of hydrogen indicates that the reaction $Hg^*+H_2=HgH+H$ takes place. R. W. LUNT.

Relative intensities of the H_α and D_3(He) lines in protuberances of the sun's chromosphere. E. J. PEREPELKIN (Z. Physik, 1928, **49**, 295—305).—Astronomical. R. W. LUNT.

Intensity distribution in the negative nitrogen band spectrum. L. S. ORNSTEIN and W. R. VAN WIJK (Z. Physik, 1928, **49**, 315—322).—Measurements have been made of the intensity distribution in the bands 3914, 4278, 3884, and 4237 Å. The intensity

distribution can be represented by a Boltzmann function of the rotational quantum number p of the form $\exp[-h^2p(p+1)/8\pi^2IkT]$, where h is the Planck constant, I the moment of inertia, k the Boltzmann constant, and T the absolute temperature.

R. W. LUNT.

Bands of the third positive group in nitrogen. R. SCHMID (Z. Physik, 1928, **49**, 428—462).—The classification of the bands (0,2), (0,3), (0,4), (1,4) by Guillery has been extended to include the bands (0,0), (0,1), (1,0), (1,1), (2,3), and (3,4).

R. W. LUNT.

Energy distribution in band spectra, especially in nitrogen bands. G. HERZBERG (Z. Physik, 1928, **49**, 761—773).—It is pointed out that the parabolic energy distribution in a band spectrum required by Condon's theory (A., 1927, 89) is attained only when the distribution of the molecules over the various vibration states in the initial condition is uniform. Generally this is not the case. From the theory developed by Franck (A., 1926, 583) considerable deviations would be expected, although at great activations approximations to the Condon distribution law can be attained. This has been shown experimentally with the nitrogen bands. This fact is explained by supposing that in the case of collisions between high-velocity electrons, Franck's rule is broken and vibrations of higher quantum number can be stimulated to a greater extent. J. W. SMITH.

Spectroscopic data relating to the afterglow in nitrogen. G. HERZBERG (Z. Physik, 1928, **49**, 512—533).—The spectrum of the afterglow in nitrogen excited by the electrodeless discharge under unspecified electrical conditions has been examined with reference to the shift of the maxima of intensity in the green, yellow, and red group of bands produced by quenching the afterglow with liquid air and by alteration of the pressure. The data obtained are reviewed at length and are thought to support the hypothesis that the afterglow is due to collisions between metastable atoms despite the difficulty of interpreting Bonhoeffer's data (cf. A., 1927, 801) on this view. R. W. LUNT.

Inverse Stark effect in the principal series of sodium. W. GROTRIAN (Z. Physik, 1928, **49**, 541—545).—The inverse Stark effect in absorption in sodium vapour at 280—320° has been measured for the doublets of the 2nd and 3rd terms of the principal in fields up to 10^2 kv. cm.$^{-1}$ In the case of the doublets 3302·94 and 3320·34 Å. the displacements are equal and linearly related with the square of the field strength; a similar relationship holds for the doublets 2852·851 and 2853·038 except that the former has a slightly greater displacement coefficient than the latter. R. W. LUNT.

Statistical derivation of the Rydberg correction for *s*-terms. E. FERMI (Z. Physik, 1928, **49**, 550—554).

Ionisation of mercury atoms by reaction with helium ions. J. STARK (Ann. Physik, 1928, [iv], **86**, 541—546).—The emission of mercury spark lines is much stronger in comparison with the emission of mercury arc lines for a mixture of mercury vapour and helium in the negative glow of a discharge tube than for a mixture of mercury vapour and neon. The same intense emission of the spark lines should apply in the case of the alkaline-earth and alkali metals.

W. E. DOWNEY.

Distribution in direction of photo-electrons from alkali metal surfaces. H. E. IVES, A. R. OLPIN, and A. L. JOHNSRUD (Physical Rev., 1928, [ii], **32**, 57—80).—A study of the distribution in direction of photo-electrons emitted from surfaces of liquid alloys of sodium and potassium, and thin films of potassium or rubidium on platinum, irradiated by light incident at various angles and polarised in different planes. Some form of surface anisotropy appears to exist. A. A. ELDRIDGE.

Complete photo-electric emission from potassium. (MISS) J. BUTTERWORTH (Phil. Mag., 1928, [vii], **6**, 1—16).—Examination of the photo-electric emission from potassium has produced no evidence for the existence of a positive emission. If such does occur it is less than 10^{-7} times the negative emission or at least a thousand times smaller than the apparent positive emission reported by Dember (Ann. Physik, 1910, **30**, 142). The photo-electric threshold of potassium has two work-functions corresponding with the wave-lengths 9700 and 60,000 Å., the results indicating that the "patches" (Richardson and Young, A., 1925, ii, 343) of lower work-function form a very small part of the total surface and under prolonged illumination are able to acquire the greater work-function. A. E. MITCHELL.

The normal photo-electric effect. P. LUKIRSKY and S. PRILEZAEV (Z. Physik, 1928, **49**, 236—258).—The photo-electric effect in aluminium, zinc, tin, nickel, silver, cadmium, lead, copper, and platinum has been investigated by measuring the currents flowing from a small sphere of the metal under investigation, when illuminated by monochromatic light in the range 2302—3130 Å., to a surrounding metal sphere, as a function of the *P.D.* between the two spheres. Under such conditions the maximum electron energy $\frac{1}{2}mv^2_{max.}$ is related to the potential V_2 producing saturation current by the equation $\frac{1}{2}mv^2_{max.}=e(V_2+K)=h\nu-p_1-p_2$, where K is the contact *P.D.* between the spheres, p_1 the work of removing an electron from an atom, and p_2 the work associated with the motion of the released electron to the metal surface. The data obtained lead to the following values respectively for the critical excitation wave-lengths: 4132, 4009, 3411, 3364, 3364, 3302, 3110, 3033, and 3018 Å.; and the mean value obtained for Planck's constant is $6{\cdot}543\times10^{-27}$ erg$\times$sec., in good agreement with the accepted value from optical data, $6{\cdot}545\times10^{-27}$. It is also shown that the contact *P.D.* between aluminium and the other metals examined is equal to the difference between the minimum quanta necessary for the excitation of photo-electrons. From this it is concluded that the electrons emitted under the influence of light are identical with those associated with electrical conduction. The velocity distribution of photo-electrons where corrected to the same maximum velocity and photo-electric current varies somewhat in the metals examined, which is thought to be due

to the different light penetration and corresponding differences in the work terms, p_2. The velocities of the photo-electrons become more uniform and approximate closely to the maximum velocity as the thickness of the irradiated metal layer is reduced.
R. W. LUNT.

Photo-electric effect with sub-microscopic drops. K. SCHARF (Z. Physik, 1928, **49**, 827—857).—The photo-electric properties of mercury, bismuth, selenium, and sulphur particles, produced by vaporisation of the element in an atmosphere of pure nitrogen, have been investigated by Ehrenhaft's condenser method. These substances show a predominant normal photo-electric effect. Inverse charging appears only rarely in single particles, but to a much greater extent in the clouds of very small particles produced by strong heating of the substance. The number of negatively-charged particles in a cloud was found to be inversely proportional to the normal sensitivity of the element, which decreases with the different elements in the order given above.
J. W. SMITH.

Nature of gaseous ions. L. B. LOEB (Physical Rev., 1928, [ii], **32**, 81—96).—For pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility on either the cluster or the small ion theory. Blanc's law is not universally valid. Mobility curves in mixtures indicate three types of effect: absence of clustering, labile clustering, and stable clustering. Clusters approaching in their stability and nature definite chemical combinations are postulated.
A. A. ELDRIDGE.

Energy of radiation excited by electronic bombardment. P. BRICOUT (J. Phys. Radium, 1928, [vi], **9**, 88—119).—An apparatus is described for the determination of the relation between the energy of the electrons emitted from a hot filament and the intensity of the radiation excited by them, and a method of measuring the absolute value of the energy emitted is developed. A theoretical explanation of the results is discussed, and a calculation made of the probability of the emission of a quantum of energy due to a collision between an electron and a neutral atom.
W. A. RICHARDSON.

New method of determining the mobility of ions or electrons in gases. R. J. VAN DE GRAAFF (Phil. Mag., 1928, [vii], **6**, 210—217).—The results of most measurements of the velocity of ions or electrons in the direction of an electric force represent the upper or lower limits of the mean velocities due to variable conditions. A method for measuring the mean velocity of a group of ions moving in a gas under a steady electric force is described. The method involves the superposition, on a plate and grid combination in the gas under examination, of the shuttering effect of an oscillating potential of known frequency which allows the transference of ions during definite time intervals. Measurements of the distances and the maximum currents in the gas then provide all the necessary data. The mobility of the positive ions of hydrogen at 760 mm. has been found to be 5·8 cm./sec., which is approximately the mean of values given by other workers.
A. E. MITCHELL.

Reflexion of electrons. S. SZCZENIEWSKI (Compt. rend., 1928, **187**, 106—109).—The reflexion of cathode rays from the cleavage surface of a bismuth crystal has been measured for different angles of incidence and accelerating potentials of 62, 139, and 240 volts. The results are in agreement with the theoretical formula $\lambda=12{\cdot}22/\sqrt{v}$, where λ is the wave-length (in Å.) associated with the beam of cathode rays, and v is the fall of potential in volts.
C. W. GIBBY.

Constitution of germanium. F. W. ASTON (Nature, 1928, **122**, 167).—Experiments with germanium tetraethyl and tetrafluoride indicate that germanium has the following isotopes, in order of descending intensity: 74, 72, 70, 73, 75, 76, 71, 77. It is unlikely that any of these lines is due to hydrogen compounds, but the intensity of Ge^{76} is in doubt. Of these mass numbers only 72 and 73 are peculiar to germanium.
A. A. ELDRIDGE.

At. wt. of proto-actinium. F. LOTZE (Naturwiss., 1928, **16**, 558).—Since 6 α-particles are lost in the degeneration of proto-actinium to actinium-*D*, and since at. wt. determinations on lead of radioactive origin lead to the mean value of 207·42 for the at. wt. of actinium-*D*, it is suggested that the most probable value for the at. wt. of protoactinium is 231.
R. W. LUNT.

Dependence of the photographic action of β-rays on their velocity. C. D. ELLIS and G. H. ASTON (Proc. Roy. Soc., 1928, **A**, **119**, 645—650).—In recent work by Ellis and Wooster (A., 1927, 393) on the relative intensities of the β-ray groups of radium-*B* and -*C*, it was assumed that photographic action ran parallel with the total ionisation per cm., *i.e.*, varied as $1/\beta^2$. This assumption has now been tested by comparing the distribution of intensity measured photographically with Gurney's data for the variation of the number of electrons with the velocity (A., 1926, 5), and it is found that photographic action varies on the whole more rapidly than $1/\beta^2$ in the region 200,000 volts and upwards. Ilford *X*-ray emulsion plates were used, and the results are expressed by a curve showing how to reduce photographic densities due to electrons of different speeds to a common basis of true exposure.
L. L. BIRCUMSHAW.

Method of determining the volume of 1 curie of radon. L. WERTENSTEIN (Phil. Mag., 1928, [vii], **6**, 17—33).—Pressure measurements on samples of radon of known radioactive power have been made by means of a Knudsen gauge, whilst the corresponding purity has been determined simultaneously by means of a quartz fibre gauge, the main impurity having been shown previously (this vol., 684) to be carbon dioxide. The volume of 1 curie of radon at N.T.P. is thus shown to be $6{\cdot}39\times10^{-4}\pm5\%$ c.c. Measurements in capillary tubes gave confirmatory results which were, however, rendered variable by the effect of rarefied radon in promoting gas evolution from the glass, whilst concentrated radon acts as a "clean-up" agent. The first effect is attributed to α-particle bombardment of the glass, whilst the second is explained by the bombardment of the gas molecules by α-particles and their subsequent adsorption. The considerably larger volumes obtained by Rutherford

and others are attributed to lack of sufficient information as to the purity of their material.

A. E. MITCHELL.

Effects produced by positive-ion bombardment of solids: metallic ions. M. L. OLIPHANT (Proc. Camb. Phil. Soc., 1928, **24**, 451—469).—Experiments have been made to determine the relation between the energy of a positive ion and the effect produced on a surface which it bombards. Considerable secondary emission occurs due to layers of adsorbed gas over the target. The deposition of metal from the positive ions causes changes of the surface bombarded which are difficult to allow for.

W. E. DOWNEY.

Recoil velocities in β-particle emission in thorium-*B*. L. WERTENSTEIN (Z. Physik, 1928, **49**, 463).—Polemical against Donat and Philipp (this vol., 343).

R. W. LUNT.

Vaporisation of polonium in a vacuum. P. BONÈT-MAURY (Compt. rend., 1928, **187**, 115—117).—A method is described for measuring the rate of vaporisation of polonium in a vacuum.

C. W. GIBBY.

Kinematographic sketch of electrically exploded wires. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 198—200).—Instead of photographing exploding wires on films rotating in a plane at right angles to the line of sight, as had been done previously, photographs were taken on a film moving round an axis parallel to the wire. Photographs are given of the explosion of copper and iron wires, and of magnesium ribbon. Luminous particles are expelled at right angles to the direction of flow of the current, not continuously, but in masses.

A. J. MEE.

Velocity of particles sputtered by disruptive discharge. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 201—204; cf. A., 1927, 1117; this vol., 97, 339, 683).—By photographing the sputtered particles on a film rotating with known velocity and measuring the tracks, the velocity of the particles can be found. The mean velocities (in m./sec.) found are, for tungsten, 43, for magnesium, 37, and for cerium, 90, but as the speed depends on voltage, current strength, and the form of the electrodes, these values are indicative only of its order of magnitude.

A. J. MEE.

Decomposition of the lead atom. A. SMITS and W. A. FREDERIKSE (Z. Elektrochem., 1928, **34**, 350—360).—Attempts have been made to effect artificial disintegration of lead, employing quartz-mercury lamps, high-tension spark discharges and low-tension arcs through gaseous and liquid dielectrics, and irradiation. The spark and arc experiments yielded definitely negative results, but some indications of breakdown were observed by *X*-ray irradiation of lead for long periods of time. Difficultly reproducible positive results were obtained by using quartz-mercury vapour lamps, and the quartz-lead lamp remains the only method which has yielded definite results. The possibility that the result is in this case due to contamination and not to transmutation is, however, recognised.

H. F. GILLBE.

Generalisation of the Kramers–Heisenberg dispersion formula for short waves in the multi-electron problem. I. WALLER (Naturwiss., 1927, **15**, 969; Chem. Zentr., 1928, i, 643).—A new dispersion formula is advanced.

A. A. ELDRIDGE.

Contraction of hydrogen under electric discharge. R. DELAPLACE (Compt. rend., 1928, **187**, 225—227).—Electrolytic hydrogen, submitted to a high-tension discharge at pressures below 11 mm., undergoes an irreversible contraction, not due to the formation of H_3. Carbon monoxide and methane are found after the discharge.

C. W. GIBBY.

Statistical deduction of some properties of the atom. Calculations of Rydberg's correction. E. FERMI (Atti R. Accad. Lincei, 1928, [vi], **7**, 726—730).—Mathematical.

Theory of electric conduction. W. H. McCREA (Proc. Camb. Phil. Soc., 1928, **24**, 438—444).—Mathematical (cf. Sommerfeld, this vol., 681).

W. E. DOWNEY.

Electronic theory of metals according to wave-mechanical statistics; Volta effect. A. SOMMERFELD (Ber., 1928, **61**, [*B*], 1171—1180).—A lecture.

H. WREN.

Wave-mechanical theory of metallic conductivity. J. FRENKEL and N. MIROLUBOW (Z. Physik, 1928, **49**, 885—893).—Mathematical (cf. Frenkel, this vol., 577).

J. W. SMITH.

Undulating theory of two-electron orbits. A. W. CONWAY (Proc. Roy. Irish Acad., 1928, **38** A, 18—28).—Mathematical.

Electron in a gravitational field. J. M. WHITTAKER (Proc. Camb. Phil. Soc., 1928, **24**, 414—420).—Mathematical.

W. E. DOWNEY.

Wave mechanics of an atom with a non-Coulomb central field. III. Term values and intensities in series in optical spectra. D. R. HARTREE (Proc. Camb. Phil. Soc., 1928, **24**, 426—437).—Mathematical.

W. E. DOWNEY.

Inversion point of the second order. W. JAZYNA (Z. Physik, **49**, 270—278).—Mathematical.

R. W. LUNT.

Impulse-energy-jump in Dirac's quantum theory of electrons. H. TETRODE (Z. Physik, 1928, **49**, 858—864).—Mathematical.

J. W. SMITH.

Measurement of light absorption. H. VON HALBAN and J. EISENBRAND (Z. wiss. Phot., 1928, **25**, 138—152; cf. A., 1927, 1017).—The factors for carrying out measurements of light absorption are critically discussed. The advantages and disadvantages of the photographic and the photo-electric methods are considered. With a sufficiently high extinction, the extinction coefficient can be determined photographically with an accuracy of a few per cent. The photographic method is not suitable for determining small differences of extinction or of concentration of absorbing material, or for the absolute measurement of small extinctions; it is, however, very suitable for the complete quantitative determination of absorption spectra, and for this it is more useful than the photo-electric method owing to its rapidity. The photo-electric method shows no lower limit of differential

sensitiveness in regard to extinction, and is therefore eminently suitable for estimating low values of extinction and small differences of extinction. In absolute measurements its sensitiveness cannot be fully utilised. In determining complete absorption spectra the limited number of lines utilisable is a disadvantage. The differences observed between the photo-electric and photographic methods at wave-lengths below λ 3000, and especially with nitrate solutions, are explained by systematic errors in the photo-electric measurements. Photo-electric cells show unexpectedly large differences in the relation of sensitivity to wave-length. The exact knowledge of the properties of the cell used is especially important if absolute measurements are to be made with impure light. W. CLARK.

Pleochroism of tourmaline. P. LE ROUX (J. Phys. Radium, 1928, [vi], **9**, 142—152).—Absorption measurements on two sections of tourmaline cut parallel and perpendicular to the optical axis have been made for the mercury arc lines 5790—3655 Å. using a photo-electric cell and quadrant electrometer. When absorption is no longer small, the coefficient of absorption varies with the direction of propagation of the light, the value being less in the direction parallel than in that perpendicular to the axis of the crystal. This has been confirmed with a second sample of yellow tourmaline. The different value obtained in this case for the coefficient of absorption indicates that the coloration of tourmaline is due to an impurity. L. S. THEOBALD.

Dielectric constants and absorption indices of ethyl alcohol for short electric waves. S. MIZUSHIMA (Proc. Imp. Acad. Tokyo, 1928, **4**, 205—207).—The dielectric constant and absorption index of ethyl alcohol were determined at various temperatures between 60° and −60° by the resonance method, using electric waves of wave-length 59 cm. The results so obtained, together with those published previously (cf. A., 1926, 560, 778, 886, 1082) for other wave-lengths, show that the region of anomalous dispersion is shifted towards longer wave-lengths as the temperature is lowered. This agrees with Debye's dipole theory. From the experimental values for the dielectric constant, and by making use of Debye's formula, the molecular radius can be calculated. It is found to be $2{\cdot}1\times10^{-8}$ cm., which is in good agreement with the value obtained by other methods. A. J. MEE.

Cathode phosphorescence of erbium in calcium oxide. S. FAGERBERG (Ann. Physik, 1928, [iv], **86**, 435—446).—The emission spectrum of an erbium sulphate phosphor has been observed over the range 6800—3100 Å. and the wave-lengths of some 150 lines and bands have been measured. J. W. SMITH.

Metallic reflexion from rock salt and sylvite in the far ultra-violet. A. H. PFUND (Physical Rev., 1928, [ii], **32**, 39—43).—The wave-lengths of the true resonance frequencies are estimated to be 1547 and 1581 Å. for sodium chloride and potassium chloride, respectively. A. A. ELDRIDGE.

Relation between molecular constitution and colour. III. Reciprocal influence of the component valency fields of a molecule. Inversion of the absorptive character of two chromogens. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1927, **3**, 373—380; Chem. Zentr., 1928, i, 696—697).—The phenyl, *p*-methoxyphenyl, and 3 : 4-methylenedioxyphenyl derivatives of benzofulvene absorb more strongly than these derivatives of dibenzofulvene, but the absorption intervals are not equal. "The absorption interval of two substances with identical substituents but different chromogens diminishes as the co-ordinatively unsaturated character of the substituents increases." In fact, bis-*p*-dimethylaminophenyldibenzofulvene absorbs more strongly than bis-*p*-dimethylaminophenylbenzofulvene, owing to the reciprocal influence of the valency fields of the chromogen and the substituents. If the co-ordinative unsaturation of the substituents disappears, *e.g.*, by salt formation, the normal absorptive character of the chromogen returns. A. A. ELDRIDGE.

Absorption spectrum of nitric oxide. M. LAMBREY (Compt. rend., 1928, **187**, 210—212; cf. A., 1927, 808).—The absorption spectrum of nitric oxide has been measured. The formulæ representing the composition of the doublet 2267·85, 2261·5 are, first component, $\nu=44082+10{\cdot}7N+2{\cdot}3N^2$ and $\nu=44077+2{\cdot}3N^2$, second component, $\nu=44196{\cdot}5+9{\cdot}12N+2{\cdot}76N^2$ and $\nu=44200+2{\cdot}76N^2$. The doublet 2153·75, 2148·15 is represented by, first component, $\nu=46419+10{\cdot}2N+2{\cdot}1N^2$ and $\nu=46413{\cdot}5+2{\cdot}1N^2$, second component, $\nu=46536+8{\cdot}72N+2{\cdot}56N^2$ and $\nu=46531{\cdot}5+2{\cdot}56N^2$. C. W. GIBBY.

Luminescence of water and carbon disulphide under the influence of γ-rays. L. MALLET (Compt. rend., 1928, **187**, 222—223).—Under the influence of γ-rays water and carbon disulphide give rise to continuous luminescence spectra. C. W. GIBBY.

Polarisation of infra-red radiation by calcite. A. M. TAYLOR (Phil. Mag., 1928, [vii], **6**, 88—97).—Infra-red radiation has been shown to be partly polarised by passage through thin plates of calcite cut parallel to the optic axis. These polarisation effects have been used to differentiate between the absorption bands of the calcite in the infra-red region due to real maxima of absorption and those which are merely the effect of interference. Six fundamental absorption bands over the range 94—7 μ with a first and second harmonic have been verified. The frequencies measured are in agreement with those calculated by ignoring the assumption of Schaefer (A., 1927, 5) of an inactive frequency which is active in combination. A. E. MITCHELL.

Influence of different nuclei on the absorption spectra of organic compounds. J. E. PURVIS (Proc. Camb. Phil. Soc., 1928, **24**, 421—425).—In the phenyl derivatives of the two naphthylamines it is found that the introduction of the phenyl group produces an additional band; in the *ar*- and *ac*-hydrogen derivatives of these two compounds the type of absorption is controlled by the saturated or unsaturated condition of each constituent ring. In the cresols, the introduction of a nitroso-group produces colour. In the anilides, the position of the typical absorption of aniline is destroyed, and it is replaced by a band due to a phenyl group. W. E. DOWNEY.

Fluorescence of mercury vapour under low excitation. (LORD) RAYLEIGH (Nature, 1928, **122**, 242).—Radiation of wave-length 3125 Å. excites the green band fluorescence of mercury vapour.

A. A. ELDRIDGE.

Absorption of light by solid and dissolved salts and absorption by ions. H. LEY [with W. HEIDBRINK] (Z. anorg. Chem., 1928, **173**, 287—296).—The absorptive power of copper sulphate solutions for ultra-violet light between 0·30 and 0·25 μ deviates appreciably from Beer's law; a similar result is obtained with concentrated solutions of copper perchlorate. The absorptive power of the solid pentahydrate is appreciably less than that of the solution, showing that the hydrated ion $[Cu4H_2O]^{\cdot\cdot}$ is present in the crystal lattice and that this forms a more normal and more optically saturated system than does the solution, the deviations in the absorptive power of which are ascribed to the formation of complex anions. The change in the colour of solutions of nickel and copper sulphates produced by the addition of sulphuric acid is shown by examination of the absorption spectrum to be due to dehydration of the coloured cation.

A. R. POWELL.

Distribution of velocity of the excited sodium atoms produced in the optical dissociation of sodium iodide. A. C. G. MITCHELL (Z. Physik, 1928, **49**, 228—235).—The Doppler effect for the *D*-light emitted by excited sodium atoms produced by passing the light from cadmium or zinc arcs through sodium iodide vapour at 650° has been measured in directions parallel and perpendicular to the direction of the beam producing dissociation. Since the effect is sensibly the same in the two directions, it follows that the velocities of the excited sodium atoms in these directions are also equal.

R. W. LUNT.

Device for measuring spectrum photographs. R. FRISCH (Z. Physik, 1928, **49**, 608).—A simple device is described suitable for the rapid determination of distances separating lines in a spectrum photograph with an accuracy of 0·01 mm.

R. W. LUNT.

Structure and activation of the formaldehyde molecule : analysis from the point of view of the ultra-violet absorption spectrum of the vapour. V. HENRI and S. A. SCHOU (Z. Physik, 1928, **49**, 774—826).—The ultra-violet absorption spectrum of formaldehyde vapour has been investigated and 35—40 bands have been located between 3700 and 2500 Å. The absorption maximum is at 2935, as for other aldehydes. The bands can be divided into 11 groups, the first 7 groups containing rotation bands, whilst the other groups are indefinite and continuous and are attributed to the pre-dissociated molecule. A double fine structure was found in the first 7 bands and is explained by assuming a doubly-quantised rotation of the molecule, corresponding with two moments of inertia J and K, the former about the C—O axis of the molecule, and the latter at right angles to it. The values deduced for the moments of inertia of the normal molecule are $J_0=1{\cdot}38\times10^{-40}$, $K_0=23\times10^{-40}$. From this the configuration of the molecule is deduced as of Y-form with the following inter-atomic distances : H—H$=1{\cdot}38\times10^{-8}$ cm.; C—O$=1{\cdot}09\times10^{-8}$; C—H$=1{\cdot}3\times10^{-8}$ cm. Similarly, there are two vibration numbers α and β, corresponding with C—O vibrations and H—H vibrations, respectively. For the normal molecule $\alpha_0=1572{\cdot}3$ and $\beta_0=441$ cm.$^{-1}$, whilst for the excited molecule $\alpha'=1231{\cdot}3$ and $\beta'=398$ cm.$^{-1}$ The band structure shows a triplet system, and the lines in each band can be arranged very exactly according to nine parabolas. The separation of the bands in these triplets is independent of the state of vibration of the atoms and is almost equal to the value calculated from the emission spectrum of the CO molecule. The carbon monoxide molecule is supposed to exist normally in the ^1S state, from which it was predicted that it would have a new absorption band at 2060·6 arising from the ^1S— change. This was found at 2060·8 Å. The deductions are drawn that the formaldehyde molecule exists normally in the ^3P state and passes through seven successive stages of vibrational activation into a pre-dissociated substance. At higher temperatures the latter condition appears at lower degrees of excitation than at normal temperatures.

Observations of the absorption spectrum of formaldehyde in solution showed that in water the formaldehyde molecule is completely hydrated, whilst in hexane at −70° it remains in the unimolecular state.

J. W. SMITH.

Optical excitation and dissociation of metallic halides. K. BUTKOV and A. TERENIN (Z. Physik, 1928, **49**, 865—884).—In continuation of previous work (A., 1926, 776; 1927, 1009) the optical dissociation of the cæsium iodide, thallous bromide and chloride, and cuprous iodide molecules into the excited metallic atom and neutral halogen atom has been investigated. The limiting frequencies at which the lines characteristic of the metallic atom are emitted when the vapour of the halide is irradiated with an intense beam of short ultra-violet light were determined, and the heat of dissociation of the molecules so deduced was found to be in satisfactory agreement with those calculated from thermochemical data. In the case of thallous iodide vapour, optical excitation causes the emission of a band spectrum of the TlI molecule besides the atomic lines. From this, the various dissociation processes are related with the energy levels in the molecules. The data obtained are compared with those found previously.

J. W. SMITH.

Titanium oxide bands. A. CHRISTY and R. T. BIRGE (Nature, 1928, **122**, 205).—Each of the blue-green titanium bands consists of three R and three P branches. The three heads of the 0—0 band lie at 19,349, 19,347, and 19,340 cm.$^{-1}$ (approx.). The bands are ascribed to neutral TiO, and are probably due to a $^3P-^3P$ transition; the lower level is assumed to be an excited level of the TiO molecule.

A. A. ELDRIDGE.

Dielectric polarisation of liquids. III. Polarisation of the isomerides of heptane. C. P. SMYTH and W. N. STOOPS (J. Amer. Chem. Soc., 1928, **50**, 1883—1890).—The densities, refractive indices, and other physical constants of *n*-heptane, its isomerides, and ββδ-trimethylpentane are recorded for 20°. The dielectric constants and densities of

n-heptane, ββ-dimethylpentane, γ-ethylpentane, and ββδ-trimethylpentane between −120° and +100° are also recorded. These molecules possess no measurable electric moments. Atoms in saturated hydrocarbons may be linked in every possible configuration without causing measurable lack of electric symmetry, although slight differences in the rigidity of the binding electrons can be detected. The electrical symmetry of the molecules gives no evidence of a difference in the electronegativities of the various constituent radicals. S. K. Tweedy.

Specific heats at low temperatures of manganous oxide, manganosomanganic oxide, and manganese dioxide. R. W. Millar (J. Amer. Chem. Soc., 1928, **50**, 1875—1883).—The specific heats were measured from 70° to 300° Abs. The specific heat–temperature curves for manganous oxide and manganese dioxide exhibit discontinuities. With the aid of the Debye and Einstein specific heat functions and the third law of thermodynamics the following entropies (in g.-cal./1°) at 25° were calculated: manganous oxide, 14·92; manganosomanganic oxide (Mn_3O_4), 35·73; manganese dioxide, 13·93. The respective free energies, ΔF, are at 25° (g.-cal./mol.): −85,830, −302,800, and −112,600. S. K. Tweedy.

Electric moment of *p*-azoxyanisole. J. Errera (Physikal. Z., 1928, **29**, 426—429).—Measurements of the electric moment are held to indicate that the optical anisotropy of *p*-azoxyanisole is due, not to molecular aggregates, but to the molecules themselves. The value obtained for the electric moment is $\mu = 2\cdot3\times10^{-18}$. J. W. Smith.

Determination of dipole moments from critical data. J. K. Syrkin (Z. anorg. Chem., 1928, **174**, 47—56).—The equation $m=1\cdot66\times10^{-20}T_cP_c^{\frac{1}{2}}$ has been deduced from the equation for the mean energy of two rigid dipoles; m is the moment of the dipole, T_c and P_c are the critical temperature and pressure. The moments of 79 substances have been calculated, and the results are in agreement with the values observed by other workers. Relationships between the dipole moments of similar compounds are discussed; *e.g.*, for homologous series the moment decreases as the number of carbon atoms in the molecule increases. Additive relationships are observable in a number of cases. H. F. Gillbe.

Molecular and atomic volumes. XX. Space occupied by hydrogen in metallic hydrides. W. Biltz (Z. anorg. Chem., 1928, **174**, 42—46).—Hydride formation by the alkali, alkaline-earth, and rare-earth metals is accompanied by a reduction to about half its value of the zero mol. volume. The mol. volumes of the rare-earth hydrides class these elements with the alkali and alkaline-earth groups. H. F. Gillbe.

Raman effect. P. Pringsheim (Naturwiss., 1928, **16**, 597—606).—Descriptive.

Dependence of refractive index on temperature and density. G. Peters (Ann. Physik, 1928, [iv], **86**, 494—510).—An interferometer method of measuring the refractive index of liquids is described. Measurements on liquid hydrogen cyanide have been made, but the results are not of sufficient accuracy to determine which of the various theoretical formulæ most accurately represents the effect of temperature and density. W. E. Downey.

Rotation polarisation of electromagnetic waves due to tetrahedral molecule models. K. F. Lindman (Acta Acad. Åboensis Math. phys., 1927, **4**, No. 1, 1—22; Chem. Zentr., 1928, i, 1146).—Experiments were carried out with isotopic three-dimensional systems of numerous small tetrahedral molecule models and waves of length greater than those of the resonators and the dimensions of the single models. In accord with Biot's corresponding law for optical activity, the rotation of the plane of polarisation of the electromagnetic waves is proportional to the number of molecule models in their path, *i.e.*, to the cross-section of the active substance. A. A. Eldridge.

Polarisation of scattered light quanta. C. V. Raman and K. S. Krishnan (Nature, 1928, **122**, 169).

New phenomenon in the scattering of light by crystals. G. Landsberg and L. Mendelstam (Naturwiss., 1928, **16**, 557—558).—While investigating the scattering of light, using a mercury arc source, from quartz crystals, a diminution in frequency of the scattered lines 2536, 3126, and 3650 Å. was observed. It is suggested that the observed diminution in frequency can be accounted for by the emission of one quantum of an infra-red frequency per quantum scattered, since in the cases recorded the diminution in frequency corresponds with emission at the known absorption region $\lambda=20\cdot7\ \mu$. R. W. Lunt.

Refractive index for electron waves. L. Rosenfeld and E. E. Witmer (Z. Physik, 1928, **49**, 534—540).—A theoretical discussion of the relationship between the values of μ, the "refractive index of a metal, e, the potential in the metal, and V derived from the equation $eV=\frac{1}{2}mv^2$, for various metals.

Valency chemistry of boron, and the constitution of the simplest boron hydride. E. Wiberg (Z. anorg. Chem., 1928, **173**, 199—221).—An electronic formulation of boron hydride, B_2H_6, is derived by postulating that (1) the octet rule is valid for boron compounds, (2) the boron atom cannot combine by covalencies with more than 4 atoms, (3) hydrogen is combined by electrovalencies only in the metallic hydrides, and in all other cases by covalencies. The conclusion is reached that in all electrovalency compounds boron is tervalent and in all covalency compounds, quinquevalent. Quadrivalent boron, in the sense of quadrivalent carbon, does not exist. The formula derived is consistent with addition of sodium and ammonia to the hydride, its reactions with water and the hydrogen halides, and the formation of hypoborates. H. F. Gillbe.

Polar conception of co-ordinated valencies. E. J. W. Verweg (Chem. Weekblad, 1928, **25**, 250—254).—It is contended that the so-called co-ordinated valencies in complex compounds are in fact polar in nature, although "deformed" to such a degree as to appear to some extent non-polar. S. I. Levy.

Structure of thin films. XI. Oxygenated derivatives of benzene. N. K. Adam (Proc. Roy. Soc., 1928, A, **119**, 628—644; cf. A., 1926, 348).—With the object of obtaining films of substances containing the benzene nucleus lying flat on the surface of water, neighbouring rings being in contact with one another, so that the cross-section of the benzene ring parallel to the plane of the ring could be measured, the surface films of a number of resorcinol and phloroglucinol derivatives, all with long side-chains, have been investigated. No films of the required type were obtained. In most of the polyhydroxy-compounds the rings stood upright, whilst in compounds containing methoxyl groups, although the rings probably did lie flat, the films were of the "expanded" type and the orientation and packing were greatly influenced by lateral compression. The cohesional force between film molecules is discussed. Hydroxyl groups greatly increase the lateral attraction between the rings packed vertically in the films. The carbonyl groups of acyl side-chains in the polyhydroxy-compounds also appear to increase the lateral attraction, but in the polymethoxy-compounds the carbonyl groups in the side-chains appear to come into contact with the water and increase the area. The compound ωω′-bis-2 : 4-dihydroxyphenyldecane forms gaseous films with the molecules lying flat, in accordance with the rule that two widely separated points of attachment to the water on the chain cause the molecules to lie flat and the films to become gaseous. The lateral attraction between the flat molecules in these gaseous films is diminished by acetylating the hydroxyl groups, and the area of the molecule is measured. Humulon (cf. Wieland, Martz, and Hock, A., 1925, i, 1422) forms a film of unique type in which the ring is probably flat on the water and in contact with adjacent rings. Although the film is of the required type, however, the substituents in the molecule are too numerous for any idea of the true cross-section of the benzene nucleus to be obtained.

L. L. Bircumshaw.

Energy distribution of complex molecules. O. K. Rice (Physical Rev., 1928, [ii], **32**, 142—149).—Theoretical. The distribution over a range of energies for a given average energy of the molecules over a range of temperatures is formulated and the results are applied to the decomposition of azomethane.

A. A. Eldridge.

Kinetics of absorption of ultra-sonic waves. D. G. Bourgin (Nature, 1928, **122**, 133).—The attenuation of ultra-sonic waves in passing through carbon dioxide, hydrogen, or helium, and the accompanying frequency variation of velocity are correlated with the mechanisms of collisions of the first and second kinds. A. A. Eldridge.

Form of molecules of cellulose and polymerised substances. J. R. Katz and P. J. P. Samwel (Naturwiss., 1928, **16**, 592—593).—A new method has been worked out by which unimolecular surface films can be prepared by spreading chloroform solutions on water. Examination of films derived from crystalline cellulose derivatives and technical preparations of high and low viscosity gave sensibly equal values for the thickness and the area per $C_6H_{10}O_5$ unit. Since the layers are only one to two carbon atoms thick, the aggregates must be in the form of threads or leaves, formed by polymerisation in one or two dimensions only. Probably, from other evidence, the former is the case. Other polymerised substances (anethole, vinyl acetate, and methyl acrylate) gave analogous results. R. K. Callow.

Chemical interactions corresponding with the constant of mass action being a function of the volume and masses of the constituents as well as of the temperature and catalytic action. R. D. Kleeman (Phil. Mag., 1928, [vii], **6**, 195—203).—By extending his previous results (this vol., 263, 470, 955) the author shows that a dense substance in contact with reacting gases of which it may occlude one or more, to any extent, renders the constant of mass action a function of the volume and masses of the constituents. Thus in addition to affecting the velocities of the changes occurring in the reacting mixture, a catalytic agent can also affect the value of the mass action constant to an extent depending on the volumes and masses of the constituents of the reacting mixture.

A. E. Mitchell.

Rate of vibration and molecular packing of organic compounds. W. Herz (Z. anorg. Chem., 1928, **173**, 358—360).—If v is the rate of vibration and z the number of molecules in unit volume just above the m. p., it is shown for about thirty organic liquids that the ratio $z^{1/7}/v$ is a constant which is approximately 3. For the hydrocarbons ethane to decane the results recorded vary from 3·02 to 3·75, for the corresponding primary alcohols from 2·90 to 3·08, and for various fatty acids and aromatic hydrocarbons from 2·77 to 3·28. Hydrogen cyanide, however, gives a value of 1·82 and iodobenzene 4·14.

A. R. Powell.

Constitution of azoimide and its esters. H. Lindemann and H. Thiele (Ber., 1928, **61**, [*B*], 1529—1534).—Determinations of the parachor of a number of derivatives of azoimide show that Thiele's formula, R·N:N:N, for these compounds and hence probably for azoimide is untenable. The assumption is thereby made that the double linking between the nitrogen atoms has the same value as the C:C, C:O, C:S, or N:O linkings, and the triple linking the same effect as the acetylenic or C:N linking. The calculated values for the cyclic form $\mathrm{R{\cdot}N}\!<\!\begin{smallmatrix}\mathrm{N}\\ \Vert\end{smallmatrix}$ agree excellently with the observed data. The following figures are recorded: ethyl azidoacetate, b. p. 74°/18 mm., d_4^{19} 1·1263, γ 34·11; azidoacetone, b. p. 71°/18 mm., 1·1228, γ 39·33; phenyl azide, b. p. 80°/30 mm., $d_4^{21\cdot5}$ 1·0959, γ 36·66; *o*-tolyl azide, b. p. 88°/23 mm., $d_4^{22\cdot2}$ 1·0709; γ 35·73; *p*-tolyl azide, b. p. 85°/22 mm., $d_4^{22\cdot5}$ 1·0527, γ 34·78.

H. Wren.

Magnetic resolution of bismuth vapour streams. A. Leu (Z. Physik, 1928, **49**, 498—536).—The magnetic resolution of streams of bismuth vapour has been investigated at temperatures in the range 1090—1430°. At the lower end of this range there is a considerable undeflected beam

thought to be due to Bi_2 molecules; this disappears completely at 1430°. The observed resolution corresponds with a magnetic moment of $0{\cdot}72_3$ Bohr unit in qualitative agreement with theory; the value of μ_1 is independent of the resolving field strength. From measurements of the temperature variation of the intensity of the undeflected beam it is shown that an approximately linear relationship exists between the dissociation constant for bismuth (Bi_2=2Bi) and the reciprocal of the absolute temperature. The corresponding value of the heat of dissociation of the Bi_2 molecule is $6\pm1{\cdot}5\times10^4$ g.-cal., whilst the value calculated by the Nernst heat theorem on analogy with iodine is $5{\cdot}6\times10^4$ g.-cal.

R. W. LUNT.

Newer measurements in the *L*-series of *X*-ray spectra. H. BRAUNS (Z. wiss. Phot., 1927, **25**, 325—344).—In *X*-ray spectroscopy, measurements of wave-length are " absolute " if they depend on the lattice constants of a crystal, which are given by the formula $d=(MeE/2\rho VSC)^{1/3}$, where M is mol. wt., e the elementary electric charge, E the equivalent wt., ρ the density of the crystal, V the volume of the elementary crystal cell, S the at. wt. of silver, and C the velocity of light. This, however, gives results correct to four figures only, whereas spectroscopic measurements are accurate to six. Moseley's calculated figure for the constants of rock salt are therefore arbitrarily accepted as standard. In " relative " measurements the lines are referred to a standard line, usually the $K\alpha_1$ line of copper, but owing to the small degree of regularity among the lines of the *X*-ray spectrum, a number of secondary reference lines at intervals of 50X are necessary. As the value for the copper line is uncertain within 1%, a table is given to facilitate conversion of the value of a line from one standard into another.

Bragg's turning crystal method and Seemann's camera method have been modified by Siegbahn to give absolute measurements. The former overcomes the difficulty due to the non-parallelism of the *X*-radiation, but as it is impossible to distinguish completely the images due to the first and the subsequent layers in the crystal, it has been largely replaced by the second method. In both cases the net error is of the order 0·05 Å.

The " relative " method was used here, the substance to be investigated being rubbed on to a copper anticathode. A film was used instead of a plate so as to fit the curved chamber. Exposure required $1\frac{1}{2}$—3 hrs., and only the $L\alpha_1$ lines were taken to sufficient intensity. The results are as follow (X): tantalum 1518·79; tungsten 1473·37; lead 1172·55; bismuth 1141·55; uranium 908·96. Except in one or two cases these agree within experimental error with the results of other workers.

S. J. GREGG.

Diffraction of cathode rays. II. G. P. THOMSON (Proc. Roy. Soc., 1928, **A**, **119**, 651—663).—A continuation of previous work (cf. this vol., 3). Using a modified apparatus, diffraction patterns have been obtained by passing a beam of cathode rays through thin films of platinum, and the results are in complete agreement with the de Broglie theory of electron waves. The values of the crystal constants of aluminium, gold, and platinum, found by applying the de Broglie theory, agree to 1% with those determined by *X*-ray analysis. Evidence is obtained which indicates that the electrons must be accompanied by a train of not less than 50 waves in length.

L. L. BIRCUMSHAW.

Diffraction of cathode rays by thin celluloid films. A. REID (Proc. Roy. Soc., 1928, **A**, **119**, 663—667; cf. preceding abstract).—The diffraction patterns obtained are in complete agreement with those predicted by the de Broglie wave theory. The energy of the ray was measured by electrostatic deflexion, and the results agree to 1% with those obtained by Thomson (preceding) where the energy was measured by spark-gap. A possible structure for the celluloid films is suggested.

L. L. BIRCUMSHAW.

Diffraction of cathode rays by thin films of copper, silver, and tin. R. IRONSIDE (Proc. Roy. Soc., 1928, **A**, **119**, 668—673).—Results in agreement with the de Broglie wave theory have been obtained by observation of the diffraction patterns formed on passing electrons through thin films of copper, silver, and tin, using the apparatus and method described by Thomson (preceding). The values of the grating constants, calculated on the de Broglie theory, agree to about 1% with those determined by *X*-ray analysis.

L. L. BIRCUMSHAW.

Critical-absorption photometer for the study of the Compton effect. C. V. RAMAN and C. M. SOGANI (Proc. Roy. Soc., 1928, **A**, **119**, 526—530).

New method of *X*-ray spectroscopy. Orientation of fatty acids on mercury. J. J. TRILLAT (Compt. rend., 1928, **187**, 168—169).—Satisfactory spectra can be obtained by using a drop of mercury covered with a very small quantity of fatty acid, melting the latter if solid. By this means orientation at liquid–liquid and liquid–solid interfaces can be investigated. It persists up to at least 100°.

C. W. GIBBY.

Absorption of *X*- and γ-rays and the secondary radiations which accompany them. DUC DE BROGLIE (Brit. J. Radiol., Roentgen Soc. Sect., 1927, **23**, 55—62).—A discussion of absorption, ionisation, and therapeutic effect.

CHEMICAL ABSTRACTS.

Relative intensities of *X*-ray lines in the *L*-spectrum of uranium. S. K. ALLISON (Physical Rev., 1928, [ii], **32**, 1—11).—The relative intensities of 17 lines in the *L*-spectrum of uranium have been studied, and the results extrapolated to voltages greater than the critical.

A. A. ELDRIDGE.

Interpretation of atomic structure factor curves in crystal reflexion of *X*-rays. G. E. M. JAUNCEY and W. D. CLAUS (Physical Rev., 1928, [ii], **32**, 12—21).—Previous work (this vol., 692) is continued. For any atom *F*-values, calculated according to the classical theory and unmodified for the Compton effect but multiplied by the Debye temperature factor, give *U*-curves the areas under which never exceed the number of electrons assumed in the model. For certain values of *D*, the grating space of a crystal of rock salt, both experimental and modified theoretical *F*-values give *U*-curves the areas under which exceed the true number of electrons.

It appears that the Compton effect is involved, and that the present Fourier analysis method is invalidated. A. A. ELDRIDGE.

Scattering of X-rays from gases. C. S. BARRETT (Physical Rev., 1928, [ii], **32**, 22—29).—Carbon dioxide, argon, oxygen, nitrogen, and helium, but not hydrogen, show excess scattering of molybdenum *X*-rays; the effect is largely due to interference arising within the atom. The effect with helium may be due to the presence of nitrogen.

A. A. ELDRIDGE.

Anomalous dispersion in the X-ray region. R. FORSTER (Naturwiss., 1927, **15**, 969—970; Chem. Zentr., 1928, i, 642).—Determinations of n for *X*-rays in the region of an absorption edge give results at variance with the theories of Lorentz and of Kallmann and Mark. A. A. ELDRIDGE.

Is crystal reflexion of X-rays entirely a classical phenomenon? I. WALLER and R. W. JAMES (Nature, 1928, **122**, 132—133).

Index of refraction of glass for X-rays of long wave-length. J. THIBAUD (Compt. rend., 1928, **187**, 219—221).—The limiting angle of total reflexion by glass of *X*-rays of wave-lengths between 1·5 and 65 Å. has been measured. As the absorption of the rays increases as the cube of the wave-length, the refractive index diminishes by an amount proportional to the square of the wave-length.

C. W. GIBBY.

Multiple ionisation and the absorption of X-rays. F. K. RICHTMYER (Phil. Mag., 1928, [vii], **6**, 64—88).—The possible existence of *X*-ray absorption spectra discontinuities corresponding with satellites analogous to the *K*, *L*, *M*, etc. discontinuities in *X*-ray spectra of the first order is discussed and it is concluded that the processes giving rise to the satellites are secondary and evidence concerning them is not to be expected in absorption spectra. Such evidence is difficult to deduce, since the satellites are weak in comparison with the parent lines and existing data on *X*-ray absorption coefficients are not sufficiently precise to demonstrate possible discontinuities. Since the square root of the difference in frequency between a satellite and its parent is directly proportional to the atomic number of the element emitting them it is suggested that the satellites arise from two-electron transfers. The importance of obviating the "slit width" error in precise measurements of *X*-ray absorption coefficient is demonstrated and it is shown that some of the published data in the region of 0·3 Å. must be several per cent. in error from this source alone.

A. E. MITCHELL.

Atomic scattering power for X-rays from powders of gold, silver, and aluminium for Cu-$K\alpha$ radiation. J. BRENTANO (Phil. Mag., 1928, [vii], **6**, 178—191).—In order to eliminate effects due to the absorption coefficient and other constants depending on the particular conditions of the measurement the comparative intensities of reflexion from different crystals have been determined under simplified conditions by working with a composite powder comprising the substance under examination and a reference substance of appreciably greater lattice constant. Cadmium oxide is a suitable reference substance for the examination of gold, silver, and aluminium. A method of interpreting the photographic results is described. The results indicate that for the elements of high at. wt. examined in the state of very fine powders the scattered intensity is practically proportional to the effective negative atomic change and not to the square of this quantity as required by the theory of Darwin and others.

A. E. MITCHELL.

Statistical derivation of the M-terms of the X-ray spectrum. F. RASETTI (Z. Physik, 1928, **49**, 546—549).

Structure of mercerised cellulose. I. Space lattice of mercerised ramie cellulose as developed from X-ray data. O. L. SPONSLER and W. H. DORE (J. Amer. Chem. Soc., 1928, **50**, 1940—1950).—*X*-Ray diffraction data indicate that there is a critical concentration of sodium hydroxide, about 13%, above which cellulose fibres become mercerised; mercerisation is not a progressive change (Herzog, A., 1926, 677). The elementary cell of mercerised cellulose is slightly monoclinic and contains two $C_6H_{10}O_5$ units; the axes are a—4·53, b=7·61, and c (long axis of fibre)=10·30 Å. Comparison with the lattice of unmercerised cellulose (Sponsler, A., 1926, 760) shows that mercerisation has caused a to decrease and b to increase, and the angle between these axes to change from 90° to 83°. Mercerisation appears to be the result of rearrangement in three different ways, viz., shift in the position of the chain with respect to the neighbouring chains, a partial rotation of the alternate glucose units in each chain (the latter remaining intact), and a shift in the position of the hydroxyl group attached to the sixth carbon atom, thus rendering it unlikely that mercerisation involves any type of molecular rearrangement of the constituent glucose (cf. Katz and Mark, B, 1925, 495). The results support a cellulose structure made up of continuous chains of glucose units held together by primary valencies, mercerisation being capable of overcoming only the secondary valencies (cf. Meyer and Mark, this vol., 621). S. K. TWEEDY.

Microstructure of ferrite. H. S. RAWDON and T. BERGLUND (U.S. Bur. Standards Sci. Papers No. 571, 1928, **22**, 649—717).—The microstructure of ferrite in re-melted electrolytic iron, open-hearth iron, and wrought iron has been investigated. Three types of structure, α, γ, and δ, are noted, associated with the three allotropic forms. α-Veining appears as a branching network within the α grains, but the size of the latter is unaffected. It is independent of the size of the ingot, and may be produced in abundance by forging at or just below the α–γ transition temperature. It has no effect on the mechanical properties of the ferrite. The δ network, a coarse network superimposed on the α grain pattern, consists of minute inclusions, and is connected with "hot-shortness." The γ network, which has no appreciable effect on the mechanical properties, also depends on minute inclusions, and is produced by heating for some time above the α–γ transition temperature. α-Veining can be suppressed by adding silicon, but not by aluminium or manganese. C. W. GIBBY.

Pleochroic haloes in biotite from near Murray Bay, P.Q. D. E. KERR-LAWSON (Univ. Toronto Studies, Geol. Ser., Contrib. Can. Min., 1927, No. 24, 54—70).—The distribution of the haloes suggests that the nuclei were formed after crystallisation and rupture of the mica. The haloes consist of shells of darkened mica, separated by lighter shells in which a bleaching or lightening effect is active. The first effect of rays from radium-*C* is to lighten the biotite. CHEMICAL ABSTRACTS.

Crystal structure of certain aromatic compounds. W. H. BRAGG (Z. Krist., 1927, **66**, 22—32; Chem. Zentr., 1928, i, 638).—A study of the relative intensities of reflexion at various planes in anthracene indicates that the molecule is of a form containing two periodicities, one being twice as great as the other. Naphthalene tetrachloride has a 7·88, b 10·30, c 14·20 Å., β 112° 40′, with four molecules in the unit cell. 1-Chloronaphthalene tetrachloride has a 8·245, b 10·1, c 15·78 Å., β 116° 12′; naphthalene tetrabromide has a 10·75, b 8·97, c 13·25 Å., β 112° 57′, with four molecules in the unit cell. A. A. ELDRIDGE.

Structure of iron nitride, Fe_4N. R. BRILL (Naturwiss., 1928, **16**, 593—594).—Contrary to the conclusions of Hägg (this vol., 605), the *X*-ray examination of an iron nitride, Fe_4N, gives definite evidence of regular spacing of the nitrogen atoms, and, therefore, of the existence of a compound. Less probably the absorption of nitrogen by iron can be regarded as an infiltration of nitrogen atoms into the iron space-lattice with minimal disturbance of the latter and a saturation-limit at the composition Fe_4N. R. K. CALLOW.

Allotropic form of silver. G. ALLARD (Compt. rend., 1928, **187**, 223—225).—Silver obtained by the action of copper on a solution of silver nitrate does not possess the usual cubic structure. The unit cell is an orthorhombic prism of height $4·23\times10^{-8}$ cm., the sides of the base being $3·76\times10^{-8}$ cm., inclined at 81° 30′ to one another. C. W. GIBBY.

Crystal structure of cryolithionite. G. MENZER (Fortschr. Min. Kryst. Petr., 1927, **12**, 58—59; Chem. Zentr., 1928, i, 1359).—The structure of cryolithionite, $Na_3Li_3Al_2F_6$, is similar to that of granite. The lattice constant is 12·10±0·025 Å. The space-centred lattice contains eight molecules; the space-group is O_h^{10}; $d_{calc.}$ is 2·79±0·02. A. A. ELDRIDGE.

***X*-Ray fine structure of cyanite and staurolite.** G. M. CARDOSO (Fortschr. Min. Kryst. Petr., 1927, **12**, 18—20; Chem. Zentr., 1928, i, 1359).—Cyanite (with rhombic pseudo-symmetry) has a_0 7·122, b_0 7·883, c_0 5·650 Å., with four molecules in the unit cell; d_{100} 6·717, d_{010} 7·575, d_{001} 5·530 Å.; on transformation a_0' 26·868, b_0' 7·883, c_0' 5·650 Å., with 16 molecules in the unit cell. A. A. ELDRIDGE.

***X*-Ray fine structure of brookite; physical properties of the three titanium dioxides.** A. SCHRODER (Fortschr. Min. Kryst. Petr., 1927, **12**, 83—84; Chem. Zentr., 1928, i, 1359).—The unit cell contains eight molecules having d_{100} 9·136±0·020, d_{010} 5·439±0·010, d_{001} 5·153±0·020 Å. A. A. ELDRIDGE.

Structure of benitoite. J. J. P. VALETON (Fortschr. Min. Kryst. Petr., 1927, **12**, 91—92; Chem. Zentr., 1928, i, 1359).—Benitoite, the only representative of the ditrigonal-bipyramidal class, has a 6·64, c 9·71 Å., $a:c$ 1·4634, with two molecules of $BaTiSi_3O_9$ in the unit cell, and space-group D_{3h}^2 or D_{3h}^4. A. A. ELDRIDGE.

Crystal structure of tetramethylammonium iodide. W. ZACHARIASEN (Norsk geol. Tidsskr., 1927, **10**, No. 1, 9 pp.; Chem. Zentr., 1928, i, 1360—1361).—The edge of the unit cell of tetragonal tetramethylammonium iodide is 5·76, and a=8·03 Å. The unit cell contains two molecules. Alternative positions of the nitrogen atoms in the space-group D_{4h}^7 are possible, but cannot be differentiated by consideration of the intensity of reflexion, although chemical relationships indicate one. Vegard's results (A., 1917, ii, 296) are criticised. The ammonium ion is considered to possess spherical symmetry, whereas the symmetry of the phosphonium, trimethylammonium, and trimethylphosphonium ions is considered to deviate from spherical. A. A. ELDRIDGE.

Evidence obtained by *X*-ray analysis of films of iron in magnetic fields as to the ultimate nature of magnetism. T. D. YENSEN (Physical Rev., 1928, [ii], **32**, 114—123).—The most minute crystal aggregates in films of electrolytic iron are not oriented in a magnetic field. The result supports the view that the ultimate magnetic particle is an intra-atomic unit. A. A. ELDRIDGE.

[Electrical conductivity of] silicates. E. CHERBULIEZ and P. ROSENBERG (Helv. Chim. Acta, 1928, **11**, 731—750).—The chemical changes occurring in silicates have been followed by measurements of electrical conductivity at 800—1200°. The conductivity of orthoclase at approximately 800° increases markedly with the duration of heating, reaching a limiting value for a definite temperature. Cooling and re-heating to the same temperature have no further effect on the conductivity, but successive increments of temperature are accompanied by similar variations in conductivity. Albite and leucite, but not nepheline, behave similarly. The increase in conductivity is explained by a dissociation of orthoclase or albite with rising temperature into silica and a silicate poorer in silica, probably of the type of nepheline. The reaction follows the unimolecular law and its reversibility is shown by a diminution in conductivity consequent on heating a mixture of nepheline and quartz at 900—1000°. With the technique used, the polymeric changes undergone by quartz on heating or the chemical changes occurring in kaolin could not be followed. L. S. THEOBALD.

Magnetic moments of the cupric ion. F. BIRCH (J. Phys. Radium, 1928, [vi], **9**, 137—141).—A thermomagnetic study of cupric chloride and sulphate has been made at various temperatures. The chief magnetic moment of the cupric ion is 10 magnetons, but one of 9 was observed in a solution of cupric chloride, and the intermediate values obtained in certain cases suggest one of 11. All the cases studied followed the law of Weiss, with the exception of anhydrous copper sulphate between 100

and 500°, and of cupric oxide which shows a steady paramagnetism. L. S. THEOBALD.

Magnetic susceptibilities of electronic isomerides. II. S. S. BHATNAGAR and R. N. MATHUR (Phil. Mag., 1928, [vii], **6**, 217—223).—The empirical equation of Bhatnagar and Dhawan (this vol., 454) has been modified to conform more closely with Langevin's theory of atomic diamagnetism. The equation becomes $x_m = -2{\cdot}86\times10^{10}\times2/3KR^2$, where x_m is the molecular diamagnetic susceptibility, K is an arbitary constant, and R is the molecular radius calculated over only part of electron orbits, as required by the general application of Langevin's theory, the extent of which is given by the value of K. Tests on a number of compounds show the general application of the revised equation and indicate that the values of K increase with the number of atoms in the molecule; for every two isomeric molecules K is the same, and in the case of groups of isomerides having the same number of atoms in the molecule the values of K increase with the atomic numbers of the groups. A. E. MITCHELL.

Existence of two magnetic rotatory powers for a uniaxial crystal along and normal to the axis. J. BECQUEREL (Compt. rend., 1928, **187**, 215—217).—The magnetic rotatory power of tysonite, the birefringence of which is very small, has been investigated for the green mercury line 5460·7 Å. The rotatory power in the direction of the axis is different from that normal to it. A formula is deduced on theoretical grounds which is in agreement with the results. C. W. GIBBY.

Influence of boric acid on the dispersion of optical glasses in the near infra-red. T. DREISCH and P. LUEG (Z. Physik, 1928, **49**, 380—385).—The refractive index to six significant figures has been determined for a number of optical glasses, with and without a boric acid content, in the range 0·5—2·5 μ; the difference between the index for 1·47 and 2·39 μ is approximately proportional to the boric acid content. R. W. LUNT.

Sulphur and selenium. E. KORINTH (Z. anorg. Chem., 1928, **174**, 57—60).—Two new modifications of sulphur are described in detail, viz., ζ-sulphur (rhombic plates), which is colourless and exhibits weak double refraction, and η-sulphur (hexagonal plates), which is almost colourless and doubly refracting. Both forms are more stable than δ-sulphur. Investigations of the modifications of selenium are described. H. F. GILLBE.

Physical properties of platinum. A. G. GRIGORIEV (Ann. Inst. Platine, 1928, **6**, 178—183).—Values obtained by various authors for the electroconductivity of platinum, its hardness, and tensile strength are compared, and shown to be very close to the corresponding figures found for Russian commercial platinum. R. TRUSZKOWSKI.

Mol. heat and entropy of hydrogen chloride calculated from band spectra data. E. HUTCHISSON (J. Amer. Chem. Soc., 1928, **50**, 1895—1900).—The mol. heats of hydrogen chloride from 1° to 000° Abs. are calculated on the basis of Kemble's values for the energy levels, using the newer quantum mechanics. The plot of the mol. heat against the temperature passes through a maximum at 12·5° Abs. The entropies are calculated by the method of Giauque and Wiebe (this vol., 228). At 0° the entropy is 44·04 or 43·72 g.-cal./1° per mol., according as the Tetrode or Lewis equation is used. S. K. TWEEDY.

Chemical constants and the new quantum statistics. G. E. GIBSON and W. HEITLER (Z. Physik, 1928, **49**, 465—472).—Mathematical. R. W. LUNT.

Boiling points of the normal paraffins at different pressures. S. YOUNG (Proc. Roy. Irish Acad., 1928, **38**, B, 65—92).—The b. p. of the normal paraffins from methane to pentatriacontane, $C_{35}H_{72}$, are calculated at various pressures from 11 to 19,950 mm. by three different methods. The first method makes use of Young's formula $\Delta=A/T^{B\sqrt{T}}$, where Δ is rise of b. p. per CH_2 group, T is b. p. Abs., and A and B are constants. It was found by using the data available that the values of Δ were reproduced with fair accuracy by the above formula when $\log A=1{\cdot}92251+0{\cdot}026187\log p+0{\cdot}013987(\log p)^2+0{\cdot}0013374(\log p)^3$, and $B=0{\cdot}01676-0{\cdot}000795\log p$, where p is the pressure. From this formula the b. p. of the paraffins were calculated, for the higher paraffins up to pressures of 30 mm., and for the lower up to 19,950 mm. The method cannot be relied on to give accurate values for the first two or three members of the series. In the second method, the equation $\log T=a+b\log n+c(\log n)^2+d(\log n)^3$ was used, the constants being calculated for the various pressures from data where available for paraffins up to nonadecane, and in other cases up to octane. In the case where there are not so many paraffins under investigation, *i.e.* for pressures above 30 mm., the last term in the equation is dropped. The b. p. of the paraffins were calculated by this method for the same pressures as in the first. The third method makes use of Ramsay and Young's equation, which is put in the form $T_A'/T_B'=a+bT_A'$, where T_A', T_B' are the absolute temperatures at which the vapour pressures of two nearly related compounds are equal, and a and b are constants. It was found necessary to add a further small term to the right-hand side of the equation in the case of the paraffins. By taking hexane as standard and calculating the constants from available data, the b. p. of the paraffins at various pressures can be calculated. The values given by the three methods are compared with the observed values and the probable b. p. is given in each case. The observed b. p. of ethane agree very well with those calculated by the third method, but are very much higher than those obtained by the other methods. It appears that either ethane has not yet been prepared in a pure state, or else its behaviour is exceptional. The observed b. p. of nonadecane are erratic, and mostly too low. The evidence is in favour of the b. p. of the higher paraffins as determined by Francis (cf. A., 1926, 816). A. J. MEE.

Density of anhydrous chromic chloride and its adsorption of water vapour from the atmosphere. M. CRESPI (Anal. Fís. Quím, 1928, **26**, 152—163).—Thirty-four determinations of the density of various

forms of anhydrous chromic chlorides have been made, and it is shown to be a unitary substance having a marked power of adsorption of water vapour, which renders it difficult to obtain consistent figures for the density. In a desiccator over sulphuric acid all the water is not lost; the anhydrous salt, obtained by heating at 100° in a current of dry air, has d 2·916. The mol. volume of the adsorbed water increases with the quantity of water retained by the salt. The velocity of adsorption shows the process to be analogous to that of the adsorption of gases by glass surfaces. H. F. GILLBE.

International Bureau of Physico-Chemical Standards. III. Physical constants of 20 organic compounds. J. TIMMERMANS and F. MARTIN (J. Chim. phys., 1928, **25**, 411—451).—The following data for the b. p., m. p., and d^0 have been determined: *n*-hexane, 68·80°, −95·1°, 0·67704; *n*-octane, 125·80°, −57°, 0·71845; *n*-butylbenzene, 183·10°, −81·2°, 0·87695; bromoform, 149·55°, 8·05°, 2·90350 (15°); ethyl iodide, 72·30°, −111·1°, 1·98065; ethylene dichloride, 83·5°, −35·5°, 1·28164; *iso*propyl chloride, 34·8°, −147·0°, 0·8869; *iso*propyl bromide, 59·35°, −89·0°, 1·34715; *sec.*-butyl chloride, 68·25°, −131·3° (racemic), −140·0° (active), 0·87556 (racemic), 0·89497 (active); *iso*butyl bromide, 91·4°, —, 1·29410; *n*-butyl alcohol, 118·0°, −90·2°, 0·82472; *iso*butyl alcohol, 108·1°, —, 0·81707; *sec.*-butyl alcohol, 99·5°, —, 0·82275 (active), 0·82273 (racemic); ethyl ether, 34·6°, −116·3°, 0·73622; *n*-amyl ether, 187·5°, −69·3°, 0·79881; methylal, 42·3°, −105·0°, 0·88545; acetone, 56·2°, —, 0·81250; methyl ethyl ketone, 79·6°, −86·6°, 0·82555; ethylene chlorohydrin, 128·6°, −67·5°, 1·22310; carbon disulphide, 46·25°, −116·8°, 1·29270. Data are also given for the variation of b. p. with pressure, the density at various temperatures, coefficients of expansion, refractive indices and dispersive powers, mol. refractions, and viscosities. The results obtained by earlier investigators are given for comparison. H. F. GILLBE.

Validity of the gas laws. W. HERZ (Z. Elektrochem., 1928, **34**, 360—362).—At the critical temperature the volume of 1 g. of a substance calculated from the simple gas laws is about 3·75 times the experimentally determined figure. At $0{\cdot}9T_c$ the ratio is about 1·45, whilst at $2/3T_c$ the two values are practically identical. These figures for the quantitative deviation from the gas laws are independent of the nature of the substance. H. F. GILLBE.

Densities of liquid elements. L. H. BORGSTROM (Finska Kemistamfundets Medd., 1927, **36**, 76—81; Chem. Zentr., 1928, i, 1254).—A comparison.

A. A. ELDRIDGE.

Atomic volume relations in certain isomorphous series. II. A. F. HALLIMOND (Min. Mag., 1928, **21**, 480—484; cf. this vol., 107).—Mol. volumes of salts of calcium, strontium, and barium and of oxygen, sulphur, selenium, and tellurium are tabulated and compared. It is shown that the ratio of the differences (Ba−Ca)/(Sr−Ca) and (Te—S)/(Se—S) is a constant in each case. The atomic volumes are then calculated. L. J. SPENCER.

Changes in the specific gravity of copper and silver [after heat treatment]. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1928, **173**, 262—267). —Repeated heating of silver and copper alternately in a vacuum and in hydrogen causes a rapid and progressive decrease in the value of d; with copper a decrease of 6% was obtained after several repetitions of this treatment. This phenomenon is attributed to adsorption of hydrogen, followed by expulsion of the adsorbed gas on subsequent heating in a vacuum with consequent swelling of the metal and the formation of internal voids. A. R. POWELL.

Physico-chemical investigations of ordinary and uranium lead chloride. W. A. ROTH and O. SCHWARTZ (Ber., 1928, **61**, [*B*], 1539—1545).—The values d_4^{18} 5·909±0·001 and 5·884±0·001 are found for ordinary lead chloride and uranium lead chloride (Pb=206·05), respectively, from which the identical molecular volumes, 47·07 c.c., are calculated. In solution in water the molecular volumes are identical, whereas differences are observed between the densities of the saturated solutions. The increases in the refractive index of water caused by addition of equal amounts of the two salts differ somewhat, whereas the molecular refractions of the dissolved salts are identical. The equivalent conductivities of the almost saturated solutions are practically equal. The heats of precipitation as chromates are identical.

H. WREN.

Accurate method for comparing the compressibilities of gases below atmospheric pressure. C. G. ADDINGLEY and R. WHYTLAW-GRAY (Trans. Faraday Soc., 1928, **24**, 378—387).—A new differential method for the measurement of compressibility has been developed and has been applied to determine the ratio of the compressibility coefficients of oxygen and hydrogen. The ratio found is 1·00148.

L. F. GILBERT.

Effect of temperature on the viscosity of neon. R. S. EDWARDS (Proc. Roy. Soc., 1928, **A**, **119**, 578—590).—The viscosity of neon has been determined over a range of temperature from 444·5° to −78·4° by means of a modification of the constant-volume method previously used by the author in the case of air (this vol., 116). The apparatus was specially designed for use with a gas available only in small quantities, and was calibrated in terms of a standard value for the viscosity of air. The standard chosen was that given by Millikan (Ann. Physik, 1913, [iv], **41**, 759), viz., $\eta_t=0{\cdot}0001824-0{\cdot}000000493(23-t)$ c.g.s. unit, over the range 23—12°, which gives $\eta_{15}=0{\cdot}00017846$ c.g.s. unit. The values $\eta_{15}=3{\cdot}076\times10^{-4}$ and $\eta_{100}=3{\cdot}656\times10^{-4}$ were obtained for the viscosity of neon, which are in satisfactory agreement with Rankine's values (A., 1910, ii, 829). The theoretical formulæ of Lennard-Jones (cf. A., 1925, ii, 91) and Sutherland are discussed, and although the temperatures reached in the present investigation are not low enough to provide a crucial test between the two formulæ, it appears that Sutherland's formula is quite satisfactory for temperatures well above the liquefying point, but as that point is approached Lennard-Jones' formula becomes superior.

L. L. BIRCUMSHAW.

Internal friction of highly viscous substances. H. LEY and U. KIRCHNER (Z. anorg. Chem., 1928,

173, 395—410).—Closely concordant results for the viscosity of glycerol have been obtained by the transpiration method and by measuring the rate of fall of glass beads through a column of the liquid in a specially constructed apparatus. The mean value of η at 0° is 120·38 and at 20° 14·56 c.g.s. units.

In order to determine the effect of molecular configuration on the internal friction (viscosity) of liquids, the value of η for various stilbene derivatives has been determined at temperatures below the true m. p., *i.e.*, in the supercooled viscous state. In the homologous series of α-alkoxyphenylstilbenes the viscosity decreases logarithmically with rise of temperature and increases in the order: butoxy-, propoxy-, methoxy-, ethoxy-phenylstilbene, indicating that the side-chain of the higher homologues is oriented in the direction of the main groups and thus allows the molecules more readily to slide over one another. The introduction of a second methoxyl group into the molecule of the methoxy-compound to give α-(*p*-methoxyphenyl)-4-methoxystilbene causes a large increase in the viscosity owing to the enlargement of the molecule in two directions. This compound crystallises only with great difficulty and readily forms a thick syrup. The α-alkoxyphenylstilbenes are readily obtained by heating with concentrated formic acid the phenylbenzyl-*p*-alkoxyphenylcarbinol produced by treating magnesium benzyl chloride with the corresponding *p*-alkoxybenzophenone. The following derivatives of α-phenylstilbene are described: α-p-*methoxyphenylstilbene*, b. p. 240—242°/14 mm., d_4^{25} 1·1015, n_D^{25} 1·6660; α-p-*ethoxyphenylstilbene*, m. p. 76°, b. p. 242—244°/14 mm., d_4^{25} 1·0829, n_D^{25} 1·6536; α-p-*propoxyphenylstilbene*, m. p. 69°, b. p. 248—250°/14 mm., d_4^{25} 1·0676, n_D^{25} 1·6437; α-p-*butoxyphenylstilbene*, m. p. 82—83°, b. p. 259—260°/14 mm., d_4^{25} 1·0551, n^{25} 1·6333; α-p-*methoxyphenyl-4-methoxystilbene*, m. p. 64°, b. p. 260—262°/14 mm., d_4^{25} 1·1269, n_D^{25} 1·6641, α-Phenylstilbene has d_4^{25} 1·0719 and n_D^{25} 1·6678.

A. R. POWELL.

Equal viscosities. II. W. HERZ (Z. anorg. Chem., 1928, **173**, 411—412; cf. A., 1925, ii, 1049).—It is shown for 18 liquids that the ratio of the density at the temperature at which the viscosity is 0·0040 c.g.s. unit to the density at the critical temperature is approximately a constant. The recorded ratios vary from 2·739 to 2·967. A. R. POWELL.

Magnetic double refraction of liquid mixtures. G. SZIVESSY and M. RICHARTZ (Ann. Physik, 1928, [iv], **86**, 393—421).—The magnetic double refraction of 13 different binary liquid mixtures has been determined as a function of their volume concentrations. Excepting the mixtures of chloronaphthalene and cumene, the observed values do not agree with Langevin's theory, being generally lower than those demanded by the latter. J. W. SMITH.

Composition of vapours from boiling binary solutions. D. F. OTHMER (Ind. Eng. Chem., 1928, **20**, 743—746).—A simple and rapid method for the determination of the composition of the liquid and vapour phases is described. The composition of the boiling liquid is maintained constant by returning the same amount of each constituent as is removed by vaporisation. Samples of the condensate and of the boiling liquid can be withdrawn separately for analysis. Vapour composition curves have been obtained for the following mixtures: water–acetic acid, benzene–acetic acid, hydrochloric acid–water, and acetone–methyl alcohol. The method is said to eliminate almost completely the errors inherent in the ordinary distillation methods.

The results suggest the existence of a second constant-b. p. mixture for the methyl alcohol–acetone series at about 94% (wt.) acetone, but definite proof of this is as yet wanting. R. A. PRATT.

Binary azeotropes. X. M. LECAT (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, i, 13—22).—A further list is given of the properties of mixtures, comprising 117 positive azeotropes (the b. p. of the azeotrope is lower than that of either component), four negative azeotropes, four eutectics, 57 non-azeotropic systems, and four systems where combination takes place. In each of the negative azeotropes a phenol is present. Acetamide is a constituent of the mixtures which show the greatest azeotropic lowering of b. p. It is pointed out that in mixtures of an ester of a mineral acid and an alcohol, double decomposition takes place, and the reaction proceeds in the direction of production of the more volatile ester. W. A. RICHARDSON.

Azeotropy in the binary systems alcohols–hydrocarbons. M. LECAT (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, ii, 105—118).—Azeotropic data are given for the 344 systems formed by 29 alcohols and 39 hydrocarbons. Equations of the type $\delta=a-b\Delta+c\Delta^2-d\Delta^3$, where δ is the azeotropic lowering, Δ the difference in b. p. of constituents, and a, b, c, and d are constants, are given for the various alcohols studied. The value of δ decreases rapidly for an equal interval Δ as a series of monohydric alcohols is ascended. L. S. THEOBALD.

Azeotropy in binary alcohol–ester mixtures. M. LECAT (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, ii, 1—16).—The relation between the azeotropic lowering of b. p. and the difference in b. p. of the constituents for binary alcohol–ester mixtures is discussed. For systems containing methyl alcohol the relation is $\delta=9-0{\cdot}88\Delta+0{\cdot}033\Delta^2-0{\cdot}000485\Delta^3$, and similar expressions hold for other alcohols. The azeotropic lowering diminishes as the mol. wt. of the alcohol increases. Isomeric alcohols have the same δ/Δ relationship. Esters of mineral acids show greater azeotropic lowering than organic esters. Acetates give smaller lowering than formates and carbonates. Many of the systems show chemical reactivity, particularly at the b. p. W. A. RICHARDSON.

Binary azeotropes. XI. M. LECAT (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, i, 54—62).—The data for 257 binary systems, azeotropic (positive), eutectic, and euzeotropic are tabulated. L. S. THEOBALD.

Sulphonitrous and sulphonitric [acid] mixtures. A. SANFOURCHE and L. RONDIER (Compt. rend., 1928, **187**, 291—293).—The vapour pressure of mixtures of sulphuric acid with nitrous and/or nitric acids within the range of those which are met with in the chamber process increases with rise in temperature and with the nitrous or nitric acid content. For all mixtures of the three acids, particu-

larly when the sulphuric acid is concentrated, the total pressure is higher than the sum of the individual pressures. The results for nitric acid may be explained by the reactions $HSO_4{\cdot}NO+HNO_3 \rightleftharpoons H_2SO_4+N_2O_4$ and $2HSO_4{\cdot}NO+H_2O \rightleftharpoons 2H_2SO_4+N_2O_3$. J. GRANT.

Solubility of potassium bromide in acetone as related to the inter-ionic attraction theory. A. L. ROBINSON (J. Physical Chem., 1928, **32**, 1089—1093).—The solubility of potassium bromide in acetone, and in acetone solutions of sodium and potassium iodides and barium iodide and bromide has been determined at 25° up to an ionic strength of 0·004*M*. Large increases in solubility, of the magnitude required by the Debye–Hückel theory, were found. L. S. THEOBALD.

Latent heat of fusion of naphthalene from new solubility data. A. A. SUNIER and C. ROSENBLUM (J. Physical Chem., 1928, **32**, 1049—1055).—The solubility of naphthalene in ethylene chloride and bromide and in ethylidene chloride and bromide has been determined between 20° and 75°. The slopes of the curves connecting log. mol. fraction with $1/T$ (Abs.) support Ward's value of 970 (A., 1926, 1200) (except in the case of ethylene dichloride, which gives a slope of 960), indicating a value of 4440 g.-cal. for the molal latent heat of fusion of naphthalene. L. S. THEOBALD.

Influence of structure on the solubilities of ethers. I. Aliphatic ethers. II. Cyclic ethers. G. M. BENNETT and W. G. PHILIP (J.C.S., 1928, 1930—1937, 1937—1942).—The mutual solubilities of a number of ethers with water have been measured over the temperature range 0—25° by a modification of Hill's volumetric method (cf. A., 1923, ii, 467). The solubility of an ether in water increases with increased branching of the carbon chains of the alkyl groups, but in a homologous series the solubility falls rapidly as the carbon chain lengthens. Closure of a ring causes a large increase in the solubility; the smaller the ring the greater is the increase. The solubility of naphthalene in some of the ethers was found not to deviate seriously from the ideal solubility curves, indicating that, in the absence of water, the liquids are normal in behaviour. The considerable solubility of the ethers in water is attributed to their union with it to form a polar compound, and the results are discussed from this point of view. J. W. SMITH.

Theory of adsorption. T. SEXL (Z. Physik, 1928, **48**, 607—610).—The adsorption formula for a gas-solid interface deduced from statistical considerations is in agreement with the Langmuir formula. J. W. SMITH.

Absorption by colloidal oxides and active carbon of sulphur dioxide present in gaseous mixtures in small proportions. C. FICAI (Giorn. Chim. Ind. Appl., 1928, **10**, 199—203).—The absorption of sulphur dioxide by gelatinous silica containing 4·8% of water, hydrated alumina with 13·5% of water, and activated carbon is reversible and depends on the temperature. Active carbon absorbs more sulphur dioxide than the colloidal oxides and has the further advantage that its absorptive capacity is not sensibly diminished by the presence of water. Silica gel is, however, activated more readily and more cheaply. T. H. POPE.

Volatility of nicotine. W. R. HARLAN and R. M. HIXON (Ind. Eng. Chem., 1928, **20**, 723—724).—The volatility was determined at 25—40° by an air-bubbling method. The nicotine vapour was absorbed in 2*N*-sulphuric acid and determined by precipitation with silicotungstic acid. The vapour concentrations range from 1·76 mg. of nicotine per 10 litres of air at 25° to 6·04 mg. at 40°. The concentrations of nicotine in the vapour phase over hydrated lime dust and over "bentonite" dust are also recorded. R. A. PRATT.

Adsorption by cadmium sulphide and its importance in the determination of cadmium. H. B. WEISER and E. J. DURHAM (J. Physical Chem., 1928, **32**, 1061—1064).—The chlorine adsorbed by cadmium sulphide precipitated from hydrochloric acid solutions of varying concentration by hydrogen sulphide at 25° and on cooling from 80° to 25° has been determined. Precipitation at 80° is incomplete. The amount of chlorine adsorbed depends on the acid concentration, the temperature, and the pressure at which precipitation is made. The phenomenon is one of adsorption and is not due to the formation of the salt $CdS,CdCl_2$ (cf. Treadwell, "Analytical Chemistry"). Continuous curves are obtained by plotting the amount of chlorine adsorbed against the concentration of hydrochloric acid for a fixed concentration of cadmium salt. The curve for 25° is a typical adsorption curve showing a maximum due to a change in the structure of the adsorbent. The curve obtained on cooling from 80° to 25° lies below that for 25° but is of a similar type; it shows, however, a minimum at an acid concentration 0·3*N*. The determination of cadmium as sulphide is of doubtful value, since it is questionable whether the conditions of precipitation can be maintained to give a product of known composition (cf. Egerton and Raleigh, J.C.S., 1923, **123**, 3019). L. S. THEOBALD.

Adsorption of simple aliphatic compounds by cellulose. K. BRASS and J. K. FREI (Kolloid-Z., 1928, **45**, 244—255).—The adsorption of aliphatic acids and other compounds by cotton wool and by precipitated cellulose (viscose) has been studied. All the acids examined, with the exception of palmitic and stearic acids, were adsorbed from aqueous solution. Formic and acetic acids, but not palmitic acid, were adsorbed by cellulose from solution in acetone. Formaldehyde, acetone, ethyl alcohol, glycol, and glycerol were not adsorbed from aqueous solution by cellulose. A few experiments conducted with aromatic compounds showed that the electrolytically dissociated acids were adsorbed and the undissociated phenols were dissolved. Benzoquinone was not adsorbed, thus resembling the aliphatic carbonyl compounds. No relation could be found between the mol. wt. of an acid and its degree of adsorption, but in most cases the acids with low dissociation constants were weakly adsorbed. Adsorbability appears to be a true function of the dissociation constant only when the acid is readily soluble.

Other investigators have found the adsorption of organic acids by filter-paper to depend mainly on the undissociated molecules, and it is suggested that the divergence of results is due to the structural differences between filter-paper and the cellulose used for these experiments. E. S. HEDGES.

Adsorption of leuco-dyes by cellulose. K. BRASS and G. TORINUS (Kolloid-Z., 1928, **45**, 256—266).—The leuco-compounds of vat dyes are dissolved reversibly by cellulose, the order of magnitude of the partition coefficient between the vat solution and the cellulose differing widely (between 6 and 800) for different compounds. The partition coefficient appears to be related to the chemical constitution of the dye, for cyclic compounds, such as thioindigotin, and especially polycyclic systems, such as indanthrene and flavanthrene, have particularly high values. Leuco-dyes with high partition coefficients show great stability towards alkaline hyposulphite solution. The degree of dispersion of the leuco-compound does not appear to affect its solubility in cellulose. E. S. HEDGES.

Influence of volume of solution and mass of adsorbent on the adsorption of arsenious acid by metallic hydroxides. K. C. SEN (Z. anorg. Chem., 1928, **174**, 75—81).—Isotherms for the adsorption by zirconium hydroxide of arsenious oxide sol have been determined under various conditions; for constant final concentration, reduction of the total volume of solution increases the extent of the adsorption, whilst increase of the total quantity of adsorbent present decreases the quantity adsorbed per unit weight of adsorbent, in addition, when the charge is considerable, to altering the curvature of the isotherms. Similar results are obtained when aluminium and chromium hydroxides are employed. It is assumed that this type of adsorption, which resembles that of cations by manganese dioxide, differs from adsorption by carbon, and is an example of chemical adsorption, in which the chemical affinity between the surfaces of the adsorbent and of the substance adsorbed plays an important part. H. F. GILLBE.

Influence of volume on the adsorption of arsenious acid by iron and aluminium hydroxides. K. C. SEN (Z anorg. Chem., 1928, **174**, 82—90).—Variation of the total volume of solution alters the adsorption isotherms and the adsorption constant. The quantity of manganese dioxide present in a solution of copper sulphate influences the isotherms of the adsorption process. H. F. GILLBE.

Equation of state for adsorbed phases. II. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1928, **3**, 142—146; cf. Rideal, A., 1925, ii, 960).—The equation of state for the adsorbed phase is $P_s(A-\beta)=iRT$, where P_s is the lowering of surface tension, A the mol. surface of the adsorbent, β a correction term, and $1/i$ the lateral cohesion of the adsorbed molecules. The potential energy due to the latter is given by $U=-(\mu^2/r^3)f(\xi_d,e_0)$, where μ is the dipole moment, r the distance between the dipole centres, and $f(\xi_d,e_0)$ a function involving temperature and polarisation. The effect of temperature is evaluated by the Maxwell–Boltzmann principle and is $\bar{U}=\int Ue^{-U/KT}d\Omega/\int e^{-U/KT}d\Omega$, where U is the mean energy and Ω the solid angle. Finally, $1-i=(\mu/r^3)KT$, where $1-i$ is the ratio between electrostatic and kinetic energy. On calculating the dipole moment μ for normal butyric, valeric, hexoic, octoic, decoic, and dodecoic acids, a constant value of 20×10^{-19} e.s.u. is obtained; it follows that μ is characteristic only of the active carboxyl group when the molecules are not closely packed, when $\mu=30-90\times10^{-19}$. β is constant at $24—25\times10^{-16}$ cm.^{2}/mol., corresponding with X-ray data for the cross-sectional area of the methyl group. For expanded films, β is greater. S. J. GREGG.

Measurement of interfacial tension of liquid–liquid systems. F. E. BARTELL and F. L. MILLER (J. Amer. Chem. Soc., 1928, **50**, 1961—1967).—Two simple forms of apparatus are described for the rapid and accurate determination of the interfacial tension between two liquids, which may be opaque. The apparatus is easy to construct and is readily cleaned. S. K. TWEEDY.

Surface tension of some molten metals against molten salts. R. LORENZ and H. ADLER (Z. anorg. Chem., 1928, **173**, 324—336).—The surface tension of molten cadmium chloride alone and admixed with potassium chloride has been determined in air at 600—750°. The value of k in the Eotvos–Ramsay–Shields formula for cadmium chloride from these results is 0·1653. The surface tension of molten cadmium against cadmium chloride at 725—730° is 3·9 dynes/cm. Addition of potassium chloride or of metallic lead causes a very rapid increase in this value and hence restrains the formation of a metal fog in the fused salt phase. A. R. POWELL.

Unimolecular films. B. C. J. G. KNIGHT and P. STAMBERGER (Nature, 1928, **122**, 97).—Experiments with films of vulcanised triolein and fatty acids indicate that in the polymerised products the molecules are joined side by side in a definitely oriented manner in long chains, leaving the polar groups unaltered. A. A. ELDRIDGE.

Condensation of molecular streams on surfaces. J. D. COCKCROFT (Proc. Roy. Soc., 1928, **A**, **119**, 293—312).—The phenomena previously studied by Wood (Phil. Mag., 1915, [vi], **30**, 300) and Knudsen (Ann. Physik, 1916, [iv], **50**, 472) have been investigated over a much wider range of temperature and by more accurate methods. In experiments with molecular streams, information is derived from the thickness of the deposit as to the intensity of the incident stream, and light is thrown on the nature and magnitude of the forces between the surface and the incident molecules. Three series of experiments were made: (1) an atomic stream of constant density was allowed to fall on a condensing surface in which a temperature gradient exists, and the region of deposition was observed; (2) an atomic stream was used of which the density varied from point to point of a condensing surface of constant temperature; (3) the effects of different surfaces and different surface conditions were studied. The first apparatus used was identical with that of Chariton and Seminoff (cf. A., 1924, ii, 723). The second apparatus consisted of a metallic oven which acts as a source of vapour for the issuing stream. The vapour

issues from a hole in the end of a metal tube, so that its density has circular symmetry round the normal to the tube end surface, but decreases as the angle from the normal increases. The stream of varying density is allowed to fall on a condensing surface held at a constant and uniform temperature, ranging in different experiments from $-70°$ to $-160°$. The results are considered from the point of view of Frenkel's adsorption theory (cf. A., 1925, ii, 194). On the basis of this theory, the method described enables the magnitude of the surface forces to be found for different adsorbed atoms and different surface materials. The true surface forces are in general masked by contaminating influences (probably gas films), so that to determine the magnitude of the real surface forces, special precautions must be taken to eliminate gas from the apparatus. It is probable that in the absence of gas films the critical temperature phenomena described by Wood and Knudsen (*loc. cit.*) would not exist for many surfaces. The experiments described show that, to ensure that practically all the atoms of the stream condense, it is sufficient to have the density of the stream about four times the critical density for the surface, but if liquid air temperatures are used for the condensing surface, the critical atomic stream density for cadmium may be so low as to require more than 10 hrs. for the first appearance of a deposit.

L. L. BIRCUMSHAW.

Surface solutions. R. DELAPLACE (J. Phys. Radium, 1928, [vi], 9, 111—119).—An apparatus is described for measuring the pressure and area of surface solutions, and the pressure–area–temperature relations of surface solutions of benzoyl benzoate are examined at pressures of 0·1—0 001 dyne/cm., and at 15° and 27°. The laws of Boyle, pS=constant, and of Gay-Lussac, $pS=kT$, where p is the surface pressure, S the area of the surface, and k a constant, were verified. The value of k is much smaller than that of R, the gas constant. Attention is directed to the difference in experimental conditions between the author's work and that of Adam and Jessop (A., 1926, 348).

W. A. RICHARDSON.

Surface activity of sodium salts of high-molecular fatty acids. P. EKWALL (Acta Acad. Åboensis Math. phys., 1927, 4, No. 6, 3—209; Chem. Zentr., 1928, i, 1156—1157).—The surface tension, conductivity, hydroxyl-ion concentration, colloid content, viscosity, and turbidity of aqueous solutions of sodium laurate, myristate, palmitate, and oleate were determined. The colloid content (acid salt) of all sodium laurate solutions less concentrated than 0·026*N* is low; in more concentrated solutions the quantity of neutral colloid rapidly increases. Between 0·008 and 0·026*N* the equivalent conductivity is practically independent of the concentration. Up to 0·026*N* the hydroxyl-ion concentration increases rapidly, and above 0·026*N* more rapidly. Below 0·006*N*, acid sodium laurate cannot exist. Sodium myristate solutions below 0·006*N* contain the acid salt, partly colloidal and partly as solid crystals. Above 0·005*N* the neutral colloid content rapidly increases and that of the crystallised acid soap diminishes. The hydroxyl-ion concentration increases in solutions up to 0·006*N*, and remains practically unchanged above this value. The equivalent conductivity is constant between 0·0015 and 0·005*N*. In sodium palmitate solution the specific conductivity is constant above 0·002*N*, and the hydroxyl-ion concentration above 0·0015*N*. Sodium oleate even in dilute solution is largely present in the colloidal condition. The relative colloid content, particularly that of the finely dispersed colloid, increases with concentration above 0·004*N*, whilst the hydroxyl-ion concentration, which has rapidly increased up to that point, becomes practically constant. Above 0·025*N* the equivalent conductivity is practically independent of concentration. Acid oleate cannot exist below 0·0009*N*. Near to the lower limit of existence the acid soap contains not more than 1 equivalent of acid to 1 equivalent of neutral soap, whilst in solutions containing larger quantities of the neutral colloid there is 1 equivalent of soap to 0·5 equivalent of fatty acid. The existence of colloid ions in sodium oleate solutions is postulated, and confirmed for concentrated solutions. McBain's ion-micelle theory is unnecessary in the case of saturated fatty acids. Soap solutions contain three kinds of surface-active substances: free fatty acid, acid soap, and undissociated soap molecules. The acid soap causes the greatest fall of surface tension. In certain cases capillary-active properties are exhibited by the three components in the colloidal form. The σ–c curves of the soap solutions are in complete accord with simultaneous structural changes. The surface tension falls rapidly with increasing soap content until the concentration above which acid soap can no longer exist is reached. It then remains practically constant until neutral colloid is present in large quantities, after which the surface activity falls again. In solutions containing so little soap that the acid soap is incapable of existence, the surface tension of the solution is determined essentially by the free fatty acid. The undissociated soap molecule aggregates also affect the value to a certain extent.

A. A. ELDRIDGE.

Surface layer. VI. Differences of potential on the border between air and solutions of some benzene derivatives. A. FRUMKIN, A. DONDE, and R. KULVARSKI (Trans. Karpov Inst. Chem., 1926, No. 5, 17—33).—The fall of surface tension and the *P.D.* at the air–solution interface of solutions of aromatic compounds were studied. The adsorption of aromatic compounds is less than that of corresponding aliphatic compounds having the same number of carbon atoms. Introduction of a methyl group increases the adsorption, but the effect depends on its position. Compounds with one nuclear polar group (phenol, cresols, anisole, nitrobenzene, aniline, methylaniline, dimethylaniline, toluidines) communicate a positive charge to the surface of water, but the magnitude of the charge is less than for aliphatic compounds, and decreases with accumulation of polar groups; the charge becomes negative with dihydroxybenzenes, *m*- and *p*-nitrophenols. Compounds substituted in the side-chain (benzoic acid, methyl benzoate, benzyl alcohol, benzylamine) produce effects similar to those of corresponding aliphatic compounds. Compounds for which the molecules occupy in the surface layer less space than the corresponding isomeric

compounds give more positive effects. Thus, *p*-cresol and *p*-toluidine give a more positive surface charge, whilst quinol and *p*-nitrophenol give a more negative surface charge, than the *ortho*-compounds. The difference is greater than can be ascribed to the change of degree of orientation of the molecules.

CHEMICAL ABSTRACTS.

Method of determining the absolute magnitude of surfaces. O. HAHN [with F. BOBEK] (Annalen, 1928, **462**, 174—185).—An extension of previous work (A., 1925, ii, 177). The methods already described have been applied to the determination of the specific surfaces of two thorium salts, using uranium-X as the radioactive indicator. Thorium oxalate, precipitated from a hot solution of thorium nitrate by means of oxalic acid and then kept under the supernatant liquid for 2½ hrs. at 100°, had a specific surface (defined as g. of substance in surface per 1 g. of substance) of 0·0205%, whilst for thorium oxalate precipitated in the cold the corresponding figure was 0·136%. Thorium hypophosphate, obtained by precipitation of a boiling solution of the nitrate with sodium hypophosphate, gave the figure 9·35%. The absolute surfaces of the three specimens are therefore 0·12, 0·78, and 52 sq. cm., respectively, since the absolute surface$=p\sqrt[3]{N/Ms^2}$, where M=mol. wt., N is Loschmidt's number, p is the specific surface, and s is the density of the substance under examination. E. E. TURNER.

Limiting surface effect in anisotropic liquids. W. KAST (Physikal. Z., 1928, **29**, 293—295).—Polemical. R. W. LUNT.

Prevalent error in the derivation of the f.-p. and b.-p. laws for dilute solutions. A. W. DAVIDSON (J. Physical Chem., 1928, **32**, 1080—1085).—Theoretical. An error frequently made consists in writing $q_0=ml$, where q_0 is the heat evolved at T_0, the f. p. of the pure solvent. Since q_0 includes not only the heat evolved when the solvent freezes, but also that evolved during the removal of the solvent by osmotic work, it equals $ml+RT_0$. The familiar f.-p. expression should be corrected to $\Delta T/T_0=RT_0/(ml+RT_0)$ or RT_0/ml', where l' is the latent heat of fusion per g. at T, the f. p. of the solution. The usual b.-p. expression should be written $\Delta T/T=RT_0/ml_v'$, where l_v' is the latent heat of vaporisation at T, the b. p. of the solution. By a slight modification of the van 't Hoff cycle, the approximate form of the f.-p. equation for ideal solutions is derived in a simple manner. L. S. THEOBALD.

Cryoscopic irregularities with phenols. G. W. RICHARDSON and P. W. ROBERTSON (J.C.S., 1928, 1775—1783).—The variation with concentration of the f.-p. constant has been determined for a number of organic substances dissolved in phenol, *o*- and *p*-cresol. It is found that the equation $K=0{\cdot}02T^2/L$ does not hold even at low concentrations. Although the values of K at low concentration are of similar magnitude in most homologous series, increasing concentration tends to produce deviations in a direction characteristic of, but showing specific variation within, the series. These are supposed to depend on internal pressure and polarity in accordance with the theory of Hildebrand (A., 1916, ii, 518; 1919, ii, 392). This is supported by the relationship between changes in mol. volume on dissolution and cryoscopic behaviour. Derived phenols show markedly different magnitudes for K, although the deviations are similar, but this is not considered to be due to solid solution formation. Data are also given for the densities of various organic liquids at 40°. J. W. SMITH.

Solutions of salts in pure acetic acid. I. A. W. DAVIDSON (J. Amer. Chem. Soc., 1928, **50**, 1890—1895).—The following salts are practically insoluble in acetic acid: sulphates (sodium and ammonium sulphates are slightly soluble), silver halides, calcium carbonate, some sulphides. Double decomposition occurs in this solvent as readily as in water. Sulphates which normally form hydrates can be precipitated in the anhydrous state from acetic acid solution, even when the latter contains water. Except in the case of sodium carbonate solvolysis does not occur to any marked extent. Certain metal acetates behave in acetic acid like the corresponding bases in water, *e.g.*, zinc acetate is insoluble in the pure acid but dissolves readily when sodium acetate is added. S. K. TWEEDY.

Osmotic pressures of concentrated solutions. J. H. HILDEBRAND (J. Physical Chem., 1928, **32**, 1086—1088).—Polemical against Bancroft and Davis (this vol., 239). L. S. THEOBALD.

Elevation in b. p. of saturated solutions at different atmospheric pressures. A. MITTENBERG (Ukraine Chem. J., 1928, **3**, [Sci.], 119—123).—The elevation of b. p., ΔU_1, of saturated sodium chloride solutions at pressures of from 0·04—0·8 atm. is calculated from the formula $\Delta U_0/\Delta U_1=U_0^2C_0L_1/U_1^2C_1L_0$, where ΔU_0 is the elevation at 1 atm., U_0 and are the b. p. of the pure solvent at 1 atm. and at the given pressure, C_0 and C_1 the concentrations of salt, and L_0 and L_1 the corresponding latent heats of vaporisation. The calculated results are in satisfactory agreement with those found by experiment. R. TRUSZKOWSKI.

Acid properties of concentrated solutions of zinc chloride. S. A. VOSNESSENSKI and T. A. STRATONOVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 771—782).—Zinc chloride forms acid complexes with water of the type $[ZnCl_2(OH)_n]H_n$ in concentrated solutions. The catalytic action of zinc chloride in those reactions which are catalysed by hydrogen ions is due to the formation of these complexes. This complex formation does not take place with the chlorides of lithium, potassium, calcium, manganese, magnesium, and cadmium. R. TRUSZKOWSKI.

Constitution of magnesium acetate solutions. II. Evidence from vapour pressures. E. A. GOODE, N. S. BAYLISS, and A. C. D. RIVETT (J.C.S., 1928, 1950—1955).—The vapour pressures of aqueous solutions of magnesium acetate up to a concentration of 4·55 g.-mol. per 1000 g. of water have been determined at 25° by a modified form of McBain and Salmon's dew-point method. The "molar fraction" calculated from the Raoult vapour-pressure formula passes through a maximum at a concentration of about 3·25 g.-mol. per 1000 g. This is explained in

terms of the theory advanced by Rivett (A., 1926, 681) that in dilute solution the magnesium radical is hydrated, whilst in more concentrated solution molecular chain complexes are formed.

J. W. SMITH.

Apparent hydration of ions. I. Densities and viscosities of saturated solutions of sodium and potassium chlorides in hydrochloric acid. J. W. INGHAM (J.C.S., 1928, 1917—1930).—The solubilities of potassium and sodium chlorides in aqueous solutions of hydrochloric acid up to $13 \cdot 5N$ have been determined at 25° and the densities and viscosities of the saturated solutions measured. From the data obtained it is deduced that the chlorine ions are not hydrated and the potassium ions hydrated only to a slight extent. The hydrogen ions may be present in the form H_3O^+, but are probably not more highly hydrated. The viscosities of the solutions containing sodium chloride cannot be accounted for without a hydration factor of about 2, which decreases as the solution becomes more strongly acid. J. W. SMITH.

State of some sparingly soluble hydroxides in solution in potassium hydroxide and ammonia solutions, as indicated by viscosity measurements. K. MOHANLAL and N. R. DHAR (Z. anorg. Chem., 1928, **174**, 1—10).—The viscosity of N- and $0 \cdot 5N$-potassium hydroxide solutions is markedly increased by the presence of beryllium, aluminium, chromium, zinc, tin, and lead hydroxides, there being simultaneously a small decrease of the specific conductivity; there is a corresponding increase of the viscosity of ammoniacal solutions in presence of copper, cadmium, zinc, and silver hydroxides. Boric and benzoic acids cause a slight increase of the viscosity of potassium hydroxide solutions, whereas hydrogen chloride produces a decrease. The results obtained lead to the conclusion that the dissolved metallic hydroxides are present to some extent in the colloidal state. H. F. GILLBE.

Properties of colloidal lead. H. Q. WOODARD (J. Amer. Chem. Soc., 1928, **50**, 1835—1840).—Lead sols prepared by the Bredig method are dark grey and fluorescent; they turn blue-black on keeping and appear brown by transmitted light. The particles are positively charged and on the passage of a current lead coagulates on the electrodes in arboriform growths. If protected by a layer of paraffin the sols are stable for 3—9 weeks, after which rapid coagulation sets in. The sols are readily coagulated by electrolytes, the coagulation time being roughly inversely proportional to the age of the sol. Shaking with air or carbon dioxide for a time which is shorter the greater the age of the sol also produces coagulation. The concentration of the colloid is proportional to the arcing current and to the p_H of the initial solution. With progressively increasing concentration of stabilising electrolyte (*e.g.*, potassium hydroxide) in the initial solution the lead concentration passes through a maximum. Contrary to the behaviour of gold, silver, and platinum sols, prolonged arcing does not diminish the maximum concentration.

S. K. TWEEDY.

Aluminium hydroxide sol. K. J. SCHEIDT (J. Russ. Phys. Chem. Soc., 1928, **60**, 617—621).—When pure aluminium foil or wire is left in contact with clean mercury in distilled water for 12—24 hrs., a very sensitive sol of aluminium hydroxide possessing a high adsorptive power is formed. Traces of salts (except aluminium chloride) inhibit the formation, whilst hydrochloric acid stabilises it. By careful evaporation a concentration of 3·17 g./litre (in the presence of hydrochloric acid 4·5 g./litre) can be obtained. The sol is electropositive, the particles reaching a diameter of 340 $\mu\mu$, and showing vigorous Brownian movement. The sol is easily precipitated by minute concentrations of ions, the hydroxyl and carbonate ions being especially effective. A theory of the mechanism of formation of the sol is discussed.

M. ZVEGINTZOV.

Herapathite suspension. E. HATSCHEK (Kolloid-Z., 1928, **45**, 195—196).—Attempts have been made to prepare suspensions of herapathite, with the object of studying the optical properties of the sol in relation to those of the crystals of the disperse phase. The substance was prepared by precipitating a hot solution of quinine hydrogen sulphate in acetic acid with alcoholic iodine solution. Attempts to obtain a stable suspension by carrying out the reaction in very dilute solutions, and also by pouring the hot reaction mixture into a number of dispersion media (glycerol, tetrachloroethane, carbon tetrachloride, and benzyl alcohol), met with failure. No success was obtained when cellulose acetate was added to the dispersion medium as a protective colloid. The following method was successful: 4 g. of finely-powdered quinine sulphate are stirred energetically with 5 c.c. of 20% iodine in alcohol and 3 c.c. of glacial acetic acid until the colour of iodine has disappeared. A few drops of this mixture are added with constant agitation to a sol containing 1·5 g. of cellulose acetate in 100 c.c. of glacial acetic acid. A stable suspension with striking optical properties is produced, which is quite opaque in thick layers and when viewed by reflected light appears grey with a weak metallic shimmer. When stirred, the liquid shows bright metallic streaming zones, which disappear slowly in consequence of the high viscosity of the sol. A layer 7—8 mm. thick appears brown and turbid in transmitted light. The optical phenomena can be explained in terms of the optical properties of the crystals of herapathite.

E. S. HEDGES.

Cerium hydroxide sols and gels. B. N. DESAI (Kolloidchem. Beih., 1928, **26**, 422—438).—Sols prepared by dialysis of cerium ammonium nitrate in Bombay (25—27°) and in Edinburgh (17—19°) are compared. The time required for gel formation in the dialyser decreases considerably, and the degree of hydration of the gel increases, with rise in the temperature at which dialysis is carried out. Ultramicroscopical observation of the gel shows that it contains only amicrons. The fact that the refractive index is the same as that of water is explained as being due to the high degree of hydration of the gel. The manner in which water is combined in the cerium hydroxide particle is discussed, and a mechanism, based on the theory of residual valency, suggested. The results obtained on using the gel as an ultrafilter confirm Zsigmondy's assumption that the gel is capillary in structure, and its behaviour on cooling

with a freezing mixture supports the view that it is polyphasic. The vapour-pressure isotherm was determined and found to be analogous to that of silica gel, except that there is no break in the cerium hydroxide curve. Viscosity measurements showed that the sol behaves as a highly hydrated colloid. On heating, the particles are dehydrated, and the viscosity–concentration curve of the heated sol is typical of a hydrophobic sol. L. L. Bircumshaw.

Behaviour of certain weak inorganic acids in solution. G. Jander (Z. angew. Chem., 1928, **41**, 201—203).—The behaviour of solutions of alkali tantalates, antimonates, and tungstates on acidification by dilute mineral acids, and the constitution of the gels which separate, have been studied by measurement of the diffusion coefficient at different hydrogen-ion concentrations and application of the equation $D_1\sqrt{M_1}=D_2\sqrt{M_2}$, where D_1 and D_2 and M_1 and M_2 are respectively the diffusion coefficients and the mol. wts. of the substance in solution at two different hydrogen-ion concentrations. The process has also been followed by the displacement of the limit of wave-length of light absorbed by the system. It is concluded that alkali tantalates contain the complex $M_7(Ta_5O_{16})$ and the gel precipitated by acids is composed of the acid $H_7(Ta_5O_{16})$. Antimonates and tungstates contain the simple ions SbO_3^- and WoO_3^-. The gel from antimonates is composed of $H_5Sb_3O_{16}$, whilst the precipitated tungstic acid may contain 5 to 12 atoms of tungsten.

W. A. Richardson.

Time of sedimentation of small particles in fluids. W. Weaver (Z. Physik, 1928, **49**, 311—314).—Polemical against Fürth (A., 1927, 1136).

R. W. Lunt.

Relation between hydration and stability of sols and the bivalent nature of the fluoride ion. S. Ghosh and N. R. Dhar (J. Indian Chem. Soc., 1928, **5**, 303—311).—Zirconium hydroxide sols have been prepared by dialysis of zirconium nitrate solution at the ordinary temperature and after boiling. The precipitation values of the chloride, bromide, and iodide ions are considerably greater for sols prepared by the first method, whilst those of the ferrocyanide, sulphate, oxalate, tartrate, and fluoride ions are but slightly greater. The sols are more readily coagulated when dilute, and the coagulation by a mixture of electrolytes is additive. The precipitation values of the sulphate, tartrate, oxalate, and fluoride ions are greater for chromium and aluminium hydroxide sols when prepared by the first method. These sols, and ferric hydroxide sols, are of lower viscosity than sols of zirconium and cerium hydroxides, and of vanadium pentoxide, whilst jellies are formed more readily by sols of the second group. High viscosity and tendency to jelly formation are ascribed to a high degree of solvation of the sol, which, however, appears not to be related to its stability. From its behaviour as a coagulating agent the fluoride ion is considered to be bivalent.

H. F. Gillbe.

Stability of disperse systems. E. N. Gapon (Ukraine Chem. J., 1928, **3**, [Sci.], 133—137).—The duration, Z, of a disperse system, the actual concentration, C, of the dispersed phase, and the degree of activity, S, of the continuous phase are related by $ZC=S$. The degree of dispersion of cupric chloride dihydrate, formed by passing dry hydrogen chloride through a solution of copper oleate in moist benzene, is uniform and the stability of this system diminishes with increasing water content. Where 12 molecules of hydrogen chloride are present to every molecule of copper oleate, the product ZC is constant, whence it follows that the activity of the medium is also constant. R. Truszkowski.

Action of α-particles on colloidal solutions of gold. J. E. Maisin (Ann. Soc. Sci. Bruxelles, 1928, **B**, **48**, 48—53).—The flocculation of a gold sol, containing 0·014 g./litre and prepared by the method of Zsigmondy, by the α-particles from radon has been followed by observations of the Tyndall effect in a specially-designed apparatus which is described. The curve obtained by plotting the relative lowering of the Tyndall effect against the quantity of radon used for coagulation rises somewhat to an arrest and then steeply, indicating a period of induction followed by coagulation proper. L. S. Theobald.

Dyeing of colloidal particles. A. Boutaric and F. Banès (Compt. rend., 1928, **187**, 117—119).—The adsorption of dyes by sols is less than that by the corresponding flocculated colloids. The particles of a sol behave like living cells in so far as the adsorption of colouring matter is concerned. Flocculated colloids behave like dead cells and fix all colouring matters. C. W. Gibby.

Reciprocal action of sols of ferric hydroxide, aluminium hydroxide, silicic acid, and manganese dioxide. I. W. N. Simakov (Kolloid-Z., 1928, **45**, 207—230).—The coagulation values of the sols used were determined with respect to univalent and bivalent anions and cations. The sols of manganese peroxide and silicic acid were found to be negatively charged, and the sols of ferric hydroxide and aluminium hydroxide carried a positive charge. A manganese dioxide sol is completely coagulated by ferric hydroxide sol when the ratio $MnO_2:Fe_2O_3=1:2{\cdot}222$ to $6{\cdot}097$, and by aluminium hydroxide sol when the ratio $MnO_2:Al_2O_3=1:0{\cdot}171$ to $0{\cdot}569$. Similarly, silicic acid sol is completely coagulated by a ferric hydroxide sol when the ratio $Fe_2O_3:SiO_2=1:1{\cdot}0$ to $1{\cdot}6$, and by aluminium hydroxide when the ratio $Al_2O_3:SiO_2=1:7{\cdot}204$ to $16{\cdot}007$. A mixture of two sols of equal sign is additive with respect to the amount of sol of opposite sign required to coagulate it. E. S. Hedges.

Ammonia test for unreduced gold compounds in red gold sols. P. P. von Weimarn (Kolloid-Z., 1928, **45**, 203—207).—The blue ring which often appears at the bounding surface of a concentrated ammonia solution and a red gold sol containing unreduced gold compounds is not produced by all gold compounds, and may not appear until after some time in other cases. Three groups of gold compounds can be distinguished in relation to this test: (*a*) those which give a blue ring in a short time, (*b*) those giving no blue ring, and (*c*) those which give a purple or blue ring after a long time. E. S. Hedges.

Influence of salts on the isoelectric behaviour of proteins. K. Kondo and T. Hayashi (Bull. Chem. Soc. Japan, 1928, 3, 146—151).—The isoelectric point of a protein is difficult to determine because the ions of the salt constituting the buffer solution may change both the mode and the extent of the ionisation of the protein molecule. Further, the salt may react with the protein, forming complex compounds which differ in solubility and ionisation from the original protein.

Experiments have been carried out on the flocculation of rice-glutelin by the addition of various inorganic chlorides. As the concentration of the salt increases, the precipitability of the protein at first diminishes, because the protein molecule is ionised and so dissolved, in proportion to the difference in "protein-ionising" powers between the anions and cations of the salt. Further increase in the salt concentration increases the precipitability, and finally diminishes it again, due to the formation of soluble dissociable complex compounds between the protein and the cations from the salt. Cupric, ferric, and aluminium salts give such compounds even at low concentrations, and this probably accounts for the poisoning effect of these salts on the soil.

S. J. Gregg.

Optical isomerides of cystine and their isoelectric solubilities. J. C. Andrews and E. J. de Beer (J. Physical Chem., 1928, 32, 1031—1039).—The solubility data obtained for isoelectric cystine in water at 25° for samples of different specific rotation indicate the existence of dextro-, lævo-, meso-, and racemic isomerides with the respective solubilities 0·32, 0·075, 0·088, and 0·152 g./litre.

L. S. Theobald.

Coagulation of thorium hydroxide sols by electrolytes. I. Kinetics of the coagulation. II. Relation between the purity of the sol and the influence of similarly charged ions on the electrolytic coagulation of thorium hydroxide sol. III. Stabilising action of alkali and alkaline-earth ions. IV. Coagulation by electrolyte mixtures. B. N. Desai (Kolloidchem. Beih., 1928, 26, 357—383, 384—404, 404—409, 410—421).—I. Details are given of a very accurate optical method, involving the use of a photo-electric vacuum cell, for measuring the coagulation velocity of thorium oxide. The ratio T_n/T is constant, as required by Smoluchowski's theory, only for a certain concentration of the coagulator. With increasing dilution the region of slow coagulation is reached, and the theory no longer holds. The results obtained are in approximate agreement with Freundlich's theory for slow and rapid coagulation. Reasons are given for the failure of previous investigators to observe the region of slow coagulation even when using dilute electrolytes, and the absence of a sigmoid curve with multivalent coagulating ions is explained by their high adsorbability. The values of the velocity coefficient K, calculated from the equation $dx/dt=K(1+bx)(1-x)$ (where $b=dx/dt$ at the turning-point of the x–t curve) are found to be fairly constant for each electrolyte, confirming the assumption that the coagulation is an autocatalytic process. On the other hand, different electrolytes give different K-values—*e.g.*, the values for potassium chloride are smaller than the corresponding values for lithium chloride. This is explained by the stronger stabilising action of the potassium as compared with the lithium ion. The values of p in the formulæ $T_n/T=(C/C_n)^p$ (Paine, *ibid.*, 1912, 4, 24) and $K/K_n=(C/C_n)^p$ (Freundlich) are found to vary with the dilution and with the electrolyte concentration taken as the normal value in calculating p.

II. In order to investigate the effect of dilution on the coagulation of thorium hydroxide sol by electrolytes, the phenomena observed on progressive dialysis were studied. Contrary to the requirements of the Schulze–Hardy law, the coagulation velocity curves for equivalent quantities of lithium, potassium, and barium chloride are not parallel for sols containing considerable quantities of a peptising agent. With increasing dialysis, the coagulation of the sol follows the Schulze–Hardy law more closely. The differences between the velocity curves are ascribed to the different adsorptions of similarly-charged ions by the sol. Deviations from the dilution rule are observed, but these diminish with rise in the concentration of the sol. The observed anomalies are most pronounced with univalent coagulating ions, but disappear with multivalent ions owing to the higher coagulating power and the greater adsorbability; the multivalent ions repress the adsorption of ions with the same charge as the sol. The assertion of Dhar (cf. A., 1924, ii, 737) that sols may be divided into two classes, according to whether they satisfy the dilution rule or not, is proved to be incorrect, since thorium hydroxide sol, according to the conditions chosen, may belong to either class.

III. The velocity of coagulation of thorium hydroxide sol by alkali and alkaline-earth chlorides has been measured. The Schulze–Hardy law does not hold in this case. The higher the valency of the ion carrying the same charge as the sol the greater is its peptising action. The ions, arranged in the order of their protective action, form the following series: $Li<Na<NH_4<K$, and $Mg<Ca<Sr<Ba$. The same order holds for the ionic mobilities.

IV. The coagulation velocity curves for the following pairs of electrolytes have been obtained: potassium and hydrogen chloride, potassium chloride and nitrate, potassium chloride and sulphate, potassium nitrate and sulphate, potassium nitrate and hydrogen chloride, hydrogen chloride and potassium sulphate, lithium and barium chloride. Ion antagonism is shown by the pairs potassium and hydrogen chloride, potassium nitrate and hydrogen chloride, potassium sulphate and hydrogen chloride, lithium and barium chloride. The antagonistic action is attributed to the adsorption of ions having the same charge as the sol, and Weiser's theory of the effect (cf. A., 1926, 242) is shown to have no experimental or theoretical support. Freundlich's view that ion antagonism is a characteristic of hydrophilic colloids is also shown to be incorrect.

L. L. Bircumshaw.

Relations between coagulation, electrokinetic migration velocity, ion hydration, and chemical effect. Investigations on clay, quartz, and permutite suspensions. P. Tuorila (Kolloidchem. Beih., 1928, 27, 44—188).—Measurements of

migration velocity have shown that the electro-endosmotic velocity of water at a glass surface is lowered by electrolytes in the following order: $LiCl < NaCl < KCl = KNO_3 < AgNO_3 = CsCl < HNO_3 < HCl$. The electrolytes retain the same order of effectiveness towards the lowering of the electrokinetic migration velocity of the particles of a paraffin sol and of a clay suspension, except for the silver ion, the position of which varies between K=Ag and Cs<Ag, depending on the concentration of the silver nitrate. Counting the particles under the ultramicroscope has shown that Smoluchowski's formula holds for the slow coagulation of polydisperse paraffin sols, but not for clay suspensions. In the coagulation of a paraffin hydrosol, a clay suspension, a quartz suspension, and a suspension of sodium-permutite the order of influence of electrolytes is that given above, the position of the silver ion again being variable. There is thus a close relation between coagulation and electrokinetic migration velocity, which can be expressed in the case of paraffin particles by the formula $d\varepsilon/d\zeta = -k(\varepsilon)^p$. For both the coagulation and the lowering of migration velocity of the particles of suspensions of clay and of quartz, bivalent cations stand in the following order of influence: $MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$. The relation between coagulation and diminution of migration velocity can be expressed by a formula similar to that given for univalent cations. The formula of Smoluchowski is valid for the slow coagulation of clay suspensions by barium chloride. A suspension of sodium-permutite is peculiar, in that the order of cations given above holds for concentrated solutions, but is reversed for dilute solutions of electrolyte; this is explained by the alkaline nature of the suspension. Suspensions of clay and sodium-permutite are stabilised by small amounts of sodium hydroxide towards coagulation by univalent cations, and a corresponding increase in migration velocity is observed. On the other hand, sodium hydroxide sensitises the suspensions towards coagulation by bivalent cations, the order of influence of the cations being reversed, according to whether the suspension is acid or alkaline. Simultaneously, the migration velocity increases, so that in this case there appears to be no relation between coagulation and migration velocity. The cause of this lies probably in the formation of colloidal hydroxides of the bivalent metals. Small amounts of sodium hydroxide sensitise the coagulation of quartz suspensions by both uni- and bi-valent cations. Experiments on the coagulation of systems, the anion of which forms an insoluble salt with the coagulating cation, showed that the coagulation may be (*a*) delayed (*e.g.*, the system copper sulphide–quartz suspension), (*b*) accelerated (copper hydroxide–clay suspension), or (*c*) unaltered (barium sulphate–sodium-permutite suspension). The chief influences are the sign of charge, the degree of dispersion, and the specific properties of the insoluble product. Systems with both positive and negative particles are readily coagulated. In a mixture containing positively-charged particles of copper hydroxide and negatively-charged particles of clay, the radius of effective sphere of action is about fifty times that of the colloidal particle.

E. S. HEDGES.

Inhibition by sugars of the precipitation of some metallic hydroxides from solution. K. C. SEN (Z. anorg. Chem., 1928, **174**, 61—74).—Sucrose aids the peptisation of zirconium, lanthanum, yttrium, and uranyl hydroxides; lactose and dextrose are effective only with the hydroxides of zirconium and uranyl, and lævulose with those of zirconium, uranium, and yttrium. In the case of lævulose and lanthanum hydroxide and lactose and yttrium hydroxide, peptisation occurs at first, but the solutions are unstable. The smaller the total volume of the solution and the greater the quantity of alkali present the smaller is the minimum quantity of sugar necessary for complete inhibition of precipitation. A certain excess of alkali is, however, necessary for peptisation to occur. The time factor is in many cases of importance, a cloudy solution often becoming clear when kept. Negative ions appear to have no influence.

H. F. GILLBE.

Acclimatisation and ionic antagonism with sheep serum and other colloids. S. PRAKASH, S. GHOSH, and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 313—328).—Negative acclimatisation is produced in all cases when arsenious sulphide, mastic, and gamboge sols are coagulated by acids, and is greater for dilute than for concentrated sols; it is ascribed to the inhibition of hydrolysis. Dilute sheep serum is much more stable towards univalent ions than is the concentrated serum, whereas the reverse is true for multivalent cations and acids. Coagulation of serum by mixtures of cations having different valencies results in ionic antagonism. Coagulation by acids, and more especially by salts, produces positive acclimatisation; potassium fluoride and oxalate are exceptional, owing to the formation of the calcium salts. For salt coagulation, the acclimatisation is more evident in the dilute serum, the reverse being true for coagulation by acids. Ionic antagonism, positive acclimatisation, and the decrease of viscosity of sols when small amounts of electrolyte are introduced are due principally to the adsorption of similarly charged ions. The abnormal dilution effect of hydrolysable sols is due to increase of hydrolysis and of the ratio of the adsorptions of oppositely charged ions on dilution. Positive acclimatisation cannot be explained in terms of the theories of Freundlich, Bancroft, and Weiser, and is apparently connected with the ease of adsorption of the coagulating ions by the sol; it occurs only when the adsorption of ions with sign opposite to that of the sol is considerable, and the adsorption of the other ion is negligible.

H. F. GILLBE.

Swelling phenomena. Swelling of caoutchouc. P. STAMBERGER (Kolloid-Z., 1928, **45**, 239—244).—Experiments on the swelling of caoutchouc in toluene, benzene, and ethyl ether show that the caoutchouc gel is no longer in equilibrium when it is raised above the swelling medium. There is thus a difference between swelling in a liquid solvation medium and in the saturated vapour.

E. S. HEDGES.

Viscosity of agar and gelatin solutions in presence of alcohols and salts. A. JANEK and B. JIRGENSONS (Latvijas Farm. Zurn., 1927, No. 3, 9 pp.; Chem. Zentr., 1928, i, 1375).—Addition of an

alcohol increases the viscosity of agar solution; addition of a salt reduces it whether alcohol is present or not. Gelatin behaves similarly, but the viscosity of alcoholic gelatin solution is lowered by potassium bromide, and raised by the sulphate or tartrate.

A. A. ELDRIDGE.

Dispersoidological investigations. XXII. Jellies and gelatinous precipitates, their classification, conditions of formation, structure, and industrial application. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1928, 9, 1—196).—Jellies may be classified according to the degree of dispersion of their primary structural elements, giving four main groups—macrocrystalline, microcrystalline, ultramicrocrystalline, sub-ultramicrocrystalline—or according to their mechanical properties—resin-like jellies, paste-jellies, soft elastic jellies, solid jellies (glasses). The classification according to the concentration of the disperse phase is rejected as unsuitable, but a division into temperature-reversible and temperature-irreversible jellies is considered to be useful. The author distinguishes between network jellies, in which the whole mass sets uniformly, and coarse cellular jellies, in which gelation proceeds only on definite surfaces within the liquid. By thorough shaking of a coarse cellular jelly it is often possible to obtain a coherent network jelly, through breaking up of the membranes, although this is neither uniform nor transparent. The membranes of the cells of coarse cellular jellies are likened to plates cut from a network jelly of the same thickness.

The conditions necessary for the formation of network jellies, cellular jellies, and mixtures of the two are discussed and illustrated by an account of experiments on the production of jellies of the sulphates of calcium, strontium, and barium. Consideration is given to the state of the water in these jellies and it is believed that there is no fundamental difference between such preparations and typical jellies such as gelatin. The total amount of water imbibed by a jelly is supposed to consist of (1) interatomic hydration, *e.g.*, water in crystal hydrates ($Al_2O_3,3H_2O$; $SrSO_4,2H_2O$), (2) surface hydration, and (3) "structure" hydration, *i.e.*, water enclosed by the pores of the structural elements of the jelly. The production of colloidal solutions in an aqueous alcohol medium of barium, strontium, and calcium salts of the following acids: sulphuric, chromic, tungstic, molybdic, hydrofluoric, oxalic, tartaric, citric, carbonic, boric, orthophosphoric, arsenic, arsenious, hydrosulphuric, and silicic, and also of silver citrate, chloride, bromide, and iodide has been studied at low temperatures (to −30°), and the following conclusions have been reached. (1) Where only one type of salt can be formed (*e.g.*, barium sulphate, silver chloride) colloidal solutions are readily obtained, and excess of one component (barium ions for barium sulphate) gives a very stable colloid, whilst excess of the other component (sulphate ions for barium sulphate) diminishes the stability or causes coagulation. (2) Where more than one salt can be formed (*e.g.*, carbonates, phosphates, silicates, etc.), instead of stable colloidal solutions there are formed voluminous gelatinous precipitates, or, under suitable conditions, network jellies.

Photomicrographs of jellies of hydrated strontium sulphate are given, and these demonstrate that the tissue of the jelly is composed of bundles of thin needles; in each bundle, the needles spread radially from one centre, and the ends of the needles of different bundles are interwoven, forming a continuous structure. The following stages in the process can be observed: (1) formation of crystallisation centres, (2) development of these centres into spheres composed of needles, (3) union of the spherical bundles into flakes, (4) filling of the entire volume by the flakes, with complete soaking up of the mother solution. On keeping, the jellies disintegrate, with formation of a flocculent precipitate composed of aggregates of tangled needles. The needles are considered as primary structure elements of a jelly, and the spherical aggregates as secondary structure elements. The jellies are easily destroyed by energetic shaking, because the interlocking of the needles is disturbed. Examples are given of other jellies which are similarly destroyed by shaking. From the study of a number of photomicrographs of precipitated gold and of some other substances it is concluded that gelatinous precipitates are particular cases of flocculent precipitates; the individual grains of the former are ultramicro-crystals, the surface layers of which are strongly solvated, and the smaller the dimensions of the ultramicro-crystals and the greater the degree of solvation the more the precipitate assumes the properties of a jelly. There is no evidence that the ultimate particles of a jelly have of themselves a gelatinous nature.

Cellulose (filter-paper) can be spontaneously dispersed to give gelatinous spherulites by heating with a concentrated aqueous solution of calcium iodide. This process has been followed photomicrographically, and the forms produced resemble the spherulites of gelatin obtained by Bradford by slow evaporation of a gelatin sol; they also show a marked similarity to spherulitic aggregates of calcium arsenate prepared by the author. Theories of the structure of jellies and gelatinous precipitates are reviewed and criticised. It is considered that the unit of all jellies is at least sub-ultramicrocrystalline, and that no true emulsoid jellies, consisting entirely of liquid phases, exist. The examination of jellies and glasses by means of X-rays is discussed, and it is concluded that the individual structure elements are not devoid of an inner vectorial structure; absolutely amorphous jellies and glasses do not exist. It is stated as a general law that any substance can under suitable conditions be obtained as a stable jelly, and reference is made to the technical importance of this generalisation.

E. S. HEDGES.

Viscosity changes at the beginning of the gelatinisation of dilute agar sols. H. G. B. DE JONG (Rec. trav. chim., 1928, 47, 797—818).—The viscosity of ½% agar sols at 43° gradually increases to a value which remains constant for a short period and then increases again. The primary increase is quantitatively reproducible, whilst the second is completely irregular. It is suggested that the former corresponds with the formation of aggregates which are small compared with the cross-section of the capillary tube of the viscosimeter, the subsequent irregularity setting in when the size of the particles becomes so large as to exert a mechanical disturbance.

Electrolytes in very dilute solution exert a capillary electric action, whilst in greater concentration their influence becomes markedly lyotropic. The bearing of these results on the stability theory of Kruyt is discussed. F. J. WILKINS.

Electrokinetic potential of silicic acid gel. II. Effect of electrolytes. S. GLIXELLI and J. WIERTELAK (Kolloid-Z., 1928, **45**, 197—203; cf. A., 1927, 1139).—A study has been made of the influence of acids (nitric, hydrochloric, sulphuric, oxalic, and phosphoric) and salts (nitrates of potassium, barium, and lanthanum) at various concentrations, on the electrokinetic potential of silicic acid gel as measured by an electro-osmotic method. The discharging effect of the salts exhibits the usual connexion with the valency of the cation, but the hydrogen ion is unusually powerful, having a greater discharging effect than a tervalent cation. The relation of the electrokinetic potential to the concentration of inorganic salt solutions can be expressed by the formula $\zeta=a-K\log c$, where a and K are constants and c is the concentration of the solution. E. S. HEDGES.

Rule for the diffusion of electrolytes in charged gels. (MLLE.) CHOUCROUN (Compt. rend., 1928, **187**, 296—297; cf. this vol., 702).—The coefficients of diffusion at 28° of potassium ferrocyanide for neutral and alkaline gelatin are in the ratio 1 : 2·5, but are equal for neutral and alkaline water. The rate of diffusion of an electrolyte in a neutral gel is decreased when the sign of the charge on the latter is the same as that of the least mobile ion. J. GRANT.

Rhythmic phenomena in stones. Rhythmic conditions. M. STORZ (Kolloid-Z., 1928, **45**, 231—238).—Stones which are produced by the subsequent aggregation of the weathering products of rocks are described. Rhythmic banding, taking the form either of alternate zones of hardness or of colour, is often observed in these stones. This phenomenon is ascribed to a rhythmic change of external conditions during the formation of the stone. E. S. HEDGES.

Influence of electrolytes on the velocity of cataphoresis, and relation between the electrokinetic and electromotive potential, of gold. N. THON (Compt. rend., 1928, **187**, 119—122).—The effects of various electrolytes on the velocity of cataphoresis of aqueous gold sols and on the electrode potential of gold have been examined. The former effect, which may be either positive or negative, is due to the anions; the latter, which is negative, to the cations. C. W. GIBBY.

Ionisation accompanying the thermal decomposition of ozone. R. RUYSSEN (Natuurwetens. Tijds., 1928, **10**, 101—116)—The ionisation associated with the thermal decomposition of 10^{-6} to 10^{-7} mol. of ozone per sec. at 240° in a field of about 845 volts corresponds with a current of 10^{-11} to 10^{-12} amp. The ionisation increases directly with the rate of decomposition, and positive and negative ions are formed in equal numbers, and must thus have equal velocities. The ionisation increases rapidly with the intensity of the field, and has by no means reached its maximum in a field of 3000 volts per cm. The thermal decomposition of ozone thus occurs in two stages. The first is the breaking up of the molecule into positive and negative ions, and occurs with a measurable velocity dependent on the number of effective molecular collisions per sec.; the second, the combination of the ions to form oxygen molecules, appears to be instantaneous. S. I. LEVY.

Influence of intensive drying on the system nitrogen peroxide-nitric oxide-oxygen. J. W. SMITH (J.C.S., 1928, 1886—1894).—It is shown that when nitrogen peroxide is heated with phosphoric oxide at least three reactions occur simultaneously: (*a*) the reactants form an additive compound; (*b*) the peroxide is dissociated into nitric oxide and oxygen to a greater extent than in the moist gas, and these products do not recombine on cooling; (*c*) the nitric oxide decomposes into its elements at a greater rate than normally. The last effect is ascribed to the catalytic effect of the large surface of phosphoric oxide. The relative extent to which these reactions proceed depends on the temperature and duration of heating.

Nitrogen peroxide which has been intensively dried at the ordinary temperature does not dissociate very considerably into nitric oxide and oxygen when heated at 550° for 24 hrs., but when heated at 620° for the same time it seems to revert to the normal state, probably owing to a superficial decomposition of the glass. In the dried gas the rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded. J. W. SMITH.

Theory of electrolytic dissociation. W. NERNST (Z. physikal. Chem., 1928, **135**, 237—250).—See this vol., 127.

Theory of strong electrolytes. A. GYEMANT (Physikal. Z., 1928, **29**, 289—293).—Measurements have been made of the conductivity of 0·002 and 0·02N-solutions of hydrogen chloride in mixtures of ethyl alcohol and benzene containing 0·2% of water. The conductivity of the solution diminishes rapidly as the benzene content of the solvent is increased. In a magnetic field such solutions show an increase in conductivity in the direction of the field, but not transversely, the increase of conductivity being of the order of 1—2% per kilovolt cm.$^{-1}$ If it be assumed that such solutions of strong electrolytes are not completely dissociated and if K denotes the dissociation constant of hydrogen chloride into ions, then the free energy of 1 g.-mol. of dissociated chloride is given by $-RT\log K$, which must also be equal to the electrical work of ionisation, A, less the work of dielectric solvatation, and the relationship takes the form $-RT\log K=A-\frac{1}{2}Ne^2(r_k^{-1}+r_a^{-1})(1-\varepsilon^{-1})$, where ε is the dielectric constant of the solvent and r_k and r_a denote the effective radius of cation and anion. It may be shown that for such very dilute solutions the molecular conductivity $\lambda=\lambda_\infty\sqrt{Kc_0}$, where denotes the molecular conductivity at infinite dilution and c_0 the total concentration of the electrolyte. From measurements of λ in a given solvent mixture (ε known) A may therefore be calculated, since the dielectric solvatation term can be calculated from known data. Using this value for A, K has been calculated as a function of c_0, *i.e.*, as a function of the composition of the solvent. These

values of K have then been used to calculate λ, by the equation $\lambda=\lambda_\infty\sqrt{Kc_0}$, as a function of the composition of the solvent for the concentrations 0·002 and 0·02N of hydrogen chloride. Since the theoretical values thus calculated agree well with experimental values the data together with the Wien effect are thought to afford evidence for the incomplete dissociation of the electrolyte in such solutions.

R. W. LUNT.

Ionisation of hydrofluoric acid solutions. M. AUMÉRAS (J. Chim. phys., 1928, **25**, 300—307).—It is shown that the conductivity of solutions of carefully purified hydrofluoric acid does not lead to a constant value of K in the equation $[H^+][F^-]=k[HF]$ (cf. Pick, Nernst Festschrift, 1912, 374). A chemical method (A., 1927, 312, 1141) leads to the value $16{\cdot}7\times10^{-5}$ for K, and it is shown that this method affords under certain conditions a means of determining the true degree of ionisation. W. A. RICHARDSON.

Influence of neutral salts on acid–salt equilibria. III. Second dissociation constant of carbonic acid and influence of salts on the activity of hydrogen ions in a hydrogen carbonate–carbonate mixture. IV. Third and fourth dissociation constants of pyrophosphoric acid and influence of neutral salts on the activity of hydrogen ions in a ter–quadrivalent and di–tervalent pyrophosphate mixture, respectively. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1928, **47**, 819—825, 826—833; cf. this vol., 589).—III. The second dissociation constant of carbonic acid has been determined by measurement of the p_H values of sodium carbonate–hydrogen carbonate mixtures at varying dilutions, and is given as pK_2—10·36 at 18°. The Debye–Hückel equation holds for these solutions up to an ionic strength of 1·25. This equation, however, does not give a quantitative description of the behaviour of solutions containing an added neutral salt. There appears to be a specific interaction of ions which is dependent on the nature of the cation of the neutral salt and the size and valency of the ions in the acid–salt mixture.

IV. Similar measurements on solutions of sodium pyrophosphate and hydrochloric acid gave values of pK_3 6·679 and pK_4 9·391 at 18°. Whilst the neutral salt effect for a dilute mixture of bi- and ter-valent pyrophosphate can be calculated fairly accurately by means of the Debye–Hückel equation, it fails in the case of ter- and quadri-valent pyrophosphate solutions. F. J. WILKINS.

Dissociation constants of the naphthylaminesulphonic acids. I. M. KOLTHOFF (Chem. Weekblad, 1928, **25**, 234).—The low values of these constants (Waterman and Groot, this vol., 407) are quite normal in the light of the "hybrid ion" conception of Bjerrum, *i.e.*, if they are regarded as the hydrolysis constants of the basic groups rather than the dissociation constants of the acid groups. The true dissociation constant of the amino-group, in the 2 : 5- and 2 : 8-acids, is calculated as about 10^{-10} and the isoelectric point as about $10^{-2\cdot5}$. S. I. LEVY.

Absolute hydration of the hydrogen, lithium, sodium, potassium, chlorine, and bromine ions in normal solutions. J. BABOROVSKY, J. VELISEK, and A. WAGNER (J. Chim. phys., 1928, **25**, 452—481).—The true transport numbers of the cations and the electrolytic transference of water have been determined for solutions of hydrogen, lithium, sodium, and potassium chlorides, and lithium, sodium, and potassium bromides. The calculated values of the absolute hydration of the ions are, in mols. of water per ion: hydrogen 1·06, lithium 13—14, sodium 8—9, potassium 5, chlorine 4, and bromine 3.

H. F. GILLBE.

Conductivity and f.-p. measurements for the dimethylpyrone salts of acetic and the three chloroacetic acids in benzene solution. M. A. RABINOVITCH (J. Russ. Phys. Chem. Soc., 1928, **60**, 623—639).—The observations were intended to throw light on the electrolytic properties of the acids. The conductivities of 0·2N-benzene solutions of acetic acid in the presence of varying amounts of dimethylpyrone (up to a ratio of dimethylpyrone : acetic acid=1·5) were determined, and found to give well-defined maxima. The conductivity of the free acids in benzene increases from trichloroacetic to acetic, but in the presence of dimethylpyrone this order is reversed, as in aqueous solutions. Cryoscopic determinations in benzene solution show that three salts are formed with dimethylpyrone: "acid" (dimethylpyrone) $(acid)_2$; "neutral" (dimethylpyrone) (acid); and "basic" $(dimethylpyrone)_2$ (acid). The stability of these salts increases from acetic to trichloroacetic, whereas the degree of polymerisation of the free acids decreases in that order. The maximum conductivity corresponds with the maximum concentration of the "acid" salt. The structure of these oxonium salts is discussed, and the nature of the ionisation in water, which is regarded as an "oxonium" base, is said to be due to complex formation. M. ZVEGINTZOV.

Iodide, iodine, tri-iodide equilibrium and the free energy of formation of silver iodide. G. JONES and B. B. KAPLAN (J. Amer. Chem. Soc., 1928, **50**, 1845—1864).—The equilibrium constant, K, of the reaction $K^{\cdot}+I'+I_2=K^{\cdot}+I'_3$ was determined directly with the aid of the "equilibrator" (this vol., 863). The value of $K(=[I'][I_2]/[I_3'])$ shows no systematic variation with the concentration of iodine between the limits of 2—33% of saturation, nor with the concentration of the iodide between the limits 0·01—0·1N. At 0°, K=0·00072, and at 25°, 0·00140; lower values are obtained when the solutions are saturated with iodine, especially when the iodide concentration is high, indicating the formation of higher polyiodides in the stronger solutions. By using a ballistic galvanometer and shunting a high-capacity condenser across it and its tapping key the measurement of potentials across a cell having an internal resistance of $1{\cdot}6\times10^6$ ohms to within 0·0- millivolt is possible; this enables cells of the Laurie type to be used. From the corrected $E.M.F.$ of the cells Pt|xN-KI satd. with I_2|xN-KI unsatd. with I_2|Pt (cf. Gerth, A., 1921, ii, 534), where x is 0·01—0·1, the unsaturated solutions being withdrawn from the equilibrator, the $E.M.F.$ of the cell Ag|AgI|I_2 is calculated. The free energy of silver iodide ($Ag+\frac{1}{2}I_2$=AgI) is 15,802 g.-cal. at 25° and 15,680 g.-cal. at 0°; this is sensibly constant for concentrations of potass-

ium iodide between $0{\cdot}01N$ and $0{\cdot}05N$. The entropy change is 4·8 g.-cal./1°, and the heat of formation at 25°, 14,354 g.-cal. All earlier work on the free energy of silver iodide is critically reviewed; it is shown that the value 2·19 g.-cal./1° for the entropy of silver iodide based on Nernst's specific heat measurements does not rest on a sound experimental basis.

S. K. TWEEDY.

Changes in inter-atomic internal energy with reference to thermodynamics and catalytic action. R. D. KLEEMAN (Phil. Mag., 1928, [vii], **5**, 1191—1198).—The equation of state for a perfect gas should be written in the form $PV=M\xi RT$, where ξ is a function both of temperature and volume, whence it follows that the kinetic energy of a molecule is not exactly proportional to the temperature, but is also a function of the volume of the gas. It then follows that if substances which interact chemically are brought into contact with another substance, a change will take place in the inter-atomic energies of the reactants which will have the effect of either increasing or decreasing the rate of reaction. Thus a thermodynamic basis of the phenomenon of contact catalysis is offered. A. E. MITCHELL.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1928, **48**, 706—715; cf. this vol., 241).—An expression is deduced thermodynamically for the contraction of liquids on mixing. The heat of mixing, contraction, and vapour pressure for the sulphuric acid–water system are deduced and compared with experimental data. J. W. SMITH.

Thermodynamic relationships concerning the constitution of compounds of ter- and multivalent elements. G. BECK (Z. anorg. Chem., 1928, **174**, 31—41).—The densities and heats of dissolution of the sulphates and chlorides of ter- and quadrivalent metals in water and in alkaline solutions have been measured. The logarithmic contraction equation $kQ=546(\log V_a/V_c)$ (see A., 1927, 520) is discussed, especially in respect of the values assumed by the constant k for various groups of compounds.

H. F. GILLBE.

Second law of thermodynamics in chemistry. R. C. CANTELO (J. Physical Chem., 1928, **32**, 982—989).—Theoretical. From the chemical point of view the second law of thermodynamics is best expressed by the statement that "heat cannot be converted into work without compensation."

L. S. THEOBALD.

Energy of formation of the compound HCl,HBr. C. DEL FRESNO (Anal. Fís. Quím., 1928, **26**, 164—167).—The heat of formation of the additive compound HCl,HBr has been calculated on the assumption that the structure is $H_2Br^+{\cdot}Cl^-$ and $H_2Cl^+{\cdot}Br^-$. The latter yields the higher figure, and is hence regarded as the more probable structure. H. F. GILLBE.

Free energy of formation in fused salts. I. Copper and thallium halides, and mercuric iodide. G. DEVOTO (Gazzetta, 1928, **58**, 359—371; cf. Cambi and Devoto, this vol., 135).—The polarisation method, previously described, may be applied to the determination of the free energy of salts at their fusion points. The polarisation potentials at the fusion point were measured for the chloride, bromide, and iodide of univalent copper and thallium, and also for mercuric iodide. The potentials calculated fromf ree energy changes agree with the measured values to within about 0·05 volt. F. G. TRYHORN.

Relationship between the different forms of calcium sulphate at high temperatures. P. N. LASCHTSCHENKO and D. J. KOMPANSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 579—616).—The heating curves and densities of various hydrated modifications of calcium sulphate have been examined. The heating curve of native insoluble anhydrous calcium sulphate ("anhydrite") shows a break between 140° and 270°; previous to this the density reaches a maximum, due to an intramolecular change. Another break occurs between 958° and 984°, when the salt begins to dissociate. At 1190° there is a transition point from a rhombic to a monoclinic form. The hemihydrate, which is very difficult to obtain free from water, is stable up to 164°, when it begins to lose water and is gradually transformed into the anhydrous salt at 260°. "Soluble" anhydrous calcium sulphate (d 2·571) is prepared by prolonged drying of the precipitated dihydrate at 100° in a desiccator. A similar product is obtained by drying the metastable dihydrate obtained in the form of a gel. It readily absorbs water to give the hemihydrate. A break in the heating curve at 440—496° indicates transformation into the insoluble anhydrous salt. Above 165° and below 260° the hemihydrate may, depending on the conditions, be transformed into the "insoluble" or "soluble" (which is always the metastable phase) forms, or into a mixture of both. Gypsum, prepared by heating native or precipitated dihydrate at 500°, gives a cooling curve with breaks at 100—140°, 640—700°, and 975°. The first is due to the formation of the unstable monohydrate, followed by polymerisation to the hemihydrate, the second corresponds with the temperature at which dead-burnt gypsum recovers the power to "set" with water, whilst the third is the point of dissociation.

The possible structural formulæ of the various modifications and the processes involved in the "setting" of plaster of Paris are discussed.

M. ZVEGINTZOV.

Tin–antimony alloys. W. BRONIEVSKI and L. SLIVOVSKI (Rev. Mét., 1928, **25**, 312—321).—A more detailed account of work already published (this vol., 829).

Gold–platinum alloys. A. G. GRIGORIEV (Ann. Inst. Platine, 1928, **6**, 184—194).—A fusion diagram is constructed for mixtures of gold and platinum. No compound formation occurs, but solid solutions are formed. The micro-structure of the alloys formed is of the ordinary type in such cases. The hardness of the alloys rises to a maximum at about 70% Pt. R. TRUSZKOWSKI.

Transformations of the β-phase in the copper–zinc system. P. SALDAU and J. SCHMIDT (Z. anorg. Chem., 1928, **173**, 273—286).—The boundaries of the β-phase in copper–zinc alloys have been determined by tempering at various temperatures for 84 days followed by quenching and examination of the microstructure. Below 600° no decomposition into $\alpha+\gamma$ was observed. Below 440° the limiting

composition of β is 55·01—51·39 at.-% Cu in cast alloys and 54·63—49 at.-% Cu in tempered alloys. At 480° the field of pure β in tempered alloys extends from 56·01 at.-% Cu to 51·39 at.-% Cu; above 480° the field broadens on both sides. In the temperature interval 440—480° a discontinuity occurs in the equilibrium diagram indicating the existence of two modifications of β, viz., β′, stable below 440°, and β, stable only above 480°. The discrepancies found by previous workers in the limiting compositions of the β-field are ascribed to insufficient time of annealing to obtain complete equilibrium being used in their work. A. R. POWELL.

Dissociation of chromium nitride. G. VALENSI (Compt. rend., 1928, **187**, 293—296).—The dissociation isotherms between 810° and 1200° of chromium nitride, prepared by heating pyrophoric chromium in pure nitrogen at 800°, are analogous to those of palladium and hydrogen, and indicate the formation of the compound CrN. The temperature (1015°) at which the dissociation pressure is 760 mm. agrees with the calculated value. J. GRANT.

Physico-chemical investigations on the higher fatty acids. I. Thermal analysis of fatty acids. A. Binary systems tristearin–tripalmitin and stearic acid–palmitic acid. N. N. EFREMOV (Ann. Inst. Polyt. Ural, 1927, **6**, 155—202).—The data given in the literature for the equilibrium in the system stearic–palmitic acids are inaccurate (cf. de Visser, A., 1898, i, 560; 1899, i, 255; Carlinfanti and Levi-Malvano, A., 1910, i, 5). The temperature–concentration diagram corresponds with Roozeboom's type III, showing the formation of two series of solid solutions and passing from one to the other through a minimum at 52·5° (68% by weight of palmitic acid) without interruption of the continuity. From the fused mixtures no chemical compound is formed on cooling. The solid solutions decompose extremely slowly, yielding either a chemical compound of varying composition of the Berthelot type or a mechanical mixture of the components with a eutectic point. The diagram of the pressure of flow (Kurnakov and others, A., 1911, ii, 18; Z. anorg. Chem., 1911, **76**, 241) for this system, which confirms the results of thermal analysis, consists of a continuous curve with a high maximum corresponding with 45% by weight of palmitic acid and the pressure 10·55 kg./mm.^{2} The pressure of flow of the solid solutions falls considerably after 2 months, owing to the decomposition of these solutions; thus the maximum pressure is reduced to 7·5 kg. per sq. mm., the corresponding composition remaining as before. Determination of the viscosity furnishes an excellent means of ascertaining the degree of purity of stearic and palmitic acids. The micro-structure is that characteristic of continuous solid solutions, no new phases indicative of the formation of a chemical compound being observed; the micro-structure also reveals incipient decomposition of the solid solutions after these have been kept for 2 months.

Both tristearin and tripalmitin exist in not less than three polymorphous modifications. The stable α-forms are obtained on rapid cooling of the molten glycerides to the solidifying temperatures (53·2° and 48·4°, respectively), and are converted into the soft, transparent, labile β-modifications if kept at 53·2—55·2° and 48·4—53·8°, respectively. When carefully heated, these do not melt, but lose their softness and transparency and change into the γ-forms. The temperature–concentration diagram of the system tristearin–tripalmitin represents one of the most perfect examples of isomorphism of the components. Continuous solid solutions are formed by the α-modifications, the curve showing a minimum at 44·9° (79·5% tripalmitin). The β-forms give a similar curve with a minimum at 47·8° for 75% of tripalmitin. A third curve is given which corresponds with the conversion of the β- into the γ-modifications, the minimum being at 52·3° (72·4% tripalmitin); all the intermediate mixtures exhibit similar relationships. On the other hand, the m. p. of the γ-forms of tristearin (69·3°) and tripalmitin (67·5°) rapidly fall in mixtures, so that the curve gradually approaches the preceding curve.

Measurement of the m. p. of fats and fatty acids by means of Schukov's apparatus and a thermometer yields only approximate figures and is useful mainly owing to its simplicity and rapidity. Prevention of supercooling by seeding and stirring leads to values more nearly in agreement with those obtained by means of a thermo-element in conjunction with a pyrometer. With these poorly crystallising substances, replacement of the cooling curves by heating curves results, even under the favourable conditions, in high values for the m. p. When these substances are heated in a capillary, the m. p. is inevitably raised and the solidifying point lowered, and differences as great as 10° between these temperatures are obtainable. T. H. POPE.

Pseudo-ternary systems containing sulphur. III. System sulphur–sulphur monochloride. D. L. HAMMICK and M. ZVEGINTZOV (J.C.S., 1928, 1785—1791).—The solubility of sulphur in sulphur monochloride has been determined both with and without previous heating of the solution to a definite higher temperature. In confirmation of the observations of Aten (A., 1913, ii, 40) it is found that the solubility is greater the higher the temperature to which the solution has been preheated. The solubility curves are said to indicate that the phenomenon is due to the formation of a subchloride S_4Cl_2 and not to a change in the inner equilibrium of the dissolved sulphur. J. W. SMITH.

System KCl–HCl–H_2O between 0° and 80°. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 738—739).—To supplement the results obtained at 25 (A., 1927, 628) the solubility of potassium chloride in hydrochloric acid solutions has been determined at 40°, 60°, and 80°. The solubility decreases with increasing acid content, but the shape of the curves does not alter with the temperature. O. J. WALKER.

System $AlCl_3$–HCl–H_2O between 0° and 80°. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 740—744).—From the f.-p. and solubility curves of the system $AlCl_3$–H_2O it is shown that between the cryohydric temperature (−55°) and 80° the saturated solution is in equilibrium with the hydrate $AlCl_3,6H_2O$ as solid phase. The heat of dissolution of this hydrate

at 20° is 4606 g.-cal. The solubility of aluminium chloride in presence of hydrochloric acid was determined at 0°, 40°, 60°, and 80°. The acid decreases the solubility of the salt, but the temperature does not affect the shape of the curves. O. J. WALKER.

System $AlCl_3$–KCl–H_2O between 0° and 80°. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 745—747; cf. preceding abstract).—The solubility of aluminium chloride in presence of potassium chloride has been measured at the same temperatures. Similar results are obtained. O. J. WALKER.

Systems $Pb(NO_3)_2$–$LiNO_3$–H_2O and $Pb(NO_3)_2$–$CsNO_3$–H_2O. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 495—496).—A preliminary note in which the equilibrium solutions at 25° are presented in the form of a triangular diagram. R. W. LUNT.

Formation of double sulphate of cerium and rubidium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1928, [vi], 7, 449—452).—From an examination of the system $Ce_2(SO_4)_3$–Rb_2SO_4–H_2O at 25° it is concluded that the only double salt formed has the composition $Ca(SO_4)_3,Rb_2SO_4,2H_2O$. Crystallographic data for this substance are given. R. W. LUNT.

System Na_2CO_3–$NaHCO_3$–H_2O and the range of existence of "trona." R. WEGSCHEIDER and J. MEHL (Monatsh., 1928, 49, 283—315; cf. Hill and Bacon, A., 1927, 1142).—A study of the equilibrium has been made at eleven temperatures between 20° and 94·5° and at 30·0°, 49·7°, and 89·5° in presence of sodium chloride. The range of existence of the double salt "trona," $NaHCO_3,Na_2CO_3,H_2O$, has been deduced from the results. One or possibly two double salts appear at 90° which have a higher carbon dioxide content than "trona." The latter yields a *labile* (β) *sodium hydrogen carbonate* when treated with water. I. VOGEL.

Equilibria in the ternary system chromium trioxide–sulphur trioxide–water. A. W. RAKOVSKI and D. N. TARASSENKOV (Z. anorg. Chem., 1928, 174, 91—96).—The solubility curves of chromium trioxide in aqueous sulphuric acid solutions have been determined at 0°, 20°, 40°, 75°, and 100°. The curves may be followed for a considerable distance into the metastable region which is entered after a minimum at 57·76% of sulphur trioxide in the liquid phase. The compound CrO_3,SO_3 exists and may be employed as an indication of moisture in closed systems, since at the ordinary temperature it decomposes with a marked change of colour if the relative humidity exceeds 1·7%. The hydrate $SO_3,2H_2O$ forms metastable mixed crystals with chromium trioxide. H. F. GILLBE.

Reduction of metallic oxides; equilibrium $Zn+CO_2 \rightleftharpoons ZnO+CO$. K. JELLINEK and B. POTIECHIN (Z. anorg. Chem., 1928, 173, 164—168).—The reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$ has been studied 565°; the quantity of carbon dioxide present at equilibrium is about 0·2%. The discrepancy between this value and that obtained by other observers is ascribed to differences in the form of the zinc oxide employed. H. F. GILLBE.

System cupric sulphate–ammonium oxalate–ammonia. M. HERSCHKOVITSCH (Z. anorg. Chem., 1928, 173, 222—224).—A 0·04*M*-solution of cupric sulphate with four times the quantity of ammonium oxalate yields an electrolyte from which a brilliant, dense, and adherent copper deposit may be obtained. The muddy deposit which is liable to form in the bath is due to excess of either ammonia or oxalic acid. In presence of an excess of ammonia the deposit consists of a mixture of crystals of the composition $Cu(CO_2)_2,NH_3$, $Cu(CO_2)_2,2NH_3$, and $Cu(CO_2)_2,2NH_3,2H_2O$, whilst if oxalic acid be present in excess, the deposit is cupric oxalate. H. F. GILLBE.

Thermochemistry of fluorine. H. VON WARTENBERG (Z. anorg. Chem., 1928, 174, 96; cf. A., 1926, 476).—The final equation should read $Cr+3/2F_2+aq.=CrF_3,aq.+283·3+a$. H. F. GILLBE.

Source of error in conductivity measurements. L. DE BROUCKÈRE (J. Chim. phys., 1928, 25, 294—299).—The conductivity of 0·01*N*-solutions of various chlorides in a vessel with freshly-platinised electrodes has been measured, and it is shown that the conductivity decreases, reaching an equilibrium value, some tenths of 1% lower than the original value, in about 12 hrs. If the solution is now replaced the conductivity rises nearly to the initial value in the first experiment, and remains very nearly constant. If the same electrodes are used for measurements in 0·001*N*-solutions a gradual increase in conductivity is observed. When the electrodes are removed from the 0·01*N*-solutions chloride can be washed out by immersion in pure water, and the amount thus obtained is equal to the amount lost from the original solution. The amount of salt adsorbed varies with each replatinisation. W. A. RICHARDSON.

Electrical conductivity of aqueous solutions of radon. E. GLEDITSCH and L. GLEDITSCH (J. Chim. phys., 1928, 25, 290—293).—Conductivity measurements on solutions containing quantities of radon varying from 13·5 to 235×10^{-9} curie per c.c. in presence or in absence of electrolytes show that the niton has no influence on the conductivity of the solutions. W. A. RICHARDSON.

Conductivity and viscosity of solutions of lithium nitrate in certain mixed solvents [at 25°]. J. L. WHITMAN and S. R. SPENCER (J. Amer. Chem. Soc., 1928, 50, 1840—1844).—Water, methyl and ethyl alcohols, and mixtures of these were used as solvents, the viscosities being measured in an Ostwald viscosimeter. The results are compared with those of Jones (A., 1905, ii, 73). The values recorded are uniformly higher than those of Jones, possibly because of the difficulty of drying lithium nitrate, which can be completely dehydrated only by prolonged heating at 150° in a vacuum. S. K. TWEEDY.

Dispersion of conductivity and dielectric constant for strong electrolytes. P. DEBYE and H. FALKENHAGEN (Physikal. Z., 1928, 29, 401—426).—The theory previously developed (this vol., 596) has been extended by taking into account the Brownian motion of the ions and the cataphoretic action. In this manner laws of a more quantitative nature are deduced. The theoretical values deduced are compared with experimental data. J. W. SMITH.

Electrochemistry of the system benzamide–bromine–nitrobenzene. V. C. Finkelstein and O. K. Kudra (J. Russ. Phys. Chem. Soc., 1928, **60**, 783—793).—The conductivity at 25° and 35° of nitrobenzene solutions containing bromine and benzamide in proportions corresponding with the compound NH_2Bz,Br_2 increases continuously with the concentration, up to 52%. The molecular conductivity curves at 35° show a maximum at $v=0{\cdot}9$ litre. The presence of bromine in excess increases the conductivity. On electrolysis, bromine is evolved at the anode and benzamide is deposited on the cathode.

R. Truszkowski.

Revision of the theory of transfer resistance. E. Newbery (Proc. Roy. Soc., 1928, **A**, **119**, 686—689).—A number of experiments have been made with a new type of electrolytic cell, designed to eliminate the disturbing effect of the fall of potential through the electrolyte obtained with the type of cell used in previous work. The table showing the relation between transfer resistance and the concentration of the electrolyte, previously recorded (*ibid.*, 1926, **A**, **111**, 188), is found to be incorrect. It is now found that transfer resistance occurs only when a gas is being liberated at an electrode. It is independent of the concentration of the electrolyte and increases with rise of temperature. The highest values are obtained with very low current densities; at high current densities, transfer resistances become very small. The theory of the effect is discussed. It is suggested that transfer resistance is the electrical resistance of a film of gas over the electrode surface.

L. L. Bircumshaw.

Apparatus for the moving boundary method of determining transference numbers. E. R. Smith (J. Amer. Chem. Soc., 1928, **50**, 1904—1906).—An apparatus is described which obviates the necessity of calibrating the measuring tube. One side of the apparatus is closed and is connected with a tube of mercury; mercury is withdrawn so as to oppose the motion of the boundary, the weight withdrawn giving the volume through which the boundary has moved. The boundary can repeatedly be returned to the starting point for a fresh determination.

S. K. Tweedy.

Measuring *P.D.* by means of dropping electrodes. A. Frumkin and A. Donde (Trans. Karpov Inst. Chem., 1926, No. 5, 34—38).—If the water electrode in Kendrick's apparatus is replaced by a mercury dropping electrode, the *P.D.* at the air–solution boundary can be measured.

Chemical Abstracts.

Influence of pressure on the potential of electrodes charged with hydrogen and on the current–potential curves. G. Tammann and E. Jenckel (Z. anorg. Chem., 1928, **173**, 337—357).—In the cell $(Pd)H_2|2N\text{-}H_2SO_4|CdSO_4|Cd$ the value of $\Delta E/p$ decreases slightly with increasing pressure, the rate of decrease being the smaller the higher is the temperature. Similar results are obtained with the cell $(Pt)H_2|0{\cdot}1N\text{-}HCl|CdCl_2|Cd$. The effect of pressure on the potential of platinum electrodes in oxidising and reducing solutions has been measured; the curves are in all cases approximately straight lines. In ferrous and ferric chloride solutions, pyrogallol, and quinhydrone the potential becomes less noble with increase of pressure and in potassium ferro- and ferri-cyanide solutions more noble. The potential of the quinhydrone electrode becomes more positive with addition of neutral salts, lithium chloride having the most pronounced effect; this effect, however, is relatively small. The potential of palladium feebly charged with hydrogen becomes more noble on keeping owing to diffusion of the surface hydrogen into the body of the metal. The effect of pressure on the current–*E.M.F.* curves of the cells Ni|KOH|Ni, $Hg|H_2SO_4|Pt$, Pb|KOH|Pt, $Pb|H_2SO_4|Pt$, and $Pt|ZnSO_4|Pt$ is shown in a series of curves; in all cases increase of pressure gives a higher *E.M.F.* for the same current.

A. R. Powell.

Electrode potential of single crystals of iron. K. Iwase and K. Miyazaki (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 163—167).—The electrode potential of the (110) face of an iron single crystal was found to be much greater than that of polycrystalline iron. With the latter the *E.M.F.* rises to a maximum and then falls, due to dissolution of the iron and contamination of the surface, whilst with the single crystal a constant value is attained representing the true *E.M.F.* between iron and the solution.

C. J. Smithells.

Change of the potential of metals, and of the colour and resistance of certain gold–silver–copper alloys, on cold rolling. G. Tammann and C. Wilson (Z. anorg. Chem., 1928, **173**, 156—163).—The surfaces of copper, silver, lead, zinc, cadmium, and molybdenum plates become less noble when polished; the effect is reversed on heating. Certain alloys of gold, silver, and copper become noticeably yellower on rolling, but on heating the colour commences to fade from about 200° upwards. At this temperature the electrical resistance also commences to decrease to a minimum, as is the case with the components. The latter, however, then show an increase of resistance until the neighbourhood of the m. p. is attained, whereas the alloys exhibit further smaller minima, which run parallel with changes in the colour of the alloys.

H. F. Gillbe.

Electrolytic reduction potentials of organic compounds. III. Nicotinic acid. M. Shikata and I. Tachi (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 95—96; cf. this vol., 648).—The first stage of the reduction of nicotinic acid consists in the reduction of the carbonyl to the formyl group, and the second stage is the reduction of the pyridine ring. Reduction does not take place in excess of alkali.

Chemical Abstracts.

Mechanism of oxidation–reduction potential. I. Oxidation-reduction potential of cysteine and cystine. E. C. Kendall and D. F. Loewen (Biochem. J., 1928, **22**, 669—682).—Dixon's hypothesis (A., 1927, 209) of a "steady state" depending on a kinetic equilibrium between the dissociation of hydrogen from cysteine and diffusion of hydrogen from the surface of the metal electrode is not supported by experimental evidence. The drift in the reduction potential with a platinum electrode is due to traces of oxygen or other oxidising agents adsorbed on the surface of the metal. The steady potential

given by a gold electrode is due to the failure of the gold to adsorb oxygen. The higher reduction potential with the mercury electrode is shown to be due to the failure of the oxidant to affect the mercury to the same extent as it does platinum and gold. The difference in potential between the gold and mercury electrodes in a solution of cysteine cannot be explained by the higher overvoltage of hydrogen on mercury.

Cysteine on oxidation does not form cystine immediately. An intermediate product which acts as the oxidant is formed. This product exists in a low concentration. In the absence of an activating agent cystine does not affect the platinum electrode and the reduction potential is a function of the logarithm of the concentration of cysteine. In a solution of cysteine and cystine containing an activating agent, cystine is brought into equilibrium with the oxidant and the reduction potential is determined by the ratio C·SH : C·S·S·C groups. S. S. ZILVA.

Reduction potential of cysteine. D. C. HARRISON and J. H. QUASTEL (Biochem. J., 1928, 22, 683—688).—Metal-free cysteine gives at a gold electrode a high negative reduction potential which is not increased by the addition of traces of catalysts such as ferric or cupric ions. This is contrary to the result which would be expected on Dixon's hypothesis (A., 1927, 209) of the mechanism by which the reduction potential of cysteine is secured at the electrode. S. S. ZILVA.

Photochemical cell containing potassium ferrocyanide solution. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, Suppl., 11—13).—A cell containing potassium ferrocyanide solution and having platinum electrodes in the two compartments, which are separated, although not completely, by a porcelain diaphragm, yields at a time t after commencement of illumination of one of the compartments a *P.D.* $\pi=\lambda(1-e^{-0\cdot8kt})$, whilst on discontinuing the illumination $\pi=\lambda(1-\gamma t)/(1+\delta\sqrt{t})$, where λ is the equilibrium potential, and γ, δ, and k are constants. The *E.M.F.* is due to displacement to the right of the equilibrium $[Fe(CN)_6]'''' + 2H_2O \rightleftharpoons [Fe(CN)_5H_2O]''' + OH' + HCN$ (cf. A., 1927, 1157). The displacement is dependent only on the light intensity, and does not obey the law of mass action. The photochemical effect is greatest at 440—450 $\mu\mu$. H. F. GILLBE.

Photochemical cells with complex cyanides of nickel or platinum. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, Suppl., 14—15; cf. preceding abstract).—A cell containing potassium nickelocyanide or platinocyanide yields an *E.M.F.* expressed by $\pi=\lambda(1-e^{-kt})$ during illumination and when the illumination is stopped. The *E.M.F.* may be due to the temporary formation of some kind of concentration cell by a change of complex dissociation or by polymerisation of complex ions or molecules. H. F. GILLBE.

Electrochemical behaviour of silicate glasses. V. Electrical properties of the anode layers. J. B. FERGUSON, M. J. MULLIGAN, and J. W. REBBECK (J. Physical Chem., 1928, 32, 1018—1030; cf. this vol., 713).—The electrical properties of various glasses with anode layers have been investigated at temperatures up to 100°. Electrolysis of a sample of glass with a sparingly soluble anode material such as mercury shows a decrease in current as electrolysis proceeds, due to a counter *E.M.F.* set up and to an increase in true resistance of the sample itself. At low voltages, the counter *E.M.F.* may nearly equal the voltage applied, but at high voltages it tends to a constant value, and the minimum voltage required in this case increases as electrolysis proceeds. The resistance of a mercury anode glass layer is many times greater than that of the original glass and changes with temperature according to the rule of Rasch and Hinricksen (A., 1908, ii, 149). With soluble anode materials, the current shows little change during electrolysis when the applied *P.D.* is constant. The smaller counter *E.M.F.* of constant value obtained under such conditions are chemical in origin. The electrical effects which accompany current reversal are described for silicate glasses with mercury-containing anode layers. Hopkinson's experiment on residual charge (Phil. Trans., 1877, 167, 599) has been repeated under new conditions. L. S. THEOBALD.

Reactions of lead in the lead accumulator. W. SMITH (Z. Elektrochem., 1928, 34, 362—363).—Investigations have been made with a cell consisting of a plate of radioactive lead (negative) and one of inactive lead (positive) immersed in 30% sulphuric acid. During the usual charge and discharge processes inactive lead is transferred to the positive plate. The same result is obtained when a stream of inert gas is bubbled through the cell on open circuit, the electrolyte having previously been saturated with inactive lead sulphate. The effect is ascribed to interchange between surface lead atoms and lead ions in the electrolyte, and the occurrence of this phenomenon has been demonstrated by other methods. The quantity of lead thus exchanged appears to be proportional to the concentration of lead in the electrolyte, independent of the direction of the current flow, and greater at the lead plate than at the lead dioxide plate. H. F. GILLBE.

Overpotentials produced by films of hydrogen less than one molecule thick. A. L. McAULAY and D. P. MELLOR (Nature, 1928, 122, 170—171).—With a mercury cathode, *N*-sulphuric acid as electrolyte, and currents of the order of 1 micro-amp./cm.^{2}, overpotentials of 0·3—0·4 volt were produced when less than one eighth of a unimolecular layer of hydrogen had been deposited. Complete elimination of oxygen was essential. A. A. ELDRIDGE.

Metal overvoltage measurements with the cathode-ray oscillograph. E. NEWBERY (Proc. Roy. Soc., 1928, A, 119, 680—686; cf. J.C.S., 1917, 111, 470).—The author's previous work on metal overvoltages, carried out with the aid of a rotating commutator, has been checked by measurements with the cathode-ray oscillograph. The apparatus was identical with that previously described with the exception of the electrode vessel, which was re-designed. The type of cell formerly used was found to give erroneous values for transfer resistance, although the values for overvoltage were correct. The electrodes used were copper, silver, zinc, cadmium,

mercury, lead, iron, nickel, and cobalt, and the electrolytes were *N*-solutions of the corresponding metallic sulphates (for iron, ferrous and ferric sulphates), except in the case of silver, lead, and mercury, where the nitrates were used. The results show that overvoltage and transfer resistance do not occur unless a gas is being liberated at the electrode. Hydrogen is always deposited along with the metals of the iron group when these are separated electrolytically from pure solutions of their respective salts, and this gives rise to hydrogen overvoltage at the cathode. The reason for the retarded deposition of the metals of the iron group is discussed, and it is shown that the hydrated ion theory, previously suggested by the author, accounts for the observed facts. Glasstone's hypothesis, that the metals are primarily deposited in a metastable form which has a different electronic arrangement from the ordinary form, appears to be very improbable.

L. L. BIRCUMSHAW.

Disperso-electricity. H. G. BOS (Chem. Weekblad, 1928, **25**, 259—263; cf. *ibid.*, 45, 66).—The factors which determine the maximum dispersion potential (dispersel Δ) are considered theoretically, and are the primary effect, q_I, the specific secondary effect, k, the partial tertiary effect, L, as well as the conductivity of the gases, capacity of the apparatus, etc. When q_I is nil, the value of the dispersel Δ reaches vanishing point with an earthed vessel whatever the values of the other factors; it is thus possible to remove risk of fire when spraying inflammable fluids in those cases in which admixture of another material will reduce the value q_I to zero.

S. I. LEVY.

Homogeneous gas reactions. II. Introduction of quantum theory. L. S. KASSEL (J. Physical Chem., 1928, **32**, 1065—1079).—Theoretical. The theory of unimolecular reactions previously advanced (this vol., 372) is extended by the introduction of quantised degrees of freedom, and the case of quantum oscillators of a single frequency, and that of two frequencies the quotient of which is an integer, are developed. When applied to the decomposition of nitrogen pentoxide, the theory accounts for the rate of this reaction at moderate pressures, but not so satisfactorily for the rate at the lowest pressures investigated. It is also applied to the decomposition of azomethane.

L. S. THEOBALD.

Homogeneous reaction between hydrogen and oxygen. C. H. GIBSON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1928, **A**, **119**, 591—606; cf. this vol., 483).—The kinetics of the reaction between oxygen and hydrogen have been investigated between 500° and 600°, porcelain reaction vessels being substituted for silica. The results confirm those previously obtained. Above 500°, a homogeneous reaction of high and variable order comes into prominence; the temperature coefficient is high, and at high temperatures and pressures the reaction is retarded by increasing the surface exposed to the gases. The rate is approximately proportional to the cube of the hydrogen concentration and to a power of the oxygen concentration which is greater than unity. Steam, argon, nitrogen, and helium accelerate the reaction markedly, the effect of the inert gas being nearly the same at all stages of the reaction and, for pressures up to 400 mm., increasing linearly with its concentration. The accelerating influence is roughly in the order 5 : 4 : 3 : 1. The results are interpreted by assuming that reaction chains are propagated through the gas. The chains are broken by deactivation of molecules in a heterogeneous reaction at the walls of the vessel, and lengthened by the presence of the inert gases, which increase the time during which any molecule in the gas phase escapes contact with the walls. The order of effectiveness of the inert gases can be correlated with the diffusion coefficients. Oxygen and hydrogen may exert an " inert gas effect " in addition to their normal mass action effects as participants in the reaction. Consideration of this throws some light on the nature of the reaction chains, and a working hypothesis of the mechanism of the reaction is constructed. The conditions affecting the transfer of internal energy from one molecule to another in collisions are discussed.

L. L. BIRCUMSHAW.

Combustion of hydrocarbons; hydroxylation and/or peroxidation. W. A. BONE (Nature, 1928, **122**, 203—204).—It is considered that normally and chiefly the combustion process is one of hydroxylation and not peroxidation, although the latter mechanism is not excluded. The evidence supporting this view is summarised.

A. A. ELDRIDGE.

[Combustion of hydrocarbons.] A. EGERTON (Nature, 1928, **122**, 204).—The behaviour of anti-knocks and pro-knocks is more easily understood if the first step in the combustion process is assumed to be the temporary formation of a peroxide. Such a process does not necessarily involve dissociation of oxygen molecules.

A. A. ELDRIDGE.

Propagation of flame in mixtures of natural gas and air. H. F. COWARD and H. P. GREENWALD (U.S. Bureau of Mines Tech. Paper, No. 427, 28 pp.; cf. A., 1927, 834).—The differences in properties of methane–air and natural gas–air mixtures with regard to the initiation and propagation of flame and the limits of inflammability have been investigated. The natural gas was composed of paraffin hydrocarbons, chiefly methane, with not more than 3% of nitrogen. Since certain properties, *e.g.*, limits of inflammability, follow the mixture rule, allowance can be made for the variations in composition which natural gas may show. Natural gas ignites somewhat more readily than methane, whether ignited by the hot walls of a quartz tube, a nickel bar, or an electric spark. With quartz, the ignition temperature is 15—55° lower, according to the proportion of inflammable gas present, and the time lag of ignition in the natural gas and air is shorter. With a nickel bar as the source of ignition, the ignition temperature is 30° lower throughout the whole range than that of methane, but 400—500° higher than in a quartz tube. A weaker electric spark is required to ignite natural gas and the percentage of natural gas in the most sensitive mixture (7·3—8·6%) is less than that required with methane. The limits of inflammability of natural gas in air are slightly less than those for methane. The maximum speed of uniform movement

of flame for natural gas in air is greater than that for methane and less natural gas is required. Details are given of experiments in a tube 100×1 ft. to determine the speeds of uniform movement of flame in natural gas, methane, ethane, propane, and butane separately. The results for methane confirm those obtained by Mason and Wheeler (J.C.S., 1917, **111**, 1050) except for a difference in speed of 9 cm./sec. near the lower limit of inflammability.

L. S. THEOBALD.

Effect of alkali-metal compounds on combustion. C. A. THOMAS and C. A. HOCHWALT.—See B., 1928, 556.

Explosions not generally guarded against. W. P. JORISSEN (Chem. Weekblad, 1928, **25**, 228—230).—The explosion limits for mixtures of air and ammonia, with and without small proportions of inflammable gases, and of other mixtures not generally recognised as explosive, have been determined under various conditions. Dichloroethylene has definite and fairly wide explosion limits with air. Trichloroethylene is non-explosive in air, but lowers the explosion limits of combustible gases.

S. I. LEVY.

Rate of decomposition of nitrogen pentoxide at very low pressures. A. G. LOOMIS and D. F. SMITH (J. Amer. Chem. Soc., 1928, **50**, 1864—1869). —Objections are raised to the method of Hirst and Rideal (A., 1926, 32); the experiments were repeated at 30° in an improved apparatus. The results show that at very low pressures adsorption and occlusion effects involve a large fraction of the gas present; the sudden increase in velocity at these pressures observed by Hirst and Rideal is probably non-existent (cf. Hibben, A., 1927, 948). All previously published information on this decomposition rate is considered to be questionable. S. K. TWEEDY.

Active nitrogen. V. Decay of the nitrogen afterglow. E. J. B. WILLEY (J.C.S., 1928, 1620—1629; cf. A., 1926, 893; 1927, 431, 1038).—Photometric studies of the decay of the nitrogen afterglow indicated that the process is bimolecular with respect to the glow-producing system between the pressures of 2 and 8 mm., a result which agrees with the statements of Angerer (A., 1921, ii, 257) and Bonhoeffer and Kaminsky (A., 1927, 801). Kinetically, however, the reaction is of the fifth order, and it is suggested that this is due to the occurrence of an initial termolecular reaction, $2N+N_2=N_2^A+N_2^B$, followed by two rapid bimolecular reactions, $N_2+N_2^A=N_2^C+N_2^D$ and $N_2+N_2^B=N_2^E+N_2^F$. F. J. WILKINS.

Velocity of thermal decomposition of malonic acid. J. LASKIN (Trans. Siberian Acad. Agric. Forestry, 1926, **6**, No. 1, 7 pp.; Chem. Zentr., 1928, i, 1254).—The thermal decomposition of malonic acid is unimolecular; the velocity coefficient at 138° is 0·021. A. A. ELDRIDGE.

Velocity coefficient for bimolecular reactions in solution. D. H. PEACOCK (Nature, 1928, **122**, 131—132; cf. Kassel, this vol., 598).—If activated molecules of solute are deactivated by collision with solvent molecules, the latter may acquire a higher velocity, or be themselves activated, or radiation may be emitted. The consequences of these postulates are discussed. The number of activated molecules present may not be given by the usual expression $e^{-E/RT}$ for complex organic substances; "electron tautomerism," with the activated and ordinary forms in equilibrium, may prevail. The velocity of reaction would then depend on the life of the activated molecules. Conditions in a solution are favourable to the stabilisation of such "tautomerides." A. A. ELDRIDGE.

Reactions in liquid hydrogen sulphide. IV. Thiohydrolysis of esters. A. W. RALSTON and J. A. WILKINSON (J. Amer. Chem. Soc., 1928, **50**, 2160—2162).—The following esters of thioacetic acid were prepared by Obermeyer's method (A., 1888, 124): methyl; ethyl, b. p. 115—116°; propyl; *iso*propyl, b. p. 122—123°; n-*butyl*, b. p. 134—135°; *phenyl*, b. p. 110—111° (8 mm.). These esters are thiohydrolysed in liquid hydrogen sulphide into free acid and mercaptan; the degree of hydrolysis, determined by conductivity measurements, increases with the mol. wt. of the ester, and even at −77° is several times the value for the hydrolysis of the analogous oxygen esters in water at the ordinary temperature.

S. K. TWEEDY.

Velocity of decomposition of tribromoacetic acid in water. O. DE GROOTE (Bull. Soc. chim. Belg., 1928, **37**, 225—239).—The velocity of decomposition of tribromoacetic acid in water has been measured by following the rate of evolution of carbon dioxide, the decrease of acidity, and the variation of the conductivity of the solution. The decomposition occurs through the intermediate formation of the tribromoacetate ion. The velocity is independent, at least in dilute solution, of the concentration of hydrogen ion. F. J. WILKINS.

Alkaline hydrolysis of esters in aqueous-alcoholic solution. II. Interaction of phenoxides and aliphatic esters. E. S. GYNGELL (J.C.S., 1928, 1784—1785; cf. A., 1926, 1134; Smith, A., 1927, 213).—The expression deduced earlier for the rate of alkaline hydrolysis of esters in aqueous-alcoholic solution has been applied with satisfactory results to a series of aliphatic esters. In all cases, except for the esters of oxalic acid, the reaction proceeded as a result of the hydrolysis of the phenoxide.

F. J. WILKINS.

Velocity of esterification of nitrobenzoic acids in ethylene glycol and of naphthoic acids in glycerol. A. KAILAN and E. KRAKAUER (Monatsh., 1928, **49**, 347—384).—The velocities of esterification of the nitrobenzoic acids in ethylene glycol and of the naphthoic acids in glycerol, each in presence of water and catalysed by hydrogen chloride, were measured at 25°, and the coefficients are expressed as empirical functions of the concentrations of water (w) and of hydrogen chloride (c). The coefficients increase proportionally to c in glycerol and glycol containing little water and in glycerol containing more water, but more rapidly in ethylene glycol containing more water (cf. Kailan and Melkus, A., 1927, 749). Combining new with earlier results (cf. Kailan and Lipkin, A., 1927, 1148), the ratios of the coefficients for benzoic acid to those for *o*-, *m*-,

and *p*-nitrobenzoic acids at $c=1/6$ and $w=0{\cdot}065$, are, in alcohol, 1 : 0·054 : 0·57 : 0·70 : 0·39 : 1·00; in glycol, 1 : 0·038 : 0·69 : 0·79 : — : —; in glycerol, 1 : 0·068 : 0·63 : 0·80 : 0·61 : 0·93. The steric hindrance of the *o*-nitro-group is thus less in glycerol and greater in ethylene glycol than in alcohol, causing more rapid esterification in glycerol than in glycol. At small values of *c* the velocities are less in glycerol than in alcohol, but at higher values greater, owing to the greater retarding action of water on the alcoholic solution. The esterifications are all practically complete: the reverse reaction is thus inconsiderable.

The velocities of chlorohydrin formation in absence and in presence of the acids (cf. Kailan and Goitein, A., 1927, 1187) are determined, and employed to correct the values from which the velocities of esterification are calculated.

At 183° the naphthoic acids are esterified in glycerol, without mineral acid, and give "sesquimolecular coefficients which are about 20% less in presence of 2 g.-mols. of water per litre than when anhydrous glycerol is used. In the latter, the ratios of $k_{1\cdot5}$ for benzoic and α- and β-naphthoic acids are 1 : 0·109 : 0·090, showing that benzoic acid must be more strongly dissociated than even α-naphthoic acid (on the assumption that the esterification is catalysed by hydrogen ions).

The following solubilities are given (at 25°, in g.-mols./litre of anhydrous solvent): *p*-nitrobenzoic acid in glycol, 0·08; α- and β-naphthoic acids in glycerol, 0·0175 and 0·0190, respectively.

E. W. Wignall.

Velocity of esterification of monoaminobenzoic acids and of pyridine-1- and 2-carboxylic acids in glycol and in glycerol. A. Kailan and Y. M. Diab (Monatsh., 1928, 49, 316—346; cf. Kailan and Lipkin, A., 1927, 1148).—The velocity of esterification at 25° of *o*-, *m*-, and *p*-aminobenzoic acids and of pyridine-1- and -2-carboxylic acids in anhydrous and moist ethylene glycol and in anhydrous glycerol in presence of hydrogen chloride as catalyst has been measured; the measurements were extended to moist glycerol for *m*- and *p*-aminobenzoic acids and for nicotinic acid. The relationship between the unimolecular velocity coefficients, the water content (*w*) of the medium, and the excess of the concentration of hydrochloric acid over that of the organic acid or that of the ester (C') is expressed by an empirical formula for the three last-named acids. Chlorohydrin formation must be taken into account in all cases for the anhydrous media and this coefficient has the value $4{\cdot}5—6{\cdot}0\times10^{-5}$. The velocity coefficients increase more rapidly in anhydrous and moist glycol and in glycerol than both the concentration of the total and of the "free" hydrogen chloride.

The velocities in glycol and in glycerol are compared with those in ethyl alcohol (Kailan, A., 1907, ii, 242). The effect of water is practically the same in glycol and in glycerol, but is less than in ethyl alcohol. The steric effect of the amino-group in the *ortho*-position is greater in glycol and less in glycerol than in ethyl alcohol. Under comparable conditions the velocity coefficients of nicotinic and picolinic acids are approximately 4 : 1 in glycol and glycerol and approximately 2 : 1 in ethyl alcohol. The differences between the velocity of esterification of benzoic acid and of the three aminobenzoic acids are practically the same in ethyl alcohol, glycol, and glycerol. Thus for $C'=1/3$ and $w=0{\cdot}03$ the ratios of the velocity coefficients of benzoic acid and *o*-, *m*-, and *p*-aminobenzoic acids are in ethyl alcohol 1 : 0·013 : 0·66 : 0·70, in ethylene glycol 1 : 0·010 : 0·67 : 0·82, and in glycerol 1 : 0·015 : 0·66 : 0·91.

I. Vogel.

Kinetic salt effect. I. Reaction between sodium monochloroacetate and sodium thiosulphate. A. N. Kappanna (J. Indian Chem. Soc., 1928, 5, 293—298).—The reaction between sodium thiosulphate and sodium monochloroacetate has been studied at 50°, 60°, and 70°. A satisfactory bimolecular velocity coefficient is obtained, which, in accord with Bronsted's theory of ionic reactions, increases as the total ionic concentration increases. The temperature coefficient is 2 in the neighbourhood of 60°. The coefficient which measures the ionic effect is practically independent of the temperature between 50° and 70°, but decreases rapidly between 25° and 50°. Alkali chlorides, sulphates, and nitrates increase the velocity coefficient, the ionic effect increasing in the order lithium, sodium, ammonium, potassium, and sulphate, nitrate, chloride.

H. F. Gillbe.

Water concentration and the rate of hydrolysis of sucrose by invertase. J. M. Nelson and M. P. Schubert (J. Amer. Chem. Soc., 1928, 50, 2188—2193).—Hydrolysis measurements on aqueous-alcoholic solutions of sucrose containing invertase indicate that the water concentration is the primary factor influencing the velocity of hydrolysis, the alcohol and sucrose concentrations being of minor significance when the sucrose concentration exceeds 20%. The affinity constant of invertase for sucrose, as measured by the method of Michaelis and Menten (A., 1913, i, 540), is inaccurate, the disturbing factor possibly being the change in water concentration.

S. K. Tweedy.

***ortho*-Effect and reactivity. I. Magnitude and cause of the *ortho*-effect in the hydrolysis of aromatic esters.** K. Kindler [with K. G. Ellinger] (Annalen, 1928, 464, 278—292).—The total effect of a radical R in the *ortho*-position with respect to carbethoxyl in a benzene nucleus is a summation of two effects: (1) the influence of R on the strength of attachment of the whole aryl grouping to the carbethoxyl group, shown in previous papers to determine the rate of hydrolysis of the ester (A., 1927, 55, 338), and (2) the direct influence of R as a centre of unsaturation on the carbonyl group. It is possible to determine the second, or "*ortho*"-effect as follows: The *ortho*-effect is negligible in esters of the type $R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Et$. The strength of attachment (*a*) of phenyl, that (*b*) of $R{\cdot}C_6H_4{\cdot}$, that (*a'*) of styryl, and that (*b'*) of $R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}$ are found to be connected by the equation

a' : *b'*. By determining the rates of hydrolysis of a series of *o*-substituted benzoic and cinnamic esters it is thus possible to calculate (*b*), and so determine the direct *ortho*-effect. For R=F, Cl, Br, I, and NO_2, the relative strengths of attachment of $R{\cdot}C_6H_4{\cdot}$ to the carbethoxyl group are given by the figures

18·2, 25·2, 10·6, 15·8, and 1·91, respectively, the relative *ortho*-effects of R being given by the figures 1, 2, 5, 7·5, and 11, respectively. These last figures assume more importance when expressed on the basis of Cl=35·5, when they become 17·8, 35·5, 88·8, and 133 for the four halogens.

New experimental work includes the measurement of the velocity coefficients for the alkaline hydrolysis of the following esters: ethyl *o*- and *p*-fluoro-, *o*-chloro-, *o*-bromo-, *o*-iodo-, and *o*-nitro-benzoates; *ethyl* o-*fluorocinnamate* (b. p. 140—141°/11 mm.; o-*fluorocinnamic acid* has m. p. 175°, corr.), *ethyl* p-*fluorocinnamate*, m. p. 30—32°, b. p. 135—140°/11 mm. (*p*-fluorocinnamic acid has m. p. 208°, corr.), ethyl *o*- and *p*-bromo-, *o*- and *p*-iodo-, and *m*-amino-cinnamates.

The cause of the *ortho*-effect is discussed. It is not steric in origin and is attributed to the unsaturated nature of the group in question. The strongly unsaturated nitro-group has a particular large *ortho*-effect. E. E. TURNER.

Carbon dioxide cleavage from acetonedicarboxylic acid. E. O. WIIG (J. Physical Chem., 1928, **32**, 961—981).—The decomposition of acetonedicarboxylic acid in various solvents alone and with catalysts has been investigated between 0° and 60°. The reaction obeys the unimolecular law, is practically independent of the nature of the walls of the reaction vessel, and is not autocatalysed by acetone, a product of the decomposition. The reaction rates in water, aniline, and various alcohols permit no relationship to be expressed between velocity of reaction and specific properties of the solvent. The curve obtained by plotting k against mol. fractions for mixtures of *iso*propyl alcohol and water is symmetrical about a maximum value of k at equimolecular composition. Small amounts of water catalyse the decomposition in the alcohol and *vice versa*. With water as solvent, the decomposition is catalysed by various nitrogen bases, especially aniline, and in both water and *iso*propyl alcohol, the efficient catalysts all contain the amino-group, but no relation between catalytic activity and the strength of the base could be detected. Contrary to the demands of Taylor's theory of negative catalysis, ethyl bromide increases the rate of reaction in aniline, the velocity coefficient rising to a maximum and then decreasing as the concentration of ethyl bromide increases. Increasing concentration of hydrochloric acid decreases the rate of decomposition in water at 50° to a constant value. Neutral salts such as potassium bromide, sodium nitrate, and sodium chloride have no effect, sodium sulphate produces a slight acceleration, and salts which hydrolyse to give an alkaline reaction increase the reaction rate. Gelatin and egg-albumin, but not starch, have an accelerating effect. The temperature coefficients in the various solvents have been determined. They decrease as temperature increases and with addition of a catalyst. The critical increments vary but slightly with temperature for a given solvent, but are different with the various solvents and also with the catalysts. A mechanism of the reaction, postulating the formation an unstable intermediate compound of the formula $(CH_2\cdot CO_2H)_2CO\cdot X$, where X is the catalyst, is discussed, together with explanations of the observed decrease in percentage decomposition with a fall in temperature. L. S. THEOBALD.

Synthesis of ammonia by the electric discharge in the presence of mercury. A. J. A. VAN DER WYK (J. Chim. phys., 1928, **25**, 251—289).—An apparatus is described for measuring the rate of formation of ammonia from its elements under the action of a silent electric discharge in presence of mercury, which acts as one of the electrodes. The influence of the area of the mercury surface, the rate of flow of the gases, the composition of the gaseous mixture, and the presence of oxygen in the gases has been studied. In any series of experiments with the same gaseous mixture the initial velocity of the reaction depends on the gaseous mixture employed in the previous series, but finally becomes constant and characteristic of the series. It is concluded that the reaction is heterogeneous and that there is intermediate formation of a hydride of mercury which is decomposed by the nitrogen. The formation and properties of this hydride are discussed. The reaction is unimolecular with respect to hydrogen and atomic with respect to nitrogen. The optimum reaction velocity is reached when the composition of the reactants is $2H_2{:}N_2$. W. A. RICHARDSON.

Oxidation of ferrous hydroxide in sodium hydroxide solution by means of air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 137—141).—A current of air was drawn through a suspension of ferrous hydroxide in sodium hydroxide solution and the quantity of ferric hydroxide determined by dissolving in acid and titrating with permanganate. The reaction velocity coefficient k is independent of the quantity of ferrous hydroxide present and its value is identical with that for the oxidation of sodium sulphite and stannous hydroxide in alkaline solution. The value of k is only slightly affected by temperature, but decreases with increasing concentration of sodium hydroxide, since the velocity is probably determined by the speed of dissolution of oxygen, which is decreased by the sodium hydroxide. S. J. GREGG.

Relationship between the velocity of deposition of radium-*F* and the condition of the precipitating metal. G. TAMMANN and C. WILSON (Z. anorg. Chem., 1928, **173**, 137—155).—Copper and nickel precipitate all radium-*F* atoms which come into contact with their surfaces, whereas with silver and soft iron the precipitation is incomplete. The precipitation velocity is greater for the hard form of a metal than for the soft, and whilst for the base metals it is proportional to the concentration of the radium-*F*, for noble metals it is approximately proportional to the square root of the concentration. Gold, palladium, and platinum, and the copper–silver and silver–gold alloys, adsorb radium-*F* to double the extent when hard than when soft. Radium-*F* is precipitated by active chromium, but to only a slight extent by the passive metal; the same is true of alloys of chromium with ferromagnetic metals. H. F. GILLBE.

Dissolution and hydration velocities of kieserite. B. UEBLER (Mitt. Kali-Forschungs-

Anst., 1927, 45—69; Chem. Zentr., 1928, i, 736—737).—The velocity of dissolution of a particular specimen of kieserite is increased by diminution of grain size only down to the natural fineness. Generally, kieserite dissolves the more rapidly the purer it is; anhydrite, however, has no marked effect. The dissolution velocity in a solution unsaturated with respect to magnesium sulphate increases with rise of temperature; the hydration velocity in a solution saturated with respect to magnesium sulphate becomes maximal at about 40°, and then falls to zero at 68°. In connexion with the effect on the velocity of dissolution of the presence of various salts in the solvent, three groups are differentiated: (*a*) dilute solutions of alkali chlorides and sulphates, in which the velocity is greater than in water, (*b*) concentrated solutions of alkali chlorides and sulphates, magnesium chloride, and saturated magnesium sulphate solutions, in which the velocity is smaller than in water, (*c*) equilibrium solutions and concentrated magnesium chloride solutions, in which the velocity is smaller than the velocity of hydration in saturated magnesium sulphate solution. For the evaluation of a kieserite (*a*) the apportionment between various grades of fineness, and (*b*) the content of impurities (particularly sludge-forming) are important. In four cases grinding increased the dissolution velocity by 20—400%. The technical significance of the results is discussed.

A. A. ELDRIDGE.

Decomposition of clays. L. WASILEWSKI (Przemysł Chem., 1928, **12**, 40—48).—The velocity of evolution of ammonia from a mixture of kaolin and ammonium sulphate rises up to a temperature of 360°, after which it drops sharply almost to zero; at this point, the mixture still contains about 3·7% of ammonia, and its aqueous extract contains almost exclusively ammonium alum. At 430° the velocity of evolution of ammonia again rises; this velocity is variable, depending on the quantity of impurities, particularly iron, present, and does not correspond with the decomposition temperature of pure ammonium alum or its mixture with alumina. Thus, using clays containing 0·5% Fe_2O_3, the mixture still contains ammonia after being heated at 450° for 10 hrs., whilst where 7% of ferric oxide is present the elimination of ammonia is complete within 4 hrs. Pure ammonium alum retains its ammonia even more tenaciously, a considerable portion remaining even after heating at 550°. If the clay–ammonium sulphate mixture be heated at 350—370°, about 0·5% of the ammonia present is oxidised, and the product still contains about 3·7% of ammonia, which is evolved at 450°, at which temperature, however, about 9% of the ammonia is oxidised to nitric acid.

R. TRUSZKOWSKI.

Silver-ion catalysis of persulphate oxidations. III. Oxidation of ammonium ion. IV. Oxidation of oxalate ion. C. V. KING (J. Amer. Chem. Soc., 1928, **50**, 2080—2088, 2089—2099; cf. this vol., 27).—III. The reaction $NH_4^{\cdot}+4S_2O_8''+3H_2O \longrightarrow 10H^{\cdot}+8SO_4''+NO_3'$ in presence of silver ions was followed by conductivity measurements. The velocity curves are not strictly reproducible and are autocatalytic in character, indicating that, contrary to previous belief, the second reaction $4Ag^{\cdot\cdot\cdot}+NH_4^{\cdot}+3H_2O \longrightarrow 4Ag^{\cdot}+NO_3'+10H^{\cdot}$ is not immeasurably rapid. A velocity equation cannot be set up in terms suitable for experimental confirmation. Irregularities in the velocity curves of other reactions may be due to slight autocatalytic effects, especially in the case of sucrose inversion, which may proceed according to the equations: $C_{12}H_{22}O_{11},nH_2O+H^{\cdot} \longrightarrow C_{12}H_{22}O_{11},nH_2O,H^{\cdot}$; $C_{12}H_{22}O_{11},nH_2O,H^{\cdot} \longrightarrow$ invert sugar $+H^{\cdot}$. If the second reaction is slow enough the velocity curve will be slightly autocatalytic in character, owing to the accumulation of the intermediate compound (cf. Pennycuick, A., 1926, 249); if it is "instantaneous" the reaction will appear unimolecular.

IV. The oxidation of oxalate ion in dilute solution by persulphate ion, which proceeds very slowly in the absence of a catalyst, was followed in the presence of the silver ion by measurement of the rate of evolution of carbon dioxide. The catalysed reaction is much faster than the analogous oxidation of ammonia, ammonium ion, and chromium ion. Duplication of the results is very difficult to attain. The glass walls of the reaction vessel exert some catalytic effect. Some of the velocity curves are autocatalytic in character, indicating that whilst an intermediate compound sometimes accumulates, at other times it decomposes with a speed comparable with its rate of formation. Livingston suggests that the persulphate and silver ions form a relatively inactive complex which can oxidise only fairly powerful reducing agents (*e.g.*, oxalate ion, but not ammonium or chromium ions), from which a more active silver ion, $Ag^{\cdot\cdot\cdot}$ or $AgO^{\cdot}$, is formed, capable of oxidising weaker reducing agents. A series of simultaneous and consecutive reactions can then be formulated which will account for all the persulphate oxidations. Other mechanisms are suggested.

S. K. TWEEDY.

Landolt's reaction. V. Catalytic influence of sodium thiosulphate on the Dushman reaction. W. ROMAN-LEVINSON (Z. Elektrochem., 1928, **34**, 333—350).—The catalytic influence is measured in terms of the percentage increase G of the reaction velocity, defined by $G=100(T_S/T_{St}-1)$, where T_S is the time of reaction without thiosulphate and T_{St} the time with thiosulphate. G is scarcely influenced by the iodide-, iodate-, or sulphite-ion concentrations, but varies with the hydrogen-ion concentration. Four reactions are recognised: the ordinary Dushman reaction, $IO_3'+5I'+6H^{\cdot}=3I_2+3H_2O$; the Dushman S-reaction, in which sulphite is present; the Dushman T-reaction, in presence of thiosulphate; and the Dushman S-T-reaction, which is the S-reaction catalysed by thiosulphate. If the concentration of thiosulphate be small compared with that of sulphite the time of reaction falls with increase of thiosulphate concentration and reaches a minimum when the two concentrations become of similar magnitude; from this point it is the T-reaction which must be considered, the reaction velocity increasing with increase of thiosulphate concentration. The calculated velocity coefficients K' and K'' of the S-T- and T-reactions are $1·86\times10^{15}$ and $1·45\times10^{10}$, respectively. The mechanisms of the reactions are discussed.

H. F. GILLBE.

Mechanism of oxidation processes. XIV. Activation of oxygen by iron. H. WIELAND and W. FRANKE (Annalen, 1928, **464**, 101—226).—The autoxidation of solutions of ferrous salts has been studied using sodium acetate and acetic acid as a buffer. Absorption of oxygen follows the unimolecular law. The temperature coefficient of the process is normal, whilst a change from p_H 5 to 7 accelerates the reaction 4- or 5-fold. At p_H 5, neutral salts have little effect on the rate of autoxidation, although sodium sulphate, possibly owing to its producing complex salts, causes diminution of the reaction velocity to half its previous value.

The rate of autoxidation of slightly hydrated ferrous chloride is greater in acetone than in ethyl alcohol or *iso*propyl alcohol, greater in these solvents than in methyl alcohol, and least in water.

The autoxidation of a number of acids in presence of iron salts has been studied. In general, ferrous sulphate is the added iron salt and an acetate buffer is used. Formic acid: Autoxidation of the ferrous salt induces autoxidation of formate, the latter ceasing when no more ferrous salt remains, since ferric iron does not oxidise formic acid. Lactic acid: Autoxidation of the lactate is more rapid than that of the formate, about one third of the oxygen absorbed by the system during the complete oxidation of the iron being used to oxidise the lactate to carbon dioxide, acetaldehyde, and (some) pyruvic acid. Autoxidation is most rapid at p_H 8·0, and is slower in air than in pure oxygen. Pyruvic acid: This case is very similar to that of lactic acid; in neither case does ferric iron oxidise the acid. Tartaric (or racemic) acid: This autoxidation is investigated very fully. Small changes in conditions very greatly affect the progress of the reaction. Ferric salts do not initiate autoxidation of tartaric acid, but play a considerable part in the autoxidation of tartaric acid in presence of ferrous salts, since the dihydroxymaleic acid formed is oxidised by ferric, producing ferrous salts. The autoxidation proceeds much further in acid than in neutral solution, and has a normal temperature coefficient up to 20°. At 30°, however, the process is not appreciably quicker than at 20°. To some extent, the process is catalytic in nature, owing to the reduction of ferric salt by the dihydroxymaleic acid formed. The last acid acts as a strong positive catalyst for a similar reason. The autoxidation process is greatly accelerated by sodium sulphate and somewhat accelerated by sodium nitrate or by cupric sulphate, whilst sodium chloride, bromide, and iodide act as strong decelerants. *p*-Benzoquinone also has a decelerating influence. Increased pressure of oxygen accelerates autoxidation, but the total amount of oxygen used is less than is the case with lower pressures (cf. Annalen, 1927, **457**, 20).

Dihydroxymaleic acid: Owing to the sparing solubility of the sodium and potassium salts of this acid, buffering is best effected using acetic acid and lithium acetate. The spontaneous decomposition of a buffered (p_H 4·8) solution of the acid (nitrogen atmosphere) is markedly accelerated by ferrous salts. Substitution of phthalate for acetate as buffer has only a slight effect. Phosphate produces marked deceleration, and addition of pyrophosphate in addition further decelerates the velocity of autoxidation (cf. Warburg, A., 1915, i, 337). Buffering with glycine causes acceleration. At p_H 1·4 and 13, autoxidation is markedly slower than at intermediate acidities, p_H 5 being the optimum condition for the process. The spontaneous autoxidation of dihydroxymaleic acid in absence of iron proceeds more rapidly in alkaline than in acid solution. The main reaction here involved is: $CO_2H{\cdot}C(OH){:}C(OH){\cdot}CO_2H \xrightarrow{1O_2} CO_2H{\cdot}CO{\cdot}CO{\cdot}CO_2H$, not that taking place as in Fenton's experiments (giving glycollaldehyde, carbon dioxide, and water), which occurs in acid solution in presence of ferric salts. Ferric salts oxidise dihydroxymaleic acid (p_H 5, lithium acetate and acetic acid) to diketosuccinic acid, which during the autoxidation process gives oxalic (1/3) and mesoxalic acid (2/3), the latter slowly giving oxalic acid.

Glyceric acid: This case is similar to that of tartaric acid. Added ferrous salt produces an effect roughly proportional to its concentration. Thioglycollic acid: Copper salts are in general more positively catalytic of the autoxidation of this acid than are those of iron, but the latter become the more effective in the neighbourhood of the neutral point. Sulphuric acid is a product of autoxidation, which is decelerated by cyanides.

Quinol: The oxidation of this substance by ferric salts renders the autoxidation of quinol in presence of ferrous salts similar to that of dihydroxymaleic acid. The velocity of change depends very largely on p_H. Near the neutral point, ferrous salts reduce *p*-benzoquinone, so that the basis of the autoxidation process is: $OH{\cdot}C_6H_4{\cdot}OH + 2Fe^{\cdot\cdot\cdot} \rightleftharpoons O{:}C_6H_4{:}O + 2Fe^{\cdot\cdot} + 2H^{\cdot}$. The buffer used may have a considerable effect on the mobility of the equilibrium. Thus, autoxidation is particularly facile in presence of a sodium acetate buffer, less so with sodium glycerate, and much less so with sodium phthalate. The catalytic action of iron salts in this process has its optimum within certain fairly narrow limits of concentration. *p*-Benzoquinone has a marked decelerating effect on the autoxidation of quinol, probably owing to the formation of an inactive iron–quinhydrone complex. As regards the mechanism of the autoxidation: it is difficult to recognise the process as one of true catalysis, and it may be that ferric salt is the effective oxidant of the quinol. This would explain why in the slow autoxidation of quinol that occurs in absence of a buffer, ferrous and ferric salts produce effects of a similar magnitude. In buffered solutions, ferrous iron is more powerful in action than ferric iron, so that probably an oxygen activation process is at work, in this case, on the part of a ferrous salt–acetate complex.

Pyrocatechol: Here the accelerative influence of iron in autoxidation is markedly stronger than with quinol. Pyrogallol: This case is similar to that of pyrocatechol, but autoxidation is more rapid. The product is not purpurogallin, but is the amorphous brown substance, resembling a humic acid, obtained in the hydrogen peroxide–iron oxidation of pyrogallol. Potassium ferrocyanide aids autoxidation, but to a much smaller extent than simple iron salts.

Experiments have been carried out on the autoxidation of dihydroxymaleic acid in complete absence of iron salts, in order to see if the known absorption of oxygen by solutions of the acid is really due to the

presence of unsuspected traces of iron. The conclusion is reached that whilst special purification of the acid (vacuum distillation in quartz vessels) renders it more stable in this respect, iron is not the initiator of the process, but merely catalyses a reaction in progress. This is substantiated by the fact that in neutral solutions of the purified material cyanide slightly accelerates autoxidation, whereas in presence of traces of iron it markedly diminishes the acceleration due to the latter.

Similar results have been obtained with quinol. The autoxidation of quinol itself produces hydrogen peroxide at p_H 3·6, whilst when iron is present no peroxide is formed.

Arsenious acid: According to Manchot (A., 1901, ii, 549) one equivalent of oxygen is activated during the oxidation of Fe^{II} to Fe^{III}, and is used for the conversion of arsenite into arsenate. This is not actually realisable under all conditions of acidity. The most concentrated weakly alkaline (p_H 6) solutions of arsenite obtainable show an activation of only 0·88 equivalent. For p_H 10, corresponding with $NaAsO_2$, activation corresponds with 0·6 equivalent, and for more strongly alkaline solutions, corresponding with Na_2HAsO_3, it corresponds with not more than one equivalent, in opposition to Gire's results (A., 1920, ii, 544). When alkalinity corresponds with Na_3AsO_3, activation exceeds 1 equivalent of oxygen, the extra ($\frac{1}{3}$ mol.) activation being due to spontaneous autoxidation and not to oxidation of arsenite by ferric salt.

Hypophosphorous acid: This acid is not appreciably oxidised by oxygen in absence of iron salts. The autoxidation in presence of iron salts seems to be an induction effect, ceasing when all ferrous salt has become oxidised. It is little affected by p_H. The results appear to show that the activation of molecular oxygen by ferrous salts cannot be due to the intermediate formation of a peroxide, as suggested by Manchot (*loc. cit.*). It is probable that the first stage in the autoxidation is the formation of a complex between the ferrous salt and the hypophosphite, rendering the hydrogen of the latter more active as regards oxidation. The second stage is the very slow reaction $2Fe^{III}+H_3PO_2 \longrightarrow 2Fe^{II}+H_3PO_3$. Phosphorous acid behaves similarly to hypophosphorous, but the activation is less pronounced and is more influenced by the acidity conditions.

Certain combined autoxidations have been studied. The autoxidation of hypophosphorous acid in presence of ferrous salts and dihydroxymaleic acid is catalytic in type, the p_H of the solution not greatly affecting the rate of change. (In absence of iron salts, solutions of mixed hypophosphorous and dihydroxymaleic acids do not absorb oxygen.) Diketosuccinic acid (not tartaric or glyceric acid) behaves similarly to dihydroxymaleic acid, but it is only slowly oxidised by ferric salt, whereas the latter acid is instantaneously oxidised by ferric salt in presence of hypophosphorous acid. The mechanism of the combined autoxidation is discussed. Possibly a readily dehydrogenated ferric salt–diketosuccinic acid complex is formed intermediately, but no final explanation can be reached on the existing evidence.

The autoxidation of formic acid in presence of ferrous salts is accelerated by dihydroxymaleic acid, but the acceleration is less than in the above case of hypophosphorous acid. Diketosuccinic acid is again an active intermediate. Relatively large amounts of dihydroxymaleic acid are required to produce acceleration, and the same is the case in the autoxidation of lactic acid in presence of ferrous salts. Dihydroxymaleic acid produces no acceleration of the autoxidation of quinol–ferrous salts.

The autoxidation of formic acid–ferrous salt in presence of thioglycollic acid is similar to the above case of formic–dihydroxymaleic acid. The experiments of Szent-Gyorgyi (A., 1924, i, 708, 1284) have been extended and put on a quantitative basis. Thioglycollic acid does not accelerate autoxidation until present in a certain concentration, but after this is reached its effect is proportional to its concentration. When lactic acid replaces formic acid there is a more pronounced mutual activation, whilst when tartaric replaces formic acid, less thioglycollic acid is required to accelerate the (more rapid) autoxidation.

The autoxidation of hypophosphorous acid and ferrous salt in presence of thioglycollic acid is a case of true catalysis, due to the equilibrium between ferric iron–thioglycollic acid and ferrous iron–dithiodiglycollic acid. This equilibrium must lie mostly on the ferrous iron side because of the marked initial activation (by thioglycollic acid) which precedes the main, catalytic, stage. Activation is ascribed to the formation of a thioglycollic acid–ferrous salt complex.

The autoxidation of hypophosphorous acid in presence of ferrous salts is not accelerated by pyruvic acid, but the autoxidation of pyruvic acid in presence of hypophosphorous acid is markedly accelerated by traces of ferrous salts, giving a case of true catalysis (ferrous salt–hypophosphorous acid complex).

Some consideration is given to cases of direct addition of oxygen to an unsaturated linking, as distinguished from the above cases, in which hydrogen is removed from a substance. The work of Meyerhof (Pfluger's Archiv, 1923, **199**, 531) on the autoxidation of linolenic acid, as accelerated by thioglycollic acid, has been extended. The autoxidation is further accelerated in presence of iron salts, in absence of which it is not rapid; it ceases when the whole of the thioglycollic has passed into dithiodiglycollic acid. In presence of traces of iron, the process is catalytic in type. The autoxidation of linolenic acid has now been studied in a buffered (p_H 4·6) solution. Ferrous iron greatly accelerates this process, but ferric iron does not do so until it has been in progress for some time. More marked acceleration is produced in presence of thioglycollic, dihydroxymaleic, or diketosuccinic acid.

The autoxidation of lecithin (cf. Meyerhof, *loc. cit.*) at p_H 4·6, in presence of ferrous salts, is catalytic in nature. In presence of ferric salts an induction effect is predominant. Added dihydroxymaleic acid produces marked acceleration, diketosuccinic acid causes deceleration when present in small, but acceleration when present in larger, quantities, whilst thioglycollic acid accelerates the reaction when it is present in small amounts and accelerates to a proportionally smaller extent when its quantity is increased.

Figures are also given for the autoxidation of crude linoleic acid under different sets of conditions.

E. E. TURNER.

Catalytic action of neutral salts. Effect of normal alkali sulphates on alkali acid sulphates in the ketonic splitting of ethyl acetoacetate. E. A. GOODHUE and H. L. DUNLAP (J. Amer. Chem. Soc., 1928, **50**, 1916—1922).—The decomposition of ethyl acetoacetate in acid solution at 80°, 90°, and 95° was investigated in a special apparatus in presence of *N*-potassium and sodium sulphates and the corresponding hydrogen sulphates (0·2*N* and 0·4*N*). The reaction proceeds at approximately half the speed when both normal and acid sulphates are present as compared with the rate when acid sulphate only is used.

S. K. TWEEDY.

Inversion of sucrose interpreted by the dualistic theory of catalysis and by activity of hydrogen ions. M. DUBOUX and R. MERMOUD (Helv. Chim. Acta, 1928, **11**, 583—597; cf. A., 1924, ii, 842).—The inversion of sucrose has been studied polarimetrically at 0°, using as catalysts 0·091—3·6*N*-hydrochloric acid and 0·74—3·69*N*-nitric acid. The velocity coefficients have been calculated from the usual logarithmic formula and the hydrogen-ion concentrations from known conductivity data of the acids concerned. The ratio $k/[H^{\cdot}]$ increases rapidly with increasing concentration of the acid used, and for concentrations greater than 0·1*N* no proportionality exists between k and $[H^{\cdot}]$. Contrary to the demands of the dual theory of catalysis, the values of k_H and in the equation $k=k_H[H^{\cdot}]+k_M(C-[H^{\cdot}])$ are not independent of the concentration of acid, neither is k_H independent of the nature of the acid. On the other hand, for hydrochloric acid as catalyst, k is proportional, as a first approximation, to the activity of the hydrogen ions a_H, according to the equation $k=k'_H a_H$. This agrees with Moran and Lewis' views of the mechanism of the inversion (J.C.S., 1922, **121**, 1613), but not with the hypothesis of Colin and Chaudun (A., 1927, 835).

L. S. THEOBALD.

Mechanism of tautomeric interchange and effect of structure on mobility and equilibrium. III. Function of alkaline and acid catalysts in the mutarotation of derivatives of tetramethylglucose. J. W. BAKER (J.C.S., 1928, 1979—1987; cf. this vol., 870).—The influence of acid and alkaline catalysts on the mutarotation of a series of *p*-substituted anilides of tetramethylglucose of the type $NHR\cdot CH\cdot[CH\cdot OMe]_3\cdot CH\cdot CH_2\cdot OMe$ has been studied. For acid catalysts, the relative velocities of mutarotation of these derivatives run parallel with the strengths as bases of the compounds NH_2R. Further, anilides of tetramethylglucose mutarotate more rapidly than the less basic derivatives of tetra-acetylglucose. It is suggested that these acid catalysts act by inducing a positive charge on the nitrogen atom which facilitates the liberation of the attached proton. With alkaline catalysts a minimum velocity of mutarotation is found at an intermediate position in the series. The following m. p. of the anilides of tetramethylglucose are recorded: p-*bromoanilide*, 154°; p-*chloroanilide*, 141°; p-*toluidide*, 151°; p-*anisidide*, 110°.

F. J. WILKINS.

Mechanism of chemical change. I. Promotion and arrest of the mutarotation of tetra-acetylglucose in ethyl acetate. T. M. LOWRY and G. G. OWEN (Proc. Roy. Soc., 1928, **A**, **119**, 505—522).—Reasons are given for the special suitability, for the study of the mechanism of chemical change, of reactions which give rise to mutarotation. A technique is developed for producing at will arrests of mutarotation. It was found possible to prepare "clean" solutions of tetra-acetylglucose in ethyl acetate in a silica flask which had been ignited in a furnace and allowed to cool in a desiccator. Under these conditions it was often found that the solution in the flask remained unchanged for some days, although the samples usually underwent a more or less rapid mutarotation when transferred to a polarimeter tube for observation. When the polarimeter tube was first filled with solution, a certain value was obtained for the velocity coefficient of the reaction; on refilling after 24 hrs., however, the rate was about 0·1 of its original value, showing that the cleanliness of the tube was increased enormously by contact with the clean solution. Further experiments showed that the addition of a drop of water to the clean solution in the flask was not sufficient to initiate mutarotation, but that water containing a trace of acid or alkali was an extremely efficient catalyst. In these catalysed solutions, however, a maximum velocity of mutarotation was developed only after 2 or 3 hrs., giving rise to inflected curves in place of the usual unimolecular type, as if the action had been resolved into two consecutive stages. The occurrence of these inflected curves is probably conditioned by the use of highly purified materials and clean apparatus. In the case of the alkaline catalyst, there is evidence that the action may be due to catalysis by the contaminated surface of the containing vessel. The progressive acceleration of the change might be due to the development of some sort of chain reaction, spreading from this surface into the interior of the liquid. Experimental details are given for the cleaning of the silica polarimeter tube, the purification of phosphoric oxide, and the preparation of dry ethyl acetate. The sugar was carefully dried in a desiccator. The source of light was an enclosed mercury arc, and all readings were made with the green line Hg 5461 Å. Special experiments showed that the light from the arc had no influence on the course of mutarotation.

L. L. BIRCUMSHAW.

Autoxidation and antioxygenic action. Catalytic properties of phosphorus compounds. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1928, **187**, 157—161).—The catalytic oxygenating activities of phosphorus trichloride, phosphorus oxychloride, phosphorus tribromide, phosphorus oxybromide, hypophosphorous acid, phosphorous acid, phosphoric acid, and several substituted phosphines have been investigated with respect to benzaldehyde and other substances. The results, particularly those obtained with phosphoric acid, are discussed in the light of the theory that an oxygenating catalyst

must be a substance itself susceptible of further oxidation. C. W. GIBBY.

Electrodynamics of surface catalysis. A. K. BREWER (J. Physical Chem., 1928, **32**, 1006—1017).—Theoretical. On the basis of previous experimental work (A., 1926, 1074; Proc. Nat. Acad. Sci., 1927, **13**, 574) concerning the emission of ions during various surface catalysed reactions, a mechanism of surface catalysis, treated as a special case of thermionic emission in gases, is advanced. The electrostatic image and intrinsic surface forces, together with the kinetic energy of agitation, dissociate the molecules of gas on the surface into ions, which are driven from the surface by kinetic agitation with a probability distribution of velocities. Chemical reaction then results from a combination of the ions of which the velocity components perpendicular to the surface are sufficient to carry them to a region of weak surface forces, which is the chemically active region. The rate of the forward reaction. developed from an electrodynamic point of view, can be represented by the equation $dC/dt=A'T^{n'/2}e^{-b'/T}$, where A' is a combination factor and b' is the complete chemical work function, the work done by the ions escaping sufficiently from the surface to react. The reverse reaction can be similarly represented, but with different values of the constants, and equilibrium is expressed by the equation $K=(A'/A'')T^{(n''-n')/2}e^{-(q-b')/T}$.

L. S. THEOBALD.

Catalysts of the reaction $CO+H_2O$ CO_2+H_2. W. DOMINIK (Przemysł Chem., 1928, **12**, 229—235).—The following equation is derived whereby the catalytic power b of a catalyst for the reaction $CO+H_2O \rightleftharpoons CO_2+H_2$ may be calculated: $b=V/[(K-1)(x_1-x_2)]\times \log_e[(x-x_2)/(x-x_1)][(x_0-x_1)/(x_0-x_2)]$, where b is constant for a given temperature and size of grain of the given catalyst, K is the velocity coefficient of the above reaction, V the velocity of flow of the reaction mixture in c.c. per hr. per g. of catalyst, x and x_0 are the partial pressures of carbon dioxide respectively during and before the reaction, and x_1 and x_2 the roots of the equation $x(p_0H_2+x-x_0)/\{p_0CO-(x-x_0)\}\{p_0H_2O-(x-x_0)\}-K=0$. The values of b are shown experimentally to be constant for a gas mixture of the above type.

R. TRUSZKOWSKI.

Catalysis in the conversion of allyl alcohol and acraldehyde into propaldehyde. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1928, **50**, 1930—1935).—The proportion of acraldehyde, as compared to that of propaldehyde, formed when allyl alcohol is passed over a zinc oxide catalyst, is the greater the slower is the rate of flow of the alcohol, indicating the possibility of the reaction (1) $CH_2{:}CH{\cdot}CHO+CH_2{:}CH{\cdot}CH_2{\cdot}OH=CH_3{\cdot}CH_2{\cdot}CHO+CH_2{:}CH{\cdot}CHO$. The reaction (2) $CH_2{:}CH{\cdot}CH_2{\cdot}OH=CH_3{\cdot}CH_2{\cdot}CHO$ (cf. Constable, A., 1927, 27) probably does not take place because the following reaction, in which (2) could not occur, takes place in presence of aluminium oxide: $CH_2{:}CH{\cdot}CHO+PrOH=2Et{\cdot}CHO$.

S. K. TWEEDY.

Catalytic hydrogenation of unsaturated compounds. III. S. V. LEBEDEV and A. O. JAKUBTSCHUK (J. Russ. Phys. Chem. Soc., 1928, **60**, 793—828).—Curves expressing velocity of catalytic absorption of hydrogen by various unsaturated hydrocarbons containing conjugated double linkings are constructed. The velocity is constant for di*iso*propenyl up to 69% of the total hydrogen necessary for saturation (termed the critical point); the curve rises and then falls sharply at 91%, after which the reaction proceeds to completion at a low velocity. The rise represents the hydrogenation of *as*-methyl*iso*propylethylene, and the third section the hydrogenation of tetramethylethylene. At 69% saturation, the reaction mixture contains no di*iso*propenyl, 38% of di*iso*propyl, 45% of *as*-methyl*iso*propylethylene, and 17% of tetramethylethylene. The quantities of all substances formed during the process of hydrogenation lie on straight lines joining the origin to various points lying on the ordinate of the critical point. Fully saturated molecules are formed from the very beginning of the reaction and are, up to the critical point, formed exclusively from the original substances. Mono-substituted ethylenes added to substances possessing conjugated double linkings such as di*iso*propenyl, isoprene, divinyl, and piperylene absorb hydrogen together with the latter substances up to the critical point, whence it follows that where such mono-substituted ethylenes are formed during the first stage, they will undergo further hydrogenation before the critical point is reached. The critical point of divinyl is at 72% saturation, the intermediate products of hydrogenation being *n*-butylene, ψ-butylene, and butane. The critical point of piperylene is at 73% saturation, and the products are propylethylene, *s*-methylethylethylene, and *n*-pentane. The nature of the products formed and their relative quantity are unaffected by the presence of substituted ethylenes in the reaction mixture.

R. TRUSZKOWSKI.

Catalytic decomposition of oleic acid. B. M. MARKS and H. C. HOWARD, jun. (J. Physical Chem., 1928, **32**, 1040—1048).—The catalytic activity of nickel towards oleic acid over the range 200—490 has been investigated. The results are best interpreted as a combination of specific catalytic and thermal effect. The main gaseous product is carbon monoxide and the predominating reaction can be represented by the scheme $2nC_{17}H_{33}{\cdot}CO_2H \rightarrow nC_{17}H_{34}+(C_{17}H_{32})_n+2nH_2O+2nCO$. Analytical data for the reaction products are given.

L. S. THEOBALD.

Reduction of oxygen at a mercury dropping-cathode. J. HEYROVSKÝ (Časopis Ceskoslov. Lek., 1928, 7, 242—251; Chem. Zentr., 1928, i, 1149).—Measurements of the current as a function of the polarisation potential for dilute solutions of electrolytes, *e.g.*, potassium chloride or sulphuric acid, in contact with air, show that the oxygen is first reduced to hydrogen peroxide at a potential corresponding approximately with that of the normal calomel electrode. The influence of p_H on this reduction potential is very small. The second stage, the reduction to water, takes place in $0{\cdot}001N$-hydrogen ion solution at $-0{\cdot}60$ volt. A. A. ELDRIDGE.

Formation of perchlorate during electrolytic production of chlorate. A. V. PAMFILOV and O. S.

FEDOROVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 765—770).—Differences observed between the results of analysis of the gases evolved and of the reaction solution in the electrolytic production of chlorates are partly due to the formation of perchlorate.

R. TRUSZKOWSKI.

Preparation of metallic alloys by electrolysis of aqueous solutions of binary electrolytes. I. Copper and cadmium. N. N. EFREMOV (Ann. Inst. Polyt. Ural, 1927, **6**, 111—148).—Only with certain complex compounds, such as the cyanides, is it found possible to obtain conditions giving the necessary levelling of potentials for the simultaneous separation of copper and cadmium by electrolysis. Investigation has been made of: the curves of the electrode potentials $Cd|Cd(CN)_2$ and $Cu|CuCN$, especially in regard to the content of potassium cyanide and to the current density; the working conditions requisite for the realisation of the electrolysis; the dependency of the current efficiency on various factors, and the most suitable materials for anode and cathode. Characteristic of the copper–cadmium alloys is the change in magnitude of the electrode potentials. The curve for copper lies almost throughout above the curve for cadmium, so that the interval of common separation is greatly narrowed; cadmium, which is deposited before copper, produces no depolarising action. Any excess of potassium cyanide in the electrolyte results in the separation of cadmium alone. Use of a copper–cadmium anode does not result in deposition of the alloy on the cathode, owing to the tardy solubility of the anodic material. The current efficiency varies little with the temperature of the bath, but increases markedly with the current density, a value 0·4—0·6 amp. per 100 cm.^{2} giving a good deposit and a high yield. With lower current densities, the brittleness of the resulting alloys increases, whilst with higher, the bath undergoes rapid exhaustion and deposition of pulverulent metal sets in. The relation between copper and cadmium in the anodic alloy scarcely affects the separation, the proportions of the two metals in the electrolyte being dependent principally on the proportion in the electrolyte. It is therefore preferable to employ an insoluble anode, such as platinum, but even then, not more than 10—12% of the bath must be used up. Moreover, soluble anodes favour slimy deposits. Since electrolytic copper–cadmium alloys alloy well with platinum, copper, cadmium, iron, lead, aluminium, zinc, and other metals, these may readily be plated in this way. If subsequent removal of the alloy from the cathode is necessary, a zinc cathode coated with graphite and then with a thin layer of cadmium or copper should be used. Tricadmium dicupride, Cd_3Cu_2, which is a stable exothermic compound, decomposes extremely readily on anodic dissolution, and it would be of interest to ascertain if this behaviour is general with intermetallic compounds and if any of these are capable of unchanged cathodic deposition.

T. H. POPE.

Influence of p_H on the electrolytic deposition of copper in presence of gelatin. C. MARIE and M. L. CLAUDEL (Compt. rend., 1928, **187**, 170—171). Copper sulphate has been electrolysed in presence of gelatin in solutions of p_H 0·88—3·57. A deposit consisting of copper sulphate, gelatin, and water is obtained, and, at 3·2, reaches a maximum weight of about 6% of the weight of copper deposited in a comparison cell. This is paralleled by the maxima which the viscosity, swelling, and osmotic pressure of gelatin pass through at about the same p_H.

C. W. GIBBY.

Anodic behaviour of copper–antimony alloys. H. NEUMARK.—See B., 1928, 611.

Addition agents in electrodeposition. V. Application of the complex cation theory of crystalloidal addition agents to base metals. I. G. FUSEYA and K. MURATA. **II.** G. FUSEYA and R. YUMOTO.—See B., 1928, 611.

Corrosion and anodic polarisation of iron. R. A. DENGG and H. J. DONKER (Korrosion u. Metallschutz, 1927, **3**, 241—248; Chem. Zentr., 1928, i, 749).—Inconclusive experiments on polarisation of various types of iron and steel in an electrolyte of $0·1N$-potassium chloride and $0·1M$-potassium carbonate are described, and the bearing of the results on corrosion is discussed.

A. A. ELDRIDGE.

Nature of the deposit formed during electrolysis of neutral and alkaline solutions with an antimony cathode. J. GRANT (J.C.S., 1928, 1987—1988).—Analyses of the deposit obtained in the cathode compartment during the electrolysis of neutral or alkaline solutions with an antimony cathode indicate that it is not, as Weeks and Druce (A., 1925, ii, 700) suggest, a solid hydride of antimony (Sb_2H_2), but finely-divided antimony containing 0·01—0·25% of adsorbed hydrogen.

F. J. WILKINS.

Direct electrolytic preparation of potassium permanganate. G. RAPIN (Compt. rend., 1928, **187**, 112—114).—The preparation of potassium permanganate by electrolysis of aqueous potassium hydroxide or carbonate with a silicomanganese anode has been investigated. The anode must be compact; pulverised silicomanganese invariably leads to the formation of manganese dioxide. If potassium carbonate is used, the solution finally contains only potassium permanganate, but if potassium hydroxide is used it contains potassium silicate also. Raising the temperature increases the efficiency. Too high a concentration of potassium hydroxide causes the formation of potassium manganate.

C. W. GIBBY.

Electrolytic oxidation of aniline. J. SLADEK (Časopis Českoslov. Lék., 1927, **7**, 299—312; Chem. Zentr., 1928, i, 1171—1172).—The oxidation of aniline to benzoquinone in presence of sulphuric acid with a lead anode, and the influence of different catalysts, current strength, temperature, anode surface, and quantity of electrolyte are discussed. The benzoquinone can be determined by Knecht and Hibbert's method. Vanadium pentoxide is the best catalyst. The electrolysis is continued for 23 hrs., with a current density of 1 amp./dm.^{2}, the temperature not exceeding 10°.

A. A. ELDRIDGE.

Electrolytic reduction of nitrosoantipyrine. M. GIORDANI (Annali Chim. Appl., 1928, **18**, 289—296).—The progress of the electrolytic reduction of nitroso-

to amino-antipyrine is studied by comparing the amounts of gas evolved at the cathode of the electrolytic cell and in a voltameter; apparatus for the comparison, and the effects of change of cathode, of current density, and of concentration are described. A spongy nickel cathode is the most effective; the amino-compound (separated as benzylidene derivative) is obtained in 65% yield. E. W. WIGNALL.

Influence of intensity of illumination on velocity of photochemical union of bromine and hydrogen, and determination of the mean life of a postulated catalyst. F. BRIERS and D. L. CHAPMAN (J.C.S., 1928, 1802—1811; cf. A., 1926, 484; Bodenstein and Lütkemeyer, A., 1925, ii, 218).—For very high light intensities the rate of union of hydrogen and bromine is approximately proportional to the square root of the intensity, whilst for low light intensities the rate of reaction is directly proportional to the intensity. The total amount of chemical change is not solely dependent on the total time of illumination for light of constant intensity, but alters when the illumination is rendered intermittent. From a quantitative study of this effect the mean life of the commonly assumed catalysts (either atoms or active molecules) has been estimated to be 0·063 sec. F. J. WILKINS.

Photochemical reaction between bromine and tartaric acid in aqueous solution. II. III. Mechanism of the reaction. J. C. GHOSH and K. P. BASU (J. Indian Chem. Soc., 1928, **5**, 342—360, 361—372).—II. The reaction in the dark between aqueous bromine and tartaric acid solutions is negligible compared with that in the light, which is characterised by a long induction period, high quantum efficiency, and a temperature coefficient of the velocity of 4·6 for 10° rise of temperature. At constant bromine concentration, increase of tartaric acid concentration results in an increase of the induction period, whilst at constant tartaric acid concentration increase of bromine concentration produces a small reduction of the induction period, but a considerable diminution of the unimolecular velocity coefficient. Sodium hydrogen tartrate greatly accelerates the reaction and decreases the induction period. By addition of hydrogen bromide at the commencement of the reaction the relatively small increase of the hydrogen-ion concentration during the reaction results in only a small decrease of the reaction velocity, whereas normally the hydrogen bromide produced during the reaction causes a rapid decrease of velocity.

III. The observed phenomena are explained by assuming as the mechanism of the reaction the sequence: (*a*) bromine molecules are photochemically activated, (*b*) part of the active bromine atoms react with oxygen present in the system, and, in the initial stages, part are used up in destroying photo-inhibitors, (*c*) the remaining active bromine atoms produce photobromination of the tartaric acid. H. F. GILLBE.

Products of the photochemical decomposition of azoimide. A. O. BECKMAN and R. G. DICKINSON (J. Amer. Chem. Soc., 1928, **50**, 1870—1875).—Brief illumination by ultra-violet radiation causes 27% of the azoimide to decompose into nitrogen and hydrogen, and the remainder into nitrogen and ammonia (the latter forming ammonium azide). By means of the quartz-fibre and McLeod gauges the mol. wt. of azoimide is found to be 43·6±2·1. S. K. TWEEDY.

Photochemistry of silver halides. I. Gravimetric determination of excess silver in photographic layers. II. Decomposition of photographic layers with neutral, acid, and alkaline hydrogen peroxide, and with ammoniacal ammonium sulphide. H. H. SCHMIDT and F. PRETSCHNER.—See B., 1928, 625.

Conversion of maleic acid into fumaric acid by bromine atoms. F. WACHHOLTZ (Z. physikal. Chem., 1928, **135**, 147—181).—See this vol., 492.

Basis of the selective chemical action of *X*-rays and light. L. SIMONS (Brit. J. Radiol., Roentgen Soc. Sect., 1927, **23**, 124—134).—There is very little variation in the ionisation produced by complete absorption of corpuscular radiation in a number of organic vapours, hydrogen, air, and sulphur dioxide, *i.e.*, there is no selective action. In the absorption of a light quantum, with *X*-rays varying in wavelength over the critical *K*-range for silver, no selective change was observed in the average energy of the photo-electrons. The observed selective rise in absorption is due to an increase in the number of atoms thus ionised. The primary ionisation in which selective effects are shown is always negligible in comparison with the total ionisation, which includes ionisation by impact. For a mixed substance, the chemical change will be proportional to the product of the true absorption coefficient of the whole and the energy density of the *X*-rays at each point. CHEMICAL ABSTRACTS.

Photochemical decomposition by *X*-radiation. R. GLOCKLER and O. RISSE (Z. Physik, 1928, **48**, 845—851).—The liberation of oxygen from dilute aqueous solutions of hydrogen peroxide and of potassium persulphate when the solution was exposed to radiation of wave-lengths 1540, 710, 560, 190 X. was examined. The amount of oxygen liberated is independent of the wave-length when the conditions of experiment are so chosen that the fraction of the energy of the *X*-ray beam which is effective for the liberation of electrons is constant. For 0·0017*N*-solutions the amount of this energy associated with the decomposition of 1 g.-mol. of hydrogen peroxide and of potassium persulphate is 70,000 and 17,500 g.-cal., respectively. R. W. LUNT.

Mechanism of chemical reactions. H. J. TAYLOR (Proc. Amer. Phil. Soc., 1926, **65**, 90—98).—Evidence is adduced in support of the view that certain reduction processes, especially in the presence of excited mercury vapour, depend on the intervention of hydrogen atoms. CHEMICAL ABSTRACTS.

Separation of krypton and xenon from atmospheric air. A. LEPAPE (Compt. rend., 1928, **187**, 231—234).—The sources of loss in the separation of krypton and xenon from air are discussed. Good yields have been obtained by fractional adsorption on coconut charcoal or silica gel, at the b. p. of oxygen. C. W. GIBBY.

Action of mixtures of salts on copper. A. LAUNERT (Compt. rend., 1928, **187**, 206—207).—The changes produced in the density and specific resistance of copper by heating in mixtures of salts have been investigated and can be explained by absorption of the vapours of the salts. The mixtures used were potassium chloride–strontium chloride, potassium chloride–barium chloride, and barium chloride–strontium chloride at temperatures below their eutectic points. C. W. GIBBY.

Reactions in the solid state. IV. Compounds resulting from the reaction between basic and acidic oxides and carbonates and the mode of compound formation. W. JANDER (Z. anorg. Chem., 1928, **174**, 11—23).—Barium carbonate and tungstic oxide heated together in any proportion in a platinum crucible at 700° in a current of carbon dioxide for 2 hrs. yield always normal barium tungstate, holding in solution a small quantity of tungstic oxide. Molybdenum trioxide and barium carbonate, and tungstic oxide and calcium carbonate, under similar conditions, yield only normal barium molybdate and calcium tungstate, respectively. Lead monoxide heated with tungstic oxide or molybdenum trioxide at 600—650° yields normal lead tungstate or molybdate, in both cases a small quantity of lead monoxide remaining in solution in the salt. When heated with excess of silicon dioxide at 950°, barium carbonate yields principally barium metasilicate, whilst if the barium carbonate be in excess the orthosilicate is the main product. The conditions necessary for chemical reaction between two solid substances are stated and discussed. H. F. GILLBE.

Mercuric tetramminopersulphate. F. FICHTER and S. STERN (Helv. Chim. Acta, 1928, **11**, 754—758; cf. Tarugi, A., 1903, ii, 481).—Mercury (10 g.), ammonium persulphate (20 g.), and concentrated ammonia solution (50—60 c.c.) react vigorously, yielding crystals of mercuric tetramminopersulphate, $[Hg^{\cdot\cdot}(NH_3)_4]S_2O_8$, which loses ammonia in air, but can be recrystallised from concentrated ammonia solution. Mercuric acetate or nitrate, but not the chloride or cyanide, can replace the mercury used as starting material. The salt prepared by Tarugi (*loc. cit.*) is considered to be identical with this salt and not a mercurous derivative. Hydrolysis results in a mixture of basic salts of varying composition. L. S. THEOBALD.

Ionium from Fergan ores. A. N. PILKOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 835—841).—Ionium is separated from other elements by adsorption on cerium oxalate, after precipitation of uranium, radium, and other radioactive elements. R. TRUSZKOWSKI.

Corroding action of sodium fluosilicate on aluminium. G. M. KRAAY (Arch. Rubbercultuur, 1928, **12**, 141—143; Med. Proefstat. v. Rubber, No. 30, 81—83).—Aluminium is slowly dissolved by a 0·1% solution of sodium fluosilicate with the evolution of hydrogen. In a 0·5% solution of the same salt corrosion is much less rapid and after a short time ceases altogether owing to the formation of a protective coating. Aluminium pans can therefore be used for the coagulation of latex with sodium fluosilicate. A. R. POWELL.

Phosphorescent aluminium nitride activated by silicon. E. TIEDE, M. THIMANN, and K. SENSSE (Ber., 1928, **61**, [*B*], 1568—1573).—Aluminium nitride is prepared by the action of ammonia on particularly pure, technical aluminium contained in a molybdenum boat heated at 1300° in a nickel tube. Admixture with silicon is obtained by adding the required amount of silica to the metal previously to its conversion into the nitride. Alternatively, the nitride is prepared by allowing the vapour of the compound $AlCl_3,NH_3$ to come into contact with a tungsten spiral heated electrically at above 1000°. Addition of silicon is effected by use of silicon tetrachloride. The presence of about 0·5% of silicon is requisite for the production of phosphorescence. The optimum amount is 5%, but this limit can be greatly exceeded before the power to phosphoresce is lost. The iron arc or mercury lamp are the best exciting sources. Cathode rays cause a dark blue luminescence. Röntgen rays and feeble radium preparations have no effect. Emission is chiefly in the blue region; three bands appear, thus giving a close analogy with the boron nitride–carbon phosphors. The distinct blue afterglow persists for about a minute and then gives place to a pale, whitish phosphorescence. Specimens of aluminium nitride which have been exposed to a high temperature but scarcely phosphoresce by reason of their low silicon content become distinctly green when exposed to the iron arc; the colour disappears when they are preserved in the dark, but can be renewed by fresh exposure. It is remarkable that whereas graphitic carbon is the excitant of the graphitic boron nitride, the diamond-like aluminium nitride is excited only by diamond-like silicon. H. WREN.

Effect of temperature on the optical properties of kaolinite. T. N. MCVAY (J. Amer. Ceram. Soc., 1928, **11**, 224—226).—Euhedral crystals of kaolinite, contained in small platinum boxes, were heated in a platinum-wound tube furnace. Samples were taken from the furnace at different temperatures and afterwards examined microscopically. Up to 600° no change, other than a slight cloudiness at the edges, was observed. At 620° a uniaxial form, which was retained up to 1400°, was produced. These crystals, probably Rinne's metanacrite, were cloudy and seemed to be broken into very thin plates. Under strong illumination interference figures were noticeable. Both the cloudiness and the interference figures vanished when the crystals were held at 1450° for 2 hrs. However, under this treatment, a development, showing a cross-hatched appearance with small crystals arranged in rhombs, became evident. These crystals were probably mullite, but they were so minute that no optical determinations could be made. The anticipated change in the nature of the substance at 900° was not observed. A. T. GREEN.

Rare earths. J. ŠVÉDA (Časopis Ceskoslov. Lék., 1927, 7, 226—232; Chem. Zentr., 1928, i, 1162).—The decomposition of praseodymium and neodymium oxalates in a current of oxygen as a function of time and temperature was investigated. The product always contains carbonate. Praseodymium oxalate decomposes the more rapidly, but in a mixture con-

taining the oxides in equal amounts the reverse is the case. The praseodymium salt yields an oxide of composition corresponding with Pr_6O_{11}, which when heated in a vacuum yields the sesquioxide, whilst the neodymium salt yields only Nd_2O_3. The presence of neodymium does not inhibit the formation of the oxide Pr_6O_{11}. A. A. ELDRIDGE.

Neodymium selenate. J. A. N. FRIEND and A. A. ROUND (J.C.S., 1928, 1820—1822).—Neodymium selenate, $Nd_2(SeO_4)_3$, has been isolated, together with the corresponding *penta-* and *octa-hydrates*. Evidence for the existence of a dodecahydrate has been obtained. F. J. WILKINS.

Chemical reactions in the electrodeless discharge. S. S. BHATNAGAR, R. K. SHARMA, and N. G. MITRA (J. Indian Chem. Soc., 1928, 5, 379—382).—The substance produced from naphthalene under the influence of the electrodeless discharge has the formula $C_{24}H_{20}O$. Other decompositions which have been observed are: $PbSO_4 \longrightarrow PbSO_3+PbS$; $CaSO_4 \longrightarrow CaSO_3$, $KBrO_3 \longrightarrow KBrO+KBr$, $KIO_3 \longrightarrow KI+I_2$, $KClO_3 \longrightarrow KClO+KCl$, and $PbSO_4+Mg$ —— $PbS+MgO_n$. H. F. GILLBE.

Reaction between nitrogen dioxide and liquid mercury. W. C. PIERCE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1928, 50, 2179—2187).—The reaction was followed by observing the time of formation, t, of a solid film on the mercury surface. The period of use of the reaction vessel and also its dimensions influence t, although the variation does not obviously depend on the surface/volume ratio of the vessel. Further, t does not depend primarily on the size of the mercury surface, but it seems to be smaller in those vessels in which dust particles from the walls can be carried direct on to this surface. Decrease in t follows the introduction of moisture or a rise in temperature. The presence of foreign gases does not influence t, but after the vessel has been in use for some time a reduction in pressure results in a reduction in t; at very low pressures t increases (cf. Moore and Noyes, A., 1924, ii, 748). Gas ions, positive or negative, accelerate the reaction when sufficient are present. Activation of the nitrogen dioxide by irradiation does not affect t. The accelerating action of light is probably due to the activation of a surface film, and seems to be associated with the photo-electric effect (cf. *loc. cit.*). S. K. TWEEDY.

Preparation and properties of pure phosphorus trioxide. (MISS) C. C. MILLER (J.C.S., 1928, 1847—1862).—Phosphorus trioxide prepared according to the method of Thorpe and Tutton (J.C.S., 1890, 57, 545) contains 1·5—2% of free phosphorus. This product may be purified by fractional crystallisation from carbon disulphide, washing with light petroleum, together with subsequent volatilisation after exposure to light. The pure oxide melts at 23·8°. Further, it neither glows nor oxidises in moist or dry oxygen at the ordinary temperature and is unaffected by sunlight. F. J. WILKINS.

Action of hydrazine on quinquevalent arsenic in faintly acid solutions. H. KUBINA and J. PLICHTA (Z. anal. Chem., 1928, 74, 235—247).—The reduction of quinquevalent arsenic by hydrazine in presence of potassium bromide has been investigated in its dependence on the acidity of the medium. In presence of hydrochloric acid the production of arsenic trichloride is quantitative only when the concentration of acid is considerable. On distillation of mixtures which are not strongly acid metallic arsenic is found in the receiver and on the condenser tube. The liquid remaining in the distillation vessel is turbid and contains free arsenic. When neutral solutions are distilled arsenic is deposited in the distillation flask, but no arsenic appears in the receiver or on the condenser tube. Addition of arsenious oxide prior to distillation causes an increased and more rapid formation of arsenic in the distillation flask, but a decreased production in the cooling arrangement. No arsenic is produced with arsenious salts alone.

It appears that when the acidity is not considerable the hydrolysis, $As^{\cdot\cdot\cdot\cdot\cdot}+4H_2O \longrightarrow AsO_4{}'''+8H^{\cdot}$, is not negligible and that part of the hydrolysed fraction is reduced to arsine. The latter reacts with arsenic trichloride produced by the normal reduction to form arsenic according to the scheme $AsH_3+AsCl_3 \longrightarrow 2As+3HCl$. This reaction occurring in the gaseous phase is responsible for the production of arsenic in the condensing apparatus. In presence of much acid the hydrolysis is repressed and reduction follows the normal course. Other reducing agents, *e.g.*, oxalates and ferrous salts, behave normally.

When acid solutions containing sulphates are distilled, arsenious sulphide and sulphur dioxide are often formed in the final stages. J. S. CARTER.

Vanadium compounds and boiling sulphuric acid. A. SIEVERTS and E. L. MÜLLER (Z. anorg. Chem., 1928, 173, 313—323).—Boiling concentrated sulphuric acid effects partial reduction of vanadium pentoxide to vanadyl sulphate and partial oxidation of vanadyl sulphate to vanadium pentoxide. If more than 0·12 g. of vanadium per 100 c.c. of acid is present the salt $VOSO_4$ separates (cf. Auger, A., 1921, ii, 554). In presence of ammonium sulphate both quinquevalent and quadrivalent vanadium are completely reduced to the tervalent state by boiling concentrated sulphuric acid and the salt $NH_4V^{III}(SO_4)_2$ separates (cf. Rosenheim and Mong, A., 1925, i, 1411). Sulphuric acid and potassium sulphate decompose vanadyl sulphate into equimolecular proportions of vanadic acid and the salt $KV^{III}(SO_4)_2$ (cf. Eichner, this vol., 34). A. R. POWELL.

Element 91. Properties and isolation. A. VON GROSSE (J. Russ. Phys. Chem. Soc., 1928, 60, 843—845, 847—854).—See this vol., 259, 495.

Phosphorescent combustion of sulphur. H. J. EMELÉUS (J.C.S., 1928, 1942—1950).—Sulphur dioxide together with a small amount of sulphur trioxide are the products of the phosphorescent combustion of sulphur. No traces of any oxide of sulphur more volatile than sulphur dioxide were found and no evidence of the formation of ozone was obtained. As distinct from arsenic (A., 1927, 497), sulphur shows no "glow pressure," above which the oxidation is non-luminous. Sulphur dioxide and a series of organic vapours inhibit the glow over definite ranges

of temperature, experiments with methyl salicylate demonstrating that the temperature at which the glow appears is the higher the greater is the concentration of inhibitant. F. J. WILKINS.

Molybdenum selenides and selenomolybdates. E. WENDEHORST (Z. anorg. Chem., 1928, **173**, 268—272).—From a sulphuric acid solution of ammonium molybdate hydrogen selenide precipitates brownish-black molybdenum triselenide, which dissolves in solutions of alkali hydroxides, selenides, and sulphides, giving deep red to brown solutions (cf. Moser and Atynski, A., 1925, ii, 583). If the acid molybdate solution is reduced with zinc until it becomes of a deep reddish-brown colour and is then saturated with hydrogen selenide, dense brownish-black leaflets of *dimolybdenum pentaselenide*, Mo_2Se_5, are precipitated. A mixture of molybdenum trioxide and selenium when heated in hydrogen to dull redness yields *molybdenum diselenide*, $MoSe_2$, in bluish-black, glistening leaflets insoluble in alkali solutions. When a mixture of potassium carbonate, selenium, and molybdenum dioxide is fused above 1200°, and the product leached with water, a residue of dark lead-grey crystals of *molybdenum sesquiselenide*, Mo_2Se_3, is obtained. Saturation of a solution of potassium molybdate in concentrated potassium hydroxide with hydrogen selenide results in the separation of red needles of *potassium selenomolybdate*, K_2MoSe_4. The sodium salt cannot be prepared under similar conditions, but the *ammonium* salt, $(NH_4)_2MoSe_4$, is obtained in glistening, blue crystals from a solution of molybdic acid in concentrated ammonia. All selenium compounds of molybdenum prepared in the wet way rapidly decompose on exposure to the air; their preparation must therefore be carried out in an atmosphere of nitrogen. A. R. POWELL.

Cyano-sulpho-compounds of molybdenum. E. CREPAZ (Gazzetta, 1928, **58**, 391—401).—Octacyano-salts of quadrivalent molybdenum (*e.g.*, $K_4[Mo(CN)_8],2H_2O$) were prepared by passing hydrogen sulphide intermittently through a solution containing potassium molybdate and potassium cyanide. The aquo-cyano-compound, $K_4[Mo(OH)_4(CN)_4],6H_2O$, was obtained on crystallising a solution of the octacyano-compound to which potassium hydroxide had been added. The exhaustive treatment with hydrogen sulphide of a solution of molybdic acid and potassium cyanide in potassium hydroxide solution gave a blue cyano-sulpho-compound, $K_3[MoS(CN)_4],2H_2O$, containing tervalent molybdenum. A method of determining the valency of the central metal atom in these compounds, based on the reduction by them of an ammoniacal solution of silver chloride, is described. In this reaction, for each equivalent of the compound involved two equivalents of silver are obtained as silver sulphide and (in the case of the above compound containing tervalent molybdenum) three equivalents of silver as metal. F. G. TRYHORN.

Thio-salts. VI. Complex molybdenum vanadium sulphides. L. FERNANDES (Atti R. Accad. Lincei, 1928, [vi], **7**, 496—501).—The preparation and analysis of a number of new complex *sulphides*, to which the following formulæ relate, is described: $[H_2(MoS_4)_4(VS_3)_2](NH_4)_5H_3,10H_2O$;
$[H_2(MoS_4)_3(VS_3)_3[(NH_4)_5H_2,12H_2O$;
$[H_2(MoS_4)_2(VS_3)_4](NH_4)_5H,25H_2O$;
$[H_2(MoS_4)_4(VS_3)_2](Guanidine)_5H_3,15H_2O$;
$[H_2(MoS_4)_3(VS_3)_3](Guanidine)_5H_2,22H_2O$;
$[H_2(MoS_4)_2(VS_3)_2](Guanidine)_5H,15H_2O$;
$[H_2(MoS_4)_2(VS_3)_4]Tl_5H,60H_2O$.
R. W. LUNT.

Sulpho-salts. V. Additive compounds with hexamethylenetetramine. F. RODOLICO (Atti R. Accad. Lincei, 1928, [vi], **7**, 660—666).—The following *compounds*, which are more stable and more easily crystallisable than the normal salts, have been prepared by a generalised method involving the addition of magnesium chloride and hexamethylenetetramine (X) to a warm solution of the alkali sulpho-salt: $MgMoO_4,X,10H_2O$; $MgMoSO_3,2X,10H_2O$; $MgMoS_2O_2,2X,10H_2O$; $MgMoS_3O,2X,10H_2O$; $MgMoS_4,2X,10H_2O$; $MgWO_4,X,10H_2O$; $MgWSO_3,2X,10H_2O$; $MgWS_2O_2,2X,10H_2O$; $MgWS_3O,2X,10H_2O$; $MgWS_4,2X,10H_2O$. From measurements of the crystallographic data for some of these compounds it was found that the morphotropic variations do not correspond with the gradual substitution of oxygen by sulphur.
F. G. TRYHORN.

Per-acids of uranium, tantalum, and niobium. A. SIEVERTS and E. L. MÜLLER (Z. anorg. Chem., 1928, **173**, 297—312).—Peruranic acid may be prepared either by addition of excess of 3% hydrogen peroxide solution to a solution of uranyl nitrate or by treating uranium trioxide with hydrogen peroxide. Pertantalic and perniobic acids are obtained by treating the corresponding potassium salts in concentrated aqueous solution with the requisite quantity of sulphuric acid. The acids are finely-divided white and yellow powders, respectively, containing one atom of active oxygen to one atom of metal. Both tantalic and niobic acids dissolve in 3% hydrogen peroxide, forming opalescent solutions; pertantalic acid is precipitated by alcohol or sodium chloride from the solution, but perniobic acid cannot thus be isolated. A. R. POWELL.

Action of fluorine on aqueous solutions of chromium and manganese salts. F. FICHTER and E. BRUNNER (J.C.S., 1928, 1862—1868).—Fluorine is as effective as a platinum anode in oxidation. Chromium alum in 1·5—7·5*N*-sulphuric acid solution is oxidised even at 0° to chromic acid. Sulphur tetroxide produced by the action of fluorine on the sulphuric acid is probably the active agent. Dilute potassium dichromate solutions are reduced, the fluorine first reacting with water to form hydrogen peroxide, which gives rise to perchromic acid which loses oxygen to form chromic salts. Manganous sulphate in the presence of sulphuric acid is oxidised to a labile sulphate of quadrivalent manganese, $Mn(SO_4)_2$. F. J. WILKINS.

Cobalticarbonates. G. A. BARBIERI (Atti R. Accad. Lincei, 1928, [vi], **7**, 747—753).—The structure of the green compound obtained by the action of an oxidising agent on a cobaltous salt in presence of alkali hydrogen carbonate is discussed. Cobalti-

nitrites dissolve in a warm solution of sodium hydrogen carbonate, giving an intensely emerald-green coloured solution. This contains a complex cobalticarbonate which is identical with the first-mentioned green compound and is not a mixture of compounds containing bi- and quadri-valent cobalt (cf. Metzl, A., 1914, ii, 472). The tervalent nature of the cobalt in the green solutions is further shown by isolating from them solid cobaltic compounds of known structure, *e.g.*, cobaltic acetylacetonate and purpureocobaltic chloride. O. J. WALKER.

Aquo-hexammine and -pentammine complexes of tervalent cobalt and chromium which crystallise in the cubic system. O. HASSEL and G. B. NAESS (Z. anorg. Chem., 1928, **174**, 24—30).—The complex salts, $[Co(NH_3)_6]SeO_4I$, $[Co(NH_3)_6]SeO_4Br$ (also $+3H_2O$), and $[Co(NH_3)_6]CrO_4Br,3H_2O$, have been prepared and their crystal structures studied; those of the first two differ from that of the corresponding sulphate only in the magnitude of the lattice constant, whilst that of the chromium complex corresponds with the structures of the trihydrates of hexamminecobaltic sulphatochloride and hexamminecobaltic selenatobromide. A series of complexes of tervalent chromium has been prepared, all the members of which have the cubic structure: $[Co(NH_3)_6]CrO_4I$, obtained by warming cobaltous carbonate with chromic acid solution, and heating the filtered solution, after addition of ammonia solution, with iodine; the analogous compound containing molybdenum in place of chromium could not be obtained, the sparingly soluble product having, after recrystallisation, the formula $2[Co(NH_3)_6]_2(MoO_4)_3,3H_2O$; $[Co(NH_3)_5,H_2O](ClO_4)_3$ (deep red), $[Cr(NH_3)_6](ClO_4)_3$ (yellow), and $[Cr(NH_3)_5,H_2O](ClO_4)_3$ (bright red), which belong to the octahedral system; $[Cr(NH_3)_5,H_2O]SO_4ClO_3$, which has the fluorspar-like structure of the complex sulphatobromides. The following lattice constants (Å.) have been determined: $[Co(NH_3)_6]SO_4I$, 10·71; $[Co(NH_3)_6]SO_4Br$, 10·51; $[Co(NH_3)_6]SeO_4I$, 10·79; $[Co(NH_3)_5H_2O]I_3$, 10·81; $[Co(NH_3)_5H_2O](ClO_4)_3$, 11·32; $[Co(NH_3)_5H_2O]SO_4I$ 10·62; $[Co(NH_3)_5H_2O]SO_4Br$, 10·45; $[Co(NH_3)_6]SeO_4Br$, 10·63; $[Co(NH_3)_6](ClO_4)_3$, 11·38. H. F. GILLBE.

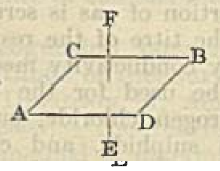
Optical activity of platinum. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 40—55).—Two of the stereoisomerides of the complex $[en\,NH_3\,Pt\,Cl_2\,NO_2]Cl$ are resolved into optical antipodes, as are the complexes $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]OH$ and $[en\,(NH_3)_2\,Pt\,Cl_2]Cl_2$. Stereoisomerism has a profound influence on the magnitude of the rotatory power and of the dispersion coefficient. The application of the amido-reaction, leading to the production of $[en\,NH_2\,Pt\,NO_2\,Cl_2]$, brings about a change of sign of rotation, the appearance or the enhancement of Cotton's effect, and an increase in the absolute value of molecular rotation. The inversion of rotation takes place with ionic velocity and is completely reversible, and the same applies to that of triammines and tetrammines. *trans*-Trichlorotriammines react with ammonia to form *cis*-dichlorotetrammines. Inversion of optical rotation is brought about by alkalis only in those complexes into the nucleus of which ammonia enters. R. TRUSZKOWSKI.

Platinum nitrites. III. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 23—39; cf. *ibid.*, 1926, **4**, 243; 1927, **5**, 102).—*cis*-Nitritochloroplatinites of the general type $[A_2\,Pt\,NO_2\,Cl]$ are produced by the action of ammonia or ethylenediamine on $K_2[Pt\,Cl_3\,NO_2]$, obtained by the action of sodium nitrite on potassium chloroplatinite. The complex $[en\,Pt\,Cl\,NO_2]$ yields on treatment with excess of ammonia the base $[en\,NH_3\,Pt\,NO_2]Cl$, which with hydrochloric acid gives the base $[en\,NH_3\,Pt\,Cl_3]Cl$, which reacts with alkali hydroxides to produce the amide $[en\,NH_2\,Pt\,Cl_3]$. Where pyridine is substituted for ammonia in the above series of reactions, the trichlorotriammine base $[en\,C_5H_5N\,Pt\,Cl_3]Cl,2H_2O$ is produced, which with dilute alkalis yields $[en\,C_5H_5N\,Pt\,Cl_3]OH$: this, when dried at 140°, loses a molecule of water to form the imide $[NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{:}(C_5H_5N)PtCl_3],H_2O$. The substance $[en\,C_5H_5N\,Pt\,NO_2]Cl$ reacts in solution with chlorine to yield $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$, whence $[en\,(C_5H_5N)\,(NO_2)_2\,Cl\,Pt]Cl,2H_2O$ is derived by the action of sodium nitrite, and this product again yields with 25% ammonia $[en\,(C_5H_5N)\,(NO_2)_2\,Cl\,Pt]OH$. Ammonia substitutes only one chlorine atom of $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$, the product being $[en\,C_5H_5N\,Pt\,NH_2\,NO_2\,Cl]Cl,2H_2O$, readily convertible into $[en\,C_5H_5N\,NH_3\,Pt\,NO_2\,Cl]Cl$ by the action of hydrochloric acid. The *cis*-tetrammines yield Cleve's salt on reduction to bivalent platinum. The tetrammine $[en\,(NH_3)_2\,Pt\,NO_2\,Cl]Cl_2$ is separated into its optical antipodes, for which $[M]_D$ is $-137°$ and $+145°$, respectively. Two stereoisomerides of $[en\,C_5H_5N\,Pt\,NO_2\,Cl_2]Cl$ are prepared, and three of $[en\,NH_3\,Pt\,NO_2\,Cl_2]Cl$. When quadrivalent is reduced to bivalent platinum in these complexes the two substituent groups which are attached to one co-ordinate are invariably eliminated. R. TRUSZKOWSKI.

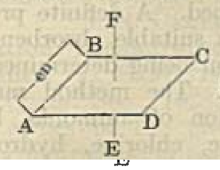
Platinum nitrites. IV. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1928, **6**, 55—97).—The following non-electrolytic nitrites of bivalent platinum have been prepared: *dinitrodihydroxylaminoplatinum*, $\begin{matrix}NO_2\\Hx\end{matrix}\!>\!Pt\!<\!\begin{matrix}Hx\\NO_2\end{matrix}$ ($Hx{=}NH_2OH$), its *stereoisomeride* $\begin{matrix}Hx\\Hx\end{matrix}\!>\!Pt\!<\!\begin{matrix}NO_2\\NO_2\end{matrix}$, *dinitroplatinumdiammine*, $\begin{matrix}NO_2\\NH_3\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_3\\NO_2\end{matrix}$, *hydroxylaminodinitroplatinum-ammine*, *pyridinodinitroplatinumammine*, *ethylenediamminodinitroplatinum*, *dihydroxylaminonitrochloroplatinum*, *hydroxylaminonitrochloroplatinumammine*, the corresponding *derivative* with pyridine substituted in place of ammonia, *pyridinonitrochloroplatinumammine*, *ethylenediamminonitrochloroplatinum*, *nitrochloroplatinumdiammine*. The following electrolytic salts of nitro-derivatives of bivalent platinum have been prepared: *trihydroxylaminonitroplatinum chloroplatinite*, *amminodihydroxylaminonitroplatinum chloroplatinite*, *diamminohydroxylaminonitroplatinum chloroplatinite*, *amminoethylenediamminonitroplatinous chloride*, *diamminopyridinonitroplatinum chloroplatinite*

$\left[\mathrm{{NH_3 \atop NH_3}\!>\!Pt\!<\!{C_5H_5N \atop NO_2}}\right]_2\mathrm{PtCl_4}$, and its *isomeride*, $\left[\mathrm{{C_5H_5N \atop NH_3}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]_2\mathrm{PtCl_4}$, *amminodipyridinonitroplatinum chloroplatinite, amminopyridinohydroxylaminonitroplatinum chloroplatinite*, $\left[\mathrm{{Hx \atop C_5H_5N}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]_2\mathrm{PtCl_4}$, its *isomerides*, $\left[\mathrm{{C_5H_5N \atop NH_3}\!>\!Pt\!<\!{Hx \atop NO_2}}\right]_2\mathrm{PtCl_4,2H_2O}$ and $\left[\mathrm{{NH_3 \atop C_5H_5N}\!>\!Pt\!<\!{Hx \atop NO_3}}\right]_2\mathrm{PtCl_4}$, and *amminopyridinomethylaminonitroplatinum chloroplatinite*. The *complex* $\left[\mathrm{{NH_3 \atop NO_2}\!>\!Pt\!<\!{NH_2\cdot CH_2\cdot CH_2\cdot NH_2 \atop NH_3\qquad\qquad NH_2}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]\mathrm{PtCl_4}$ is obtained by the interaction of the complex $\mathrm{{NO_2 \atop NH_3}\!>\!Pt\!<\!{NH_3 \atop Cl}}$ with 1 mol. of ethylenediamine and the addition of potassium chloroplatinite. The *complex* $\left[\mathrm{{Hx \atop NO_2}\!>\!Pt\!<\!{NH_2\cdot CH_2\cdot CH_2\cdot NH_2 \atop NH_3\qquad\qquad NH_3}\!>\!Pt\!<\!{Hx \atop NO_2}}\right]\mathrm{PtCl_4}$ is obtained in an analogous way from $\mathrm{{NO_2 \atop Hx}\!>\!Pt\!<\!{NH_3 \atop Cl}}$, and the following complexes are prepared similarly: $\left[\mathrm{{NH_3 \atop NO_2}\!>\!Pt\!<\!{NH_2\cdot CH_2\cdot CH_2\cdot NH_2 \atop C_5H_5N\qquad\quad C_5H_5N}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]\mathrm{PtCl_4}$, $\left[\mathrm{{NH_3 \atop NO_2}\!>\!Pt\!<\!{NH_2{:}NH_2 \atop Hx\quad Hx}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]\mathrm{SO_4}$, and $\left[\mathrm{{NH_3 \atop NO_2}\!>\!Pt\!<\!{NH_2{:}NH_2 \atop NH_3\,NH_3}\!>\!Pt\!<\!{NH_3 \atop NO_2}}\right]\mathrm{SO_4}$. Formulæ indicating the space orientation of quadrivalent platinum bases are written [ABCDEFPt], where A to F represents groups substituted within the octahedron in the order shown in formulæ (I) and (II), the latter

(I.)



(II.)



applying to ring derivatives containing ethylenediamine. The following non-electrolytic derivatives of quadrivalent platinum are prepared and described: *nitrotrichloroplatinumdiammine*, $[\mathrm{NH_3\,Cl\,NH_3\,NO_2\,Cl_2\,Pt}]$, *pyridinonitrotrichloroplatinumammine*, $[\mathrm{C_5H_5N\,NH_3\,NO_2\,Cl_3\,Pt}]$, and *ethylenediaminonitrotrichloroplatinum*, $[\mathrm{en\,NO_2\,Cl_3\,Pt}]$. The following electrolytic quadrivalent platinum derivatives are prepared and described: *triamminonitrodichloroplatinum chloride*, $[\mathrm{(NH_3)_3\,NO_2\,Cl_2\,Pt}]\mathrm{Cl}$, *triamminodinitrochloroplatinum chloride*, $[\mathrm{(NH_3)_3\,(NO_2)_2\,Cl\,Pt}]\mathrm{Cl}$, *diamminopyridinonitrodichloroplatinum chloride*, $[\mathrm{C_5H_5N\,NH_3\,NO_2\,NH_3\,Cl\,Pt}]\mathrm{Cl}$, optically active *diamminopyridinodinitrochloroplatinum chloride*, $[\mathrm{C_5H_5N\,NH_3\,NO_2\,NH_3\,NO_2\,Cl\,Pt}]\mathrm{Cl}$, *amminopyridinomethylaminonitrodichloroplatinumammine chloride*, $[\mathrm{C_5H_5N\,NH_3\,NH_2Me\,NO_2\,Cl_2\,Pt}]\mathrm{Cl}$, optically active *amminopyridinomethylaminodinitrochloroplatinum chloride*, $[\mathrm{C_5H_5N\,NH_3\,NH_2Me\,NO_2\,NO_2\,Cl\,Pt}]\mathrm{Cl}$, *ethylenediaminopyridinonitrodichloroplatinum chloride*, $[\mathrm{en\,C_5H_5N\,NO_2\,Cl_2\,Pt}]\mathrm{Cl}$, its dextrorotatory *stereoisomeride*, $[\mathrm{en\,C_5H_5N\,Cl\,NO_2\,Cl\,Pt}]\mathrm{Cl,2H_2O}$, d-*ethylenediaminopyridinodinitrochloroplatinum chloride*, $[\mathrm{en\,C_5H_5N\,NO_2\,Cl\,NO_2\,Pt}]\mathrm{Cl,2H_2O}$, *ethylenediaminopyridinotrichloroplatinum chloride*, $[\mathrm{en\,C_5H_5N\,Cl_3\,Pt}]\mathrm{Cl}$, *amminoethylenediaminonitrodichloroplatinum chloride*, $[\mathrm{en\,NO_2\,NH_3\,Cl_2\,Pt}]\mathrm{Cl}$, its d- and l-*isomerides*, $[\mathrm{en\,NH_3\,Cl\,NO_2\,Cl\,Pt}]\mathrm{Cl}$ and $[\mathrm{en\,NO_2\,Cl\,NH_3\,Cl\,Pt}]\mathrm{Cl,H_2O}$, *amminoethylenediaminotrichloroplatinum chloride*, $[\mathrm{en\,NH_3\,Cl_3\,Pt}]\mathrm{Cl}$, *tetramminonitrochloroplatinum chloride*, $[\mathrm{(NH_3)_2\,NO_2\,NH_3\,Cl\,NH_3\,Pt}]\mathrm{Cl_2}$, optically active *triamminopyridinonitrochloroplatinum chloride*, $[\mathrm{NH_3\,C_5H_5N\,NH_3\,NO_2\,NH_3\,Cl\,Pt}]\mathrm{Cl_2,H_2O}$, l-*diamminoethylenediaminodichloroplatinum chloride*, $[\mathrm{en\,NH_3\,Cl\,NH_3\,Cl\,Pt}]\mathrm{Cl}$, l-*diamminoethylenediaminonitrochloroplatinum chloride*, $[\mathrm{en\,NH_3\,NO_2\,NH_3\,Cl\,Pt}]\mathrm{Cl_2}$, optically active *amminoethylenediaminopyridinodichloroplatinum chloride*, $[\mathrm{en\,C_5H_5N\,Cl\,NH_3\,Cl\,Pt}]\mathrm{Cl_2,H_2O}$, and optically active *amminoethylenediaminopyridinonitrochloroplatinum chloride*, $[\mathrm{en\,C_5H_5N\,NO_2\,NH_3\,Cl\,Pt}]\mathrm{Cl}$.

R. Truszkowski.

Thiocyanates of bivalent platinum. A. A. Grunberg (Ann. Inst. Platine, 1928, **6**, 122—177).—The following compounds are prepared and described: cis- and trans-*dithiocyanoplatinumdiammine*, $\mathrm{{SCN \atop SCN}\!>\!Pt\!<\!{NH_3 \atop NH_3}}$ and $\mathrm{{SCN \atop NH_3}\!>\!Pt\!<\!{NH_3 \atop SCN}}$, cis- and trans-*dipyridinodithiocyanoplatinum*, and *ethylenediamminodithiocyanoplatinum*. Ammonia and amines react with potassium thiocyanoplatinite to yield analogues of Peyronne's salt, possessing the *cis*-configuration. Complexes of the above type react with thiocarbamide according to Kurnakov's rules. Jørgensen's rule, whereby tetrammino bases should yield *trans*-derivatives on heating, is not followed by thiocyano-salts. *cis*-Dithiocyanoplatinumdiammine is less stable than the *trans*-isomeride, although direct transformation of the less to the more stable form was not observed. The stabilising influence of the ethylenediamine ring on bases of the above type is shown also by the thiocyano-derivatives. Potassium chloroplatinite reacts with potassium thiocyanoplatinite to form platinous thiocyanate and potassium chloride. *cis*-Dithiocyanoplatinumdiammine combines with silver nitrate to yield $\left[\mathrm{{NH_3 \atop NH_3}\!>\!Pt\!<\!{S\;\;N \atop SCNAg}}\right]\mathrm{NO_3}$, the *trans*-isomeride yielding a more complex product. Peyronne's rule is explained on the assumption that salts of the type $\mathrm{PtX_2}$ have the *cis*-configuration. Measurements of the mol. wt. of the above isomerides of the type $\mathrm{PtA_2(SCN)_2}$, dissolved in acetone, show that these bases are isomerides and not polymerides, as found in liquid ammonia solution by Reihlen and Nestle (cf. A., 1926, 699). In bromoform, *cis*-dipyridinodithiocyanoplatinum exhibits association not found for the *trans*-isomeride.

R. Truszkowski.

[Ruthenium chlorides.] H. Gall and G. Lehmann (Ber., 1928, **61**, [*B*], 1573—1576).—A reply to Remy and Lührs (this vol., 722). It is shown that the product obtained by the action of hydrochloric acid on ruthenium tetroxide is not an individual, but corresponds analytically with a mixture of ruthenium tri- and tetra-chlorides. The green colour of ruthenium chloride solution has been attributed by Remy

to the tervalent metal. Since, however, such solutions of the metal are brown, the supposition involves the assumption of isomeric ruthenium trichlorides, which does not appear justified. The colour is attributed by the authors to the mixture of brown and blue. H. WREN.

Stability of rhodium sesquioxide and of iridium dioxide. S. PASTORELLO (Atti R. Accad. Lincei, 1928, [vi], **7**, 754—757).—The behaviour of the above oxides in a current of sulphur dioxide at temperatures above 350° has been examined by *X*-ray methods. The oxide of rhodium is stable up to 450° but is reduced to the metal above this temperature. Iridium dioxide is stable up to 650°. The results support the view that the decreased activity of platinum containing rhodium or iridium in the catalytic oxidation of sulphur dioxide to sulphur trioxide is due to the formation of rhodium sesquioxide and iridium dioxide, respectively (cf. Levi and Faldini, B., 1927, 651). O. J. WALKER.

Distillation of osmium tetroxide in aqueous solution, and oxidation of osmium and its compounds. E. FRITZMANN (Ann. Inst. Platine, 1928. **6**, 101—115).—See A., 1927, 742. R. TRUSZKOWSKI.

Magnitude of observation errors in chemical analysis. A. E. KORVEZEE and N. H. J. M. VOOGD (Chem. Weekblad, 1928, **25**, 242—247; cf. Goudriaan, this vol., 262; Hartong, *ibid.*, 382).—A mathematical analysis of the probability and effect of errors of observation. S. I. LEVY.

Natural classification of the elements and the qualitative analysis grouping. J. GILLIS (Natuurwetensch. Tijds., 1928, **10**, 47—52).—The arrangement of the elements in the form proposed by Antropoff (A., 1926, 773) may be employed to throw up the division usually adopted in analytical work into groups based on the solubilities of the sulphides and carbonates. S. I. LEVY.

Quantitative analysis depending on change in density. A. SHESTKOV (J. Chem. Ind. [Russia], 1927, **4**, 762—763; Chem. Zentr., 1928, i, 1306).—The quantity of solid precipitated or gas evolved in a reaction is determined by measurement of the density change of the solutions. The method can be applied to oxidation reactions by precipitation of an ionic product of the reaction. A. A. ELDRIDGE.

Electronic interpretation of oxidation and reduction in analytical chemistry. L. DUPARC, E. ROGOVINE, and P. WENGER (Helv. Chim. Acta, 1928, **11**, 577—583).—Oxidation is regarded as an increase in positive valency of the substance oxidised and a decrease in positive valency of the oxidising agent, the former signifying a loss and the latter a fixing of electrons. The reduction of potassium permanganate and dichromate, and the oxidation of ferrous iron, oxalic acid, alcohol, and potassium iodide are discussed on these lines, together with the more complex case of arsenious sulphide and nitric acid. L. S. THEOBALD.

Reduction of the weight of powdered substances weighed in air to that in a vacuum. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1928, **173**, 233—261; cf. A., 1927, 1134).—Neither calcium chloride nor sodium nitrate adsorbs air on the surface. Finely-divided silver, copper, and iron reduced from their oxides at 750° have no adsorptive power for air, but silver and iron adsorb 5 mg./100 g. of carbon dioxide. Exposure to pure dry air, however, results in slight oxidation, 100 g. of iron increasing in weight 30 mg., 100 g. of copper 10 mg., and 100 g. of silver 4 mg. Oxidation of filings of iron and copper also takes place in dry air but not nearly to the same extent as with the powders. For exact chemical work, *e.g.*, the determination of at. wts., no measurable error is introduced by omitting to take into account this slight oxidation. A. R. POWELL.

Analytical application of iodine trichloride to oxidation and of sodium formate to reduction. E. BIRK (Z. angew. Chem., 1928, **41**, 751).—A 20% solution of iodine trichloride in concentrated hydrochloric acid may be used for analytical oxidations, *e.g.*, of finely-divided sulphur in solutions. Fusion with sodium formate and consequent reduction is recommended as a means of solubilising certain insoluble substances; *e.g.*, anhydrous chromic chloride is thus converted into a soluble mixture of chromium formate and chloride. Fusion of a tungsten ore with sodium formate and lithium carbonate yields a characteristic deep blue lithium tungsten bronze. A. DAVIDSON.

Apparatus for continuous gas analysis. E. C. WHITE (J. Amer. Chem. Soc., 1928, **50**, 2148—2154).—An apparatus which affords a continuous determination of moderate concentrations of a given constituent in a flowing gas mixture, and registers the concentration automatically by electrical means, is described. A definite proportion of gas is scrubbed with a suitable absorbent, the titre of the resulting solution being determined by conductivity measurements. The method may be used for the determination of ammonia, hydrogen chloride, sulphur dioxide, chlorine, hydrogen sulphide, and carbon dioxide, and also may be adapted to the determination of carbon monoxide in presence of hydrogen and hydrocarbons. S. K. TWEEDY.

Microscopical examination of metallic minerals. J. ORCEL (Bull. Soc. d'Encour., 1928, **127**, 503—527).—A description of the technique of the preparation, etching, and microscopical examination of sections of minerals. C. W. GIBBY.

Spectrophotometric determination of hydrogen-ion concentrations and of the apparent dissociation constants of indicators. V. Fast-green FCF [" *p*-hydroxyerioglucine *A* "]. W. C. HOLMES and E. F. SNYDER (J. Amer. Chem. Soc., 1928, **50**, 1907—1910).—Data are supplied for the determination of hydrogen-ion concentrations at p_H 6·7—10·0 with the aid of fast-green FCF. The apparent dissociation constant of the dye in this range is approximately 8·1(5) at 29° (cf. A., 1925, ii, 999). S. K. TWEEDY.

Apparatus for potentiometric titration. E. LINDE (Svensk Kem. Tidskr., 1927, **39**, 285—287; Chem. Zentr., 1928, i, 725—726).—A method depending on the use of a triode valve is described. A. A. ELDRIDGE.

Potentiometric micro-titrations. E. ZINTL and K. BETZ (Z. anal. Chem., 1928, **74**, 330—342).—It is shown mathematically that the potentiometric end-point of a process involving precipitation is premature by an amount Δ c.c., such that $\Delta = 8Lv/N^2$, where L is the solubility product involved, v the volume of the solution, and N the normality of the titrating solution. The value of Δ is usually negligible under ordinary conditions, but is often not inconsiderable in micro-determinations. It is possible, however, using a silvered platinum wire as indicator electrode, to titrate chlorides and bromides with $0{\cdot}001N$-silver nitrate and iodides with $0{\cdot}0001N$-silver nitrate without involving any serious error. The volume of the solution should, however, be kept small. Potentiometric micro-titration of mixtures of two halides is possible, but titrations of solutions containing all three halides yield untrustworthy results. Contrary to the statement of Mislowitzer and Vogt (A., 1925, i, 1485), it is possible to determine chloride in presence of serum potentiometrically.

When the amount of arsenic is less than 0·1 mg. the indicator correction is such that the visual titration with potassium bromate yields untrustworthy results. When the volume of the solution is kept small, *e.g.*, 5—10 c.c., amounts of arsenic of this order may be determined with considerable accuracy by the potentiometric method, using $0{\cdot}001N$-potassium bromate. The titrated solution should contain 10% of hydrochloric acid. Smaller quantities of arsenic, *e.g.*, 0·002 mg., may be determined using $0{\cdot}0001N$-bromate. The observed values are, however, about 8% too high. Quantities of arsenic of the order 0·1 mg. may be determined with accuracy in presence of considerable quantities of copper salts.

J. S. CARTER.

Hydrogen-ion concentration measurements. I. Methods of measurements. C. E. DAVIS and G. M. DAVIDSON (J. Amer. Chem. Soc., 1928, **50**, 2053—2065).—The inherent errors of the electrometric method of determining hydrogen-ion concentrations with a condenser apparatus are investigated (cf. Beans and Oakes, A., 1921, ii, 12). The method is useless for precise work; errors due to humidity, the galvanometer throw, and the method of calculation arise. A mathematical discussion of the important errors is given, and their significance illustrated by graphs representing the titration of sulphuric and orthophosphoric acids by $0{\cdot}1N$-sodium hydroxide. The accumulated errors may attain ±4 millivolts.

S. K. TWEEDY.

Differential potentiometric titration. N. F. HALL, M. A. JENSEN, and S. A. BAECKSTROM (J. Amer. Chem. Soc., 1928, **50**, 2217).—The glass isolation vessel in MacInnes and Jones' method of differential potentiometric titration (A., 1927, 35) may be replaced by a fountain-pen filler having a small side arm near the bulb. One wire is wrapped round the filler, whilst the other passes into the interior through the side arm, which is then sealed.

S. K. TWEEDY.

Volumetric determination of acids and bases in various solvents. K. LINDERSTRØM-LANG (Dansk Tidsskr. Farm., 1928, **2**, 201—232).—A theoretical paper on the errors involved in the titration of acids and bases, Brønsted's views (Rec. trav. chim., 1923, **42**, 718) regarding the nature of these substances being adopted. The errors of titration can frequently be greatly reduced by carrying out the operation in a non-aqueous medium. Thus in the titration of glycine with hydrochloric acid the error may amount to as much as 5% if the determination is carried out in aqueous solution, but this can be reduced to 0·4% by employing 90% ethyl alcohol as solvent. Most amino-acids can also be determined practically quantitatively by titration with hydrochloric acid if they are dissolved in 90—95% acetone, naphthol-red being used as indicator.

H. F. HARWOOD.

Indicators. XII. Azo-indicators. A. THIEL and O. PETER (Z. anorg. Chem., 1928, **173**, 169—198).—Methyl-orange exists as a yellow, purely azo-form and as a red, practically completely quinonoid, form. The electrochemical and colour equilibria coincide almost exactly, the indicator thus satisfying the modified Ostwald theory of indicators. The double change is limited to the *p*-aminoazobenzene-*o*-carboxylic acid derivatives. Considerable evidence has been obtained for the hypothesis of closed ring formation. A number of relationships exist between the indicator properties of a substance and its constitution. The half-way stages of all sulphonic and *m'*- and *p'*-carboxylic acids are practically identical and are in accord with those of the free bases having similar amino-complexes. The *o'*-carboxylic acids are bivalent indicators, of which the half stage of the first change (basic) lies below that of substances of the first group having the same amino-complexes. The colour change of the yellow forms of the acidic indicators increases in the order *o'*-, *m'*-, *p'*-, whilst for the red forms the order is *o'*-, *m'*-, *p'*- for the sulphonic acids and *m'*-, *p'*-, *o'*- for the carboxylic acids, successive increases being produced in all cases by substitution in the amino-group in the order: unsubstituted, dimethyl and monophenyl, diethyl, for the yellow forms, and unsubstituted, diethyl, dimethyl, monophenyl for the red forms. The depth of colour of all the indicators increases by substitution in the amino-group in the order unsubstituted, monophenyl, dimethyl, diethyl for the yellow forms and unsubstituted, dimethyl or diethyl, monophenyl for the red forms.

H. F. GILLBE.

Electrometric determination of hydrogen peroxide and the associated peracids. A. RIUS (Trans. Amer. Electrochem. Soc., Sept. 1928, advance copy, 15—28).—In a solution containing hydrogen peroxide, permonosulphuric acid, and perdisulphuric acid the three constituents may be determined as follows: The permono-acid is determined by electrometric titration with sodium sulphite solution (containing 5% of 96% alcohol, which renders the solution more stable to atmospheric oxidation). As indicator electrode a strip of platinum 2×2·5 cm. is used, and the sample to be titrated is diluted to 200 c.c. with $2N$-sulphuric acid. This method is also satisfactory for the determination of permonophosphoric acid. Electrometric titration of permonosulphuric acid by means of ferrous sulphate in presence of manganous

sulphate is accurate only in the absence of hydrogen peroxide. The presence of much perdisulphuric acid interferes. Hydrogen peroxide in presence of the persulphuric acids is determined by a modification of Birkenbach's method of titration with potassium permanganate, the latter being added rapidly to the peroxide solution. By determination of the total oxidising value of the solution and subtraction of the equivalents of hydrogen peroxide and permonosulphuric acid as determined above the amount of perdisulphuric acid may be determined. The *E.M.F.* change in a *N*-calomel Pt,H_2SO_5 cell on addition of small amounts of hydrogen peroxide forms a sensitive method for the detection of the peroxide.

O. J. WALKER.

Microchemical reactions of the acids of chlorine, bromine, and iodine. E. M. CHAMOT and C. W. MASON (Mikrochem., 1928, **6**, 82—91).—A characteristic test for periodates in neutral solution is the formation, on addition of silver nitrate, of a fine-grained yellow to orange precipitate which becomes nearly black when heated and consists of small hexagonal prisms and triangular plates; as confirmatory tests the precipitation of the potassium salt and the starch test after reduction are recommended. Iodates are distinguished from periodates by the formation of a precipitate with barium chloride. Perchlorates are distinguished by their reaction with potassium salts and by the formation of thin rectangular crystals with strychnine sulphate. Chlorates should be reduced to chlorides for testing and bromates are distinguished in the presence of chlorates by the *m*-phenylenediamine test. Numerous other well-known tests for these and other halogen acids are also useful for microchemical work.

A. R. POWELL.

Determination of small quantities of free chlorine. K. ALFTHAN (Finska Kemistamfundets Medd., 1927, **36**, 109—112; Chem. Zentr., 1928, i, 1306—1307).—*as*-Dimethyl-*p*-phenylenediamine hydrochloride (1 c.c. of 0·1% solution) is added to the acidified tap water (100 c.c.) and the colour compared with a standard solution of methyl-red.

A. A. ELDRIDGE.

Iodometric determination of ozone and chlorine. A. JULIARD and S. SILBERSCHATZ (Bull. Soc. chim. Belg., 1928, **37**, 205—224).—The use of neutral or alkaline solutions of potassium iodide for the determination of ozone is attended by considerable error. Trustworthy results are obtained only by keeping the iodide solution at a hydrogen-ion concentration of p_H 7 by means of a suitable buffer mixture, or by making acid with an excess of boric acid. Since the presence of the buffer mixtures interferes in no way with the determination of chlorine by potassium iodide, such solutions may be used for the analysis of mixtures of chlorine and ozone.

F. J. WILKINS.

Detection of minute traces of iodine. A. N. SCHUKAREV and SYSOEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 669—671).—On placing a small electrolytic cell provided with a very sensitive galvanometer in an electromagnetic field, a minute current is induced in the cell circuit. 0·1*N*-Potassium iodide, potassium chloride, or sodium chloride solutions gave *E.M.F.* of about $3·8\times10^{-6}$ volt. On addition of traces of iodine ($8\times10^{-5}\%$) the *E.M.F.* is increased threefold. The phenomenon is due to depolarisation by the iodine of the electrodes, with a consequent increase in the current. The method is shown to be sensitive to $3\times10^{-5}\%$ of iodine.

M. ZVEGINTZOV.

Detection of sulphur and sulphurous acid. A. NOLL.—See B., 1928, 567.

Quantitative precipitations in concentrated solutions. V. NJEGOVAN and V. MARJANOVIC (Z. anal. Chem., 1928, **74**, 191).—In the method previously described 1 c.c. of saturated barium chloride solution is added for every 0·125 g. of sulphate ion present (cf. this vol., 497).

A. R. POWELL.

Determination of sulphur trioxide in natural waters and soil extracts. B. G. ZAPROMETOV (Bull. Univ. Asie. Centr., 1927, 91—95).—Raschig's benzidine method (A., 1903, ii, 572, 691) is preferred; the filtration with suction of the benzidine sulphate is omitted.

CHEMICAL ABSTRACTS.

Stable sodium thiosulphate solution. L. W. WINKLER.—See B., 1928, 567.

Determination of active oxygen in a mixture of persulphuric acid and hydrogen peroxide. G. D. LUBARSKI and M. G. DIKOVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 735—741).—Le Blanc and Eckhardt's method (A., 1900, ii, 45) for the determination of active peroxide and persulphate oxygen gives low results, probably as a result of formation of molecular oxygen. Ferber's method (Diss., Dresden, 1913) gives high results, owing to the catalytic action of ferric salts, which liberate iodine from iodides even in the absence of active oxygen. Wolffenstein and Makow's method (A., 1923, ii, 652) also gives low results. The only method which gives results comparable with those obtained by gasometric analysis is the following. Five c.c. of the solution under examination are left in a flask with 150 c.c. of water and 5 c.c. of 10% potassium iodide for 24 hrs. below 20°, and shielded from direct sunlight, after which iodine is determined volumetrically.

R. TRUSZKOWSKI.

Sources of error in organic micro-elementary analysis. I. Determination of nitrogen by Dumas' method. F. BOCK and K. BEAUCOURT (Mikrochem., 1928, **6**, 69—81).—The occasional slightly high results obtained in Pregl's microchemical method of determining nitrogen are attributed to incomplete removal of adsorbed gases in the copper oxide packing in the tube by a cold current of carbon dioxide. This source of error is avoided by carrying out a blank analysis at the beginning of a series of tests and using the same coarse copper oxide for a number of tests, changing only the fine copper oxide with every test. There is no advantage in arranging the copper column at the end of the tube as recommended by Dubsky, for Pregl's original arrangement of this column between two columns of copper oxide is equally satisfactory.

A. R. POWELL.

Modified digestion acid for non-protein nitrogen determination. M. DUPRAY (J. Lab. Clin. Med. 1927, **12**, 387).—A mixture of sulphuric, perchloric,

and phosphoric acids is employed, so that no precipitate is formed. CHEMICAL ABSTRACTS.

Determination of nitrates. II. L. SZEBELLÉDY (Z. anal. Chem., 1928, **74**, 232—235).—Arsenates, sodium, ammonium, magnesium, calcium, strontium, aluminium, manganous, zinc, antimony, silver, or cadmium salts do not interfere with the determination of nitrate by the author's method (this vol., 498). In presence of lead, mercuric, bismuth, and often barium salts the end-point is somewhat obscured by the white precipitate formed and a comparison solution is advisable. In presence of copper and nickel the colour changes are from yellowish-green to blue and green, respectively, and the use of a comparison solution is essential. Determinations are impossible in presence of cobalt and chromium salts and determinations in presence of mercurous salts are not entirely satisfactory. In absence of free arsenic, arsenious oxide does not interfere. J. S. CARTER.

Determination of nitrites in soil. R. P. BARTHOLOMEW.—See B., 1928, 538.

Ciurea's modification of Deniges' method for the micro-determination of phosphorus. I. VOICU (Bul. Soc. Chim. Romania, 1928, **10**, 50—54).—Polemical against Ciurea (this vol., 384). It is alleged that there is no proportionality between the amount of phosphorus and the amount of chlorine water used to destroy the blue colour. Decolorisation is never complete. J. S. CARTER.

Indicator for volumetric determination of phosphoric acid. L. DUPARC and E. ROGOVINE (Helv. Chim. Acta, 1928, **11**, 598—599).—The intense orange coloration produced by adding uranyl acetate to an aqueous solution of sodium salicylate is used for the determination of phosphoric acid. To 20 c.c. of the solution to be analysed, and 20 c.c. of a standard solution of 5·46 g. of calcium phosphate dissolved in nitric acid and diluted to 1 litre, are added 50 c.c. of water and 10 c.c. of a 10% aqueous solution of sodium salicylate. The solutions are heated to boiling and the uranyl acetate (13—15 g./litre) solution is added to each until an orange-yellow colour is obtained. The colours are matched either in the presence of the heavy precipitates which form during titration or in the clear liquids. Centrifuging can be employed, but is not essential. The method can be applied to the determination of phosphoric acid in urine when the latter is diluted six times with water to reduce the depth of colour. The standard solution is similarly diluted in this case. L. S. THEOBALD.

Microchemical determination of phosphoric acid as strychnine phosphomolybdate. C. ANTONIANI and R. B. JONA (Giorn. Chim. Ind. Appl., 1928, **10**, 203—205).—Modifications of Embden's method (A., 1921, ii, 462) are found advisable. The time of sedimentation of the precipitate is without effect, provided that it is at least 30—40 min., and the precipitation is not impaired by excess of the strychnine–molybdic acid reagent, but 6 parts of strychnine to 1 part of P_2O_5 represent the best conditions. Excess either of nitric acid beyond that of the reagent or of other free acid is harmful, but salts of organic acids, extraneous inorganic salts, and silicic acid are without influence; arsenic acid behaves like phosphoric acid. The results obtained are more constant if the precipitate is washed with 10% nitric acid solution instead of with the fivefold diluted reagent, and the method is applicable to quantities of P_2O_5 ranging from 1 to 6·3 mg. Good results are obtained with nitric–hydrochloric acid extracts of soil or mineral superphosphate and with sulphuric acid solutions of Thomas slag, the acid solutions being neutralised with sodium hydroxide solution and then re-acidified with nitric acid to dissolve the separated hydroxides, prior to precipitation of the phosphate with the strychnine–molybdic acid reagent. T. H. POPE.

Titration of phosphoric and boric acids present in the same solution by the citrate method. W. M. DEERNS (Chem. Weekblad, 1928, **25**, 268—271).—The end-points are not sharp, and the colour change interval is influenced, not only by the quantities of the various materials present, but also by the concentration of the indicator itself. The chemistry of the changes is very complicated, and equilibrium is attained in some cases only after considerable intervals. S. I. LEVY.

Apparatus for micro-determination of carbon dioxide. L. LESCŒUR (J. Pharm. Chim., 1928, [viii], 8, 11—18).—An apparatus for circulating a gas in a closed circuit over a suitable absorption reagent is described. The circulation of the gas is effected by a small mercury pump, consisting of a reservoir of mercury which is allowed to empty itself slowly through the atmosphere of carbon dioxide formed by the action of hydrochloric acid on the test solution. The drops of mercury falling through a tube of calculated diameter aspirate the gas over their upper surface while compressing it on the lower surface, thus behaving as a series of pistons. Generally not more than 25 min. are required for the complete absorption of carbon dioxide. R. A. PRATT.

Determination of alkalis in sub-soil waters. K. L. MALIAROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 829—834).—The alkali metal content of sub-soil water is determined, after precipitating sulphates with barium and elimination of chlorides by heating to dryness with excess of oxalic acid, by converting the remaining oxalates into carbonates, the quantity of which is determined by titration with standard acid. R. TRUSZKOWSKI.

Use of dihydroxytartaric acid for the detection and determination of sodium. A. P. OKATOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 661—668).—Dihydroxytartaric acid was obtained in 90% yield by Fenton's method of oxidising dihydroxymaleic acid with bromine in glacial acetic acid solution. The solubility of the sodium salt was determined at 0° (0·032%) and 10° (0·053%) by titrating the solution with potassium permanganate. A solution of the potassium salt is a qualitative reagent for sodium up to 0·05*N*-concentration at 12·5° and 0·025*N* at 0°. The solution, however, decomposes in a few days. It can be used for the determination of sodium, provided the determination is carried out at 0°, and a correction introduced for the solubility of the sodium salt. M. ZVEGINTZOV.

Influence of impurities from glass on the titre of sodium hydroxide. W. BOTTGER (Schweiz. Apoth. Ztg., 1927, **65**, 549—553; Chem. Zentr., 1928, i, 726).—Ampoules which had contained 5*N*-sodium hydroxide solution for 3 yrs. showed a change of more than 1—1·8% only when dimethyl-yellow was used as indicator. A. A. ELDRIDGE.

Apparatus for titration with carbonate-free sodium hydroxide. H. W. VAN URK (Pharm. Weekblad, 1928, **65**, 390).—The burette is provided with a lower side-arm and tap, by means of which the solution is measured out. Below the ordinary bottom tap the burette is prolonged into a capillary which dips below the surface of the solution contained in a Woulf's bottle, the joint being air-tight. The second neck of the bottle is closed by a cork bearing a soda-lime tube, through which, by means of a pump, pressure can be exerted to refill the burette, which is also provided with a soda-lime tube at the top. S. I. LEVY.

Volumetric determination of potassium. G. JANDER and O. PFUNDT (Chem. Fabr., 1928, 435—436, 446—448).—An account of work already published (A., 1927, 1046), with a description of modified apparatus.

Rapid gasometric determination of potassium. G. JANDER and H. FABER (Z. anorg. Chem., 1928, **173**, 225—232).—The difficulties in employing sodium cobaltinitrite as a quantitative reagent for potassium are discussed. In order to obtain a precipitate having a constant sodium : potassium ratio it is necessary to work with solutions saturated with sodium chloride and to stir vigorously during the formation of the precipitate. By treating the washed precipitate with a concentrated solution of ferrous sulphate in 2*N*-sulphuric acid, potassium may be rapidly determined by measuring the volume of nitric oxide evolved. H. F. GILLBE.

Microchemical detection of silver as sulphate. O. HACKL (Mikrochem., 1928, **6**, 106—107).—The characteristic rhombic crystals of silver sulphate serve for the microchemical detection of silver in concentrations exceeding 2 mg. per c.c. if 1 drop of the solution is evaporated with 1 drop of 2% sulphuric acid. A. R. POWELL.

Potentiometric analysis. II. Determination of silver and the halogens. T. HECZKO (Z. anal. Chem., 1928, **74**, 289—308; cf. this vol., 726).—The principle of the method is the same as that previously described for the potentiometric determination of iron with permanganate, but for argentometric work a silver indicator electrode is used and the absorbent electrode consists of a thin rod of pine-wood. The end-point may be determined either by measuring the throw of the galvanometer needle for every addition of solution or by measuring the strength of the residual current after each addition. For the determination of chloride, bromide, iodide, or silver, 5% of ammonium nitrate is added to the liquid to be titrated to increase the conductivity, and for the determination of two halogens consecutively in the same solution 6% of barium nitrate is added to render the two maxima more pronounced and to reduce errors due to adsorption by the first silver salt precipitated. A. R. POWELL.

Microchemical determination of calcium. F. ROGOZINSKI (Bull. Soc. chim., 1928, [iv], **43**, 464—469).—A microchemical method for the determination of calcium (*e.g.*, 0·27—1·1 mg.) by precipitation with sulphuric acid in presence of alcohol is described. After 12—21 hrs. the supernatant liquid is removed; the precipitate, $CaSO_4,2H_2O$, is filtered through a Pregl filter, washed with 96% alcohol, and dried at 105° in a current of filtered air. The presence of moderate amounts of hydrochloric acid or magnesium salts has no influence on the accuracy of the process. W. A. RICHARDSON.

Use of oxalic acid in microchemical analysis. K. L. MALJAROV (Mikrochem., 1928, **6**, 92—96).—The property of oxalic acid of expelling volatile acids from their salts affords a useful method of separating alkalis from alkaline earths and both these groups from the heavy metals. Thus, if a chloride or nitrate solution is evaporated with an excess of oxalic acid and the residue is heated until the excess is expelled, the alkaline earths are converted into insoluble carbonates and the alkalis into soluble carbonates. To separate alkaline earths from magnesia the oxalate residue is ignited to obtain the oxides, from which the alkaline earths may be extracted with water free from carbon dioxide. Zinc, copper, and manganese are dissolved from admixture with iron and aluminium by extracting the ignited oxalate residue with dilute hydrochloric acid. Chromium and manganese solutions are freed from chlorides by evaporation with oxalic acid and ignition of the residue. A. R. POWELL.

Rapid determination of magnesium. L. GALIMBERTI and E. ZOCCHEDDU (Annali Chim. Appl., 1928, **18**, 286—288).—Either in presence or in absence of alkali chlorides or sulphates, magnesium may be determined alkalimetrically, the results obtained agreeing closely with those furnished by gravimetric determinations. An excess of 0·1*N*-sodium hydroxide solution is run from a burette into a 250 c.c. flask containing a definite volume of the solution together with methyl-orange, practically complete precipitation of magnesium hydroxide being thus effected. The liquid is diluted to 250 c.c. with water, shaken vigorously, left for some minutes, and filtered rapidly through a hard, pleated filter, 100 c.c. of the filtrate being carefully titrated with 0·1*N*-hydrochloric acid in presence of methyl-orange until the yellow colour just begins to change to orange; addition of a few drops of phenolphthalein to the liquid facilitates the titration, as this indicator becomes colourless just before the change of the methyl-orange. The difference between the volume of alkali first used and that of the acid ultimately required for neutralisation corresponds with the magnesium present in accordance with the equation, $2NaOH+MgCl_2=NaCl+Mg(OH)_2$. T. H. POPE.

Electro-analytical determination of lead. A. V. PAMFILOV and A. A. BLAGONRAVONA (J. Russ. Phys. Chem. Soc., 1928, **60**, 699—706).—Various electro-analytical methods of determining lead are discussed, and their accuracy is compared with gravimetric and volumetric methods. Deposition of lead as the peroxide at the anode, with subsequent weighing of the deposit, gives inaccurate results,

but this can be avoided if the peroxide is reduced by heat to the monoxide. For cathodic deposition in hydrochloric acid solution various depolarisers, such as gallic acid and hydroxylamine hydrochloride, have been tried with moderate success. The deposits, however, are generally spongy and corrode the platinum cathodes. Coating the latter with copper and the use of mercury amalgams is not very successful. Further, it is almost impossible to avoid some lead peroxide deposition on the anode, consequently the cathode deposition method is greatly inferior in accuracy to the anode method.

M. ZVEGINTZOV.

Toxicology of lead and its compounds. IV. Electrolytic detection of lead. V. Nephelometric determination of lead. P. W. DANCKWORTT and E. JURGENS (Arch. Pharm., 1928, **266**, 367—374, 374—382).—IV. Methods of detecting lead by colour reactions with organic compounds (cf. A., 1923, ii, 508; 1925, ii, 1095; 1927, 277) were unsuccessful when used with animal organs or foodstuffs and the "triple-nitrite test" (A., 1922, ii, 659; 1924, ii, 61) had also to be abandoned. The accurate chromate method (Arch. Pharm., 1927, **265**, 424) is troublesome and the following simple electrolytic method was adopted. On a glass slide with hollowed part 0·5 cm. in diameter were fixed two platinum wires with ends 5 mm. apart and placed so that no liquid could rise between the sides of the hollow part and the wires. A current of 2·4 amp. at 4 volts was employed and the separation of metallic lead in tree-form noted at the cathode under the microscope, whilst lead dioxide deposited at the anode. The latter when mixed with tetramethyl-*p*-diaminodiphenylmethane (cf. A., 1902, ii, 352) developed a blue colour at the edges. To study the behaviour of other metals, especially those occurring with lead, 0·2*N*-solutions of lead, bismuth, mercury, iron, copper, manganese, and cadmium nitrates were electrolysed under the same conditions, using 3 drops of the solution. The metals all behave characteristically, manganese and lead alone being deposited as dioxides, which gave a blue colour with the above base. The results of electrolysis in nitric acid solution and with the addition of phosphoric acid are also described. The solutions examined contained 1 mg. of metal per 1 c.c. Phosphoric acid may be used to give only cathodic deposition with lead, and 0·010 mg. of lead can be detected. By anodic deposition 0·003 mg. of lead can be detected by the colour method. Since the presence and separation of other metals during electrolysis hinders the detection of lead, their influence on the cathodic and anodic deposition of the latter metal is described from the results of electrolysis of lead nitrate along with those of the above metals in turn, in neutral, nitric and phosphoric acid solutions. Lead in each case can be detected, and in acid solution manganese was easily recognised by conversion into permanganate. As iron and copper occur most often in biological material with lead, different mixtures of these metals were electrolysed, and whilst cathodic deposition is of no value, yet lead can be detected by the colour reaction in quantities of 0·005 mg. per drop in presence of ten times this amount of copper and iron. The detection of lead can be made in each case directly after destruction of organic material in the nitric acid solution.

V. The colour reaction of lead salts with hæmatin (A., 1907, ii, 653) is affected by the presence of copper and zinc, and whilst the colorimetric method with Arnold's reagent (A., 1902, ii, 352) is delicate the apparatus is expensive, so the nephelometric method (cf. A., 1907, ii, 398) was applied to the toxicological determination of lead, using Kleinmann's apparatus (A., 1925, i, 473). Optically clear 1% potassium dichromate solution (5 c.c.) is mixed with 5 drops of acetic acid. The lead solution (1 c.c. containing 0·0558 mg. of lead) is added and allowed to react for 20 min.; the volume is then made up to 20 c.c. with distilled water. Nephelometric readings can be taken between 10 and 60 min. after mixing; consistent results are obtained when the conditions are standardised. Favourable results were also obtained by diluting a mixture of 10 c.c. of 1% potassium dichromate solution, 15 drops of acetic acid, and 2 c.c. of the above lead solution. The presence of sodium or copper acetate has no effect, but copper nitrate may not be present. Except in acid solution the presence of iron gives rise to inaccuracy (A., 1908, ii, 633). By the above method 0·006 mg. of lead can be determined.

J. D. FULTON.

Volumetric determination of mercury. L. MARICQ (Bull. Soc. chim. Belg., 1928, **37**, 241—251).—The only satisfactory method of determining mercury in concentrations of 0·1—0·001*N* is an electrometric modification of the Personne–Denigès method, in which the mercury salt is titrated against potassium iodide. The results are accurate to within 1% even in presence of relatively large amounts of nitric and sulphuric acids, and chlorides, acetates, and phosphates.

F. J. WILKINS.

Rapid separation of aluminium and beryllium. I. M. KOLTHOFF and E. B. SANDELL (J. Amer. Chem. Soc., 1928, **50**, 1900—1904).—From a slightly acid solution containing aluminium and beryllium the former is quantitatively precipitated as $Al(C_9H_6ON)_3$ by the addition of an acetic acid solution of 8-hydroxyquinoline ("oxine") and an excess of ammonium acetate, the precipitate being weighed after drying at 120—140°. Beryllium hydroxide is precipitated from the filtrate by the addition of ammonia solution and ignited to the oxide. The method may also be used to separate beryllium from ferric iron.

S. K. TWEEDY.

Gallium. III. Quantitative separation of [ferric] iron from gallium by means of 1-nitroso-β-naphthol. J. PAPISH and L. E. HOAG (J. Amer. Chem. Soc., 1928, **50**, 2118—2121).—The solution is just acidified with hydrochloric acid and excess of 50% acetic acid, or ammonium acetate, is added. A solution of 1 g. of 1-nitroso-β-naphthol in 50 c.c. of 50% acetic acid is then added. After some hours the precipitate of ferric 1-nitroso-β-naphthoxide is washed and ignited to ferric oxide, which is spectroscopically free from gallium. The filtrate is evaporated to dryness, the residue dissolved in hot aqua regia, boiled with hydrochloric acid, and the gallium precipitated as hydroxide, which is then ignited to oxide. The latter contains only negligible traces of iron.

S. K. TWEEDY.

Rapid determination of manganese. G. SPACU and J. DICK (Z. anal. Chem., 1928, 74, 188—191).—The cold, neutral solution is treated with 1·5 g. of solid ammonium thiocyanate and 4 c.c. of pyridine. After vigorous stirring the crystalline precipitate, $Mn(SCN)_2,4C_5H_5N$, is collected in a porous filtering crucible, washed in succession with water, dilute alcohol, absolute alcohol, and ether containing small quantities of the precipitants, dried in a vacuum desiccator, and weighed; it contains 11·27% Mn. A. R. POWELL.

Determination of manganese dioxide etc. by Bunsen's method. E. RUPP (Chem.-Ztg., 1928, 52, 429—430).—Manganese dioxide and fuming hydrochloric acid are heated in a 30-c.c. distillation flask, the neck of which is closed by a stopper provided with a boiling capillary; the gases evolved are passed into a solution of potassium iodide contained in a bottle closed by an absorption tube containing glass wool and potassium iodide crystals. In order to prevent "sucking back," the side tube of the flask is cut to a length of 5 cm. and 18—20 cm. of capillary tube of diameter 2·5—2·8 mm. are joined on at a suitable angle. Satisfactory results may also be obtained by distilling into alkaline arsenite or alkaline iodide solution contained in an open vessel and titrating with potassium bromate or thiosulphate after acidifying, as the case may be, provided that sodium hydroxide and not carbonate is used as the alkaline reagent. F. R. ENNOS.

Volumetric analysis of chromates. P. SOKOLOV and T. ARISTOVA (J. Chem. Ind. [Russia], 1927, 4, 905—906; Chem. Zentr., 1928, i, 1307).—The determination of chromate by addition of excess of ferrous sulphate and titration with permanganate is more accurate than titration of dichromate solution into ferrous sulphate, using ferricyanide as external indicator. A. A. ELDRIDGE.

Electrometric determination of chromic acid in presence of vanadic acid by application of induction and catalysis. R. LANG and J. SWERINA (Z. Elektrochem., 1928, 34, 364—367).—Chromic acid may be determined by titrating in approximately *N*-hydrochloric acid solution with arsenious oxide solution in presence of manganese sulphate; immediately before the end-point is reached 1 drop of 0·0025*M*-potassium iodide or iodate is added and the titration completed. When a mixture of chromium and vanadium is to be dealt with, the metals, including the iron which is usually present, are oxidised in acid solution to their highest valency state by hydrogen peroxide or nitric acid; a little potassium permanganate is added to the neutralised solution, which is heated to boiling, and silver nitrate, sulphuric acid, and hydrochloric acid are added. Complete reduction of the manganese takes place in a few minutes, and the solution is boiled to drive off chlorine and to coagulate the silver chloride formed. Chromium may then be determined as above, whilst the vanadium determination is carried out by the ferrous sulphate method. H. F. GILLBE.

Detection of tin, zinc, chlorine and, [bromine]. E. EEGRIWE (Z. anal. Chem., 1928, 74, 225—231).—The hydrochloric acid solution of antimony and tin sulphides is evaporated to small volume. A few c.c. of concentrated hydrochloric acid are added and the whole is treated with iron to remove antimony and to reduce tin to the stannous state. A few drops of the solution are allowed to run down the sides of a test-tube containing 5 c.c. of a 0·01% solution of diazine-green S(K) previously acidified (to obtain a blue coloration) with a few drops of hydrochloric acid. After a short time a violet, and later a red, coloration appears at the surface of separation. Quantities of tin of the order of 0·002 mg. may be thus detected.

Minute quantities of zinc may be detected by the use of metanil-yellow or orange IV. To each drop of a 0·01% solution of dye are added 3 drops of a 2% solution of potassium ferricyanide. The whole is made faintly acid with mineral acid, when a red colour develops. On addition of a drop of a faintly acid solution of a zinc salt the colour disappears. If chromate is present this must first be reduced to chromium salt by treatment of the acidified solution with hydrogen peroxide. Zinc may also be detected by the use of diethylaniline. Ten drops of a solution of 0·5 c.c. of diethylaniline in 200 c.c. of 50% phosphoric acid are added to 15 drops of the ferricyanide solution. On addition of a drop of a faintly acid solution of a zinc salt the initial yellow colour gradually becomes reddish-brown. Alternatively, the diethylaniline (0·25 c.c.) may be dissolved in 200 c.c. of 1 : 1 sulphuric acid. In this case 15 drops are added to 15 drops of ferricyanide solution, to give an orange liquid yielding an orange or reddish-brown turbidity on addition of a drop of the solution of zinc salt. If the amount of zinc exceeds 0·01 mg. precipitation occurs. As before, chromate interferes and must be reduced. Cations forming coloured precipitates with ferricyanide must be excluded. Quantities of zinc of the order 0·002 mg. may be readily detected in presence of chromium and aluminium.

Quantities of chlorine of the order 0·03 mg. are detectable by the use of filter-paper treated with acid-fuchsin. The change is from red to yellow. Bromine and nitrogen peroxide interfere. Quantities of the order 0·002 mg. may be detected by the use of azo-carmine B(B) or rosindulin 2B. Papers stained red by aqueous solutions of the dyes become yellow. If the process be interrupted when still incomplete and the dried paper held for an instant in the neck of a bottle containing concentrated hydrochloric acid the yellow colour is changed to violet or blue. Bromine gives the same reaction. This reaction may be used for the detection of hypochlorites and hypobromites. The solution to be tested is added to a solution of the dye until an orange colour is produced. The solution is then acidified. Bromides can be detected in presence of chlorides by this reaction, bromine being liberated by treatment with manganese dioxide and glacial acetic acid, lead dioxide, and 2*N*-acetic acid, or potassium dichromate and dilute sulphuric acid. J. S. CARTER.

Colorimetric determination of titanium by the hydrogen peroxide method. F. G. GERMUTH (J. Amer. Chem. Soc., 1928, 50, 1910).—The colour fading produced by phosphate ion (Faber, A., 1907,

ii, 557) may be prevented by the addition of 1 c.c. of 0·1% uranium acetate solution for each 0·1 mg. of titanium. The temperature should be between 20° and 50°. S. K. TWEEDY.

Volumetric determination of germanic acid. A. TCHAKIRIAN (Compt. rend., 1928, **187**, 229—231).—An aqueous solution is prepared by boiling, the solubility being increased by adding 2 g. of mannitol per g. of germanium dioxide. The solution may then be titrated with alkali, using phenolphthalein as indicator. In the absence of mannitol, glycerol, or dextrose only about 0·4 of the germanic acid is neutralised. The mannitol–germanic acid compound liberates iodine from a mixture of potassium iodide and potassium iodate, and hence may be determined with sodium thiosulphate. Both methods have an accuracy of about 1%. The formula $H_2[Ge_2O_5M_n]$ is suggested for the mannitol–germanic acid compound, M representing mannitol, and n being at least 2. C. W. GIBBY.

Detection of vanadium, [uranium, and titanium]. J. ROLL (Z. anal. Chem., 1928, **74**, 342—345).—The customary method for the detection of vanadium, *i.e.*, examination of the filtrate after treatment with ammonium sulphide, is held to be unsatisfactory. It is preferable to precipitate vanadium along with iron, aluminium, and chromium as the metavanadate of these metals. Uranium and titanium will, if present, be also found in the precipitate. The washed precipitate is treated with a hot solution of sodium hydroxide, when vanadium and aluminium are removed as vanadate and aluminate, respectively. The presence of vanadium is confirmed by treating a portion of the acidified filtrate with hydrogen peroxide. The residue insoluble in sodium hydroxide is treated with a hot solution of sodium carbonate. The presence of uranium in the filtrate is confirmed by adding a few c.c. of a solution of ferrocyanide and neutralising with hydrochloric acid. Iron, chromium, and titanium are detected in the insoluble residue by specific tests. Titanium is conveniently detected by dissolving in acid and testing with hydrogen peroxide in presence of phosphoric acid. The absence of vanadium should be confirmed by testing with ammonium fluoride before making the test for titanium. J. S. CARTER.

Blowpipe test for metals. O. PROSCHOLD (Z. physikal. chem. Unterr., 1928, **41**, 40—44; Chem. Zentr., 1928, i, 1209).—The appearance of the pellets which fall into a paper box when the material is heated on charcoal serves to differentiate antimony, bismuth, cadmium, lead, tin, zinc, silver, and Wood's alloy. A. A. ELDRIDGE.

Determination of traces of antimony in copper. H. BLUMENTHAL.—See B., 1928, 573.

Colorimetric determinations of small quantities of antimony, and their separation from tin. S. G. CLARKE (Analyst, 1928, **53**, 373—379).—To determine amounts of antimony in tin of the order 0·001—0·05%, 5 g. of tin are dissolved in 50 c.c. of concentrated hydrochloric acid, with excess of bromine while the tin is dissolving; 10 g. of oxalic acid are then added and 350 c.c. of water, the liquid is boiled, all free bromine reduced with sodium hypophosphite, and a piece of coiled cleaned copper foil 15×12 cm. added. Boiling is continued for 1·5—2 hrs., the coil removed and washed successively in 5% hydrochloric acid and water, covered with water, about 1 g. of sodium peroxide added, warmed until the deposit is dissolved, the solution poured off, and the coil tested by immersion in 1 : 1 hydrochloric acid. The antimony is precipitated by passing a current of hydrogen sulphide for 15 sec., the precipitate coagulated, and the liquid filtered. The filter is washed with a dilute solution of an electrolyte and 5 c.c. of concentrated sulphuric acid are added to the filtrate; after addition of a few drops of nitric acid near the end stage, the solution is evaporated just to fuming. After cooling, 15 c.c. of water are added and the antimony is determined colorimetrically by addition to a solution of 10 c.c. of 1% gum arabic, 5 c.c. of 20% potassium iodide, 1 c.c. of 10% aqueous pyridine, and 1 c.c. of a dilute solution of sulphur dioxide in 60 c.c. of cold dilute (1 : 3) sulphuric acid, the comparison solution requiring 80 c.c. of sulphuric acid. As little as 0·05 mg. of antimony can be determined by this method. D. G. HEWER.

Separation of iridium and rhodium by fusion with bismuth. B. KARPOV (Ann. Inst. Platine, 1928, **6**, 98—100).—Alloys containing metals of the platinum group are analysed for rhodium by fusing the residue remaining after treatment of the silver alloy with nitric acid and aqua regia with bismuth in a carbon crucible at 1000° for about 2—3 hrs., in a reducing atmosphere. The aqua regia solution of the bismuth alloy contains the rhodium, whilst the insoluble residue consists of iridium. The use of bismuth in place of lead usually used shortens the time necessary for carrying out this analysis by at least 40%. R. TRUSZKOWSKI.

Determination of osmium. E. FRITZMANN (Ann. Inst. Platine, 1928, **6**, 116—122).—See this vol., 388. R. TRUSZKOWSKI.

Nomography. IV. O. LIESCHE (Chem. Fabr., 1928, 450—451, 463—465).—Nomograms on three linear scales effect graphical addition and subtraction, on logarithmic scales multiplication and division. The first can be used for the solution of linear equations with two independent variables as in the "indirect" analysis of a mixture of antimony tri- and penta-sulphides. An example of the use of logarithmic scales is given by the determination of the volume-% of converted ammonia in the Haber process, given the pressure, temperature, and equilibrium constant. C. IRWIN.

Drying apparatus. F. FRIEDRICHS (Chem.-Ztg., 1928, **52**, 601).—A modification of Abderhalden's drying apparatus is illustrated. The connexion to the vacuum pump is joined directly to the drying chamber instead of to the container holding the drying substance, so that the drying can be conducted in a vacuum or in an atmosphere of any suitable gas. A. R. POWELL.

Aspirator. O. RODE (Chem.-Ztg., 1928, **52**, 601).—The apparatus comprises two 5—6-litre glass bottles each provided with a rubber stopper carrying a short tube with stopcock and a long tube reaching

to the bottom. The two long tubes are connected together by means of a length of rubber tubing and, when filled with water, act as a siphon to permit the transfer of water from one bottle to the other.

A. R. POWELL.

[Laboratory] gas generator. V. T. JACKSON (Ind. Eng. Chem., 1928, **20**, 771).—The aspirator which serves as generator is so attached to the acid vessel that the opening of a stopcock allows the acid to descend into the generator and its closing with the resultant gas pressure forces it back again. The apparatus also includes a large acid reservoir and a glass-wool filter for catching spray. C. IRWIN.

Saybolt-type micro-viscosimeter. S. M. ROGERS and L. R. ADKINS (Ind. Eng. Chem., 1928, **20**, 742).—The viscosimeter has a barrel of capacity 8·5 c.c. of proportions similar to the Saybolt instrument. The viscosities of a number of oils were tested with both the usual and micro instrument and ratios varying from 4·8 to 5·1 were obtained. The cooling error on the apparatus described was very slight even at 99°. C. IRWIN.

Measurement of the viscosity of fluids. R. O. BOSWALL (J. Mun. Coll. Tech. Manchester, 1928, **13**, 10—21).—A description of a robust viscosimeter giving continuous readings of the viscosity of fluids under viscous flow. The fluid under examination passes through a special nozzle from one reservoir to another, vertically below it, through a narrow tube of uniform bore. These reservoirs are fitted with pressure gauges and the viscosity of the fluid is obtained from readings of the pressures in the reservoirs, and by making reference to experimental calibration charts on which the viscosity is expressed as a function of the ratio of the pressures in the reservoirs and of the density of the fluid. F. G. TRYHORN.

Laboratory uses of monel metal. L. F. BATES and R. C. BROWN (Nature, 1928, **122**, 240).—Various uses are described. A. A. ELDRIDGE.

Carbon resistor furnaces for laboratory use. H. C. KREMERS and L. F. YNTEMA (Ind. Eng. Chem., 1928, **20**, 770—771).—A granular carbon resistor furnace constructed of concentric alundum tubes and graphite electrodes is suitable for temperatures up to 1200°, and especially for alloy research. It is best used with a step-down transformer with variable secondary winding. C. IRWIN.

Heraeus electric micro-combustion furnace. B. FLASCHENTRAGER (Z. angew. Chem., 1928, **41**, 840—841).—The apparatus comprises three small heating units mounted in alinement on a stand in such a way that the middle and right-hand furnaces are movable along the combustion tube. The right-hand unit is fixed to the stand and is filled with cymene as a heating liquid which is maintained at 180° by an electric heating element. The combustion boat is placed in the tube about 2 cm. to the right of the middle furnace (19 cm. long), the right-hand small furnace (7 cm. long) is heated to redness and slowly moved towards the middle until combustion ceases, and, finally, this is moved back and the middle furnace moved along to cover the boat so as to ensure complete combustion. A. R. POWELL.

Valve for use with currents of gas. E. BLECHSCHMIDT (Physikal. Z., 1928, **29**, 441).—A new type of glass valve is described simplifying the regulation of a stream of gas. It is constructed in the form of a tap, the lower portion of the barrel forming one lead and a side tube the other. The key is not bored, but is ground in such a manner that the upper part forms a seal against the atmosphere, whereas the lower portion separates the two sides of the apparatus only when in one position, other positions enabling gas to stream through from one part of the apparatus to another at a known rate. A scale attached to the barrel enables comparative experiments to be carried out. J. W. SMITH.

Adjustable needle valve leaks. C. T. KNIPP (Nature, 1928, **122**, 131).—Three forms of needle valve, one of which admits of calibration, and all being constructed with very long and narrow needles, are described and figured. A. A. ELDRIDGE.

Electric crucible furnace with air-inlet at the bottom. G. ABELS and E. TITOV (Ann. Inst. Polyt. Ural, 1927, **6**, 351—352).—The laboratory furnace described consists of a threaded cylinder 5 cm. in diameter on which a chromium–nickel wire is wound. The inner space is connected with the air by channels in the double cover and in the foot. By displacement of a disc the air supply may be regulated or completely stopped. A current of 3 amp. at 120 volts gives the temperature 950°. The furnace is patented.

T. H. POPE.

Physical methods in the chemical laboratory. V. Production and measurement of high temperatures. E. SCHROER (Z. angew. Chem., 1928, **41**, 757—760).—A review of the different methods of producing and measuring high temperatures. Heating by the burning of gaseous mixtures (*e.g.* oxygen–hydrogen flame), the recombination of atomic hydrogen, the explosion of gaseous mixtures, the " thermite " process, resistance ovens, induction furnaces, the concentration of cathode rays on a substance to be heated, and the use of the electric arc are described. For measurement, the use of the gas thermometer, resistance thermometer, thermo-couple, and optical pyrometer are described, and a special method depending on the thermionic emission from a filament is mentioned. A. J. MEE.

Laboratory condenser. E. S. WEST (Ind. Eng. Chem., 1928, **20**, 737).—A condenser is constructed of an inner tube of light Pyrex glass sealed at each end to a jacket of thicker glass carrying an adapter. The narrow space between the two tubes renders cooling very efficient. C. IRWIN.

Pressure regulation in vacuum distillation. G. H. RICHTER (Ind. Eng. Chem., 1928, **20**, 682).—As the b. p. of a substance is usually recorded only under one pressure some convenient means of adjusting the pressure to this point in a distillation under reduced pressure is desirable. This is given by the needle valve of a Tirrill burner well greased and connected to the vacuum line by thick suction tubing and a T-piece. C. IRWIN.

Apparatus for sampling powdered solids. J. VON MEERSCHEIDT-HULLESSEM.—See B., 1928, 589.

Automatic sample-collecting vacuum pump. E. R. WEAVER and M. SHEPHERD (J. Amer. Chem. Soc., 1928, **50**, 1829—1835).—An automatic Topler pump is arranged as the backing unit of a high-speed mercury-vapour pump; the mercury delivered by the former is restored to the cycle by the alternate application of vacuum and atmospheric pressure to the pump reservoir by means of an auxiliary system operating on the suction of a water aspirator or a mechanical vacuum pump. The gas pumped out is automatically collected. Stopcocks are eliminated from the pumping cycle. S. K. TWEEDY.

Device for the preparation of solutions of constant density. J. HAMOUS.—See B., 1928, 589.

Rapid evaporation at the ordinary temperature. E. JANTZEN and H. SCHMALFUSS.—See B., 1928, 589.

Calorimeter for determination of heats of combustion. A. EUCKEN and L. MEYER.—See B., 1928, 589.

Method for detecting leaks in glass vacuum apparatus. P. SELENYI (Z. Physik, 1928, **48**, 733—734).—The residual gas inside the vacuum apparatus is excited by a Tesla current while another gas leaks into the apparatus. If the light emitted by the two gases is markedly different, as with carbon dioxide and air, the leaking spot can be detected directly by the change in colour in its vicinity. J. W. SMITH.

Action of the Geiger counter. L. F. CURTISS (Physical Rev., 1928, [ii], **31**, 1060—1071).—When the point of the Geiger point counter is negative, the sensitive surface is on the point. A sensitive surface is obtained only when the point has been treated with a catalyst, *e.g.*, iron oxide, copper oxide, or platinum or palladium-black, which may be poisoned by mercury, sulphur dioxide, or hydrogen sulphide. The adsorbed gas layer plays an important part in the action of the counter. A. A. ELDRIDGE.

Apparatus for determining mol. wt. by the b.-p. method. H. RUPE and N. VASSLIEV (Helv. Chim. Acta, 1928, **11**, 713—716).—The apparatus described is easy to construct and is suitable for ordinary laboratory use. The method can be used for a variety of solutes in such solvents as water, acetone, benzene, and chloroform with an error not greater than 10% and usually much less; the longest time required for a determination is 1 hr. L. S. THEOBALD.

Determination of mol. wts. by the Barger-Rast method. A. FRIEDRICH (Mikrochem., 1928, **6**, 97—102).—The original method of Barger (J.C.S., 1904, **86**, 286) is shown to give more satisfactory results than the modification proposed by Rast (A., 1921, ii, 623). An alternative procedure is to use a tube drawn out to a capillary at both ends; this is half filled with the standard solution by suction, a small air bubble is admitted, and the remainder of the tube is filled with the test solution by continuing the suction. Both capillary ends are then sealed and the observation of the movement of the bubble is carried out as usual. Various precautions for obtaining accurate results are described and sources of error in the three modifications are discussed. A. R. POWELL.

Magnetic micro-balance. E. WEDEKIND (Z. angew. Chem., 1928, **41**, 771—774).—The construction of an instrument for magneto-chemical work, in which the ordinary analytical balance previously used is replaced by a micro-balance, is described. The electro-magnets are also greatly improved. The method of using the balance is described. The reproducibility of the instrument for differences in weight in the same field is in general $\pm 0 \cdot 002$ mg. For powders the susceptibility can be estimated to within about 1%. A. J. MEE.

Apparatus for micro-filtration. K. L. MALJAROV (Mikrochem., 1928, **6**, 103—105).—The apparatus comprises two pieces of thick-walled glass tubing, the lower end of the longer piece and the upper end of the shorter piece being thickened and ground flat so as to form a perfect joint between the two. The lower end of the shorter piece is drawn out to a capillary jet and the two pieces are held together with a bow-shaped spring clamp after inserting a small piece of any type of filter-paper between them. The filter is placed with the jet in the liquid and suction is applied by means of the mouth at the upper end. The filtrate collects above the paper and the collecting tube may, if desired, be provided with a small bulb to increase its capacity. A. R. POWELL.

Ultrafiltration. R. WASMUHT (Chem. Fabr., 1928, 405—406).—Amongst the advantages of the membrane filter is that adsorption effects, such as the staining brown of filter paper by iron bromide solution from the formation of basic salt, do not occur. Two methods of securing a membrane filter held between two filter papers and resting on a perforated porcelain plate are described. Another apparatus is designed for the treatment of steel turnings with bromine solution and the ultrafiltration of the insoluble residue, with exclusion of air. C. IRWIN.

Self-acting filters. J. V. DUBSKÝ and A. RABAS (Chem. Weekblad, 1928, **25**, 293—294).—Forms of apparatus are described, based on the method in which the material to be filtered is contained in a closed vessel inverted with its mouth below the level of the liquid in the filter funnel, in which the necessity of removing the closed vessel for refilling is obviated. S. I. LEVY.

Automatic addition of a fluid. W. P. JORISSEN (Chem. Weekblad, 1928, **25**, 294—295; cf. preceding abstract).—Several very early forms of apparatus, designed to secure the continuous flow of liquid to a filter, are recalled; the original form is attributed to Berzelius. S. I. LEVY.

Burette for titration. N. M. KETOV (Ann. Inst. Polyt. Ural, 1927, **6**, 355—356).—A stopcock in the upper end of a constricted (jet) tube is connected by means of a rubber tube with the exit tube of a stoppered flask into which passes the jet of a burette. The volume of liquid run (without contact with rubber tube or stopcock grease) from the constricted tube is equal to that of the distilled water which is thereby drawn from the burette into the flask. The pinchcock may be placed between the burette and the flask. The constricted tube is filled from the top after removal of the ground-in cap and stopcock, and closure of the jet with rubber tubing and a glass plug. T. H. POPE.

Weight burette for the micro-measurement of liquid volumes. M. SHEPHERD (U.S. Bur. Stand.,

Sci. Papers, No. 555, 1927, **22**, 287—292).—Volume is measured by determining the weight of mercury used to displace the liquid concerned. Liquids are condensed into the evacuated burette by subjecting a portion of the burette to liquid-air temperatures. The method is applicable to liquids the vapour pressures of which are not excessive at the ordinary temperature. It is accurate to within 0·001 c.c. J. S. CARTER.

Hartmann and Braun's spring balance. J. E. VERSCHAFFELT and E. VAN DE CASTEELE (Natuurwetensch. Tijds., 1928, **10**, 35—46).—The balance is described, and the relation between load and reading under ordinary working conditions considered mathematically. The influence of temperature is important, and varies linearly with the load. A method of calibrating is described, and the effect of altering the adjustments examined. S. I. LEVY.

High-resistance liquid. A. GYEMANT (Z. tech. Physik, 1927, **8**, 491—493; Chem. Zentr., 1928, i, 734).—A solution of a strong electrolyte in a mixture of two organic solvents of differing dielectric constant, *e.g.*, picric acid in benzene and alcohol, gives a liquid the high resistance of which (10^4—10^{12} ohms) can be varied within wide limits. Applications are described. A. A. ELDRIDGE.

Continuous extractor. D. HENVILLE (Analyst, 1928, **53**, 380—382).—An apparatus suitable for the extraction of about 50 g. of material consists of a wide glass extractor (*a*), tapering at the bottom to a narrow tube, bent round and inserted into a rather wider tube which connects from a higher point in (*a*) to the extraction flask below. The apparatus is attached to a reflux condenser, and is packed at the bottom of (*a*) with cotton wool or asbestos, or a thimble may be used. Space is left for formation of a " head " and the material being extracted is always totally immersed in solvent, but the quantity of the latter must not be sufficient to overflow through the large side tube. D. G. HEWER.

Method of heating extraction apparatus. S. REINER (Chem.-Ztg., 1928, **52**, 529).—Six separately controlled electric hot plates arranged on a rack serve the same number of Soxhlet extractors. These are held by hinged clamps allowing the condensers to be lifted and the flasks removed. C. IRWIN.

Constant-drop apparatus. A. H. BURR (J. Soc. Dyers and Col., 1928, **44**, 18—19).—The apparatus consists of an inverted bell-jar, or a wide-mouthed bottle with the bottom cut away, fitted with a rubber stopper carrying two tubes. The first tube, the outflow to waste, controls the height of water in the vessel. The second tube, which rises sufficiently above the bottom of the reservoir to avoid dirt carried in by the water supply, is connected by rubber tubing to a capillary tube previously tested to give approximately the desired number of drops per min. Agitation of the water in the reservoir is prevented as far as possible by carrying the water inlet tube practically to the bottom, and reducing the inflow to the minimum to maintain the constant level. Constancy of dropping is maintained indefinitely if the head of water is maintained constant and the water supply kept free from dirt. R. BRIGHTMAN.

Preparation and use of the hydrogen electrode. S. POPOFF, A. H. KUNZ, and R. D. SNOW (J. Physical Chem., 1928, **32**, 1056—1060).—Various conditions affecting the preparation of hydrogen electrodes have been studied. The electrode should be cleaned by electrolysing as anode in concentrated hydrochloric acid to remove the old deposit, and then plated with gold by electrolysis in Clark's cyanide solution. This plating does not affect the time of attainment of equilibrium but results in a more adherent coating of platinum, which is also more easily removed on cleaning. The electrode is then used as cathode for 5 min. in 3% chloroplatinic acid containing 0·5 c.c. of 0·1*N*-lead acetate in 100 c.c., with a current density of 1·35 amp. per dm.^{2}, electrolysed in dilute sodium hydroxide for a few seconds and then in dilute sulphuric acid for 1 min. The lead acetate is essential for a good deposit. The electrode attains equilibrium more quickly in a Bovie titration cell than in an open beaker. Thinly-coated electrodes are preferable to those thickly coated, since the latter require greater time for the attainment of equilibrium and are more susceptible to poisoning. Treatment with nitric acid or dichromate cleaning mixture removes poisoning due to mercuric chloride, but with the repurified chemicals used, poisoning of the electrodes was difficult to effect. The maximum variation in potential of electrodes prepared by the above method was $\pm$0·1 millivolt. L. S. THEOBALD.

Oxygen electrode as a quasi-quantitative instrument. W. T. RICHARDS (J. Physical Chem., 1928, **32**, 990—1005).—The preparation of an oxygen–platinum electrode giving reproducible results is discussed, and a cell chain having a flowing junction and requiring small volumes of liquid is described. The electrode surface should be as large as possible with a constant area immersed, and solutions not easily reduced, such as phosphate or borate, should be employed if reproducible results are to be obtained. Nitrate and sulphate solutions show a continuous fall in potential. Under suitable conditions, oxygen electrode potentials constant to 1 millivolt for many days, but below the thermodynamic value for the oxygen–hydrogen, can be obtained. The oxygen potential varies quantitatively with the partial pressure of gaseous oxygen between 0 and 1 atm. Details are given of a method for measuring activities of the hydroxyl ion with an accuracy of a few millivolts. The effect of increasing concentration of electrolytes on the potential of the hydrogen–oxygen chain has also been measured. L. S. THEOBALD.

Determination of the m. p. of paraffins and the preparation of paraffin mixtures of definite m. p. J. KISSER (Z. wiss. Mikros., 1927, **44**, 443—451; Chem. Zentr., 1928, i, 1204—1205).—Halle's method for the determination of m. p. of paraffins is very accurate, although the ordinary capillary method is good. Formulæ are given for the preparation of mixtures of definite m. p. A. A. ELDRIDGE.

Demonstration of crystallisation processes by the streak method. I. II. W. KRAEMER (Z. wiss. Mikros., 1927, **44**, 476—477, 477; Chem. Zentr., 1928, i, 1206).

Geochemistry.

Inter-relation between diatoms, their chemical environment, and upwelling water in the sea, off the coast of Southern California. E. G. MOBERG (Proc. Nat. Acad. Sci., 1928, **14**, 511—518).

Dissolved and suspended mineral matter in Colorado River. W. D. COLLINS and C. S. HOWARD (Ind. Eng. Chem., 1928, **20**, 746—748).—In 1925—1927 the dissolved solids varied from 250 to 1500 in 10^6, the total hardness calculated as calcium carbonate ranged from 130 to 640 in 10^6, and the non-carbonate hardness from 38 to 400 in 10^6.

R. A. PRATT.

Rare gases from thermal springs and the earthquakes of April 14 and 18, 1928, in Bulgaria. N. P. PENTCHEV (Compt. rend., 1928, **187**, 243—244).—The composition of rare gases evolved from thermal springs in Bulgaria has been found to be unchanged by earthquakes. No certain conclusion can be reached concerning the constancy or otherwise of their radioactive properties. C. W. GIBBY.

Probable identity of gageite with tephroite. S. G. GORDON (Proc. Acad. Nat. Sci. Philadelphia, 1928, **79** (for 1927), 207—208).—A tabulation of the chemical composition, optical data, crystal angles, etc. of gageite from Franklin Furnace, New Jersey (A., 1910, ii, 968), suggests that this mineral is the same as tephroite. L. J. SPENCER.

Arfvedsonite, riebeckite, and crocidolite from Greenland. S. G. GORDON (Proc. Acad. Nat. Sci. Philadelphia, 1928, **79** (for 1927), 193—205).—Descriptions with optical data are given for these amphiboles from the nepheline-syenites of south Greenland. The following analyses are given of arfvedsonite from different localities. I by H. S. WASHINGTON, II by E. V. SHANNON, and III by F. WYNKOOP. They are interpreted as mixtures of the arfvedsonite molecule ($R_2O,3RO,4SiO_2$) and riebeckite molecule ($R_2O,R_2O_3,4SiO_2$), usually with an excess of R_2O_3, where R_2O is largely Na_2O, and RO and R_2O_3 are chiefly FeO and Fe_2O_3.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
I.	43·52	1·73	5·30	11·12	22·39	1·13	1·09
II.	43 08	0·83	4·44	8·06	28·97	0·70	0·32
III.	49·11	0·78	1·16	9·23	25·50	1·13	0·18

	CaO.	Na_2O.	K_2O.	F.	H_2O.	Total.	*d*.
I.	2·21	7·39	1·83	0·88	1·20	100·26	3·465
II.	4·08	5·88	3·28	—	1·10	100·74	3·447
III.	0·77	8·01	2·89	0·29	1·12	100·05	4·410

Totals less O for F_2. I, also ZrO_2 0·84. II, also BaO trace.

Riebeckite occurs in parallel growth on ægirine crystals, and crocidolite in parallel growth on arfvedsonite. L. J. SPENCER.

Olivine of Linosa (Pelagic Islands). G. CAROBBI (Atti R. Accad. Lincei, 1928, [vi], **7**, 654—660).—Crystallographic and analytical data are given for two specimens of transparent olivine, one greenish-yellow (*d* 3·410), the other reddish-yellow (*d* 3·462). These contained respectively: FeO, 12·43 and 11·06%; NiO, 0·12 and 0·18%; CoO, 0·13 and 0·10%; and, more noteworthy, PbO, 0·20 and 0·26%. It is suggested that the lead occurs as the result of an isomorphic substitution of magnesium. The two compounds $(Fe,Co,Ni,Mn)_2SiO_4$ and $(Mg,Ca,Pb)_2SiO_4$ constitute 77·5% and 22·5%, respectively, of the specimens analysed. F. G. TRYHORN.

Intrusive rock of Muno (Luxemburg) and metamorphism produced by it. A. L. HACQUAERT (Natuurwetensch. Tijds., 1928, **10**, 73—88).—The intrusive veins consist chiefly of felspar and biotite, with inclusions of calcite, quartz, apatite, zircon, chlorite, and pyrites, and the material is classed as a kersantite. The inclusions of calcite are of magmatic origin. It is deduced that the intrusions occurred at relatively low temperatures, and that the whole was subsequently subjected to hydrothermal action. The action of the solutions, which were rich in magnesium salts, has resulted in considerable impregnation of the surrounding rock with biotite.

S. I. LEVY.

Series of lavas of Southern Serbia. J. TOMITCH (Compt. rend., 1928, **187**, 133—136).—Analyses of five specimens are recorded. C. W. GIBBY.

Alkali-lavas from Mount Nimrud, Armenia. G. T. PRIOR (Min. Mag., 1928, **21**, 485—488).—Micro-sections of rocks from Mount Nimrud showed the presence of anorthoclase, ægirine, and soda-amphiboles. Complete chemical analyses were therefore made of three of the rocks (soda-rhyolite, pantelleritic trachyte, and trachyandesite), showing about 6% Na_2O, and a relation to the soda-rocks of the Rift Valley in East Africa is suggested.

L. J. SPENCER.

Julienite. A. SCHOEP (Natuurwetensch. Tijds., **10**, 58—59).—Blue microscopic needles, forming a thin layer on a white talcose schist at Chamibumba, near Katanga, having refractive indices of 1·645 parallel to and 1·556 perpendicular to the elongation, respectively, and readily soluble in cold water, appear to consist of a hydrated cobalt chloronitrate.

S. I. LEVY.

Organic Chemistry.

Steric hindrance. W. HUCKEL (Ber., 1928, **61**, [*B*], 1517—1524).—An attempt is made to differentiate between the spatial and chemical factors generally confusedly involved under the term "steric hindrance." The modified Trautz formula $k=\alpha e^{-q/RT}$ is used in which *q*, the activation energy (mean energy required to bring the reacting molecule into the active condition), is usually calculated from the temperature coefficient of the velocity coefficient *k*. The "action constant" α, which expresses the probability of encounter of the active surfaces of the molecules and, in addition to the activation energy, controls the velocity coefficient, is obtained by substituting the calculated value of *q* in the value

of k determined at any definite temperature. Examination of the data recorded by Vavon for the hydrolysis of the *cis*- and *trans-o-iso*propyl*cyclo*hexyl hydrogen succinates, *cis*- and *trans-o-n*-propyl*cyclo*hexyl hydrogen phthalates, and bornyl and *iso*bornyl hydrogen phthalates shows that considerable differences in the rates of reaction may depend on great differences between q or α but a uniform interpretation of steric hindrance cannot be deduced from the results. Examination of the rates of hydrolysis of n-propyl, n- and *iso*-butyl, *iso*amyl, *iso*propyl, *sec.*- and *tert.*-butyl acetates shows that the activation energy and action constants are approximately the same for esters of primary alcohols. The activation energy of esters of tertiary alcohols is much greater and the action constants are much smaller than those of esters of primary alcohols, both influences diminishing the rate of hydrolysis. H. WREN.

Thermal dissociation of ethane, propane, n- and *iso*-butane. R. N. PEASE (J. Amer. Chem. Soc., 1928, **50**, 1779—1785).—The gases are passed through Pyrex glass tubes at 625° and 650° under 1 atm. pressure. The total rate of dissociation increases with the complexity of the molecule. The two main reactions are dehydrogenation and demethanation. The ratios of hydrogen to methane decrease in the sequence, ethane, propane, n-butane. *iso*Butane decomposes at about the same rate as n-butane but gives relatively much more hydrogen. n-Butane does not undergo appreciable secondary reaction. Reactions appear to be somewhat more rapid than normal in the first few seconds, but dilution experiments indicate a change of the first order. The temperature coefficients are, as a minimum, 1·5—2 per 25°, giving a minimum activation energy of 25,000—50,000 g.-cal. H. WREN.

Control of the mol. wt. of liquid hydrocarbons produced by electrical discharge in ethane. S. C. LIND and G. GLOCKLER (J. Amer. Chem. Soc., 1928, **50**, 1767—1772).—Silent, corona, and high-frequency discharges all cause the condensation of ethane to liquid products with liberation of permanent gases. The average mol. wt. of the liquid products has been regulated between 467 and 105 by controlling the time that the first products, either gaseous or liquid, are allowed to remain in the discharge tube. Prolongation of the action causes increase in mol. wt. of the products. H. WREN.

Wurtz reaction. Factors involved in the preparation of octane. H. F. LEWIS, R. HENDRICKS, and G. R. YOHE (J. Amer. Chem. Soc., 1928, **50**, 1993—1998).—A method has been developed for preparing octane, b. p. 124·2—124·8°, d_4^{20} 0·7044, n_D^{20} 1·3961, from n-butyl bromide and sodium in 65—70% yield based on the butyl bromide. Optimal conditions consist in the use of an excess of sodium which need not exceed 50%, a volume of ether two and a half times that of the butyl bromide, low temperature, a period appropriate to each set of conditions, and fine sodium wire. Agitation is of material advantage. Traces of water are unexpectedly detrimental, but sufficient dehydration is secured if the ether is dried over calcium chloride and distilled over sodium. The presence of acetonitrile does not favour the formation of octane. Butene and at least two higher saturated hydrocarbons, possibly dodecane and hexadecane, are also produced. H. WREN.

Hexa-*tert.*-butylethinylethane. P. L. SALZBERG and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 1737—1744).—The hydrocarbon is undissociated at the ordinary temperature and undergoes rearrangement when the temperature is raised. Cleavage by alkali metals indicates that the stability of the central ethane linking is intermediate between that of the corresponding linking in dibenzyl and hexaphenylethane.

tert.-Butylacetylene is converted by the successive action of magnesium ethyl bromide and ethyl chloroformate into *tri*-tert.-*butylethinylcarbinol*, $(CMe_3\cdot C:C)_3C\cdot OH$, m. p. 100—102·2° (corr.) (additive *compound* with stannic chloride), which is isomerised by concentrated sulphuric acid to the *ketone* $(CMe_3\cdot C:C)_2\cdot C:CH\cdot CO\cdot CMe_3$, m. p. 109·5—110·5° (corr.). The carbinol in light petroleum is transformed by phosphorus tribromide into the corresponding *bromide*, apparently existing in two forms, m. p. 69—70° (corr.) and 177—178° (corr.), respectively. *Tri*-tert.-*butylethinylmethyl acetate*, m. p. 144·5—145·5° (corr.), from the carbinol, potassium, and acetic anhydride or from the bromide and silver acetate, is hydrolysed by potassium ethoxide to the original carbinol. With molecular silver in the presence of ether the bromide affords *hexa*-tert.-*butylethinylethane*, $(CMe_3\cdot C:C)_3C\cdot C(C:C\cdot CMe_3)_3$, m. p. 130—131° (corr.), rearranged in xylene at 140° to a *hydrocarbon*, $C_{38}H_{54}$, m. p. 174—175° (corr.). *Tri*-tert.-*butylethinylacetic acid*, $(CMe_3\cdot C:C)_3C\cdot CO_2H$, m. p. 202—205°, is prepared from the ethane by the successive action of sodium–potassium alloy and carbon dioxide or from the bromide by treatment with magnesium and carbon dioxide. H. WREN.

Action of nascent thiocyanogen on isoprene and dimethylbutadiene. H. A. BRUSON and W. A. CALVERT (J. Amer. Chem. Soc., 1928, **50**, 1735—1737).—An additive *compound*, $C_7H_8N_2S_2$, m. p. 76—77° (corr.), is formed by the addition of bromine to isoprene and sodium thiocyanate in glacial acetic acid at 5—6°. A similar *substance*, $C_8H_{10}N_2S_2$, m. p. 130° (corr.), is produced from $\beta\gamma$-dimethylbutadiene. The compounds are useful for the identification of the hydrocarbons. H. WREN.

Rearrangements of the triple linking. H. H. GUEST (J. Amer. Chem. Soc., 1928, **50**, 1744—1746).—Δ^{α}-Heptinene is prepared in 74% yield by the addition of dibromoheptane to finely-divided potassium hydroxide covered with mineral oil at 250°. It is converted into an isomeric hydrocarbon by passage over soda–lime at 380° or over pumice at 350°. The reverse transformation is apparently effected by sodamide suspended in mineral oil at 160°. H. WREN.

Modification of the Adams' method of preparing alkyl iodides. H. S. KING (Proc. Nova Scotian Inst. Sci., 1927, **16**, 87—91).—A modified form of apparatus is described which can be constructed from commonly available parts. H. WREN.

Colorimetric determination of ethylene chlorohydrin. M. B. SAPADINSKI (Z. anal. Chem., 1928, **74**, 273—275, and J. Russ. Phys. Chem. Soc., 1928, **60**, 695—697).—The solution containing ethylene chlorohydrin is mixed with diazobenzenesulphonic acid and warmed to 25°, whereby complete oxidation of the $\cdot CH_2\cdot OH$ group to >C:O occurs. The alkali hydroxide, which induces condensation, is not added until the first change is complete; subsequently the mixture is heated at 50°. For measurement, a solution of "Bordeaux-Lafitte" in benzene, standardised by use of known amounts of ethylene chlorohydrin, is employed. H. WREN.

Derivatives of *n*-heptane. R. T. DILLON and H. J. LUCAS (J. Amer. Chem. Soc., 1928, **50**, 1171—1714).—*Heptan-δ-ol*, m. p. −37·2° to −41·5°, b. p. 153·4—154·4° (corr.)/745 mm., d_4^{25} 0·8175, n_D^{25} 1·4173, is prepared from magnesium *n*-propyl bromide and ethyl formate. *Heptan-γ-ol*, from magnesium *n*-butyl bromide and propaldehyde, has b. p. 152·7—154° (corr.)/745 mm., n_D^{20} 1·4201. H. WREN.

Constitution of phytol. F. G. FISCHER [with K. LOWENBERG] (Annalen, 1928, **464**, 69—90).—The ketone obtained by Willstatter and co-workers (A., 1911, i, 144; 1919, i, 448) by the oxidation of phytol, and regarded by them as having the formula $C_{17}H_{34}O$, is now shown to be $C_{18}H_{36}O$, since glycollaldehyde is formed when phytol ozonide, a C_{20} compound, is reduced either by means of zinc and acetic acid or by means of hydrogen and palladised calcium carbonate. If phytol is regarded as being built up of reduced isoprene units, it is most likely to be (cf. geraniol and farnesol) tetramethyl-Δ^{β}-hexadecen-α-ol, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CMe{:}CH\cdot CH_2\cdot OH$, which when ozonised etc. would produce glycollaldehyde and ζκξ-trimethylpentadecan-β-one. The latter substance has accordingly been synthesised: Hydrogenation of farnesol in methyl alcohol in presence of palladised calcium carbonate affords a 40%, whilst hydrogenation in 80% methyl alcohol in presence of palladous chloride gives not less than an 80% yield of *farnesane* [*βζκ-trimethyldodecane*], b. p. 119·5—120°/11 mm., d_4^{25} 0·7682, n_4^{25} 1·4303. Reduction of farnesyl acetate in ethyl acetate in presence of palladised calcium carbonate gives a little farnesane, but mainly the desired *hexahydrofarnesol* [*γηλ-trimethyldodecanol*], b. p. 151—152·5°/10 mm., d_4^{25} 0·8491, n_D^{25} 1·4487. The latter is converted by phosphorus tribromide in light petroleum into *γηλ-trimethyldodecyl bromide*, b. p. 150—154°/10 mm., which with ethyl sodioacetoacetate gives *ethyl γηλ-trimethyldodecylacetoacetate*, b. p. 192—195°/10 mm. The latter, when hydrolysed by cold and then by warm 3% methyl-alcoholic potassium hydroxide, affords ζκξ-trimethylpentadecan-β-one, identical in properties with the ketone, $C_{18}H_{36}O$ (b. p. 173·5—174°/10 mm. or 294—295°/708 mm., d_4^{25} 0·8323, n_D^{25} 1·4432). The two semicarbazones melted alone, or when mixed, at 66—67°. The ketone and phytol therefore have the constitutions mentioned above. E. E. TURNER.

Spatial configuration of two *cis-trans*-ethylenic isomerides [βε-dimethyl-Δ^{γ}-hexene-βε-diols]. BOURGUEL and RAMBAUD (Compt. rend., 1928, **187**, 383—384).—The *trans*(α)-form, m. p. 76—77°, of βε-dimethyl-Δ^{γ}-hexene-βε-diol (Zalkind, A., 1923, i, 176) is shown to be a solid solution of 5 parts of the *cis*(β)-form, m. p. 69—70°, and 1 part of the true trans(γ)-*modification*, m. p. 101°, obtained also by reducing βε-dimethyl-Δ^{γ}-hexinene-βε-diol with sodium and alcohol. Whilst dehydration of the *cis*-modification gives a γ-oxide (Zalkind, *loc. cit.*), the *trans*-compound affords a mixture of βε-dimethyl-$\Delta^{\gamma\epsilon}$-hexadien-β-ol and βε-dimethyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene. H. BURTON.

Condensations of glycerol. RANGIER (Compt. rend., 1928, **187**, 345—346).—The action of fused sodium acetate on heated 95% glycerol followed by treatment of the product with acetic anhydride affords the following compounds: *diglyceryl tetra-acetate*, $(C_3H_5)_2O(OAc)_4$, b. p. 164—165°/2 mm.; *triglyceryl penta-acetate*, $(C_3H_5)_3O_2(OAc)_5$, b. p. 194—195°/2 mm.; *tetraglyceryl hexa-acetate*, b. p. 224—225°/2 mm.; *pentaglyceryl hepta-acetate*, b. p. 254—255°/2 mm.; *hexaglyceryl octa-acetate*, b. p. 284—285°/2 mm.; *heptaglyceryl nona-acetate*. H. WREN.

Acetylenic glycerols containing a straight chain of five carbon atoms. R. LESPIEAU (Bull. Soc. chem., 1928, [iv], **43**, 607—662).—*δε-Dichloro-Δ^{α}-pentinen-γ-ol*, b. p. 90—91°/12 mm., d^{23} 1·306, n_D 1·500, is obtained from dimagnesium acetylenyl bromide and acraldehyde dichloride. It is converted by 10% potassium hydroxide into *ε-chloro-γδ-oxido-Δ^{α}-pentinene*, b. p. 58—60°/20 mm., d^{23} 1·159, n_D 1·472, which is hydrated to *ε-chloro-Δ^{α}-pentinene-γδ-diol*, b. p. 131—132°/16 mm., d^{16} 1·289, n_D^{16} 1·501. The latter substance with sodium methoxide affords *ε-methoxy-Δ^{α}-pentinene-γδ-diol*, b. p. 100°/3 mm., d^{17} 1·12, n_D^{17} 1·473, whereas it is hydrolysed by water in presence of calcium carbonate to *Δ^{α}-pentinene-γδε-triol*, b. p. 156—159°/4 mm., d^{25} 1·217, n_D^{25} 1·489 (*triphenylurethane*, m. p. 204—206°). All the acetylenic compounds react with alcoholic silver nitrate, whereas only the dichlorohydrin and epichlorohydrin yield precipitates with ammoniacal cuprous chloride. The isolation of two *αβηθ-tetrachloro-Δ^{δ}-octinene-γζ-diols*, m. p. 139—139·5° and 96·5—97·5°, respectively, is described.

ε-Methoxy-αβ-oxido-Δ^{γ}-pentinene, b. p. 75—76°/15 mm., d^{26} 4·024, 1·4573, is prepared from chloroacetaldehyde and the compound $OMe\cdot CH_2\cdot C{:}C\cdot MgBr$. It is converted by hydrogen chloride into *α-chloro-ε-methoxy-Δ^{γ}-pentinene-β-ol*, b. p. 117·5—118·5°/12 mm., d^{24} 1·172, n_D^{24} 1·485, and by water into *ε-methoxy-Δ^{γ}-pentinene-αβ-diol*, b. p. 155—156°/12 mm., d^{22} 1·1274, n_D^{22} 1·481; with boiling methyl alcohol containing a little sulphuric acid it affords *αε-dimethoxy-Δ^{γ}-pentinene-β-ol*, b. p. 207—210°/10 mm., d^{23} 1·0508, n_D^{23} 1·4608. *γδ-Dibromo-ε-methoxy-Δ^{γ}-pentinene-αβ-diol* has m. p. 51—52°, b. p. 192°/11 mm. H. WREN.

Use of magnesium alkoxides in the preparation of ethers. V. CERCHEZ (Bull. Soc. chim., 1928, [iv], **43**, 762—768).—When treated on a brine-bath with 2 mols. of methyl sulphate, magnesium alkoxides afford methyl ethers in 70 80% yield. With ethyl sulphate at 120—130° the corresponding

ethyl ethers are obtained in 60% yield. The following ethers have been prepared by this method: methyl *n*-butyl ether, b. p. 70°; methyl *iso*amyl ether, b. p. 90—91°; methyl *cyclo*hexyl ether, b. p. 133—135°; *methyl* sec.-*octyl ether*, b. p. 158° (yield 15%), octene, b. p. 125°, being also produced; ethyl *n*-propyl ether, b. p. 63·6°; ethyl *n*-butyl ether, b. p. 91°. Magnesium benzyloxide and methyl sulphate give no definite product. The alkoxides are readily obtained by treating magnesium amalgam, prepared in the dry way, with the alcohol, the action proceeding very readily with propyl and benzyl alcohols and *cyclo*hexanol, less readily with butyl, *iso*amyl, and octyl alcohols. When *cyclo*hexanol is heated at 120° with 2 mols. of methyl alcohol and 1 mol. of sulphuric acid a considerable amount of *cyclo*hexene is formed.
R. BRIGHTMAN.

Hydrogenation of ethers. A. MARTY (Compt. rend., 1928, **187**, 47—49).—Propyl, *iso*propyl, butyl, amyl, and *iso*amyl ethers suffer fission when passed with hydrogen over reduced nickel at 250—300°. At 180°, phenetole is smoothly converted into *cyclo*hexane and ethyl alcohol, whereas at 250° this reaction is accompanied by the production of ethane and phenol. β-Naphthyl methyl and ethyl ethers decompose at 280° in both directions; the aromatic components are further hydrogenated to di- and tetra-hydronaphthalene and tetrahydro-β-naphthol. Guaiacol at 180° under 300 mm. gives the mixed ether $OH\cdot C_6H_{10}\cdot OMe$, together with pyrocatechol and phenol (partly reduced to *cyclo*hexanol). Under similar conditions, diphenyl ether affords di*cyclo*hexyl ether, phenol, *cyclo*hexanol, benzene, and *cyclo*hexane.
H. WREN.

Action of disilicon hexachloride on ether. S. KIPPING and R. A. THOMPSON (J.C.S., 1928, 1989—1990).—Disilicon hexachloride, like silicon tetrachloride (Kipping and Murray, this vol., 79), reacts to a slight extent with pure ether to yield a compound from which alcohol is formed on hydrolysis with sodium hydroxide. It is suggested that an additive compound is first formed which is partly decomposed into ethyl chloride and chloroethoxysilicon derivatives.
J. W. BAKER.

Preparation of normal sulphuric esters. R. LEVAILLANT (Compt. rend., 1928, **187**, 234—236).—Alkyl sulphates are prepared by the action of alkyl nitrites on alkyl chlorosulphonates, $Cl\cdot SO_2\cdot OR + O.N\cdot OR' = OR\cdot SO_2\cdot OR' + NOCl$. Thus methyl chlorosulphonate and methyl nitrite at 80—145° give methyl sulphate in 40% yield. Ethyl sulphate, in 55% yield, is derived from ethyl nitrite and ethyl chlorosulphonate at 80—100°.
H. WREN.

Organic titanous compound and the preparation of solutions of titanous salts. D. W. MACCORQUODALE and H. ADKINS (J. Amer. Chem. Soc., 1928, **50**, 1938—1939).—Tetraethyl titanate is reduced by sodium and ethyl alcohol to impure ethyl titanite, Et_3TiO_3, which can be further purified by heating at 156°/8—10 mm., whereby some unchanged ethyl titanate distils. The final product is a dark blue, amorphous solid containing about 87·4% of titanite. It reduces aromatic nitro-compounds to amines very readily and aromatic aldehydes to alcohols somewhat more slowly.
H. WREN.

Preparation of esters. M. KOTAKE and Y. FUJITA (Bull. Inst. Phys. Chem. Res., Japan, 1928, **7**, 734—739).—Nearly quantitative yields of various esters (including those of stearic, succinic, benzoic, malonic, maleic, cinnamic, pyromucic, and salicylic acids) are obtained by heating the acid with a slight excess of alcohol, a quantity of sulphuric acid equivalent to the alcohol used, and anhydrous aluminium sulphate at 100°. Only a 71% yield was obtained in the case of oxalic acid.
J. W. BAKER.

Action of hydrogen bromide on organic esters at the ordinary pressure. M. SÉON (Compt. rend., 1928, **187**, 131—133).—The action of hydrogen bromide under varied conditions of temperature but at atmospheric pressure on amyl formate, amyl salicylate, benzyl acetate, benzyl benzoate, allyl acetate, ethyl acetoacetate, and *cyclo*hexyl acetate leads to the formation of the organic acid and the alkyl, benzyl, or *cyclo*hexyl bromide. Phenyl acetate or benzoate is not decomposed under these conditions.
H. WREN.

Catalytic decomposition of oleic acid. B. M. MARKS and H. C. HOWARD, jun.—See this vol., 968.

Presence of a new fatty acid in a fish oil. H. MARCELET (Compt. rend., 1928, **187**, 145—146).—In addition to stearic, palmitic, and an unidentified acid, m. p. 46—47°, *dorosomic acid*, $C_{17}H_{34}O_2$, m. p. 55°, is isolated from *Dorosoma vasus*, Bloch; the *methyl* ester, m. p. 30°, and the *barium* salt are described.
H. WREN.

Ketazines of lævulic acid and lævulhydrazide. C. W. BENNETT (J. Amer. Chem. Soc., 1928, **50**, 1747—1748).—Sodium lævulate and hydrazine hydrate in boiling alcohol afford *lævulic acid ketazine*, $C_{10}H_{16}O_4N_2$, m. p. 119—120° (corr.). Lævulhydrazide and hydrazine hydrate give *lævulhydrazide ketazine*, $C_{10}H_{20}O_2N_4$, m. p. 219—220° (corr.).
H. WREN.

Structures of convolvulinolic and japalinolic acids. Synthesis of κ-hydroxypentadecoic and κ-hydroxyhexadecoic acids. L. A. DAVIES and R. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 1749—1755).—Methyl ι-aldehydododecoate, b. p. 141—143°/4 mm., is converted by magnesium *n*-amyl bromide into *methyl κ-hydroxyhexadecoate*, m. p. 40·5—41·5°, b. p. 183—186°/3 mm. *κ-Hydroxyhexadecoic acid*, m. p. 68—69°, prepared by hydrolysis of the ester, is oxidised by chromic acid in glacial acetic acid to *κ-ketohexadecoic acid*, m. p. 74—75°. Since these acids are obtained also from japalinolic acid by oxidation and subsequent reduction of the keto-acid thus produced, it follows that this acid is *d*-κ-hydroxyhexadecoic acid. Similarly, methyl ι-aldehydododecoate and magnesium *n*-butyl bromide afford *methyl κ-hydroxypentadecoate*, b. p. 166°/2 mm., m. p. 29—32°, from which *κ-hydroxypentadecoic acid*, m. p. 63·5—64°, and *κ-ketopentadecoic acid*, m. p. 70—71°, are derived. Convolvulinolic acid has a structure different from that of κ-hydroxypentadecoic acid. θ-*Ketohexadecoic acid*, m. p. 73·5—74·5°, is described.
H. WREN.

Synthesis of heptane-ϰε-dicarboxylic acid. A. S. CARTER (J. Amer. Chem. Soc., 1928, **50**, 1967—1970).—*Ethyl δ-phenoxypropylmalonate*, b. p. 228

235°/26 mm., is converted successively into *δ-phenoxypropylmalonic acid*, m. p. 72—78° (decomp.), and δ-phenoxyvaleric acid, m. p. 55—56° (*silver* salt). The latter acid is transformed into δ-iodovaleric acid and thence into *ethyl δ-iodovalerate*, b. p. 108—118°/20 mm., which is condensed with ethyl ethylsodiomalonate to *ethyl heptane-αεε-tricarboxylate*, b. p. 195—200°/20 mm., from which *heptane-αεε-tricarboxylic acid*, m. p. 86—88°, and *heptane-αε-dicarboxylic acid*, b. p. 218—223°/17 mm., m. p. 41·5—43° (*silver* salt), are derived. H. WREN.

Rotatory dispersion of derivatives of tartaric acid. IV. Propyl and butyl tartrates. P. C. AUSTIN (J.C.S., 1928, 1831—1834).—The rotatory dispersions of di-*n*-propyl, di*iso*propyl, di-*n*-butyl, and di*iso*butyl tartrates have been measured. In each case the rotatory dispersion is both complex and anomalous and is expressed by Drude equations with two terms, the same dispersion constants being used as were determined by Lowry and Abram for the dimethyl (J.C.S., 1915, **107**, 1187) and by Lowry and Cutter for the diethyl ester (*ibid.*, 1922, **121**, 542). No simple relation is found between the rotation constants. The following revised physical data for the esters are given: methyl, m. p. 48° and 61·5° (dimorphous); ethyl, m. p. 18·7°, d_4^{20} 1·2028; *n*-propyl, b. p. 177°/17 mm., d_4^{20} 1·1186; *iso*propyl, b. p. 152°/12 mm., d_4^{20} 1·1136; *n*-butyl, m. p. 21·8°, b. p. 182°/11 mm., d_4^{20} 1·0909; *iso*butyl, m. p. 66°, b. p. 171°/11 mm. J. W. BAKER.

Rotatory dispersion of derivatives of tartaric acid. III. Diacetyltartaric acid and its esters. P. C. AUSTIN (J.C.S., 1928, 1825—1831).—Re-examination of the rotatory dispersion of diacetyltartaric acid (cf. Austin and Park, A., 1925, ii, 1028) in ether in place of acetone allows the measurements to be extended further into the ultra-violet, and evidence of its complex dispersion is thus obtained. The rotations in this solvent ($[\alpha]_D$ −17·01°) are much lower than in acetone ($[\alpha]_D$ −24·5°) and it is suggested that the latter may react with the acid to give a bridged compound. The enhanced lævorotations obtained by addition of water to the solution in acetone may be ascribed, as in the case of tartaric acid itself, to an alteration in the equilibrium between two components of opposite sign. The rotatory dispersions of the methyl, ethyl, *n*- and *iso*-propyl, and *n*- and *iso*-butyl esters have been determined. The dispersion of the methyl ester is complex but normal, whilst the other esters exhibit anomalous dispersion. The following revised physical data for esters of diacetyltartaric acid are given: *methyl*, m. p. 118°, $[\alpha]_D$ −17·87° in acetone; ethyl, m. p. 103°, b. p. 179°/17 mm., $[\alpha]_D$ −0·50° in ether; *n*-propyl, m. p. 67°, b. p. 181°/10 mm., d_4^{20} 1·1114, $[\alpha]_D$ (supercooled) +11·02°; *iso*propyl, m. p. 21·5°, b. p. 167°/11 mm., $[\alpha]_D$ +8·63° in ether; *n*-butyl, m. p. 31·4°, b. p. 205°/15 mm., d_4^{20} 1·0823, $[\alpha]_D$ (liquid) +22·20°; *iso*butyl, b. p. 193°/13 mm., d_4^{20} 1·0816, $[\alpha]_D$ (liquid) +67·18°. J. W. BAKER.

Oxidation of alcohols to aldehydes and condensation of aldehydes and alcohols to mixed esters. I. S. N. DANILOV (Trans. State Inst. Appl. Chem., Moscow, 1927, No. 5, 66—88).—The best results in the catalytic oxidation of amyl and *iso*butyl alcohols were obtained with zinc as catalyst, when 40—70% yields resulted at 580° and a speed of 50—100 g. of alcohol per hr.; with birch charcoal at 320—330°, the yield was 56—57%. Esters were obtained in 94—96% yield by Tischenko's method. Thus, aluminium turnings (0·4 g.) were activated by exposure to a stream of hydrogen chloride, preceded and followed by hydrogen; amyl alcohol (18 c.c.) was added, the metal dissolving in 20 min. Valeraldehyde (100 g.) was then added with cooling and stirring, the mixture being finally heated for 30 min. at 80°, and distilled at 100 mm.

CHEMICAL ABSTRACTS.

Catalysis in the conversion of allyl alcohol and acraldehyde into propaldehyde. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1928, **50**, 1930—1935).—Study has been made of the behaviour of allyl alcohol and mixtures of it with acraldehyde in presence of a zinc oxide catalyst and of *n*-propyl alcohol and acraldehyde in presence of aluminium oxide. Formation of propaldehyde by passing allyl alcohol over zinc oxide results, at least in part, from the reaction of the alcohol with acraldehyde and not through hydrogenation of acraldehyde or intramolecular rearrangement of allyl alcohol.

H. WREN.

Reactions relating to carbohydrates and polysaccharides. XIV. Polymerisation of aldehydes. H. HIBBERT, W. F. GILLESPIE, and R. E. MONTONNA (J. Amer. Chem. Soc., 1928, **50**, 1950—1955).—Chloral alone or, preferably, in presence of a trace of hydrogen chloride combines with propaldehyde, *iso*butaldehyde, and trimethylacetaldehyde giving substituted *paraldehydes*, CCl_3·CHO,2R·CHO, m. p. 62·5°, 68·5—69°, and 114—115°, respectively, which are stable towards alkali hydroxide but are decomposed by boiling dilute sulphuric acid. Paraldehydes could not be prepared from three different aldehydes or from acetaldol and chloral. H. WREN.

Relations between rotatory power and structure in the sugar group. XVIII. α-Methyl-*d*-lyxoside triacetate. F. P. PHELPS and C. S. HUDSON (J. Amer. Chem. Soc., 1928, **50**, 2049—2051).—*α-Methyl-*d*-lyxoside triacetate*, m. p. 96°, $[\alpha]_D^{20}$ +30·1° in chloroform, is prepared from α-methyl-*d*-lyxoside and acetic anhydride in warm pyridine. Comparison of its rotation with that of α-methyl-*d*-xyloside triacetate indicates that the lyxoside derivative has a butylene oxide-ring and that crystalline α-lyxose, $[\alpha]_D$ +5·5°, also has this ring structure, since its rotation differs normally from that of α-methyl-*d*-lyxoside. H. WREN.

Acetylmonoses. IV. Two isomeric triacetylmethyl-lyxosides. P. A. LEVENE and M. L. WOLFROM (J. Biol. Chem., 1928, **78**, 525—533).—α-Methyl-*d*-lyxoside is converted by acetic anhydride in pyridine at 0° into *α-methyl-*d*-lyxoside triacetate*, m. p. 96°, $[\alpha]_D^{0}$ +30·6° in chloroform. α-*d*-Lyxoside tetraacetate is treated with an almost saturated solution of hydrogen bromide in glacial acetic acid giving a syrupy bromo-compound which is treated with methyl alcohol and quinoline; the liberated acid is neutralised by silver carbonate or, preferably, sodium methoxide,

whereby *γ-methyl-*d*-lyxoside triacetate*, m. p. 90°, $[\alpha]_D$ $-103{\cdot}1°$ in chloroform, is obtained. The syrupy bromoacetyl-lyxose is converted by silver carbonate and methyl alcohol into the α- and γ-methyl-*d*-lyxoside triacetates. The γ-form is very rapidly de-acetylated by treatment with dry methyl alcohol containing 0·1% of hydrogen chloride. H. WREN.

α- and β-Forms of diacetone methylmannoside [methylmannoside di*iso*propylidene ether]. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1928, **78**, 363—367).—α-Methylmannoside is slowly converted by acetone containing 1% of hydrogen chloride into methylmannoside di*iso*propylidene ether, b. p. 105°/0·2 mm., $[\alpha]_D^{20}$ $+56{\cdot}0°$, whereas the same product is very rapidly formed from γ-methylmannoside; it is probably identical with the product, $[\alpha]_D^{20}$ $+46{\cdot}6°$, obtained by the action of silver oxide and methyl iodide on mannose di*iso*propylidene ether. The specific rotation of the methylmannoside di*iso*propylidene ether prepared from di*iso*propylidenemannose by Freudenberg's method could not be increased beyond $-41°$. All three products are hydrolysed at the same rate and hence all have the butylene-oxide structure. It follows therefore that the amylene-oxide structure of methylmannoside is changed under the influence of acetone. H. WREN.

Ameliaroside, a new glucoside from *Amelanchier vulgaris*, Moench. M. BRIDEL, C. CHARAUX, and G. RABATE (Compt. rend., 1928, **187**, 56—57).—The *glucoside* crystallises in small prisms containing 4·54% H_2O, m. p. 195°, $[\alpha]_D$ $-86{\cdot}56°$ (anhydrous). It is hydrolysed by dilute sulphuric acid at 100° or by emulsin to dextrose and *ameliarol*, m. p. 110°, which gives a strong violet coloration with ferric chloride. H. WREN.

Production of furfuraldehyde from oxycellulose. F. W. KLINGSTEDT (Zellstoff u. Papier, 1928, 8, 471—474).—Distillation of oxycelluloses with hydrochloric acid appears to yield furfuraldehyde when the phloroglucinol method of determination is followed, but the amount has generally been overestimated owing to non-appreciation of the production of hydroxymethylfurfuraldehyde. If the barbituric acid method is used, it appears that cellulose which has not been oxidised too powerfully does not contain groups capable of yielding furfuraldehyde in appreciable amount. The furfuraldehyde, obtained from highly oxidised cellulose in small amount, is derived from non-cellulosic components. H. WREN.

Lignin. II. Fractional extraction of lignin from corn [maize] cobs. M. PHILLIPS (J. Amer Chem. Soc., 1928, **50**, 1986—1989).—The ground material is subject to a preliminary treatment with boiling alcohol and benzene (1 : 1). Lignin is fractionally extracted by 2% alcoholic sodium hydroxide at the ordinary temperature, by 2% aqueous sodium hydroxide at 100° and 135°, and finally by 4% aqueous sodium hydroxide at 180°, each process being continued until lignin is not further removed before the next process is applied. The lignin is unequally combined with the carbohydrates, part of it being loosely bound possibly in the form of an ester and the remainder more formly retained, probably in ether-like combination. H. WREN.

Effect of the cyano-group on the basicity of aliphatic amines as determined in aqueous and alcoholic solutions. T. D. STEWART and V. COOK (J. Amer. Chem. Soc., 1928, **50**, 1973—1983).—The constants are determined by electrometric titration in water and by colorimetric measurements in alcohol. The basic dissociation constants of α-diethylaminoacetonitrile and of α-diethylaminophenylacetonitrile in water are $1{\cdot}0\times10^{-10}$ and $1{\cdot}7\times10^{-11}$, respectively. In alcoholic solution, the acidic dissociation constants of their salts (chlorides) are $3{\cdot}4\times10^{-5}$ and $5{\cdot}2\times10^{-4}$, respectively, whilst those of α-diethylaminopropionitrile and of α-diethylamino*iso*butyronitrile are $3{\cdot}4\times10^{-5}$ and 2×10^{-6}, respectively. The following compounds are prepared from sodium hydrogen sulphite, diethylamine, potassium cyanide, and the requisite aldehyde or ketone: *α-diethylaminoacetonitrile*, b. p. 62—63°/14 mm.; *α-diethylaminopropionitrile*, b. p. 67—68°/17 mm.; *α-diethylaminophenylacetonitrile*, b. p. 130—131°/11 mm.; *α-diethylamino*iso*butyronitrile*, b. p. 75—77°/23 mm. H. WREN.

Catalytic preparation of methylamine from methyl alcohol and ammonia. T. L. DAVIS and R. C. ELDERFIELD (J. Amer. Chem. Soc., 1928, **50**, 1786—1789).—Methylamine is formed when methyl alcohol and ammonia are passed over a heated thorium oxide catalyst. Under optimal conditions (325—330°; relative concentration about 0·80—0·83 mol. of ammonia per mol. of methyl alcohol) nearly one third of the methyl alcohol is transformed into methylamine. H. WREN.

Action of organo-magnesium compounds on certain fatty dialkylamides. M. MONTAGNE (Compt. rend., 1928, **187**, 128—130).—The action of butyl bromide or iodide on a mixture of butyrdiethylamide and magnesium methyl iodide yields β-diethylamino-β-methylpentane and *δ-diethylamino-δ-methylnonane*, b. p. 128—129°/20 mm. (*picrate*, m. p. 78—79°; *chloroaurate*, m. p. 54°); the *hydrochloride* of the latter is decomposed by heat into diethylammonium chloride and a *hydrocarbon*, $C_3H_7{\cdot}CMe{:}CH{\cdot}C_5H_9$ or $CHEt{:}CMe{\cdot}CH_2{\cdot}C_5H_9$, b. p. 161—164°. If benzyl chloride is employed, the products are β-diethylamino-β-methylpentane and *γ-diethylamino-α-phenyl-γ-methylhexane*, b. p. 163°/10 mm. (*picrate*, m. p. 99°; *chloroaurate*, m. p. 101°). H. WREN.

Additive compounds of cadmium halides with hexamethylenetetramine. VI. G. SCAGLIARINI and E. BRASI (Atti R. Accad. Lincei, 1928, [vi], 7, 509—511).—In order to trace the influence of the solvent particularly with respect to the dielectric constant the formation of additive *compounds* between cadmium halides and hexamethylenetetramine has been examined in water and in acetone. Dilute aqueous solutions of cadmium halides when mixed with a dilute aqueous solution of hexamethylenetetramine leads to the precipitation of the crystalline substances $2CdCl_2,C_6H_{12}N_4$, $CdBr_2,2C_6H_{12}N_4$, and $CdI_2,C_6H_{12}N_4,8H_2O$. Gradual addition of a concentrated acetone solution of the base to a concentrated acetone solution of cadmium chloride leads to the formation of the complex $CdCl_2,C_6H_{12}N_4$. A similar procedure in the case of cadmium bromide furnishes the compound $3CdBr_2,2C_6H_{12}N_4$, whilst

the addition of the halide solution to the base gives rise to the substance $CdBr_2,C_6H_{12}N_4$. From cadmium iodide only one substance is formed, viz., $2CdI_2,C_6H_{12}N_4$. R. W. LUNT.

Action of thiocyanogen on *ON*-disubstituted hydroxylamines and primary amines. L. W. JONES and E. E. FLECK (J. Amer. Chem. Soc., 1928, **50**, 2018—2028).—N-*Thiocyano*-ON-*diethylhydroxylamine*, b. p. 45—46°/2 mm., prepared by the action of thiocyanogen on *ON*-diethylhydroxylamine in ether, is hydrolysed by 2% hydrochloric acid at 0° to hydrocyanic, thiocyanic, and sulphuric acids and ethoxyethylammonium chloride (identified as β-ethoxy-α-phenyl-β-ethylcarbamide, m. p. 63°), and by 2% potassium hydroxide to ammonia, ethylamine, acetaldehyde, and potassium thiosulphate. *Ethyl* ON-*carbethoxydibenzylhydroxamate*, b. p. 200—203°/7 mm., prepared from carbethoxyhydroxamic acid, benzyl chloride, and potassium hydroxide, is hydrolysed to ON-*dibenzylhydroxylamine*, b. p. 145—146°/3 mm., which, with thiocyanogen, affords N-*thiocyano*-ON-*dibenzylhydroxylamine*, m. p. 91°, and *benzyloxybenzylammonium thiocyanate*, m. p. 50—52°. The hydroxylamine is hydrolysed in exactly the same manner as the corresponding diethyl compound. At an elevated temperature *ON*-disubstituted hydroxylamines are hydrolysed by alkali hydroxide to the corresponding aldehyde and amine.

Thiocyanotriphenylmethylamine, $CPh_3{\cdot}NH{\cdot}SCN$, m.p. 142° (*thiocyanate*, m. p. 173°), is prepared from thiocyanogen and triphenylmethylamine in ether. It suffers rearrangement when heated with calcium oxide at 440—450° yielding benzophenoneanil (identified by hydrolysis to aniline and benzophenone). Thiocyanobenzylamine could not be obtained homogeneous. The preparation of *α-benzyloxy-α-benzylcarbamide*, m. p. 98—99°, and *α-benzyloxy-α-benzylthiocarbamide*, m. p. 94—95°, is recorded. H. WREN.

Action of nitrous acid on amino-compounds. II. Aliphatic amino-acids. T. W. J. TAYLOR (J.C.S., 1928, 1897—1906).—The velocity of reaction of nitrous acid with glycine and α- and β-alanine has been measured in dilute aqueous solution at 25°, the reaction being followed by determination of the amino-acid by a modification of Sorensen's formaldehyde titration method (A., 1908, i, 115). The reaction velocity with 1 equivalent of nitrous acid is diminished by addition of mineral acids or neutral salts. The hydroxy-acid formed in the reaction has no negative autocatalytic effect. The reaction velocity was measured in $0{\cdot}05N$- and $0{\cdot}025N$-solution in the case of glycine and α-alanine, and in $0{\cdot}05N$- and $0{\cdot}04N$-solution with β-alanine where the reaction is much slower. In every case the reaction is approximately of the third order. Doubling the concentration of nitrous acid increases the velocity to a greater extent than does doubling that of the amino-acid. Hence two of the molecular species involved must be nitrous acid, and the third some form of the amino-acid. The latter is present in two forms, $NH_3^+{\cdot}RCO_2^-$ (A^{+-}) and $NH_3^+{\cdot}RCO_2H$ (A^+), and mathematical analysis of the kinetics of the reaction shows that the ratio of the concentrations of these two forms is almost independent of the concentration, the values in $0{\cdot}05N$- and $0{\cdot}025N$-solution being for glycine, 0·786 and 0·800, α-alanine, 0·721 and 0·718, and for β-alanine 0·444 and 0·444, respectively. The reaction velocity was measured in the presence of $0{\cdot}05N$- and $0{\cdot}1N$-sulphuric acid, the presence of which lowers the reaction velocity, and would increase the concentration of A^+ and decrease the concentration of the nitrite ion and A^{+-}, and the velocity coefficients were calculated with various assumptions regarding the molecular species involved in the reaction. Agreement between the various experiments is reached only if the reacting species are (A^{+-}) and HNO_2, and the reaction velocity is thus proportional to the product $[A^{+-}][HNO_2]^2$. The apparent difference in the speeds of reaction in the three cases studied arises mainly from the difference in the acid dissociation constants; the smaller is the value of these, the smaller is the concentration of the form A^{+-} present. J. W. BAKER.

Preparation of *d*-arginine monohydrochloride. G. J. COX (J. Biol. Chem., 1928, **78**, 475—479).—Gelatin is hydrolysed by concentrated hydrochloric acid and the solution is concentrated to a thick syrup under reduced pressure. The residue is dissolved in water, neutralised with concentrated sodium hydroxide to Congo-red, and the arginine is precipitated as the flavianate. The precipitate is heated with concentrated hydrochloric acid, separated from flavianic acid, and again concentrated to a thick syrup in a vacuum. The syrup is dissolved in 95% alcohol and the solution cooled to cause the separation of residual flavianic acid as the arginine salt. After removal of the latter, the solution is treated with aniline, which causes the separation of *d*-arginine monohydrochloride. The latter substance is purified by crystallisation from a mixture of alcohol and water; it has m. p. 222° (corr.). H. WREN.

Action of picric acid on glycylglycine. A. MOREL, P. PRECEPTIS, and A. GALY (Compt. rend., 1928, **187**, 173—174).—Glycylglycine affords a crystalline monopicrate when its aqueous solution is mixed with picric acid and evaporated to dryness in a vacuum at the ordinary temperature; the residue is washed with ether and crystallised by slow evaporation of its aqueous solution. Alternatively, glycylglycine and picric acid are dissolved in aqueous barium hydroxide, the mixture is boiled, and the barium quantitatively removed by sulphuric acid; after removal of barium sulphate, the filtrate is slowly concentrated. Under the first set of conditions, glycine affords the monopicrate of diglycine. H. WREN.

Reciprocal action of picric acid and *cyclo*-glycylglycine. A. MOREL and P. PRECEPTIS (Compt. rend., 1928, **187**, 236—239).—In acid solution, the monopicrate of monoglycylglycine is obtained from the substances mentioned in the title. In faintly alkaline solution the same substance is obtained but reduction of picric acid also occurs. H. WREN.

Carbonic acid azides. C. V. HART (J. Amer. Chem. Soc., 1928, **50**, 1922—1930).—*Dicyanodiazide*, $CN{\cdot}N{:}C(N_3)_2$, m. p. 40·3° (corr.), prepared by the action of cyanogen bromide on an aqueous solution of sodium azide (previously regarded as carbon pernitride), is

converted by ammonia into ammonium azide and *dicyanoamidoazide*, m. p. 151—152° (decomp.). It is hydrolysed by boiling water to azoimide and cyanamide, but reaction is not quantitative owing to formation of 5-aminotetrazole; if sodium hydroxide is used, sodium azide and sodium cyanamide are quantitatively formed. Dicyanodiazide is reduced by hydrogen sulphide to dicyanodiamide, m. p. 207·4°, which is similarly produced from dicyanoamidoazide. The ability of a substance to form sodium azide with sodium hydroxide and to yield an amine, sulphur, and nitrogen when reduced with hydrogen sulphide is regarded as specific evidence of the presence of azide groups, since these reactions are not shown by the isomeric tetrazoles. Treatment of an alcoholic solution of dicyanodiazide with aniline causes production of *dicyanophenylamidoazide*, decomp. 145° (*sodium* salt), reduced by hydrogen sulphide to phenyldicyanodiamide, m. p. 195—196° (probably identical with phenylcyanoguanidine). With α-naphthylamine, dicyanodiazide affords *dicyano-α-naphthylamidoazide* (*sodium* salt). Unexpectedly, the action of cyanogen bromide on the sodium salt of 5-aminotetrazole yields dicyanoamidoazide. Cyanurtriazide, $C_3N_3(N_3)_3$, is hydrolysed by sodium hydroxide to sodium azide and cyanuric acid and reduced by hydrogen sulphide to melamine, thus establishing the complete absence of tetrazole groups. *Cyanuramidodiazide*, $C_3N_3(NH_2)(N_3)_2$, decomp. above 200°, is formed by the action of ammonia on cyanurtriazide in ether. *Cyanuric dichloride azide*, m. p. 85°, is prepared from cyanuric trichloride and sodium azide. H. Wren.

Preparation of cyanogen by the wet method. C. Noir and Tching-Datchong (Compt. rend., 1928, **187**, 126—128).—The following procedure is adopted in analysis of the gas evolved by the action of potassium cyanide on copper sulphate. The gases are absorbed in 0·5*N*-potassium hydroxide and cyanogen is determined by addition of an excess of silver nitrate, removal of silver cyanide after acidification with nitric acid, and measurement of the residual silver. Carbon dioxide is determined by passing a known volume of gas into barium hydroxide and titration of the precipitated barium carbonate. Determination of hydrocyanic acid depends on passage of the gases into an excess of silver nitrate, removal of silver cyanide, and measurement of residual silver. The gas is found to contain 78% of cyanogen, 20% of carbon dioxide, and 1—2% of hydrocyanic acid. Carbon dioxide appears to be formed by hydrolysis of the cyanate. H. Wren.

Luminescence of aliphatic Grignard compounds. R. T. Dufford (J. Amer. Chem. Soc., 1928, **50**, 1822—1824).—Magnesium methyl, ethyl, propyl, and butyl bromides all emit faint light when oxidised. The effects are observed only at dilutions considerably greater than those used with magnesium aryl halides. H. Wren.

Preparation of mercury dimethyl. K. Fuchs (J. pr. Chem., 1928, [ii], **119**, 209—210).—A mixture of acid-free methyl sulphate (1 mol.), methyl acetate, and 0·5% sodium amalgam (1 mol. Na) is shaken in a pressure flask, at first cautiously, until the temperature, which rises to 60—70°, has fallen to 15°. The yield of pure mercury dimethyl, b. p. 91·5—92·5°/745 mm., is 60—65%, calculated on the sodium used. Methyl acetoacetate cannot replace the methyl acetate as catalyst. Addition of mercuric chloride and a corresponding excess of methyl sulphate gives only a 55% yield of mercury dimethyl, accompanied by some mercury methyl chloride. Ethyl sulphate has no advantage over ethyl bromide for mercury diethyl. C. Hollins.

Use of platinum oxide–platinum-black in the catalytic reduction of aromatic hydrocarbons. XVII. R. Adams and J. R. Marshall (J. Amer. Chem. Soc., 1928, **50**, 1970—1973).—Excellent results are recorded for the hydrogenation of the following aromatic compounds in presence of the catalyst and glacial acetic acid at 25—30° and 2—3 atm.: benzene, toluene, ethylbenzene, *m*-xylene, mixed xylenes, mesitylene, cymene, di- and tri-phenylmethane, αα-diphenylethane, dibenzyl, phenylacetic and β-phenylpropionic acids. H. Wren.

Tetraphenylditert.-butylethane. J. B. Conant and N. M. Bigelow (J. Amer. Chem. Soc., 1928, **50**, 2041—2049).—Diphenyl*tert.*-butylmethyl chloride, m. p. 71—72°, is rapidly converted by 40% sodium amalgam in ether in an atmosphere of nitrogen into the brick-red *sodium diphenyl*tert.*-butylmethyl*, the constitution of which is established by its transformation into *diphenyl*tert.*-butylacetic acid*, m. p. 160° (p-*nitrobenzyl* ester, m. p. 77°). The sodium salt is transformed by tetramethylethylene dibromide into *tetraphenyldi*tert.*-butylethane*, m. p. 138—141° (in an atmosphere of nitrogen), from which the sodium compound is readily re-formed. The hydrocarbon rapidly absorbs oxygen in solution at 25°, but a peroxide could not be isolated. On heating a dilute solution to 55°, a reversible colour change indicative of dissociation appears. When heated for a few minutes in solution at 100° in absence of air, it disproportionates completely. The effect of the tertiary alkyl group in promoting dissociation of the C–C linking is thus similar to that of secondary groups in the dixanthyl series. If an insufficient amount of sodium–potassium alloy is employed in place of sodium amalgam in the preparation of *potassium diphenyl*tert.*-butylmethyl*, the yield is much lowered and about half the chloride is converted into a *hydrocarbon*, $C_{34}H_{38}$, m. p. 145°, isomeric with tetraphenyldi*tert.*-butylethane; this substance does not react with oxygen or with sodium–potassium alloy. Treatment of the isomeric diphenyl*tert.*-butylmethyl chloride, m. p. 103—106°, or of γγ-diphenyl-β-methyl-Δ^{α}-butene with sodium–potassium alloy in ether gives a red metallic *derivative* differing from the sodium compound described above, since it is converted by carbon dioxide into an *acid*, $C_{18}H_{20}O_2$, m. p. 218—224° (decomp.) (non-crystalline p-*nitrobenzyl* ester), and by tetramethylethylene dibromide into an oil which does not absorb oxygen. H. Wren.

Effects induced by the phenyl group. I. Addition of polar reagents to styrene and the behaviour of the halogenated benzenes. F. Ashworth and N. Burkhardt (J.C.S., 1928, 1791—1802).—The interaction of styrene with hydrogen bromide, ammonium hydrogen sulphite, and thio-

phenol, and of α- and β-bromoethylbenzenes and αβ-dibromoethylbenzene with aqueous-alcoholic potassium hydroxide has been studied. Addition of hydrogen bromide and ammonium hydrogen sulphite to styrene occurs in accordance with the Markownikoff rule and requires negative free affinity on the ω-carbon atom in styrene, the sole products being, respectively, α-bromoethylbenzene and, after treatment with barium hydroxide, *barium α-phenylethanesulphonate* (+H_2O and anhydrous). The latter was identical with the product obtained by the action of ammonium sulphite on α-bromoethylbenzene, and was different from *barium β-phenylethanesulphonate* (+H_2O and anhydrous), similarly prepared from β-bromoethylbenzene. Posner's conclusion (A., 1905, i, 279) that the addition of thiophenol to styrene takes place quantitatively in the opposite sense to that of hydrobromic acid is confirmed, since the product is phenyl β-phenylethyl sulphide, b. p. 188—189°/15 mm., n_D 1·6082, contaminated, as measurements of its refractive index show, with less than 2% of phenyl α-phenylethyl sulphide, b. p. 163—164°/15 mm., n_D 1·6042. By oxidation the reaction product yields only phenyl β-phenylethyl sulphone identical with that obtained by the action of sodium benzenesulphinate on β-bromoethylbenzene. The reaction is accompanied by a 10% contraction and can thus be followed dilatometrically. It is greatly accelerated by the action of light, the increase in the rate of addition produced by exposure to sunlight continuing for some time after the reaction mixture is returned to diffuse daylight. Piperidine is a powerful retarding agent. Cryoscopic measurements of thiophenol, styrene, and mixtures of these in benzene show that no association takes place. By the action of boiling aqueous-alcoholic potassium hydroxide solution (0·4*N*) α-bromoethylbenzene is converted quantitatively into phenylmethylcarbinol; the β-compound yields only styrene, whilst styrene dibromide yields only α-bromostyrene. The conjugative electronic displacements which may occur in styrene in its various reactions are discussed. J. W. Baker.

Derivatives of *n*-butylbenzene. R. R. Read and D. B. Mullen (J. Amer. Chem. Soc., 1928, **50**, 1763—1765).—*n*-Butylbenzene is converted by nitration in presence of sulphuric acid into a mixture of o-*nitro*-n-*butylbenzene*, b. p. 131—133°/15 mm., d_4^{20} 1·071, and p-*nitro*-n-*butylbenzene*, b. p. 143—145°/15 mm., d_4^{20} 1·065. o-n-*Butylaniline*, b. p. 122—125°/12 mm., d_4^{20} 0·953 (*hydrochloride*, m. p. 137°), is prepared in the usual manner. o-n-*Butylphenol*, b. p. 113—115°/14 mm., d_4^{20} 0·975, and p-n-*butylphenyl* p-*nitrobenzoate*, m. p. 67—68°, are described. m-n-*Butylphenol* has b. p. 247—249°/758 mm., d_4^{23} 0·974. H. Wren.

Dichloro-*o*-xylenes. L. E. Hinkel, E. E. Ayling, and L. C. Bevan (J.C.S., 1928, 1874—1878). Dichlorination of pure *o*-xylene with gaseous chlorine in presence of iron filings at −10° yields mainly 4 : 5-dichloro- (I), m. p. 76°, b. p. 240° (corr.), and 3 : 4-*dichloro-* (II), m. p. 9°, b. p. 234° (corr.), together with a small quantity of 3 : 6-*dichloro-* (III), m. p. 68°, b. p. 227° (corr.), -*o-xylenes*. All on further chlorination yield the same tetrachloro-*o*-xylene, m. p. 227°. Oxidation of (I) yields 4 : 5-dichlorophthalic acid (Villiger, A., 1909, i, 930). Nitration with a mixture of fuming nitric and acetic acids converts it into 4 : 5-*dichloro*-3-*nitro*-o-*xylene*, m. p. 117°, which is reduced by iron and glacial acetic acid to 4 : 5-*dichloro*-3-o-*xylidine*, m. p. 88° (*acetyl* derivative, m. p. 197°). This is converted by the Sandmeyer reaction into a mixture of 3 : 4 : 5-trichloro-*o*-xylene and tetrachloro-*o*-xylene. When heated for 10 min. with nitric and sulphuric acids, (I) yields 4 : 5-*dichloro*-3 : 6-*dinitro*-o-*xylene*, m. p. 210°, which by reduction in alcoholic solution with sodium hydrosulphite yields the *diamine*, m. p. 186°. Nitration of (II) yields 3 : 4-*dichloro*-5-*nitro*-o-*xylene*, m. p. 78° (together with a little of the 6-nitro-isomeride), dinitration yielding 3 : 4-*dichloro*-5 : 6-*dinitro*-o-*xylene*, m. p. 172°. Reduction of the 5-nitro-compound yields 5 : 6-*dichloro*-o-4-*xylidine*, m. p. 63° (*acetyl* derivative, m. p. 147°), whilst from the dinitro-compound is obtained 3 : 4-*dichloro*-5 : 6-*diamino*-o-*xylene*, m. p. 176°, which reacts with phenanthraquinone. Nitration of (III) yields 3 : 6-*dichloro*-4-*nitro*-o-*xylene*, m. p. 220°. Nitration of 3 : 5-dichloro-*o*-xylene (Crossley, J.C.S., 1902, **81**, 1533) with a mixture of fuming nitric and glacial acetic acids on a water-bath yields 3 : 5-*dichloro*-4-*nitro*-o-*xylene*, m. p. 92° (contaminated with a little 6-nitro-isomeride), which is reduced to 3 : 5-dichloro-4-*o*-xylidine, m. p. 47·5° [acetyl derivative, m. p. 196°; Crossley (*loc. cit.*) gives 44·5° and 186°, respectively]. J. W. Baker.

M. p. of *m*-dinitrobenzene. F. McCamish and A. Salathe (J. Amer. Chem. Soc., 1928, **50**, 1785).—The value m. p. 89·85° is determined. H. Wren.

Arylsulphonphenylchloroamides. E. Gebauer-Fülnegg and E. Jusa (Monatsh., 1928, **50**, 61—67).—Benzenesulphonphenylchloroamide, m. p. 61°, is stable when pure and acid-free, but readily changes into benzenesulphon-*p*-chloroanilide, m. p. 121°, in presence of traces of acid. The activity of the halogen atom towards reagents is governed by the relative speed of this isomerisation. Electrolysis of the chloroamide in solution in liquid sulphur dioxide leads to a little benzenesulphonanilide in the cathode chamber and benzenesulphon-*p*-chloroanilide in both cathode and anode chambers. Pyridine, potassium hydroxide, and sodium methoxide give in that order increasing amounts of benzenesulphon-*o*-chloroanilide and diminished quantities of the above two products; sodium in dry ether gives exclusively the *o*-chloroanilide. On the other hand, the isomerisation is completely excluded when the chloroamide is treated with ammonia or with mercury, benzenesulphonanilide being the only product. Sodium iodide yields benzenesulphon-*p*-iodoanilide, sodium nitrite the *p*-nitroanilide, and sodium cyanide a mixture of products. With aluminium chloride isomerisation, but no condensation, occurs. C. Hollins.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. IV. E. de B. Barnett and J. L. Wiltshire (J.C.S., 1928, 1822—1825).—Addition of zinc dust and a few c.c. of copper sulphate solution to a solution of 4-chloro-*o*-benzoylbenzoic acid in ammonia (*d* 0·880) yields 4-*chlorodiphenylmethane*-2′-*carboxylic acid*, m. p. 132°, which is con-

verted by cold concentrated sulphuric acid into 2-*chloro*-9-*anthrone*, m. p. 155°, from which 2-*chloro*-9-*anthranyl acetate*, m. p. 143°, is obtained by the acetic anhydride–pyridine method (Barnett and Matthews, J.C.S., 1923, **123**, 389). 3-*Chloro*-9-*anthranyl acetate*, m. p. 146° (depressing m. p. of 2-chloro-compound), is prepared similarly. By the action of the Grignard reagent on 2-chloro-9-anthrone are obtained 2-*chloro*-9-*methyl*-, m. p. 184°, 2-*chloro*-9-*ethyl*-, m. p. 79° (which by bromination yields 2-*chloro*-10-*bromo*-9-*ethylanthracene*, m. p. 128°), 2-*chloro*-9-n-*propyl*-, m. p. 82°, or 2-*chloro*-9-*benzyl*-, m. p. 132° [which by bromination yields 2-*chloro*-10-*bromo*-9-*benzylanthracene*, m. p. 167° (*dibromide*, decomp. 150°)], *anthracene*. Good yields could be obtained only with magnesium ethyl bromide and magnesium benzyl chloride. J. W. Baker.

Coloured rubrene hydrocarbons. C. Moureu, C. Dufraisse, and A. Willemart (Compt. rend., 1928, **187**, 266).—The preparation of a *dimethylrubrene*, m. p. 315°, from *p*-tolylacetylene and benzophenone and of a *dibenzorubrene*, m. p. 280°, from β-naphthylacetylene and benzophenone is indicated. H. Wren.

Coloured rubrene hydrocarbons. A. Willemart (Compt. rend., 1928, **187**, 385—387; cf. A., 1926, 945, and preceding abstract).—The formation of rubrene hydrocarbons (II) from chloro-compounds of the type CR‴:C·CR′R″Cl is explained by elimination of 1 mol. of hydrogen chloride from the tautomeric allene derivative CR′R″:C:CR‴Cl, and subsequent production of a dimeride from the unstable cyclic intermediate (I).

$$\text{(I.)}\quad 2C_6H_4<\substack{CR\\CR}>C \longrightarrow \left[C_6H_4<\substack{CR\\CR}>C\colon\right]_2 \quad \text{(II.)}$$

H. Burton.

Electrolytic oxidation of aniline. J. Sladek. See this vol., 969.

Condensation of phenylenediamines with acetanilide. Salts of tolylphenylethenylamidines. H. Becker (Rocz. Chem., 1928, **8**, 242—249).—Diphenylethenylamidine (*hydrochloride*, m. p. 218°; *hydrobromide*, m. p. 200°) is prepared by condensing acetanilide with aniline in the presence of phosphoryl chloride. Using *m*-phenylenediamine the product is m-*phenylenedi(phenylethenylamidine)*, m. p. 213° (*hydrochloride*, m. p. 275°). When *o*-phenylenediamine was used, no condensation product was obtained. The *hydrochlorides* of *o*- and *p*-tolylphenylethenylamidine melt respectively at 154—156° and 194°, and the *hydrobromide* of the corresponding *m*-compound at 152°. R. Truszkowski.

Action of aromatic sulphonyl chlorides on tertiary bases. A. Wahl (Rev. gén. Mat. Col., 1928, **32**, 176—177; cf. A., 1902, i, 822; 1905, i, 194; this vol., 878).—Toluene *o*- and *p*-, and probably all, sulphonyl chlorides react with dimethylaniline, giving crystal-violet in small yield, tetramethyldiaminodiphenylmethane, and probably 4′-dimethylamino-4-methyldiphenylsulphone. Methyl-violet is not produced (cf. A., 1880, 75, 108). Similarly, diethylaniline and methyldiphenylamine yield violet and blue dyes, respectively. A. McGookin.

***ar*-α-Substituted hydrindenes.** E. Goth (Ber., 1928, **61**, [*B*], 1459—1460).—*ar*-1-Aminohydrindene, its acetyl and benzoyl derivatives have m. p. −3°, 126°, and 136°, respectively. 1-Hydroxyhydrindene melts at 47—51°. H. Wren.

Syntheses in the diphenyl series. L. E. Hinkel and D. H. Hey (J.C.S., 1928, 1838—1840).—The decomposition products of 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one (this vol., 760) have now been proved to be 5-bromo- and 4 : 5-dibromo-3-hydroxydiphenyl, respectively, by synthesis of these compounds from 5-bromo-3-nitro-4-aminodiphenyl (I) [m. p. (pure) 100°; cf. Scarborough and Waters, A., 1927, 656]. Acetylation yields 5-bromo-3-nitro-4-acetamidodiphenyl, identical with the compound described by Bell and Robinson (A., 1927, 657). Reduction of 5-bromo-3-nitrodiphenyl yields 5-*bromo*-3-*aminodiphenyl*, m. p. 88° (*acetyl* derivative, m. p. 140°), converted by diazotisation into 5-bromo-3-hydroxydiphenyl, which yields a benzoyl derivative identical with that prepared from one of the decomposition products of 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one. Diazotisation of (I) in hydrobromic acid solution yielded no trace of 4 : 5-dibromo-3-nitrodiphenyl (cf. Crossley, J.C.S., 1904, **85**, 278). 5 : 4′-Dibromo-3-nitro-4-aminodiphenyl (II), m. p. 154° (cf. Scarborough and Waters, *loc. cit.*), is obtained. Acetylation of (II) yields 5 : 4′-dibromo-3-nitro-4-acetamidodiphenyl, identical with the compound described by Bell and Robinson (*loc. cit.*) as (5? : 4′)-dibromo-3-nitro-4-acetamidodiphenyl. Reduction of (II) gives 5 : 4′-*dibromo*-3 : 4-*diaminodiphenyl*, m. p. 120° (*dibenzoyl* derivative, m. p. 278°). Diazotised 5-bromo-3-nitro-4-aminodiphenyl reacts with a solution of cuprous bromide in hydrobromic acid, giving 4 : 5-*dibromo*-3-*nitrodiphenyl*, m. p. 125°. Reduction of this compound yields 4 : 5-*dibromo*-3-*aminodiphenyl* (*acetyl* derivative, m. p. 177°), which is converted into 4 : 5-dibromo-3-hydroxydiphenyl identical with the second decomposition product from 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one. M. Clark.

Azochromophores. I and II. J. S. P. Blumberger (Chem. Weekblad, 1928, **25**, 282—286, 315—318).—An examination of the effect of the hydroxyl, amino-, and methyl groups as substituents in azo-dyes on the absorption spectra has been made by collecting examples and data from the literature. The effects are explained on the author's theory of the deformation of the valency-electron fields as the result of substitution. Substituents are divided into two classes. The first, which includes the hydroxyl and amino-groups, repel the electrons of the chromophore when introduced in the *ortho*- and *para*-positions, the effect being reversed when *meta*-substitution occurs. With the second class, the opposite effects are produced. The methyl group is classed as neutral. The effects of the halogen, nitro-, aldehydo-, carboxyl, and sulphonic acid groups are considered. The halogens also repel the valency electrons of the chromophore when present in the *ortho*- and *para*-positions. S. I. Levy.

Copper compounds of some aminoazo- and hydroxyazo-derivatives. A. Cremonini (Gazzetta, 1928, **58**, 372—379).—1-Benzeneazo-2-benzyl-

naphthylamine (this vol., 629) gives with ammoniacal copper sulphate a *copper* derivative, as does the corresponding 1-*p*-nitrobenzeneazo-compound: definite compounds are, however, not obtained.

The copper derivatives of benzeneazo-β-naphthylamine (cf. Charrier and Beretta, A., 1927, 237) and benzeneazo-β-naphthol (cf. Schaposchnikoff and Svientoslavski, A., 1905, i, 161) are reinvestigated. Whereas Charrier obtained a red compound, m. p. 130°, *copper bisbenzeneazo-β-naphthylamine*, green, m. p. 174°, is now obtained. This when heated under reflux at 250—260° yields aniline, ammonia, αβ-naphthylenediamine, and 2-phenyl-αβ-naphthotriazole, with copper and copper oxide. *Copper bisbenzeneazo-β-naphthol*, brown, m. p. 288°, is prepared. These compounds are violently oxidised by nitric acid; when treated with hydrochloric acid they yield cupric chloride and the parent substance, with no hydrogen or reduced product, which shows that the formulæ ascribed by Charrier (*loc. cit.*; hydrogen remains unreplaced) are erroneous. The compounds are considered to have tautomeric forms, in which copper either (*a*) replaces hydrogen in the amino- or hydroxyl group, and is co-ordinately attached to the nitrogen atom adjacent to the phenyl group, or (*b*) is attached in the reverse manner to the *o*-quinonoid tautomeride: in each form a 6-membered ring is present. Attempts to determine the number of active hydrogen atoms (cf. Ciusa, A., 1920, i, 665) were unsuccessful. E. W. WIGNALL.

Coupling of diazonium salts in the side-chains of unsaturated compounds. I. A. QUILICO and (SIGNA.) M. FRERI (Gazzetta, 1928, **58**, 380—390).—*p*-Nitrobenzenediazonium sulphate dissolved in acetic acid, or, better, suspended in alcohol, reacts with anethole to give anisaldehyde-*p*-nitrophenylhydrazone, m. p. 161°, identified by oxidation and by synthesis, and with *iso*safrole to give *piperonal*-p-*nitrophenylhydrazone*, m. p. 199—200°, also oxidised and synthesised (m. p. 201°); in each reaction a small amount of a red *substance*, m. p. 222—223° (decomp.), regarded as a decomposition product of the diazo-compound, is obtained. Using 2 : 4-dinitrobenzenediazonium sulphate, *anisaldehyde*- and *piperonal*-2 : 4-*dinitrophenylhydrazones*, m. p. 243° and 265° (decomp.), respectively, are obtained, and are also synthesised. From *iso*apiole, *apiolaldehyde*-p-*nitrophenylhydrazone*, m. p. 228—229°, is prepared. It is suggested that the diazo-compound forms an unstable product by addition at the double linking, followed by loss of acetaldehyde; substances with side-chains of the allyl type (*e.g.*, safrole) give uncertain or negative results. E. W. WIGNALL.

Phenacylhydrazine. M. BUSCH and W. FOERST [with W. STENGEL] (J. pr. Chem., 1928, [ii], **119**, 287—302).—*Phenacylhydrazine*, $CH_2Bz{\cdot}NH{\cdot}NH_2$, m. p. 85—86° (decomp.) [*oxalate*, m. p. 150° (decomp.)], is obtained by condensing phenacyl bromide with hydrazine hydrate in absolute alcohol at −5° and removing hydrazine hydrobromide by ice-water. It is very reactive, and when heated in alcoholic solution loses ammonia, forming 2 : 5-diphenyl-3 : 4-dihydro-1 : 4 : 3-pyrazone (cf. Gastaldi, A., 1921, i, 604). It is suggested that the intermediate products

$$\begin{array}{l}\mathrm{CPh{\cdot}CH_2{\cdot}NH{\cdot}N}\\ \mathrm{N{-}NH{\cdot}CH_2{-}CPh}\end{array},\quad \begin{array}{l}\mathrm{CPh{\cdot}C{\cdot}N}\\ \mathrm{N{-}\!\!-C{\cdot}CPh}\end{array},\ \text{and}\ \begin{array}{l}\mathrm{CPh{\cdot}C(OH){\cdot}N}\\ \mathrm{N{-}\!\!-CH{-}\!\!-CPh}\end{array}$$

are formed.

By the action of acetic acid and anhydride, *diacetylphenacylhydrazine*, m. p. 123°, is prepared; and, with the appropriate aldehydes, o- and m-*nitrobenzaldehyde*-, m. p. 156° (decomp.) and 146—147°, respectively, and *salicylaldehyde*-, m. p. 110° (decomp.), *phenacylhydrazones*, in imperfect yield, owing to decomposition of the reagent. Similarly are prepared: p-*bromophenacylhydrazine*, m. p. 135—136° (decomp.) (*hydrochloride*, decomp. from 170°, sintering 210°; *perchlorate*, m. p. 270°; *oxalate*), decomposing in alcohol to 2 : 5-*di*-p-*bromophenyl*-3 : 4-*dihydro*-1 : 4 : 3-*pyrazone*, m. p. 248—249°, with a *substance* of similar nitrogen content, m. p. 252—254°; and *salicylaldehyde*-, m. p. 125° (decomp.), m-*nitrobenzaldehyde*-, m. p. 136° (decomp.), and p-*chlorobenzaldehyde*-, darkens 128°, m. p. 134° (decomp.), p-*bromophenacylhydrazones*. The last substance reacts at its carbonyl group with phenylhydrazine to give its *phenylhydrazone*, m. p. 214° (decomp.), to which the *syn*-formula,

$$\begin{array}{l}\mathrm{C_6H_4Br{\cdot}C{\cdot}CH_2{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4Cl}\\ \qquad\ \ \mathrm{N{\cdot}NHPh}\end{array}$$

, is given, since it combines with formaldehyde, acetaldehyde, or benzaldehyde, in alcoholic solution under the influence of a trace of hydrogen chloride, to furnish, respectively, 1-p-*chlorobenzylideneamino*-3-*phenyl*-, m. p. 180° (decomp.), -3-*phenyl*-2-*methyl*-, m. p. 166°, and -2 : 3-*diphenyl*-, m. p. 163—164°, -5-p-*bromophenyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 3 : 4-*triazines*.

m-*Nitrophenacylhydrazine*, m. p. 100° (decomp.), decomposes readily, *e.g.*, when an attempt is made to combine it with *p*-chlorobenzaldehyde, giving only bis-*p*-chlorobenzylideneazine. E. W. WIGNALL.

Preparation of phenyl and tolyl oxalates. J. MIKSIC and Z. PINTEROVIC (J. pr. Chem., 1928, [ii], **119**, 231—234).—Aryl oxalates are readily obtained pure by the action of oxalyl chloride (1 mol.) on phenols (2 mols.) in dry ether in presence of sodium or potassium, cooling in a freezing-mixture being necessary to control the vigorous reaction which begins after a few hrs. with *m*- and *p*-cresols, or after 24 hrs. with *o*-cresol and phenol. C. HOLLINS.

Preparation of derivatives of phenolsulphonyl chloride. E. GEBAUER-FULNEGG and F. VON MEISSNER (Monatsh., 1928, **50**, 55—60).—All attempts to obtain a monosulphonyl chloride from phenol, anisole, phenetole, phenyl acetate, thioanisole, or acetylthiolbenzene by the action of chlorosulphonic acid were unsuccessful, disulphonyl chlorides being obtained. Anisole gives anisole-2 : 4-disulphonyl chloride, m. p. 86°, from which the 2 : 4-*disulphonamide*, m. p. 239—240°, and 2 : 4-*disulphanilide*, m. p. 209°, are obtained; the chloride is reduced with zinc and sulphuric acid to 2 : 4-*dithiolanisole*, m. p. 51°. Phenetole gives the 2 : 4-disulphonyl chloride, m. p. 102—104°, and thence the 2 : 4-*disulphanilide*, m. p. 202—204°, is obtained. *Acetoxybenzene*-2 : 4-*disulphonyl chloride*, m. p. 91°, is obtained by acetylation of phenol-2 : 4-disulphonyl chloride, which is the only product of the action of chlorosulphonic acid on phenyl acetate; 3-*acetoxytoluene*-4 : 6(?2)-*disulphonyl chloride*, m. p. 109°, is similarly prepared. Acetyl-

thiolbenzene and chlorosulphonic acid give only 4 : 4′-di(chlorosulphonyl)diphenyl disulphide, m. p. 131°. C. HOLLINS.

Nitration of *m*-fluorophenol. H. H. HODGSON and J. NIXON (J.C.S., 1928, 1879—1882).—The methods of preparation of the undermentioned compounds are those described for the corresponding chloro- and bromo-compounds with appropriate modifications (cf. A., 1925, i, 1144; 1926, 281). The following are described: *3-fluoro-6-nitrophenol*, m. p. 32° (*sodium* and *silver* salts; *methyl ether*, m. p. 52°; *benzoate*, m. p. 110—111°); *3-fluoro-4-nitrophenol*, m. p. 42° (*sodium* and *silver* salts; *methyl ether*, m. p. 56·5°; *benzoate*, m. p. 118°); *3-fluoro-2-nitrophenol*, m. p. 39° (*sodium* and *silver* salts; *methyl ether*, m. p. 43·5°; *benzoate*, m. p. 114°); *3-fluoro-4 : 6-dinitrophenol*, m. p. 80° (*silver* salt); *3-fluoro-2 : 6-dinitrophenol*, m. p. 68·5° (*silver* salt); *3-fluoro-2 : 4-dinitrophenol*, m. p. 138—139° (*silver* salt); *3-fluoro-2 : 4 : 6-trinitrophenol*, m. p. 173° (*silver* salt). The 3-fluoro-2-, -4-, and -6-nitrophenols resist acetylation. Monosulphonation of 3-fluoro-2-nitrophenol in the cold or at 100—120° appears to give exclusively 3-fluoro-2-nitrophenol-4-sulphonic acid, since only 3-fluoro-2 : 6-dinitrophenol could be obtained by further mononitration. The differences in behaviour of the fluoro- and the other halogeno-analogues, more especially of their silver salts, are discussed. A trustworthy method for the preparation of *m*-fluoronitrobenzene from *m*-nitroaniline is described. M. CLARK.

Basicity of nitrophenoxymalonic acids. J. S. TELETOV and N. N. ANDRONIKOV (J. Russ. Phys. Chem. Soc., 1927, 59, 1199—1204).—The conductivities of the sodium salts of bis-*o*-, -*p*-, and -*m*-nitrophenoxymalonic acids were investigated by the Ostwald–Walden method, to determine their basicity, $(V_{1024}-V_{32})/10$.

The ultra-violet absorption spectra of Bischoff's isomerides of the methyl and ethyl esters of bis-*p*-phenoxymalonic acids showed that these were mixed crystals of the malonic and corresponding disubstituted acetic esters formed by loss of a carboxyl group. The sodium salts of the *o*- and *m*-acids, prepared from their methyl esters, gave values 1·98—1·99 for the basicity. The sodium salt of the *p*-acid, prepared by five different methods, gave values for the basicity from 2·18 to 2·06, *i.e.*, the acid is somewhat stronger than the *o*- and *m*-isomerides. Investigation of the mono-substituted *p*-phenoxymalonic acid showed it to be a distinctly weaker dibasic acid than the disubstituted acids, the value obtained being 1·54. M. ZVEGINTZOV.

Complex isomerism and complex salt isomerism. E. HERTEL and J. VAN CLEEF (Ber., 1928, **61**, [*B*], 1545—1549).—The Debye–Scherrer diagrams of the yellow, m. p. 91·5°, and the red form, m. p. 84·5°, of the compound formed from 2 : 6-dinitrophenol and 4-bromo-α-naphthylamine are so different from one another that the existence of different crystal lattices is placed beyond doubt. The case is classified as complex isomerism.

2 : 4 : 6-Trinitroanisole and β-naphthyldimethylamine afford a *compound*, m. p. 68—69°, to which the constitution $OMe{\cdot}C_6H_2(NO_2)_3 \ldots C_{10}H_7{\cdot}NMe_2$ is ascribed. When heated above its m. p., it becomes converted into *trimethyl-β-naphthylammonium picrate*, m. p. 190° (decomp.), identical with the product derived from trimethyl-β-naphthylammonium iodide and silver picrate. The reverse transformation cannot be effected. To this relationship the term "complex salt isomerism" is applied. The types of isomerism are illustrated by the phase diagrams of the compounds. H. WREN.

Interaction of picric acid and 2 : 5-diketopiperazine. A. MOREL and P. PRECEPTIS (Compt. rend., 1928, **187**, 236—239).—When boiled in aqueous solution picric acid and diketopiperazine give glycylglycine picrate, the reaction thus involving hydrolysis of a ·CO·NH· group in the diketopiperazine ring, followed by salt formation. The coloration afforded in presence of sodium carbonate (Sasaki, A., 1921, ii, 358) or barium hydroxide is due to the formation of azo-derivatives, in addition to the picrate of glycylglycine, a reaction comparable with that observed by Seyewetz and Mounier (this vol., 167), and also resembling the reduction caused by creatinine. The formation of azo-derivatives in these conditions is regarded as confirming the reasons already advanced by Abderhalden and Komm (A., 1924, i, 1361) for the existence in the proteins of rings containing equivalent carbonyl groups. R. BRIGHTMAN.

[Nuclear condensation of phenols with nitriles.] J. HOUBEN (Ber., 1928, **61**, [*B*], 1597).—A reply to Hoesch (this vol., 169). H. WREN.

Reactions of Friedel and Crafts, Fries, and Gattermann. K. VON AUWERS and W. MAUSS (Ber., 1928, **61**, [*B*], 1495—1507).—The Friedel–Crafts reaction occurs in very differing ways with various polyalkylated phenolic ethers and the constitution of the products must be elucidated in each individual case. With phenols of certain structure, *meta*-derivatives may be the main products of the change. In the case of the Fries displacement this has never been observed. A difference appears therefore to be involved according as the acid residue is introduced from without into the molecule or is originally present therein. In contrast to the Friedel–Crafts change, the Fries displacement takes place within the molecule; the reactions are essentially different. There is little evidence of the formation of *meta*-derivatives in the Gattermann synthesis, but displacement of alkyl groups occurs as readily as during the Fries reaction.

as-*m*-Xylyl methyl ether is converted by acetyl chloride in the presence of carbon disulphide and aluminium chloride into a mixture of 5-acetyl-*as*-m-xylenol, m. p. 53—54°, and *6-acetyl*-as-m-*xylenyl methyl ether*, b. p. 140—142°/13 mm., m. p. 50—51°. Hydrolysis of the latter compound with aluminium chloride affords 6-acetyl-*as*-*m*-xylenol, m. p. 130—131·5° (*oxime*, m. p. 142—146°, and its *hydrochloride*), converted by 80% phosphoric acid at 170—190° into *as*-*m*-xylenol. Similarly, chloroacetyl chloride affords 5-chloroacetyl-*as*-*m*-xylenol and *6-chloroacetyl*-as-m-*xylenol*, m. p. 107—107·5°, reduced by zinc dust and acetic acid to 6-acetyl-*as*-*m*-xylenol. *4-Methyl-*-*ethylphenyl methyl ether*, b. p. 206—208°, is transformed by the Friedel–Crafts reaction into *5-acetyl-*

4-*methyl*-2-*ethylphenyl methyl ether*, b. p. 148—150°/16 mm., 6-acetyl-4-methyl-2-ethylphenol, b. p. 144—146°/25 mm. (*p*-nitrophenylhydrazone, m. p. 175—176°), and 5-*acetyl*-4-*methyl*-2-*ethylphenol*, m. p. 120—121° (converted by phosphoric acid into 4-methyl-2-ethylphenol, identified as its phenylurethane, m. p. 100—101°). The *oxime* of the hydroxyphenol yields a *hydrochloride*. Reduction of the hydroxy-ketone by Clemmensen's method affords 4-*methyl*-2 : 5-*diethylphenol*, b. p. 248—250°, m. p. 54—54·5° (*methyl ether*, b. p. 234—236°). Mesityl methyl ether reacts with difficulty with aluminium chloride in presence of carbon disulphide, forming m-*acetylmesitol*, m. p. 81—82°.

as-*m*-Xylenyl benzoate is converted by aluminium chloride at 130—140° into *o*-*benzoyl*-as-m-*xylenol*, m. p. 40—41° (*oxime*, m. p. 153—154°), and 6-*benzoyl*-as-m-*xylenol*, m. p. 140—141°. *p*-Xylenyl acetate and aluminium chloride at 80—90° afford 6-acetyl-*p*-xylenol, m. p. 130—131°, and 5-acetyl-*as*-*m*-xylenol, m. p. 54°. 2 : 5-*Dimethyl*-4-*ethylphenol*, m. p. 39—40°, is converted into its *acetate*, b. p. 248—250°, which, with aluminium chloride at 250°, yields 6-acetyl-2 : 4-dimethyl-3-ethylphenol. 2 : 5-*Diethyl*-4-*methylphenyl acetate*, b. p. 260—262°, and aluminium chloride at 130° give 6-acetyl-4-methyl-2 : 3-diethylphenol amongst other products.

Mesityl methyl ether is not readily brought into reaction with hydrocyanic acid in Gattermann's synthesis, but appears to yield small amounts of 3-hydroxy-2 : 4 : 6-trimethylbenzaldehyde, m. p. 108—109°, reduced by Clemmensen's method to (?) 2 : 3 : 4 : 6-tetramethylphenol. Under somewhat different conditions a *hydroxydimethylbenzaldehyde*, m. p. 106—107° (*oxime*, m. p. 164·5—165°), is obtained. *vic*-*o*-Xylenol gives mainly 4-hydroxy-2 : 3-dimethylbenzaldehyde; an *o*-hydroxyaldehyde is produced in small amount. *vic*-Hemellithenol yields *p*-hydroxydimethylbenzaldehyde and 2-*hydroxy*-3 : 4 : 5-*trimethylbenzaldehyde*, m. p. 36—37°.

H. Wren.

Flueckiger's test for thymol and carvacrol. H. G. Hewitt (J. Amer. Pharm. Assoc., 1928, **17**, 524—525).—The test consists in warming the substance in chloroform solution with solid sodium hydroxide. Thymol or carvacrol gives a red coloration, due to the formation of an aldehyde and the condensation of the latter with the phenol (Flueckiger, Pharm. Chem., 1888, **2**, 101). E. W. Wignall.

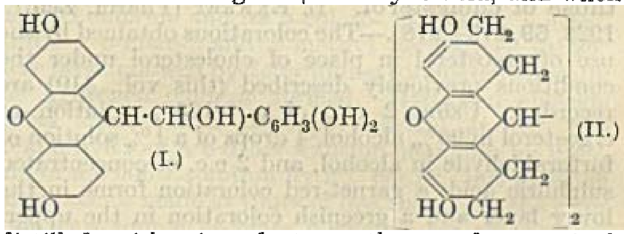
[Oil from] corolla of *Monarda fistulosa*, L. K. H. Rang (J. Amer. Pharm. Assoc., 1928, **17**, 525—528).—The volatile oil from the florets of this species has $d^{23\cdot3}$ 0·9740 and contains carvacrol and some hydroxythymoquinone; the alcoholic extract contains two *substances*, m. p. 139—141° and 235—237°.

E. W. Wignall.

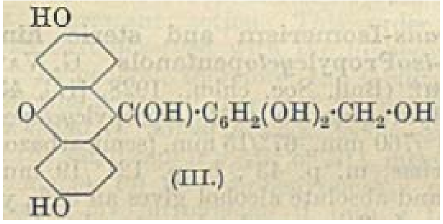
Sclareol, the chief constituent of oil of sage. Y. Volmar and A. Jermstad (J. Pharm. Chim., 1928, [viii], **8**, 55—57).—See this vol., 524.

Oxidation of sulphides with perbenzoic acid. II. Preparation of sulphoxides and sulphones and a titrimetric method for determination of sulphoxides. L. N. Lewin (J. pr. Chem., 1928, [ii], **119**, 211—217).—ββ′-Dichlorodiethyl sulphide, diphenyl sulphide, and dibenzyl sulphide are oxidised quantitatively to sulphoxides provided that the theoretical quantity of perbenzoic acid is used in dilute, well-cooled chloroform solution. The sulphoxides are converted by 15% excess of perbenzoic acid into sulphones, the yields being 100%, 100%, and 80%, respectively. C. Hollins.

Action of oxalyl chloride on resorcinol. J. Miksic (J. pr. Chem., 1928, [ii], **119**, 218—230).—By the action of sodium and excess of oxalyl chloride on resorcinol in moist ether, first with cooling and finally at the boil for a few days, there is obtained "β-*resemin*," $C_{20}H_{16}O_6$ (I), m. p. 155—160° (decomp.) (*penta-acetyl* derivative, m. p. 197°), which by fusion with alkali at 200° gives β-resorcylic acid, and when



distilled with zinc dust xanthen and resorcinol. From oxalyl chloride (1 mol.), resorcinol (2 mols.), and potassium (2 atoms) in moist ether there are obtained "*resjankin*," $C_{26}H_{26}O_6$ (II), decomp. 280° (*tetra-acetyl* derivative, m. p. 170—172°, and "*res-*



perin," $C_{20}H_{16}O_7$ (III), m. p. 210° (decomp.; *hexa-acetyl* derivative, m. p. 159—159·5°). The absorption spectra of the three compounds are compared with those of phenolphthalein and fluorescein.

C. Hollins.

Aromatic allyl and propenyl compounds. I. Safrole and *iso*safrole. H. I. Waterman and R. Priester (Rec. trav. chim., 1928, **47**, 849—860).—Safrole, purified through its mercuriacetate (Manchot, A., 1920, i, 780), has m. p. and setting point 11·0°, b. p. 38—40° in a cathode-vacuum, or 125—126°/25 mm., d_4^{20} 1·100, n_D^{20} 1·5383. *iso*Safrole, purified through the picrate, shows b. p. 46·8° in a cathode-vacuum, d_4^{20} 1·122, n_D^{20} 1·5782. The pure compounds do not react with iodine in the dark, and unsaturated impurities may thus be detected. In the light safrole takes up more iodine than *iso*safrole and reaches equilibrium more quickly. A method for analysing mixtures of the two isomerides based on their different affinities for iodine is described. C. Hollins.

Action of ethylamine and diethylamine on *iso*safrole oxide. J. S. Kusner (J. Russ. Phys. Chem. Soc., 1928, **60**, 655—659).—The formation by the action of ethylamines on *iso*safrole oxide of amino-alcohols was studied, with the view of investigating their possible physiological properties. *iso*-Safrole oxide, b. p. 147—149°/15 mm. (prepared by

the action of alcoholic potassium hydroxide on the bromohydrin), gave with ethylamine on keeping for 3 days at 30—40° in a solution of aqueous alcohol, a white *compound*, m. p. 67°, b. p. 175—180°/15 mm., with the properties of a secondary alcohol and a base, probably having the constitution $CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NHEt$ (*hydrochloride*, m. p. 181°; *picrate*, m. p. 168—169°). With ethylamine, the reaction was more difficult, requiring heating for 4 hrs. at 100°. A very viscous *liquid*, b. p. 174—178°/15 mm., soluble in ether, acetone, and alcohol was obtained, giving a *picrate*, m. p. 160°, and *hydrochloride*, m. p. 196—197°.

M. ZVEGINTZOV.

Colour reactions of ergosterol as distinct from those of cholesterol. L. EKKERT (Pharm. Zentr., 1928, **69**, 276—278).—The colorations obtained by the use of ergosterol in place of cholesterol under the conditions previously described (this vol., 410) are recorded. Using 2 c.c. of a 0·125% solution of ergosterol in 96% alcohol, 4 drops of a 1% solution of furfuraldehyde in alcohol, and 2 c.c. of concentrated sulphuric acid, a garnet-red coloration forms in the lower layer and a greenish coloration in the upper. Treatment of 2 c.c. of a dilute acetic anhydride solution of the sterol with 2 c.c. of 85% phosphoric acid gives a greenish-yellow coloration after long keeping in the case of cholesterol and a brilliant green coloration in the case of ergosterol.

G. A. C. GOUGH.

***cis–trans*-Isomerism and steric hindrance. VII. 2-*iso*Propyl*cyclo*pentanols.** G. VAVON and A. APCHIE (Bull. Soc. chim., 1928, [iv], **43**, 667—677).—Hydrogenation of 2-*iso*propyl*cyclo*pentanone, b. p. 174°/760 mm., 67°/15 mm. (semicarbazone, m. p. 202°; *oxime*, m. p. 43°, b. p. 121°/19 mm.), with sodium and absolute alcohol gives an 85% yield of a mixture of 2-*iso*propyl*cyclo*pentanols, b. p. 85°/18 mm., in which the *trans*-isomeride predominates. trans-2-iso*Propyl*cyclo*pentanol*, isolated by means of the *hydrogen phthalate*, m. p. 69°, has b. p. 93—94°/27 mm., d_4^{11} 0·910, n_D^{11} 1·4583; the trans-*hydrogen succinate*, d_4^{11} 1·073, n^{11} 1·463, and *phenylurethane*, m. p. 63°, are described. Hydrogenation in presence of platinum-black in acetic acid containing 10% of aqueous hydrochloric acid affords a mixture of 2-*iso*propyl*cyclo*pentanols (together with some acetate) in which the cis-*isomeride*, b. p. 84—85°/20 mm., d_4^{11} 0·9145, n_D^{11} 1·4578 (*hydrogen phthalate*, m. p. 105°; *phenylurethane*, m. p. 103°; *hydrogen succinate*, m. p. 48—49°), preponderates, but not to the extent obtaining with the 2-*iso*propyl*cyclo*hexanols (A., 1927, 455). When heated in nitrogen at 180—190° for 6 hrs. the sodium derivative of the *cis*- is largely converted into the *trans*-isomeride. With acetic acid at 0° in presence of 2% of sulphuric acid the *trans*- is esterified about three times as rapidly as the *cis*-isomeride; at 39° or in the absence of a catalyst the difference is less marked. Similarly, the *trans*-hydrogen phthalate and -hydrogen succinate are hydrolysed more rapidly than the corresponding *cis*-compounds, the ratio of the velocity coefficients varying from 4·5 to 5 for the hydrogen phthalates in 75% alcohol at 39° and 68°, and from 9 to 16 in water at 68° and 0°. For the hydrogen succinate the corresponding ratios at 0° and 39° are 18 and 10 in 75% alcohol, respectively, and 19 and 15 in water. Since these ratios are smaller than those observed (*loc. cit.*) for the corresponding 2-*iso*propyl*cyclo*hexanols although the velocity coefficients themselves are larger, it is concluded that the steric effect of the *iso*propyl group is less marked in the *cyclo*pentanols than in the *cyclo*hexanols, a view which is supported by the lesser formation of the *cis-iso*propyl*cyclo*pentanol in catalytic hydrogenation.

*cyclo*Pentanone, b. p. 129°, is obtained in 87% yield by treatment of adipic acid for 16 hrs. with 1·5% of barium hydroxide; larger amounts of barium lower the yield. Condensation of *cyclo*pentanone with excess of acetone at −10° in presence of dilute sodium methoxide gives a 39% yield of 2-*iso*propylidene*cyclo*pentanone, b. p. 78—79°/10 mm. (*oxime*, m. p. 83°), together with 2-*cyclo*pentylidene*cyclo*pentanone, b. p. 115—118°/10 mm. (oxime, m. p. 122°), di-iso*propylidene*cyclo*pentanone*, m. p. 41°, b. p. 130—140°/11 mm., and iso*propylidene*cyclo*pentylidene*cyclo*pentanone*, m. p. 37°, b. p. 167—175°/11 mm.

R. BRIGHTMAN.

Relative stability of isomerides and absorption spectra. Transformations in the glycol and aldehyde series. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1928, **186**, 1848—1850; cf. this vol., 760).—Rules given for the prediction of intramolecular transformations from absorption spectra (*loc. cit.*) have been followed to obtain aldehydes or ketones by the dehydration of glycols by heat, and also to transform an aldehyde into a ketone. From these rules dehydration of glycols at one temperature should yield aldehydes and at a higher temperature ketones. The dehydration of αα-diphenylethyleneglycol, β-phenylbutane-αβ-diol, and hydrobenzoin was effected by passing their vapours through a tube containing infusorial earth, at reduced pressure, whereby secondary reactions were avoided. At 250—300° primary–tertiary glycols yielded only aldehydes and at 400—450° only ketones. At 250—300° hydrobenzoin yielded diphenylacetaldehyde, a little deoxybenzoin, and unchanged glycol, whilst at 400—450° phenyl benzyl ketone and a little benzaldehyde (from the dissociation of hydrobenzoin) were obtained. It is suggested that an aldehyde is first formed on dehydration and equilibrium between aldehyde and ketone is set up, with displacement in the direction of ketone at higher temperatures, the latter substance having absorption bands nearer the visible region. Thus diphenylacetaldehyde when treated in the same manner as the glycols was converted into deoxybenzoin at 400—450°, which result supports the theory. An ethylene oxide is suggested as intermediate in the change from glycol to aldehyde.

J. D. FULTON.

Reactivity of atoms and groups in organic compounds; the carbon–chlorine bond. J. F. NORRIS. **III.** [with A. A. MORTON]. **Rate of reaction between diphenylmethyl chloride and ethyl alcohol. IV** [with C. BANTAL]; **V** [with J. T. BLAKE]. **Rates of reaction between derivatives of diphenylmethyl chloride and ethyl or *iso*propyl alcohol. VI** [with D. V. GREGORY]. **Rates of reaction of benzoyl chloride and some derivatives**

with *iso*propyl alcohol (J. Amer. Chem. Soc., 1928, **50**, 1795—1803, 1804—1808, 1808—1812, 1813—1816). III.—In order to examine the effect of substituents on the strength of the carbon–chlorine linking, the rates of formation of hydrogen chloride from a large number of alkyl or acyl chlorides and ethyl or *iso*propyl alcohol have been conductometrically determined. Goldschmidt's values for the conductivity of absolute ethyl-alcoholic hydrogen chloride (A., 1915, ii, 136) have been confirmed by further measurements. An approximate correction for the effect of non-electrolytes on the conductivity of alcoholic hydrogen chloride has been obtained by correlating the percentage lowering of the specific conductivity produced by 8 hydrocarbons and halogenobenzenes with their mol. volumes. The velocity of reaction of diphenylmethyl chloride with ethyl alcohol in 0·1—0·02N solution at 25° corresponds closely with that required for a reversible unimolecular reaction. The velocity coefficient in the forward direction (k_1), calculated by a new method, is not affected by as much as 10% of impurity in the diphenylmethyl chloride, but is increased by traces of water. On this account, higher values are obtained for k_1 by titration measurements. Experiments at 0° give a value of about 4 for the temperature coefficient, k_{t+10}/k_t, of the forward reaction.

IV. The values of k_1, calculated by the above method, are tabulated for 15 mono- and di-substituted diphenylmethyl chlorides and ethyl alcohol at 25°, diphenylmethyl chloride itself being unity. The positive effect of substituents on the mobility of the chlorine atom is greatest in the *p*-position and is not parallel with the orienting effect in aromatic substitution. The order of influence of *p*-substituents is OMe>OPh>Et>Me>Ph>$C_{10}H_7$>Cl>Br, the last two having a depressant effect which is greatest in the *o*-position. This is in good agreement with the order found by Olivier (A., 1923, i, 197, 908) for the hydrolysis of substituted benzyl chlorides. The methoxy- and phenoxy-diphenylmethyl chlorides are coloured and react much more readily with water and alcohols than does benzoyl chloride. There is no relation between the activating effect of a radical and its effect on the dissociation constant of an acid. Thus, *p*-toluic acid and phenylacetic acid are nearly equal in strength, but the values of for phenyl-*p*-tolylmethyl chloride and αβ-diphenylethyl chloride with ethyl alcohol are 16·2 and 0·0004, respectively. The velocity coefficients of the *pp'*-dichloro- and *pp'*-dimethyl-diphenylmethyl chlorides are approximately the squares of those for the corresponding monosubstituted derivatives. The mobility of the hydroxylic hydrogen in *iso*propyl alcohol calculated from for the reactions between this alcohol and diphenylmethyl chloride and its *pp'*-dichloro-derivative is 11% and 15%, respectively, of that of the hydroxylic hydrogen in ethyl alcohol (cf. A., 1925, i, 626). The following derivatives of diphenylmethyl chloride have been prepared from the corresponding carbinols by Montagne's method (A., 1907, i, 141): p-*phenyl*-, m. p. 71—72·5°; p-*chloro*-, b. p. 172—173°/6 mm.; p-*methyl*-, b. p. 147—148°/2 mm.; oily o-*chloro*-, decomp. 90°; pp'-*dimethyl*-, m. p. 41—43·5°, and p-*bromo*-, b. p. 188—191°/10 mm.

V. The following are described: *phenyl*-o-*tolylmethyl chloride*, m. p. 40—40·5°, red, oily *phenyl*-p-*anisylmethyl chloride*; *di*-p-*tolylmethyl chloride*, m. p. 45—46°; p-*phenoxydiphenylcarbinol*, m. p. 75°; orange p-*phenoxydiphenylmethyl chloride*, m. p. 49—50°; p-*ethyldiphenylcarbinol*, m. p. 33°; p-*ethyldiphenylmethyl chloride*, b. p. 122°/1—2 mm.; pink, oily *phenyl*-o-*anisylmethyl chloride*, *phenyl*-α-*naphthylmethyl chloride*, m. p. 64—64·5°; p-*bromodiphenylcarbinol*, m. p. 63°; oily *phenyl*-m-*tolylmethyl chloride*, and m-*chlorodiphenylmethyl chloride*. The reaction velocities of these chlorides with ethyl alcohol are tabulated and the results are discussed in the preceding section.

VI. The reactions between *iso*propyl alcohol and benzoyl chloride and its *p*-chloro-, *p*-bromo-, *p*-iodo-, *o*-nitro-, *p*-nitro-, and *p*-methyl derivatives at 25° have been followed by determining conductometrically the hydrogen chloride formed. Hydrogen chloride reacts slowly with *iso*propyl alcohol at 25°, the conductivity of a 0·075N-solution changing by 0·4% and of a 0·006N-solution by 2% per hr., but by using observations made at times of less than 1 hr. the error from this source becomes negligible for the present purpose. A correction is also introduced for the effect of the non-electrolytes. The reactions are unimolecular up to 30% conversion. The effect of *p*-substituents in increasing the mobility of the chlorine atom is in the order NO_2>Br>Cl>I>Me, the last having a depressant action. This order is the opposite to that observed with the diphenylmethyl chlorides. In general, therefore, the lability of the carbon–chlorine linking is increased by introducing a positive or negative radical into a molecule containing groups of the same sign (*e.g.*, Br or NO_2 into benzoyl chloride; Me or Ph into diphenylmethyl chloride) and decreased by introducing it into a molecule containing groups of opposite sign.

H. E. F. Notton.

Colour, mol. wt., and electrolyte character of derivatives of triphenylmethane. I. Lifschitz and G. Girbes (Ber., 1928, **61**, [*B*], 1463—1491).—Triphenylmethane derivatives can be divided into two classes of compounds, Ar_3CX. In the first series, the C–X linking is homopolar as far as can be ascertained. The substances are non-electrolytes and do not yield triphenylmethyl ions. Triphenylmethane, triphenylethane, their cyanides, azides, and sulphonic acids, belong to this series. In the second class, the C–X linking is heteropolar and can give rise to ions. This occurs only by intrusion of solvent or other molecules $[Ar_3CX]+R \quad [Ar_3C\cdots R]^{\cdot}+X'$. The incidence and extent of such intrusion depend on the nature of R and the tenacity of the group X in the first sphere. The electrolytes II are naturally not optically identical with the initial substances I, but the difference can usually be appreciated only in the ultra-violet. According to the nature of R, the electrolytes II may be colourless or coloured. Greatly deformable molecules R may cause absorption in the region of greater wave-length. Thus the thiocyanates are colourless when dissolved in alcohol or acetone, but yield more or less intense yellow or orange solutions in phenol. More pronounced colour may further be occasioned by structural modification of the cation,

e.g., by transformation to the quinonoid form, thus yielding compounds,  Diarylquinols show selective absorption in the visible part of the spectrum which does not, however, resemble that of dyes. Finally, an intruded molecule R (from a second molecule of the solvent) can function, thus giving *meri*quinonoid ions with pronounced dye-like absorption. Such autocomplex formation is particularly marked when the concentration is great, X has a pronounced tendency to ionisation, and the medium has slight intrusive power.

The derivatives of triarylmethylcarbinols exist in a colourless and a coloured series. Apart from the actual dye salts, the colour of the solutions depends on the concentration, temperature, and medium, the sequence of the latter being: ether, alcohol, acetone, nitrobenzene, acetonitrile, camphor, chloroform. Other things being equal, the colour increases with the concentration and, particularly, with the temperature. Among the actual dye salts of the rosaniline and malachite-green series, the transition colourless coloured by change of medium and temperature has not previously been observed. In addition to the coloured forms, however, colourless varieties are observed with the azides, ferrocyanides, and thiocyanates of malachite-green and crystal-violet which are particularly stable in the diamino-series in the increasing sequence, thiocyanate $\longrightarrow$ ferrocyanide $\longrightarrow$ azide. The photochemical transition, colourless $\rightleftharpoons$ coloured, cannot be studied with the azides which undergo decomposition under the influence of ultra-violet light. Solutions of malachite-green azide contain an equilibrium mixture of true dye salt and of a colourless form; this equilibrium is established with remarkable rapidity. If to such an almost colourless solution mercuric cyanide or thiocyanate is added, an intense colour is immediately developed owing to the formation of double salts with the dye salt. Similar equilibria exist in the cases of the salts of malachite-green etc. with mineral acids as evidenced by the production of the more intensely coloured complex compounds containing heavy metals, but in these cases the balance is displaced greatly towards the dye salt side. Only the typical, true methane compounds, particularly the cyanides, maintain an individual position. With these, transformation can be effected only by illumination. Precisely similar relationships are observed among the cyanides and azides of triphenylcarbinol and its methoxy-derivatives.

The cyanides of triphenyl-, diphenylanisyl-, phenyldianisyl-, and trianisyl-carbinols give colourless solutions with normal mol. wt. in all media. In the almost non-dissociating chloroform, the thiocyanates are unimolecular, although the solutions are slightly coloured; the values are independent of the concentration within experimental limits. In alcohol, the thiocyanates give values corresponding with 60—75% of the theoretical; the dissociation increases with increasing dilution and since the substances are completely stable in boiling alcohol, the phenomenon must be regarded as electrolytic dissociation. In confirmation, the solutions in contrast with those of the cyanides exhibit marked electrolytic conductivity. The compounds are therefore sharply differentiated from the typical, coloured carbonium salts of which the stable perchlorates of methoxylated triphenylcarbinols have been investigated. Their solutions in chloroform exhibit greatly exalted mol. wts. which increase markedly with increasing concentration. The relative intensity of colour increases in a similar manner. Identical relationships are found cryoscopically in camphor. In less intensely coloured solution in acetone, the mol. wt. is much lower and almost completely independent of the concentration. In freezing nitrobenzene (orange solution) trianisylcarbonium perchlorate exhibits low mol. wt. (the solution is a good conductor of electricity); in the boiling solvent (almost blackish-red solution) the results are much higher. The strongly coloured solutions of the perchlorates therefore invariably contain associated polymeric salt, the mol. wt. approaching the normal more closely as the solutions become less absorptive.

Under all conditions the cyanides and azides of triphenylcarbinol and methoxytriphenylcarbinols are non-electrolytes. This is also true of the cyanides of diamino- and triamino-triphenylmethane dyes. Preservation of the solutions, addition of complex-forming salts, and protracted heating do not induce electrolytic conductivity, which can be caused only by irradiation. In alcoholic solution malachite-green azide exhibits distinct electrolytic conductivity, which is less pronounced in its less intensely coloured solution in nitrobenzene. Colour and conductivity appear parallel. In harmony, both are increased by the addition of anionic-complex-forming substances, such as mercuric cyanide. Comparison of the behaviour of solutions of malachite-green chloride with those of normal electrolytes shows that the former must contain a proportion of undissociated colourless form. In these cases, the position of the equilibrium depends on the medium; the relative conductivity diminishes in the sequence alcohol, acetone, acetonitrile, nitrobenzene. This is most clearly shown with the ferrocyanides of triphenyl- and the methoxytriphenyl-carbinols. These colourless salts afford colourless or very feebly coloured triarylmethyl ions and thus are completely analogous to the corresponding thiocyanates. Solutions of the latter do not immediately attain their maximum conductivity unless heated. The perchlorates, as typical carbonium salts, have been investigated in the same media. In alcohol, the slight difference in conductivity between the yellow trianisylcarbonium salts and the colourless mono- and di-anisyl compounds is remarkable. The relatively high values of μ, in comparison with tetraethylammonium salts, is probably not due to alcoholysis. In acetone, the colour disappears or diminishes abnormally with dilution, whereas conductivity increases normally. This is possible only if the triarylmethyl ion, $[Ar_3C\cdots COMe_2]$, is colourless or only faintly coloured and the intensely coloured ions produced at a higher temperature are more highly complex or *meri*quinonoid. Similar observations are made in acetonitrile. In nitrobenzene, between 5° and 150°, the temperature coefficients of carbonium and ammonium salts diminish continuously with rise of temperature, whereas the colour of the carbonium

solutions deepens from orange to dark red. Colour therefore has no influence on conductivity but is intimately associated with increase of mol. wt.

The following new compounds or amended data are recorded: tri-*p*-anisylmethane, m. p. 49°, which gives a red colour with sulphuric acid; tri-*p*-anisylcarbinol, m. p. 82°; phenyldi-*p*-anisylmethane, m. p. 99—100°; phenyldi-*p*-anisylcarbinol; *tri*-p-*anisylmethyl perchlorate*, m. p. 193°; phenyldi-*p*-anisylmethyl perchlorate, m. p. 210° (instead of m. p. 113—114°, as recorded); *diphenyl*-p-*anisylmethyl perchlorate*, m. p. 191°; triphenylmethyl perchlorate, m. p. 150°; tri-*p*-anisylacetonitrile, m. p. 128°; *phenyldi*-p-*anisylacetonitrile*, m. p. 95°; *diphenyl*-p-*anisylacetonitrile*, m. p. 117—118°; from the chloride and mercuric cyanide; *tri*-p-*anisylmethyl thiocyanate*; *phenyldi*-p-*anisylmethyl thiocyanate*, m. p. 112°, from the corresponding perchlorate in chloroform and potassium thiocyanate; *diphenyl*-p-*anisylmethyl thiocyanate*, m. p. 72°; *triphenylmethyl azide*, m. p. 65°, from the perchlorate in chloroform and sodium azide; *tri*-p-*anisylmethyl azide*, m. p. 74°; *malachite-green azide*, m. p. 118—119°; *tri*-p-*anisylmethyl ferrocyanide*, m. p. 230° (decomp.); *phenyldi*-p-*anisylmethyl ferrocyanide*, m. p. 192° (also $+CHCl_3$); *diphenyl*-p-*anisylmethyl ferrocyanide*, m. p. 238° (decomp.) (also $+ CHCl_3$); *triphenylmethyl ferrocyanide*, m. p. 280° after darkening at 270° (also $+2CHCl_3$); *p*-dimethylaminobenzylideneacetone, tile-red crystals, m. p. 128°, or yellow leaflets. m. p. 135°. H. Wren.

Preparation of phenolsulphonephthalein and bromo[phenol]sulphonephthalein. R. Freas and E. A. Provine (J. Amer. Chem. Soc., 1928, **50**, 2014—2017).—Phenolsulphonephthalein is conveniently prepared by heating together saccharin (1 mol.), phenol (5 mols.), and sulphuric acid (4 mols.) at 120° for at least 48 hrs. More colouring matter is produced at higher temperatures, but it contains sulphonic acids. Addition of metallic sulphates affects the yield unfavourably. Aluminium, zinc, and ferric chlorides, and phosphoric acid (85%) are inferior to sulphuric acid as condensing agents. The dye is purified by repeated precipitation from sodium carbonate solution, and is then suitable for conversion into pure bromophenol-blue (tetrabromophenolsulphonephthalein).
H. E. F. Notton.

Benzyl chloromethyl ether and dibenzylformal. P. Carré (Bull. Soc. chim., 1928, [iv], **43**, 767—768).—See this vol., 880.

***cyclo*Propylmethyl-alkylacetic acids, and their bactericidal action towards *B. lepræ*. XIII.** J. A. Arvin and R. Adams (J. Amer. Chem. Soc., 1928, **50**, 1983—1985).—Toxicity towards *B. lepræ* is not evident in members below *cyclo*propylmethyloctylacetic acid and reaches a maximum in the acids containing 16 or 17 carbon atoms. The bactericidal effect does not differ markedly from that of acids of the same mol. wt. containing 5- or 6-membered rings. *cyclo*Propylmethyl bromide (cf. von Braun, A., 1925, i, 1401), the preparation of which is detailed, is converted by standard methods into *ethyl* cyclo*propylmethylmalonate*, b. p. 129—133°/18 mm., n_D^{20} 1·4363, d_4^{20} 1·0216, and the following *ethyl* cyclo*propylmethyl*-n-*alkyl-malonates* (the b. p. n_D^{20}, and d_4^{20} of each being given): -*amyl*-, 122—125°/1·7 mm., 1·4459, 0·9770; -*hexyl*-, 139—142°/2·9 mm., 1·4470, 0·9685; -*heptyl*-, 146—149°/2·7 mm., 1·4481, 0·9613; -*octyl*-, 149—154°/2·3 mm., 1·4491, 0·9559; -*nonyl*-, 165—168°/2·5 mm., 1·4503, 0·9512; -*decyl*-, 162—166°/1·9 mm., 1·4510, 0·9460; -*undecyl*-, 186—189°/3 mm., 1·4519, 0·9419; -*dodecyl*-, 183—187°/2 mm., 1·4526, 0·9395; -*tetradecyl*-, 192—195°/1·9 mm., 1·4530, 0·9377; and cyclo*propylmethyl*-n-*alkyl-acetic acids*: -*amyl*, 112—115°/1·4 mm., 1·4469, 0·9375; -*hexyl*-, 130—132°/1·8 mm., 1·4498, 0·9253; -*heptyl*-, 136—139°/2 mm., 1·4509, 0·9236; -*octyl*-, 146—149°/2·1 mm., 1·4529, 0·9142; -*nonyl*-, 162—164°/2·3 mm., 1·4545, 0·9105; -*decyl*-, 176—178°/2·7 mm., 1·4553, 0·9064; -*undecyl*-, m. p. 27—28°, b. p. 186—189°/3 mm.; -*dodecyl*-, m. p. 29—30°, b. p. 191—195°/3 mm.; and -*tetradecyl*-, m. p. 35—37°, b. p. 176—179°/1·3 mm. H. E. F. Notton.

β-Δ²-*cyclo*Pentenylethyl-alkylacetic acids and their bactericidal action towards *B. lepræ*. XII. J. A. Arvin and R. Adams (J. Amer. Chem. Soc., 1928, **50**, 1790—1794; cf. this vol., 754).—As in other series, the toxicity of these acids, and of some new *cyclo*pentenyl-alkylacetic acids, reaches a maximum with the members containing 16—18 carbon atoms. In all series hitherto examined, acids of approximately the same mol. wt., whether saturated or unsaturated, are nearly equal in bactericidal power. β-Δ²-*cyclo*Pentenylethyl alcohol (cf. Noller and Adams, A., 1926, 1137) is converted by standard methods into β-Δ²-cyclo*pentenylethyl bromide*, b. p. 71—72°/16 mm., 1·4995, d_4^{20} 1·2869; δ-Δ²-cyclo*pentenylbutyl alcohol*, b. p. 118—123°/24 mm., n_D^{20} 1·4723, d_4^{20} 0·9317 (*by-product*, b. p. 98—103°/24 mm.); δ-Δ²-cyclo*pentenylbutyl bromide*, b. p. 82—86°/5 mm., n_D^{20} 1·4942, d_4^{20} 1·2229; *ethyl* δ-Δ²-cyclo*pentenylbutylmalonate*, b. p. 152—155/3 mm., n_D^{0} 1·4598, d_4^{20} 1·0077, and δ-Δ²-cyclo*pentenylbutylacetic acid*, b. p. 149—154°/5 mm., n_D^{20} 1·4740, d_4^{20} 0·8962. The b. p., n_D^{20} and d_4^{20}, respectively, of the following are: *ethyl* β-Δ²-cyclo*pentenylethyl-alkyl-malonates*: -n-*hexyl*-, 152—155°/2 mm., 1·4598, 0·9742; -n-*heptyl*-, 159—162°/1·4 mm., 1·4602, 0·9649; -n-*octyl*-, 178—181°/2 mm., 1·4605, 0·9624; -n-*nonyl*-, 176—180°/1·5 mm., 1·4609, 0·9567; -n-*decyl*-, 183—187°/2·1 mm., 1·4613, 0·9531; -n-*undecyl*-, 190—194°/2·1 mm., 1·4616, 0·9486, and -n-*dodecyl*-, 197—201°/2·2 mm., 1·4618, 0·9460; *ethyl* Δ²-cyclo*pentenyl-alkyl-malonates*: -n-*decyl*-, 170—172°/1·5 mm., 1·4616, 0·9642; -n-*undecyl*-, 176—180°/1 mm., 1·4622, 0·9598, and -n-*dodecyl*-, 193—196°/2 mm., 1·4627, 0·9559; β-Δ²-cyclo*pentenylethyl-alkyl-acetic acids*: -n-*hexyl*-, 160—163°/2·3 mm., 1·4697, 0·9426; -n-*heptyl*-, 166—168°/2·2 mm., 1·4698, 0·9358; -n-*octyl*-, 174—176°/1·8 mm., 1·4700, 0·9315; -n-*nonyl*-, 183—185°/2 mm., 1·4701, 0·9269; -n-*decyl*-, 186—188°/1·5 mm., 1·4702, 0·9227; -n-*undecyl*-, 190—193°/1·3 mm., 1·4703, 0·9196, and -n-*dodecyl*, 199—203°/1·5 mm. (m. p. 30—31·5°); Δ²-cyclo*pentenyl-alkyl-acetic acids*: -n-*decyl*-, 183—186°/1·5 mm., 1·4692, 0·9319; -n-*undecyl*-, 188—190°/1·5 mm. (m. p. 36—38°); -n-*dodecyl*-, 202—204°/2 mm. (m. p. 38—39°); and β-Δ²-cyclo*pentenylethylacetic acid*, 125—126°/4 mm., 1·4718, 0·9904. [With C. R. Noller]. Magnesium β-Δ²-*cyclo*pentenylethyl bromide and methyl η-aldehydo-octoate yield θ-*hydroxy*-κ-Δ²-cyclo*pentenyl*-

undecoate, b. p. 177—179°/2 mm., 1·4720, d_4^{20} 0·9874, which is hydrolysed by alcoholic potassium hydroxide to θ-*hydroxy*-κ-Δ^2-cyclo*pentenylundecoic acid* (θ-*hydroxy*-dl-*hydnocarpic acid*), m. p. 62·0—62·8°. H. E. F. NOTTON.

Thermal decomposition of thiobenzanilide. A. W. CHAPMAN (J.C.S., 1928, 1894—1897).—Thiobenzanilide decomposes when heated at 250° or higher temperatures yielding hydrogen sulphide (37—40%), 1-phenylbenzthiazole (I), (38—58%), *s*-diphenylbenzamidine (II) (11—19%), stilbene, and tetraphenylthiophen (III) (cf. Jacobson, A., 1886, 700). The following mechanism is suggested: $Ph{\cdot}CS{\cdot}NHPh \longrightarrow PhC{<}{}^{N}_{S}{>}C_6H_4$ (I) $+2H$. $2H+Ph{\cdot}CS{\cdot}NHPh \longrightarrow NH_2Ph+Ph{\cdot}CHS$. $NH_2{\cdot}Ph+Ph{\cdot}CS{\cdot}NHPh \longrightarrow NPh{:}CPh{\cdot}NHPh$ (II) $+H_2S$. $Ph{\cdot}CHS$ ——— $CHPh{:}CHPh+\begin{matrix}CPh.CPh\\ CPh{\cdot}CPh\end{matrix}{>}S$ (III) $+H_2S$ (cf. Baumann and Klett, A., 1892, 185). M. CLARK.

Bromination of *p*-aminobenzoic acid and its ethyl and butyl esters. A. LEULIER and J. DINET (J. Pharm. Chim., 1928, **8**, [viii], 57—61; cf. A., 1927, 1186).—According to the concentration of hydrobromic acid employed, *monobromo*-, m. p. 225° (Maquenne block), and dibromo- (chars 320°) derivatives of *p*-aminobenzoic acid have been obtained in yields of 60% and 57%, respectively, by the action of hydrogen peroxide on a solution of the amino-acid in aqueous hydrobromic acid. Bromination of the ethyl ester gave 80% of the monobromo-compound, m. p. 92°, and the butyl ester gave 90% of monobromo-derivative, m. p. 63°. The esters did not appear to have lost their anæsthetic properties nor did the toxicity appear to be increased by bromination. Under similar conditions, the nitrobenzoic acids are not brominated. E. H. SHARPLES.

Action of organo-magnesium compounds on *N*-substituted cinnamic anilides. N. MAXIM and N. IOANID (Bul. Soc. Chim. Romania, 1928, **10**, 29—48; cf. Maxim, this vol., 519).—Cinnamic methyl- and ethyl-anilides and diphenylamide react quantitatively, like the diethylamide (*loc. cit.*), with organo-magnesium halides to give after hydrolysis the corresponding amides of β-substituted β-phenylpropionic acids, and a cheaper route to these acids is thus provided. *Cinnamic methylanilide*, m. p. 70°, b. p. 231°/15 mm., *ethylanilide*, m. p. 46°, b. p. 234°/15 mm., and diphenylamide, m. p. 150°, are prepared from cinnamoyl chloride and the appropriate amines. By their interaction with magnesium ethyl and phenyl bromides the following compounds are obtained: β-*phenylvaleric methylanilide*, b. p. 206°/12 mm. (free acid, m. p. 66°), *ethylanilide*, b. p. 244°/15 mm., and *diphenylamide*, m. p. 52—53°, b. p. 265°/18 mm.; ββ-*diphenylpropionic methylanilide*, b. p. 261°/13 mm. (free acid, m. p. 155°), *ethylanilide*, b. p. 278°/25 mm., and *diphenylamide*, m. p. 130°. Magnesium methyl iodide, on the other hand, reacts only slowly with the cinnamic anilides, addition taking place at the carbonyl group with elimination of amine and production of styryl methyl ketone. C. HOLLINS.

Addition of halogens to unsaturated acids and esters. I. Addition of equimolecular mixtures of bromine and chlorine to cinnamic acid and its derivatives in non-hydroxylic solvents. N. W. HANSON and T. C. JAMES (J.C.S., 1928, 1955—1960).—An equimolecular mixture of bromine and chlorine, dissolved in carbon tetrachloride, reacts additively with cinnamic acid, behaving as a solution of hypothetical bromine monochloride. Two acids are obtained and these are shown, by analysis and by their reactions with two equivalents of methyl-alcoholic potassium hydroxide, to be the two stereoisomeric β-chloro-α-bromo-β-phenylpropionic acids, analogous with cinnamic acid dihalides (higher-melting) and *allo*-dihalides (lower-melting), respectively. The higher-melting acid (I) has m. p. 182° (Erlenmeyer, A., 1896, i, 302). allo-β-*Chloro*-α-*bromo*-β-*phenylpropionic acid* (II) has m. p. 75°. When treated with methyl-alcoholic potassium hydroxide, the acid (I) evolved 39% by weight of the available hydrogen bromide, and 61% of the available hydrogen chloride, the product of this elimination being a mixture of acids from which α-bromo-, α-bromo-*allo*-, and β-chloro-*allo*-cinnamic acids were isolated. The acid (II) evolved 15% of hydrogen bromide and 84% of hydrogen chloride, the only product isolated being α-bromocinnamic acid. The isomeric α-chloro-β-bromo-β-phenylpropionic acid (Erlenmeyer, *loc. cit.*), m. p. 184·5°, evolved hydrogen bromide only, to the extent of 95% by weight of the available amount. Kinetic experiments showed that " bromine chloride " solution reacts with cinnamic acid much more rapidly than either of the halogens separately and with α-methylcinnamic, α-bromo-*o*-methoxycinnamic, and *m*-methoxycinnamic acids and methyl *o*-methoxy-, *o*-methoxy-*iso*-, and *m*-methoxy-cinnamates much more rapidly than bromine alone. M. CLARK.

Influence of substituents in the benzene nucleus on mode of reaction of silver salts of *o*-hydroxycarboxylic acids with acetobromoglucose. K. JOSEPHSON (Annalen, 1928, **464**, 227—236).—An investigation of the effect of the grouping R on the reaction between the silver salt of a substituted salicylic acid and acetobromoglucose. This reaction (cf. Karrer and co-workers, A., 1921, i, 260) mav take either or both of two courses, (I) and (II): (I) $OH{\cdot}C_6H_3R{\cdot}CO_2Ag+Br{\cdot}C_6H_7O_5Ac_4 \longrightarrow AgBr+OH{\cdot}C_6H_3R{\cdot}CO_2{\cdot}C_6H_7O_5Ac_4$; (II) $AgO{\cdot}C_6H_3R{\cdot}CO_2H+Br{\cdot}C_6H_7O_5Ac_4 \longrightarrow AgBr+CO_2H{\cdot}C_6H_3R{\cdot}O{\cdot}C_6H_7O_5Ac_4$. The three silver salts having R—H, R—Me in position 4 and R=Me in position 5 all react according to courses (I) and (II), whilst the three silver salts having R=Me in position 3, R=NO_2 in position 3, and R=NO_2 in position 5 all react in accordance with course (I) only (cf. Josephson, Arkiv Kemi, Min., Geol., 1927, **9**, No. 36). It would therefore appear that a 3-methyl or a 3- or 5-nitro-group hinders salt formation of the type suggested by Karrer (*loc. cit.*). Silver 4 : 5-dimethoxysalicylate reacts only along the lines of (I).

Tetra-acetylglucose m-*hydroxytoluate* has m. p. 151°, $[\alpha]_D^{20}$ —46·5°. The corresponding glucoside, *tetra-acetylglucosido*-m-*hydroxytoluic acid*, has m. p. 145°, $[\alpha]_D^{20}$ —28·3°, and is hydrolysed by barium hydroxide

solution to β-*glucosido*-m-*hydroxytoluic acid*, m. p. 142°, $[\alpha]^{20}$ −56·2°.

Tetra-acetylglucose 3-*nitrosalicylate*, m. p. 140°, has $[\alpha]_D^{20}$ −42·8° (*acetate*, m. p. 145°, $[\alpha]^{20}$ −73·5°). *Tetra-acetylglucose* 5-*nitrosalicylate*, m. p. 174°, $[\alpha]_D^{20}$ −47·2°, forms an *acetate*, m. p. 166°, $[\alpha]_D^{20}$ −44·3°. All rotations are for chloroform solutions. E. E. TURNER.

Chaulmoogroyl derivatives of lactates and salicylates. S. SANTIAGO and A. P. WEST (Philippine J. Sci., 1928, **35**, 405—409).—Chaulmoogroyl chloride (*ibid.*, 1927, **33**, 265) reacts with hydroxy-esters to give *methyl* and *ethyl chaulmoogroyl-lactates*, m. p. 51—54° and 54—57°, respectively, *ethyl* and *butyl chaulmoogroylsalicylates*, m. p. 48—51° and 49—50°, respectively, and the corresponding *methyl*, *phenyl*, *amyl*, and iso*amyl* esters, all unstable, decomposing at about 40°. E. W. WIGNALL.

Catalytic reduction of hydroxybenzoic acids. F. BALAŠ and A. KOSIK (Časopis Českoslov. Lek., 1927, **7**, 118—121, 136—138, 191—192; Chem. Zentr., 1928, i, 1173).—Reduction of aqueous salicylic acid by hydrogen and colloidal platinum at 60° yields finally *cyclo*hexanol in 50% yield. Similarly, *m*- and *p*-hydroxybenzoic acids yield hexahydro-*m*- and -*p*-hydroxybenzoic acids, respectively.

A. A. ELDRIDGE.

***ortho*-Effect and reactivity. I. Magnitude and cause of the *ortho*-effect in the hydrolysis of aromatic esters.** K. KINDLER [with K. G. ELLINGER].—See this vol., 962.

Condensation product of salicylic acid and *iso*valeric anhydride. J. DALIETOS (Arch. Pharm., 1928, **266**, 325—328).—The *iso*valeryl analogue of acetylsalicylic acid, which should have interesting physiological properties, is not formed by treating a salicylate with *iso*valeryl chloride, nor by heating salicylic acid and *iso*valeric anhydride at atmospheric or higher pressure, for here extensive decomposition, if anything, takes place. When, however, the anhydride and salicylic acid are heated at 150° in presence of a small quantity of sulphuric acid, iso*valerylsalicylic acid*, m. p. 225° (*sodium* salt, m. p. 233—236°), is formed. W. A. SILVESTER.

Catalytic reduction of mandelic acids. K. W. ROSENMUND and H. SCHINDLER (Arch. Pharm., 1928, **266**, 281—283).—When benzyl benzoate is reduced in boiling xylene solution by hydrogen and palladium, toluene and benzoic acid are produced (Rosenmund and Heise, A., 1921, ii, 631). The esters of other alcohols do not similarly give the corresponding hydrocarbon, at least only those which can be regarded as substituted benzyl alcohols in containing an α-phenyl group. Acetylmandelic acid, *i.e.*, α-carboxybenzyl acetate, is similarly smoothly reduced to acetic acid and phenylacetic acid (yield 20% in boiling xylene, 60% in boiling tetralin). *p*-Methoxy- and *o*-chloro-phenylacetic acids are similarly obtained from the acetates of the corresponding mandelic acids. The diacetyl derivative of *o*-hydroxymandelic acid gives directly *o*-hydroxyphenylacetic acid, the *o*-acetyl group being simultaneously removed, in the form of acetaldehyde. The method affords a ready means of obtaining substituted phenylacetic acids.

W. A. SILVESTER.

Chemical constitution and pungency. Syntheses of ethyl hydroferulate [β-4-hydroxy-3-methoxyphenylpropionate] and β-4-hydroxy-3-methoxyphenylpropyl alcohol. H. NOMURA and S. HOTTA (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 693—694).—*Ethyl* β-4-*hydroxy*-3-*methoxyphenylpropionate*, b. p. 192·5—193°/17 mm., was prepared by esterification of the acid with alcohol and sulphuric acid. Reduction by sodium and alcohol yielded γ-4-*hydroxy*-3-*methoxyphenylpropyl alcohol*, b. p. 196°/16 mm. The acid, ester, and alcohol are all pungent. R. K. CALLOW.

Attempted synthesis of isomerides of piperic acid. H. LOHAUS (J. pr. Chem., 1928, [ii], **119**, 235—271).—An attempt to synthesise chavicic and *iso*chavicic acids, the $\Delta^{\alpha\beta}$-*cis*-, $\Delta^{\gamma\delta}$-*cis*- and $\Delta^{\alpha\beta}$-*trans*-$\Delta^{\gamma\delta}$-*cis*-isomerides of piperic acid, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$ (cf. Ott and others, A., 1922, i, 1026; 1924, i, 418), could not be based on direct methods, as in these the *cis*- would invert to the *trans*-compounds (cf. the formation of *trans*-cinnamoyl chloride by the action of thionyl chloride on *allo*cinnamic acid; G. MAAS, unpublished). Hydrogenation of an acetylenic compound would, however, be expected to furnish first the less stable product. Accordingly the hydrogenation of *piperonylpropargylidenemalonic acid* has been investigated.

Phenylpropargylidenemalonic acid is prepared by condensing phenylpropargylaldehyde diethylacetal with malonic acid, filtering, and adding sulphuric acid to the mother-liquor; contrary to the statement of Driessen (Diss., Kiel, 1898), the acid is soluble in dilute sodium hydroxide solution without decomposition. Its *pyridine* salt, decomp. 114—116° (from alcohol), is soluble in water which contains pyridine.

The starting-material for the preparation of the piperonyl analogue was 3 : 4-methylenedioxycinnamic acid, obtained in improved yield by eliminating carbon dioxide from piperonylidenemalonic acid in a vacuum. The dibromide was then prepared, and thence 3 : 4-methylenedioxy-ω-bromostyrene. From this, piperonylacetylene was obtained with constant b. p. 103°/11 mm.; the action of magnesium ethyl bromide then furnished the corresponding *magnesyl bromide*, which was treated with ethyl orthoformate in an ether–benzene mixture to give, after addition of sulphuric acid, *piperonylpropargylaldehyde diethylacetal*, b. p. 188—190°/16 mm. (decomp. during isolation), with resinous products and some bis-piperonyldiacetylene.

Magnesium piperonylacetylenyl bromide and ethyl formate in ether at −20° gave, after addition of sulphuric acid, the original acetylene and *piperonylpropargylaldehyde*, m. p. 76°, b. p. 159—160°/15 mm., with, under some conditions, an unknown *substance*, m. p. 220°. The aldehyde was also obtained by hydrolysing the above acetal with very dilute sulphuric acid; decomposition accompanied the hydrolysis. The aldehyde could be prepared from the acetylene by means of the *sodium* derivative only by use of a solution of sodium in liquid ammonia: it did not, however, react with ethyl formate.

Piperonylpropargylidenemalonic acid, brown, m. p. 250° (decomp.), was obtained from the acetal and

malonic acid in acetic acid, in best yield by using the crude product from the acetylene, without distillation. The yellow *dipyridine* salt, decomp. 231°, when treated with dilute hydrochloric acid yielded a *monopyridine* salt, m. p. 204°, yellow, which on keeping with water was converted into a red *form*, m. p. 237°.

The preparation of 3 : 4-methylenedioxycinnamaldehyde (piperonylacraldehyde) (Ladenburg and Scholtz, A., 1895, i, 42; Winzheimer, A., 1908, i, 656) was repeated, and the m. p. 77—78°, b. p. 175—190°/1 mm., obtained. A *by-product*, m. p. 100—105°, gave with *p*-nitrophenylhydrazine a *compound*, m. p. 258°. From the aldehyde and malonic acid, piperonylidene-ethylidenemalonic acid (Scholtz, A., 1895, i, 468), new m. p. 231—232° (decomp.) (*pyridine* salt, decomp. 191—192°), was prepared.

Catalytic hydrogenation of phenylpropargylaldehyde diethylacetal, employing palladium adsorbed on charcoal, yielded only *trans*-cinnamaldehyde diethylacetal, identified by condensation with malonic acid; the free aldehyde gave similar results. Piperonylpropargylaldehyde yielded oily products; piperonylacraldehyde was reduced to piperonylpropane. Phenylpropargylidenemalonic acid gave in methyl alcohol an oily product, in acetic acid an oil regarded as *cis-cis*-cinnamylideneacetic acid, with some cinnamylidenemalonic acid; the sodium salt yielded an oily product, and the pyridine salt a *cis*-cinnamylidenemalonic acid, decomp. about 106°, which was also obtained, in less pure condition, when palladium adsorbed on barium sulphate was employed.

From piperonylpropargylidenemalonic acid, amorphous products were obtained: it is thought that carbon dioxide was lost. The products from the pyridine and piperidine salts were also unsatisfactory; from the last, *trans*-piperonylethylidenemalonic acid could be obtained. A small quantity of a product regarded as the *cis*-form was obtained, and was heated; carbon dioxide was lost, and a resinous mass obtained, from which an amorphous substance, m. p. 160° (possibly impure *iso*chavicic acid), was separated by extraction with benzene.

The preparation of *iso*piperic acid (Ott, Eichler, and Heimann, A., 1922, i, 1027) was repeated. Piperonylidene-ethylidenemalonic acid was heated with quinoline at 160°: the product had m. p. 155° (softens 145°). *iso*Piperic acid with thionyl chloride gave piperoyl chloride, identified by conversion into piperic acid, and, by piperidine, into piperin. *iso*Chavicic acid, on the other hand, undergoes no inversion when treated with thionyl chloride. E. W. Wignall.

Sensitive differentiation of phthalic and terephthalic acids. R. Ripan (Bul. Soc. Stiinte Cluj, 1927, **3**, 308—310; Chem. Zentr., 1927, ii, 2466).—On treatment of a fairly concentrated solution of a copper salt with the acid in 2% aqueous solution in presence of pyridine, terephthalic acid gives an immediate precipitate of the compound $[C_6H_4(CO_2)_2][Cu(H_2O)_3(C_5H_5N)_3]$, whereas phthalic acid yields a precipitate of the compound $[Cu(C_5H_5N)_2][C_6H_4(CO_2)CO_2H]_2$ only after some hours; the test is very sensitive. The cobalt salts differ even more markedly in solubility.

A. A. Eldridge.

Hydrolysis of esters by solid alkali hydroxides. E. Tassilly, A. Belot, and M. Descombes (Compt. rend., 1928, **186**, 1846—1848).—The method of hydrolysis of ethyl phenylethylmalonate by solid alkali hydroxides (this vol., 290) has been extended. The ester is added, with shaking, to finely-powdered potassium hydroxide (2 mols. for each carboxyl group) in a covered crucible; the mass gradually solidifies and the heat generated has occasionally to be controlled. The reaction is generally finished after 1 hr. Solid esters usually react only above their m. p., although methyl oxalate reacts energetically in the cold. Ethyl acetate and the esters of benzoic, phenylacetic, hydrocinnamic, cinnamic, and salicylic acids react in the cold, but methyl cinnamate must be heated at 100°, and likewise the esters of *o*-, *m*-, and *p*-nitrobenzoic acid. The yields of acid are quantitative. The difficultly hydrolysable methyl *allo*camphorate yields camphoric acid quantitatively at 200° by this method. J. D. Fulton.

Molecular configurations of polynuclear aromatic compounds. VII. 5 : 5'-Dichlorodiphenyl-3 : 3'-dicarboxylic acid. F. B. McAlister and J. Kenner (J.C.S., 1928, 1913—1916).—No diphenyl derivative could be prepared from the *ethyl* ester, m. p. 59—60°, of *5-iodo-3-nitrobenzoic acid*, m. p. 166—167°, which is obtained by successive treatment of 3-nitro-5-aminobenzoic acid with potassium metabisulphite in fuming nitric acid and a solution of iodine in potassium iodide. *3-Bromo-5-iodotoluene* (I), prepared from 5-bromo-*m*-toluidine, has m. p. 23°, b. p. 150°/29 mm. *3-Bromo-5-acetamidobenzoic acid*, m. p. 279—281°, obtained by oxidation of *5-bromoaceto-*m*-toluidide*, m. p. 171—172°, with an aqueous solution of potassium permanganate and hydrated magnesium sulphate, is successively converted into *3-bromo-5-aminobenzoic acid*, m. p. 220—222° (*hydrochloride*), and *3-bromo-5-iodobenzoic acid*, m. p. 209—211° [*methyl* ester (II), m. p. 59—61°]. When either (I) or (II) was heated with copper powder, bromine as well as iodine was eliminated, so that no definite diphenyl derivative could be prepared in either case. *3-Chloro-5-iodotoluene*, m. p. 0°, b. p. 138—140°/26 mm., from 5-chloro-*m*-toluidine, is readily converted when heated with copper powder into *5 : 5'-dichloro-3 : 3'-ditolyl*, m. p. 101—102°. Oxidation failed to yield the corresponding dicarboxylic acid. *3-Chloro-5-acetamidobenzoic acid*, m. p. 265—267°, is converted into *3-chloro-5-aminobenzoic acid hydrochloride*, m. p. 118—121°, and thence by successive treatment with potassium metabisulphite in fuming nitric acid and a solution of iodine in potassium iodide, into *3-chloro-5-iodobenzoic acid*, m. p. 190—191° [*methyl* ester (III), m. p. 43—44°]. When (III) is heated with copper powder, *methyl 5 : 5'-dichlorodiphenyl-3 : 3'-dicarboxylate*, m. p. 156°, is obtained. *5 : 5'-Dichlorodiphenyl-3 : 3'-dicarboxylic acid*, m. p. 358—360°, yields a *brucine* salt, m. p. 178—179°, decomp. 191—193°, $[\alpha]_D$ —5·2° in chloroform, a *quinine* salt, m. p. 170—172°, decomp. 174°, $[\alpha]_D$ —132° in alcohol, and an *acid morphine* salt, m. p. 218—219°, decomp. 223—225°, $[\alpha]_D$ —30° in alcohol. The solutions of ammonium 5 : 5'-dichlorodiphenyl-3 : 3'-dicarboxylate prepared

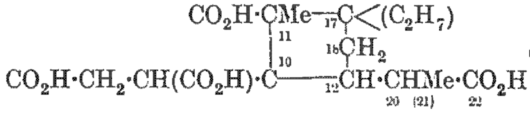
from these salts were in each case optically inactive. The acid therefore does not exhibit the asymmetry of its 2 : 2′-6 : 6′-structural isomeride (cf. A., 1926, 518).. M. CLARK.

Action of phthaloyl chloride on *m*-methoxybenzoic acid and *m*-tolyl methyl ether. R. WEISS and W. KNAPP (Monatsh., 1928, **50**, 10—15).—From *m*-methoxybenzoic acid or its methyl ester, phthaloyl chloride, and aluminium chloride there is obtained the *dilactone* of dihydroxy-4-methoxydiphenylmethane-2 : 2′-dicarboxylic acid,

, m. p. 183°. With *m*-tolyl methyl ether condensation occurs *ortho* to the methoxyl group, giving 3′ : 3″-*dimethoxydi*-p-*tolylphthalide*, which is reduced by sodium amalgam in methyl alcohol to 2′ : 2″-*dimethoxy*-4′ : 4″-*dimethyltriphenylmethane-2-carboxylic acid*, m. p. 170° (+0·75MeOH; *compound* with 0·25CHCl:CHCl, and *potassium* salt described). Oxidation of this phthalin with alkaline permanganate gives 2 : 2′-*dimethoxytriphenylmethane*-4 : 4′ : 4″-*tricarboxylic acid* (*methyl* ester, *sodium* and *potassium* salts described), which is converted by zinc chloride at 200° into 1 : 2′-*dimethoxy-9-phenylanthrone*-3 : 4′-*dicarboxylic acid* (decomp. 250°). C. HOLLINS.

Complex anions of meconic and quinic acid with heavy metals. R. WEINLAND and H. FRIEDE (Arch. Pharm., 1928, **266**, 353—366).—By adding aqueous ferric chloride to a methyl-alcoholic solution of meconic acid and then sodium hydroxide, ammonia, or an organic base in calculated amount (short of alkaline reaction), or by adding aqueous ferric acetate to an aqueous solution of meconic acid containing excess of sodium acetate or to an aqueous solution of meconic acid in sodium hydrogen carbonate, guanidine, or piperidine containing acetic acid, crystalline salts (usually red to brown) of tribasic ferridimeconic acid are obtained. The following are described: *trisodium* salt, $[Fe\{O\cdot C_5HO_2(CO_2)_2\}_2]Na_3,10H_2O$; *triguanidine* salt, $+6H_2O$; *tripiperidine* salt, $+5H_2O$; *ammonium dihydrogen* salt, $+5H_2O$; *monopyridine dihydrogen* salt, $+5H_2O$; *monoguanidine* salt, $+5H_2O$; *monoquinoline* salt, $+6H_2O$; also a *sodium* and a *pyridine* salt in which 4 mols. of acid are present to 7 of base, $+20H_2O$. A green *pyridine chlorochromidimeconate*, $[Cr\{O\cdot C_5HO_2(CO_2)_2\}_2Cl]H_4,C_5H_5N,7H_2O$, is obtained in small yield by adding pyridine to an aqueous methyl-alcoholic solution of meconic acid and green chromic chloride hexahydrate. From a solution of copper sulphate and meconic acid, excess of ammonia precipitates a blue *hexammonium tricupridimeconate*, $+8H_2O$; the green *pyridine* salt contains only 4 mols. of base; a corresponding white *tetrammonium trizincidimeconate* ($+8H_2O$) is described. Quinic acid [1 : 2 : 4 : 5-tetrahydroxy*cyclo*hexane-1-carboxylic acid], although it contains no benzene ring and gives no coloration with ferric salts, yields green *tripotassium* and *trirubidium ferritriquinates*, $[Fe\{O\cdot C_6H_7(OH)_3CO_2\}_3]M_3,12H_2O$. C. HOLLINS.

Bile acids. XXVIII. Nature of the fourth ring. H. WIELAND and F. VOCKE (Z. physiol. Chem., 1928, **177**, 68—85; cf. Wieland, Schlichting, and Jacobi, A., 1927, 247).—Oxidation of the tetracarboxylic acid, $C_{16}H_{24}O_8$ (Wieland and Schlichting, A., 1924, i, 857), with 6% hydrogen peroxide gives, in addition to much acetic acid, acetaldehyde and acetone. Since β-methyladipic and α-methylglutaric acids similarly yield acetone, this is in keeping with the suggested structure (I) for the tetracarboxylic acid.

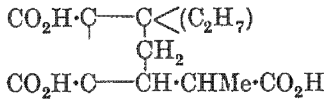


(I.)

The mother-liquors from the preparation of this acid (residues from working-up of 10 kg. of deoxycholic acid) contain succinic acid, α-methylglutaric acid, and an *acid*, $C_7H_{10}O_6$, m. p. 134°, which is not identical with *cis*-α-methyltricarballylic acid, but which by decarboxylation yields α-methylglutaric acid. An identical acid is obtained by hydrolysis of Auwers' ethyl butane-αγγ-tricarboxylate (A., 1896, i, 642). It is concluded that the C_{11} atom in cholanic acid carries a methyl group.

The tetracarboxylic acid gives a trimethyl ester, m. p. 100°, a *triethyl* ester, m. p. 108°, a *dimethyl* ester, m. p. 167°, by esterification, and a *monomethyl* ester, m. p. 163° (*potassium* salt described), by hydrolysis of the tetramethyl ester (*loc. cit.*); hydrolysis of the trimethyl ester, on the other hand, regenerates the free acid. Oxidation with chromic acid of the product of the action of magnesium phenyl bromide on the trimethyl ester gives an *acid*, $C_{28}H_{30}O_4$, m. p. 226—227°; from the tetramethyl ester an isomeric *acid*, m. p. 155°, is similarly obtained.

The *methyl ester trihydrazide*, $C_{17}H_{32}O_5N_6$, m. p. 145° ($+H_2O$; decomp.), prepared from the tetramethyl ester, gives by the Curtius reaction the *trihydrochloride* of a *triamino-acid*, $C_{13}H_{27}O_2N_3,3HCl$, m. p. 250° (decomp.), the oxidation of which by hypochlorous or hypobromous acid gave no useful result.



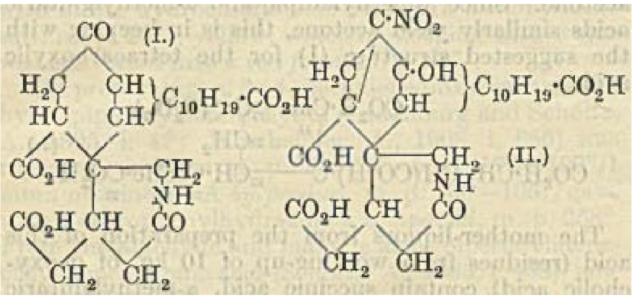
(II.)

The tricarboxylic acid, $C_{13}H_{20}O_6$ (II), obtained by oxidation of the pyro-acid, $C_{15}H_{22}O_5$ (*loc. cit.*), yields by the usual esterification method only a *dimethyl* ester, b. p. 208—210°/1 mm., which is converted by diazomethane into the *trimethyl* ester, b. p. 170° in high vacuum. The *methyl ester dihydrazide* from this gives by the Curtius reaction a *diamino-acid*, decomp. 280°.

In the preparation of pyrodeoxybilianic acid by thermal decomposition of deoxybilianic acid a stereoisomeric "β"-*deoxybilianic acid*, m. p. 221—222°, is obtained as a by-product; it is possibly an intermediate in the conversion into the pyro-acid. C. HOLLINS.

Bile acids. XX. Nitrogenous derivatives of bilianic acid. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1928, **176**, 187—199; cf. this vol., 764).—The white compound, $C_{24}H_{35}O_8N$, precipitated by acids from the alkaline solution of the blue nitroso-compound obtained from bilianic acid di*iso*oxime (*loc. cit.*) is a tricarboxylic acid (I) formed by exchange of

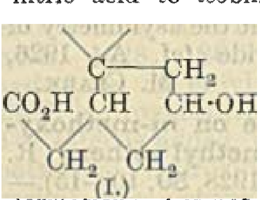
hydroxyl for the nitroso-group, probably followed by ketonisation. It exists in two forms, (*a*) small crystals, m. p. 200—205° (decomp.; sintering at



185°), containing H_2O, and (*b*) needles, m. p. 260° (decomp.; anhydrous). Under similar conditions bilianic acid dioxime gives a blue *nitroso*-compound, $C_{24}H_{33}O_8N$, m. p. 236—238° (decomp.; sinters at 220—230°), which by the action of alkali yields bilianic acid [as (I) with omission of the NH]. The substance (I) is also obtained by oxidation of bilianic di*iso*oxime with permanganate. Oxidation of the di*iso*oxime or of the blue nitroso-compound therefrom with nitric acid (*d* 1·4) at 15° yields a hydroxytricarboxylic *acid*, $C_{21}H_{31}O_{10}N_2$, m. p. 212—214° (decomp.), of probable structure (II).

C. Hollins.

Bile acids. XIII. Catalytic reduction of ketonic acids of the bile acid group. W. Borsche and E. Feske (Z. physiol. Chem., 1928, **176**, 109—121; cf. Borsche and Frank, A., 1926, 1140).—By means of an exceptionally active platinum-black catalyst dehydrocholic acid, m. p. 237—238°, is reduced with hydrogen in glacial acetic acid to 3 : 7 : 12-trihydroxycholanic acid, m. p. 196—197°, $[\alpha]_D$ +35·91° in alcohol (identical with that of natural cholic acid); the previously recorded high rotation is probably due to the presence of *dihydroxyketocholanic acid*, m. p. 219—220°, $[\alpha]_D^{20}$ +73° in alcohol (*methyl* ester, m. p. 160°; methyl ester *oxime*, m. p. 111—112°), which is formed in larger amount when a less active platinum-black is used. Oxidation of methyl deoxycholate, m. p. 130° (the m. p. and rotation given by Borsche and Frank are erroneous), with chromic acid yields the dehydro-ester together with *methyl hydrogen deoxybilianate*, $C_{19}H_{27}O_5$·CHMe·CH_2·CH_2·CO_2Me, m. p. 278°. Dehydrodeoxycholic acid, m. p. 189°, is reduced to deoxycholic acid, m. p. 141—143° (+AcOH), $[\alpha]_D^{20}$ +49·33°, identical with the natural product, whilst bilianic acid yields reductobiliobanic acid, m. p. 243° (Windaus and van Schoor, A., 1926, 169; *methyl* ester, m. p. 135°), which is oxidised by chromic acid to biliobanic acid, m. p. 307°. The reduction of deoxybilianic acid to 7-*hydroxylithobilianic acid*, m. p. 269—271° (*trimethyl* ester, m. p. 105°), of pyrodeoxybilianic acid to the corresponding *dihydroxy-acid*, $C_{23}H_{38}O_4$, m. p. 211—213° (*methyl* ester, m. p. 168°), and of *iso*bilianic acid to reducto*iso*biliobanic acid, m. p. 278°, is described. The last-mentioned acid is converted by warm alkali into 7 : 12-*dihydroxylithobilianic acid*, melting and decomposing at 162° with regeneration of the lactonic acid, m. p. 278°. Reducto*iso*biliobanic acid is oxidised by chromic or nitric acid to *iso*biliobanic acid, m. p. 264—265° [*oxime*, m. p. 215°; dimethyl ester, m. p. 172°; dimethyl ester oxime, m. p. 188° (decomp.)].



Reductobiliobanic acid and hydroxylithobilianic acid, which both contain the grouping (I), show no tendency to δ-lactone formation; it is not safe, however, to conclude from this that reducto*iso*biliobanic acid has a γ- rather than a δ-lactone bridge.

C. Hollins.

Colour and constitution. III. Influence of the methylthiol, methoxy-, and chlorine groups on the colours of the nitrobenzaldehydephenylhydrazones. H. H. Hodgson and F. W. Handley (J.C.S., 1928, 1882—1886).—The influence of the methylthiol, methoxy-, and chlorine groups on the colours of certain nitrobenzaldehydephenylhydrazones containing these substituents in the *ortho*- and *para*-positions in the benzaldehyde and phenylhydrazine residues, respectively, is investigated. Equimolecular alcoholic solutions exhibit a well-defined order which is the same whether the groups are present in the aldehyde or hydrazine residue and is independent of the position of the nitro-group in the remaining residue, viz., *o*-Cl (lemon-yellow), *o*-SMe, *p*-Cl, H, *o*-OMe, *p*-SMe (increasing depth), *p*-OMe (deep reddish-orange). The absorption spectra curves of the *o*-nitrobenzaldehydephenylhydrazones confirm the results of the visual observations. The influence of the substituents is, in general, less marked than in the case of the azo-dyes (cf. this vol., 284). *p*-Nitrobenzaldehydephenylhydrazone, already shown to exist in two polymorphic forms (Ciusa and Vecciotti, A., 1911, i, 810), crystallises from glacial acetic acid in yellow needles, m. p. 194°, which slowly change to a pale orange modification of unchanged m. p. Exposure to ultra-violet light is without effect. Addition of water to a solution of the substance in glacial acetic acid precipitates a yellow variety changing in a few seconds into the red form of Ciusa and Vecciotti. Attempts to prepare *o*-methylthiolbenzaldehyde were unsuccessful. The following are described: 4-*methylthiolphenylhydrazine*, m. p. 60° (*hydrochloride*), obtained by reduction of the diazonium compound from 4-thioanisidine hydrochloride; 2-*methylthiolphenylhydrazine*, m. p. 40°, similarly prepared from 2-thioanisidine hydrochloride (an amorphous by-product, m. p. below 100°, was also obtained); o- and p-*chlorobenzaldehyde*-o-*nitrophenylhydrazones*, m. p. 178° and 203—204°; o- and p-*methoxybenzaldehyde*-o-*nitrophenylhydrazones*, m. p. 176—177° and 204°; p-*methylthiolbenzaldehyde*-o-*nitrophenylhydrazone*, m. p. 225—226°; o- and p-*chlorobenzaldehyde*-m-*nitrophenylhydrazones*, m. p. 171 and 172°; o- and p-*methoxybenzaldehyde*-m-*nitrophenylhydrazones*, m. p. 176° and 156°; p-*methylthiolbenzaldehyde*-m-*nitrophenylhydrazone*, m. p. 146°; p-*chlorobenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 224°; o-*methoxybenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 204—205°; p-*methylthiolbenzaldehyde*-p-*nitrophenylhydrazone*, m. p. 183°; o-*nitrobenzaldehyde*-o- and -p-*methylthiolphenylhydrazones*, m. p. 87—88° and 204°; m-*nitrobenzaldehyde*-o- and *ethylthiolphenyl*-

hydrazones, m. p. 118° and 152°; p-*nitrobenzaldehyde-o-* and -p-*methylthiolphenylhydrazones*, m. p. 147° and 179°; *benzaldehyde-p-methylthiolphenylhydrazone*, m. p. 93°; p-*methylthiolbenzaldehydephenylhydrazone*, m. p. 138°. M. CLARK.

Condensation of heptaldehyde with aromatic aldehydes. B. N. RUTOWSKI and A. I. KOROLEW (J. pr. Chem., 1928, [ii], **119**, 272—274).—Heptaldehyde and benzaldehyde in aqueous alcohol condense under the influence of sodium hydroxide to give β-*phenyl-α-amylacraldehyde*, b. p. 174—175°/20 mm., d_{20}^{20} 0·97108, n^{20} 1·5381, of pleasant odour when diluted (*oxime*, m. p. 72·5—73°; *semicarbazone*, m. p. 117·5—118°). This further condenses with benzoylglycine to give 2-*phenyl*-4-β-*benzylideneheptylidene-5-oxazolone*, m. p. 97—98°. E. W. WIGNALL.

Physical properties of salicylaldehyde. T. S. CARSWELL and C. E. PFEIFER (J. Amer. Chem. Soc., 1928, **50**, 1765—1766).—Purification of a sample, f. p. −7° (the accepted value), by vacuum fractionation, conversion into the hydrogen sulphite compound, and redistillation, gives pure salicylaldehyde, f. p. 1·6°, b. p. 196·4—196·5°/751 mm., d^{20} 1·1690.
H. E. F. NOTTON.

Catalytic nuclear hydrogenation of acetals of aromatic and semi-aromatic aldehydes. I. F. SIGMUND (Monatsh., 1928, **49**, 271—282; cf. A., 1927, 1054).—Hydrogenation of phenylacetaldehyde diethylacetal with platinum-black in anhydrous acetic acid yields chiefly a mixture of hexahydrophenylacetaldehyde diethylacetal and unreduced acetal, b. p. 222—230°, together with small quantities of liquids, b. p. 195—202° (chiefly hexahydrophenylethyl ethyl ether) and b. p. 202—210° (probably a mixture of the latter ether and reduced acetal). Phenylacetaldehyde dimethylacetal under similar conditions gives an 81% yield of hexahydrophenylacetaldehyde dimethylacetal (I), b. p. 204·5—206°, and a small quantity of a fraction of b. p. 194—197° (probably a mixture of hexahydrophenylethyl methyl ether and the reduced acetal). Treatment of (I) with sulphuric and acetic acids gives hexahydrophenylacetaldehyde, b. p. 179—182° (semicarbazone, m. p. 162°; cf. Skita, Ber., 1915, **48**, 2, 1694), and a small, less volatile fraction probably produced by the slight polymerisation of the aldehyde. I. VOGEL.

Analysis of vanillin and vanillin sugar. J. PRITZKER and R. JUNGKUNZ (Chem.-Ztg., 1928, **52**, 537).—The most suitable qualitative test for vanillin is the mercuric nitrite test of Nickel, as modified by Kreis and Studinger. For gravimetric determination, precipitation with *m*-nitrobenzhydrazide is recommended. A suitable volumetric method consists in titration with 0·1*N*-sodium hydroxide, using thymolphthalein as indicator. S. I. LEVY.

Synthesis of a new [methylated] gallaldehyde. F. MAUTHNER (J. pr. Chem., 1928, [ii], **119**, 306—310).—*Gallaldehyde 4-methyl ether* (3 : 5-*dihydroxy*-4-*methoxybenzaldehyde*), m. p. 139—140° (p-*nitrophenylhydrazone*, m. p. 222—223°), is obtained as follows. Methyl gallate is methylated by diazomethane (cf. Herzig and Pollak, A., 1903, i, 89) and the product hydrolysed to gallic acid 4-methyl ether (Graebe and Martz, A., 1903, i, 262); this is treated in alkaline solution with methyl chloroformate, yielding OO′-*dicarbomethoxy-4-methoxy-α-resorcylic acid*, m. p. 120—121°, of which the acid *chloride*, m. p. 58—59°, is reduced in toluene by hydrogen in the presence of palladium, at 110°, to the corresponding *aldehyde*. The last is hydrolysed by alkali, in presence of hydrogen, to the new derivative. E. W. WIGNALL.

Nierenstein reaction. W. BRADLEY and R. ROBINSON (Nature, 1928, **122**, 130—131).—Polemical against Nierenstein (this vol., 739). In the interaction of diazomethane and benzoyl chloride, the reaction $PhCO·Cl+CH_2N_2=PhCO·CH_2Cl+N_2$ (*a*) is not the primary action; the reactions $PhCO·Cl+CH_2N_2=PhCO·CHN_2+HCl$ (*b*) and $HCl+CH_2N_2=CH_3Cl+N_2$ (*c*) are much more rapid than $PhCO·CHN_2+HCl=PhCO·CH_2Cl+N_2$ (*d*). Hence the observed evolution of nitrogen is a measure of the extent to which the final yield of chloroacetophenone by (*b*) and (*d*) falls short of the theoretical. Under favourable conditions the yield of chloroacetophenone from equimolecular proportions of benzoyl chloride and diazomethane is 9% of the theoretical. It is recommended that the reagents should be mixed as rapidly as possible. A. A. ELDRIDGE.

Degradation of *o*-substituted aromatic acid azides. H. LINDEMANN and W. SCHULTHEIS.—See this vol., 1028.

Sulphur-containing derivatives of acetophenone. E. RIESZ and W. FRANKFURTER (Monatsh., 1928, **50**, 68—75).—By the action of chlorosulphonic acid acetophenone yields a *disulphonyl chloride*, m. p. 195—196° (decomp.), from which the *disulphonanilide*, m. p. 195—196° (decomp.), and dithiolacetophenone, m. p. 128° (*lead* salt described), are obtained. *p*-Aminoacetophenone, diazotised and treated with alkaline xanthate, gives after hydrolysis p-*thiolacetophenone*; this is condensed with chloroacetic acid to give p-*acetophenylthioglycollic acid*, m. p. 155—156°, which by treatment with chlorosulphonic acid is converted into 5 : 5′-diacetothioindigotin. The *p*-thiolacetophenone is oxidised to acetophenone-*p*-sulphonic acid, which on sulphonation with chlorosulphonic acid yields an *acetophenonedisulphonyl chloride*, m. p. 210° (decomp.) [*anilide*, m. p. 235° (decomp.)], which is thus different from the direct sulphonation; it gives on reduction a *dithiolacetophenone*, m. p. 215° (*lead* salt described).
C. HOLLINS.

Action of bromine on phenyl β-phenylstyryl ketone. R. BARRÉ and E. P. KOHLER (J. Amer. Chem. Soc., 1928, **50**, 2036—2040).—The results differ from those of previous workers (cf. Dilthey and Last, A., 1916, i, 821; Vorländer, A., 1923, i, 682; Moureu, A., 1923, i, 921). When bromine and phenyl β-phenylstyryl ketone are refluxed together in chloroform *phenyl α-bromo-β-phenylstyryl ketone*, m. p. 88—89° (rapid heating), is obtained in 90% of the theoretical yield. It is reduced by zinc dust and acetic acid to phenyl ββ-diphenylethyl ketone. If, however, bromination is carried out at the ordinary temperature for 15—20 hrs., the bromo-derivative is partly dehydrated by the hydrogen bromide formed to 1 : 2-*dibromo*-1 : 3-*diphenylindene*, m. p. 104—105°.

This has a reactive bromine atom and forms with alcohol 2-*bromo*-1-*ethoxy*-1 : 3-*diphenylindene*, m. p. 130—131°. It is ozonised to *o*-dibenzoylbenzene.

H. E. F. NOTTON.

Nitrogen trichloride and unsaturated ketones. II. G. H. COLEMAN and D. CRAIG (J. Amer. Chem. Soc., 1928, **50**, 1816—1820).—Solutions of nitrogen trichloride in carbon tetrachloride are conveniently analysed by conversion into ammonium chloride by evaporation with hydrochloric acid in a current of air. Styryl methyl ketone and nitrogen trichloride in carbon tetrachloride (cf. A., 1927, 1190) at –10° form ammonium chloride, αβ-dichloro-β-phenylethyl methyl ketone, which decomposes at the ordinary temperature into β-chlorostyryl methyl ketone, and α-*chloro*-β-*amino*-β-*phenylethyl methyl ketone hydrochloride* (I) (5% of the theoretical yield), m. p. 176—177° (decomp.), which is converted by the Schotten–Baumann method into a *by-product*, m. p. 204°, and a *benzamido*-derivative, m. p. 160—161°. This is reduced by sodium amalgam and alcohol to α-*benzamido*-α-*phenylbutan*-γ-*ol*, m. p. 150—151°. The hydrochloride (I) is reduced similarly to α-*amino*-α-*phenylbutan*-γ-*ol*, m. p. 74—76° (*dibenzoyl* derivative, m. p. 139—141°). β-*Amino*-α-*phenylbutan*-γ-*ol*, m. p. 62—64° (*hydrochloride*, m. p. 114—116°), and β-*benzamido*-α-*phenylbutan*-γ-*ol*, m. p. 177—179°, were prepared for comparison from α-amino-β-phenylethyl methyl ketone (cf. Sonn, A., 1908, i, 55).

H. E. F. NOTTON.

2 : 4 : 7-Trinitrofluorenone. F. BELL (J.C.S., 1928, 1990).—Nitration of fluorenone by the method of Schmidt and Bauer (A., 1906, i, 27) yields, not 2 : 3 : 7-trinitro-, but 2 : 4 : 7-*trinitro-fluorenone*, m. p. 175°, identical with the product obtained by nitration of 4-nitrofluorenone with nitric acid (*d* 1·5) on the steam-bath.

J. W. BAKER.

Thiobenzophenone. H. STAUDINGER and H. FREUDENBERGER [with E. SENN, S. VENDRELL, and I. SIEGWART] (Ber., 1928, **61**, [*B*], 1576—1583).—The action of benzophenone chloride on potassium sulphide affords a mixture of thiobenzophenone and unchanged benzophenone which can scarcely be separated into its components by fractional distillation. If the product is treated with diphenylketen, the compound $CPh_2<^{CO}_{S}>CPh_2$, m. p. 180—181°, separates, which is decomposed by distillation with benzylideneaniline in a vacuum into thiobenzophenone, m. p. 54—55°, and the β-lactam, $CPh_2<^{CO-}_{CHPh}>NPh$. The preparation of thiobenzophenone from benzophenone chloride and sodium sulphide suffers under the disadvantage that benzophenone is formed by the action of alkali on the chloride; better results are obtained by the gradual addition of sodium hydrogen sulphide to the chloride dissolved in alcohol in the complete absence of air. The polymeric thiobenzophenone of Siegwart (Diss., Zurich, 1917) is a mixture of sulphur and dibenzhydryl disulphide, m. p. 152—153°. Thiobenzophenone can be prepared in 75% yield by the action of hydrogen sulphide on benzophenone dichloride at 150°; if the reaction is prolonged, the products are sulphur and tetraphenylethylene. The readiest method for the preparation of thiobenzophenone consists in the treatment of benzophenone in alcohol with hydrogen chloride and hydrogen sulphide. Thiobenzophenone forms dark violet needles, m. p. 54—55°, and possibly exists in a polymeric form, m. p. 51° It is far more reactive than benzophenone, readily undergoing change with diphenylketen and aliphatic diazo-compounds. With aniline and phenylhydrazine it affords benzophenone-anil and -phenylhydrazone, respectively. It does not condense with acetaldehyde, acetone, or ethyl acetate in the presence of tertiary bases, whereas it is decomposed if sodium ethoxide is employed. It does not give an additive compound with triethylphosphine. At 160—170° it yields tetraphenylethylene and sulphur. It readily undergoes auto-oxidation to benzophenone, a little sulphur dioxide and sulphur, and a trisulphide, m. p. 124°. Pure thiobenzophenone does not polymerise if preserved for years and is not affected by addition of pyridine, trimethylamine, triethylphosphine, or hydrogen chloride. It is reduced by sodium sulphide, sodium hydrogen sulphide, ammonium sulphide, or sodium ethoxide in alcoholic solution to dibenzhydryl disulphide, m. p. 152—153°. The last-named compound is prepared in quantitative yield by the action of excess of sodium hydrogen sulphide on benzophenone dichloride. Its constitution is established by its formation from thiobenzhydrol (from hydrogen sulphide and diphenyldiazomethane) and iodine. It is further formed from benzophenone and ammonium sulphide. It is reduced by aluminium amalgam to thiobenzhydrol and converted when heated into thiobenzophenone, diphenylmethane, and sulphur.

H. WREN.

Carvacryl [2-hydroxy-5-*p*-cymyl] ketones. K. W. ROSENMUND and C. WHA (Arch. Pharm., 1928, **266**, 407—411).—The following ketones have been prepared from carvacrol by the method used with other phenols by Rosenmund and Schulz (A., 1927, 667): 2-*hydroxy*-5-p-*cymyl methyl ketone*, m. p. 120° (*methyl ether*, b. p. 164°/18 mm.); *ethyl ketone*, m. p. 110°, b. p. 201°/15 mm. (*oxime*, m. p. 145°); *propyl ketone*, m. p. 90°, b. p. 200°/15 mm. (*oxime*, m. p. 120°). The ethyl and propyl ketones are reduced by Clemmensen's method to *o*-*propylcarvacrol*, b. p. 150°/14·5 mm., and *o*-*butylcarvacrol*, b. p. 158°/12 mm., respectively. 2-Hydroxy-5-*p*-cymyl methyl ketone condenses with benzaldehyde in presence of alkali to give 2-*hydroxy*-*o*-p-*cymyl* β-*hydroxy*-β-*phenylethyl ketone*, m. p. 158°. The corresponding 2-*methoxy*-compound, m. p. 72°, is similarly prepared. 2-Methoxy-5-*p*-cymyl methyl ketone is also condensed with ethyl mesoxalate, giving after hydrolysis 4-*methoxy*-3-*methyl*-6-iso*propylphenacylmalic acid*, m. p. 96 (*ethyl* ester, b. p. 190°/0·5 mm.), which by decarboxylation at 96—110° is converted into the corresponding *glycollic acid* (*ethyl* ester, b. p. 180—184°/0·36 mm.).

C. HOLLINS.

Acyl wandering with phenols. K. W. ROSENMUND and W. SCHNURR (Annalen, 1928, **460**, 56 98).—The synthesis of phenolic ketones by the Behn method (G.P. 95,901, 1897), which was recently improved (A., 1927, 667), is now shown to take place as a result of intermediate ester formation; for,

when thymol, acetyl chloride, nitrobenzene, and aluminium chloride are used, thymyl acetate is formed intermediately and may actually be isolated. For the conversion of the ester of a phenol into the ketone, the former is treated with 1·2—1·3 mols. of aluminium chloride in 5 parts of nitrobenzene (1 day in the cold).

It is also shown that the conditions previously used for effecting the Fries transformation are unnecessary. Thus, in the case of the conversion of *p*-tolyl benzoate into 2-hydroxy-5-methylbenzophenone only 1 mol. of aluminium chloride (corrected for purity of the sample used) need be used. Moreover, complete reaction is usually effected by heating the mixture at 120° for 10 min. Details for this "baking" process are given.

The acetyl group in thymyl acetate shows a marked tendency to migrate to the *p*-position with respect to the hydroxyl group. The change occurs in the cold in little more than a day, whilst at 60° it is complete in 10 min. Most aliphatic acyl radicals migrate at about the same rate as the acetyl group. The approximate rates of formation of the following ketones by the nitrobenzene method have been determined: 4-hydroxy-2-methyl-5-*iso*propyl-acetophenone, and the corresponding -propiophenone, -butyrophenone, -*iso*valerophenone, -*octophenone* (m. p. 81—82°, b. p. 217—220°/9 mm.), -*phenylacetophenone* (m. p. 105°), -cinnamophenone, and -β-*phenylpropiophenone*, m. p. 122° (from thymol esters, b. p. as follows: acetate, 131°/21 mm., propionate, 248°/760 mm., butyrate, 265°/760 mm., iso*valerate*, 143°/9 mm., *octoate*, 186°/9 mm., *phenylacetate*, 188°/9 mm., β-*phenylpropionate*, 218°/13 mm.). 4-Hydroxy-5-methyl-2-*iso*propyl-acetophenone (m. p. 120°), and the corresponding -propiophenone, -butyrophenone, and -iso*valerophenone*, m. p. 108°, b. p. 201°/13 mm., are obtained, respectively, from the acetate, b. p. 238°/750 mm., *propionate*, b. p. 250°/760 mm., *butyrate*. b. p. 263°/760 mm., and iso*valerate*, b. p. 271°/760 mm., of carvacrol. Clemmensen reduction of 2-hydroxy-4-methylpropiophenone affords 5-*methyl*-2-*propylphenol*, b. p. 129°/16 mm., the *acetate* (b. p. 124°/14 mm.) of which is very readily converted into 4-*hydroxy*-2-*methyl*-5-*propylacetophenone*, m. p. 113°, b. p. 194°/13 mm.

Aromatic acyl radicals migrate with considerably greater difficulty. From thymyl benzoate and carvacryl benzoate (b. p. 191°/14 mm.), 4-*hydroxy*-2-*methyl*-5-iso*propylbenzophenone*, m. p. 153°, and 4-hydroxy-5-methyl-2-*iso*propylbenzophenone, m. p. 172—173°, are obtained.

The rate of migration of acyl radicals into the *p*-position in the case of thymol esters is given by the order: ·Ac, ·COEt and homologues $>$·CO·CH_2Ph, ·CO·$[CH_2]_2$Ph, ·CO·CH:CHPh$>$Bz.

Migration of an acyl group into an *o*-position (the *p*-position being blocked) is markedly less facile than *p*-migration. The migration proceeds rapidly (10 min. at 120°) in absence of nitrobenzene, however. In this way, from *p*-tolyl esters (b. p. as follows: *hexoate*, 142—143°/14 mm., *heptoate*, 168°/17 mm., *octoate*, 175°/12 mm.), the following have been prepared: 2-hydroxy-5-methyl-acetophenone and the corresponding -propiophenone, -butyrophenone, -*iso*valerophenone, -*hexophenone* (b. p. 163°/15 mm.), -*heptophenone* (b. p. 168°/10 mm.), and -*octophenone*, m. p. 36°. From 6-chloro-*m*-tolyl esters (b. p. as follows: *acetate*, 121°/15 mm., *propionate*, 250°/760 mm., *butyrate*, 263°/760 mm.) there are produced the following: 5-*chloro*-2-*hydroxy*-4-*methyl*-*acetophenone* (m. p. 71—72, b. p. 137°/15 mm.) and the corresponding -*propiophenone* (m. p. 76°) and -*butyrophenone* (m. p. 61—62°).

3-*Chloro*-2-*hydroxy*-5-*methyl*-*acetophenone*, m. p. 91°, has been obtained from 3-*chloro*-p-*tolyl acetate*, b. p. 238°/760 mm., the corresponding -*propiophenone*, m. p. 115°, from the *propionate*, b. p. 248°/760 mm., and the -*butyrophenone*, m. p. 62°, from the *butyrate*, b. p. 260°/760 mm.

Reduction of 4-hydroxy-2-methylacetophenone by Clemmensen's method produces 3-*methyl*-4-*ethylphenol*, b. p. 122°/15 mm., the *acetate* (b. p. 124°/15 mm.) of which is converted into 2-*hydroxy*-4-*methyl*-5-*ethylacetophenone*, m. p. 96—97°, b. p. 142—143°/15 mm., by aluminium chloride. Similarly, the acetate of 2-hydroxy-5-methylacetophenone is readily converted into 3 : 5-diacetyl-*p*-cresol, m. p. 83°, b. p. 194°/13 mm., although the benzoate refuses to undergo a similar change.

Aromatic residues undergo *o*-migration less readily than aliphatic residues. The following have been prepared by heating the appropriate ester for 10 min. at 140° with aluminium chloride: 2-hydroxy-5-methyl-, 2′-*chloro*-2-*hydroxy*-5-*methyl*- (m. p. 78°, b. p. 195°/15 mm.), 2′-*bromo*-2-*hydroxy*-5-*methyl*- (m. p. 76—77°) and 4′-*bromo*-2-*hydroxy*-5-*methyl*- (m. p. 79°, b. p. 210°/14 mm.), 5-*chloro*-2-*hydroxy*-4-*methyl*- (m. p. 142°), and 3-*chloro*-2-*hydroxy*-5-*methyl*-*benzophenone*, m. p. 71°.

Various determinations of relative rates of *o*-migration have been made. True aliphatic radicals migrate more rapidly than the phenylacetyl group, and the benzoyl and bromobenzoyl radicals migrate much less rapidly than the latter.

Although it is known that 2 : 4 : 6-trimethylphenyl esters undergo the Fries change, which is accompanied by displacement of a methyl group by acyl, 2 : 4 : 6-tribromophenol is unaffected under similar conditions.

With phenyl esters possessing free *o*- and *p*-positions either migration may take place. Mild conditions favour *p*-migration, drastic conditions *o*-migration. Thus when *m*-tolyl acetate is treated in nitrobenzene with aluminium chloride at 25°, only *p*-migration occurs; at 90—100° approximately equal amounts of *o*- and *p*-change take place, whilst at 165° only *o*-change occurs. Similar results are obtained using *o*-tolyl and *p*-hydroxyacetophenone acetates, and the corresponding homologous esters (propionates to octoates; no details given).

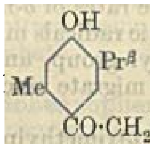
In the case of aromatic residues, temperature again may be used to control the course of the migration. At 165°, *m*-tolyl benzoate is quantitatively converted into 2-hydroxy-4-methylbenzophenone, whilst at lower temperatures the 4 : 2-isomeride is the main product. The other ketones produced in this part of the investigation are *p*-hydroxy- and 4-hydroxy-3-methyl-benzophenone.

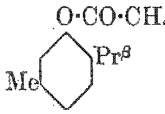
The tendency, present in phenyl esters, for *o*-migration is decreased by introducing (*o*-tolyl esters)

a 2-methyl group, but is markedly increased (*m*-tolyl esters) by introducing a *m*-methyl radical (figures given for "baking" in the cases of the acetates and benzoates of the three phenols at 120°). The nitro-group (*o*-nitrophenyl esters) completely inhibits migration, which is also inhibited by an *o*-acyl group. The carboxyl group is inhibiting when in the *m*- or *p*-position with respect to the hydroxyl, but acetylsalicylic acid is convertible into 4-hydroxyacetophenone-3-carboxylic acid. The corresponding benzoate does not give a migration reaction. The action of aluminium chloride on phenyl anisate gives only 4 : 4′-dihydroxybenzophenone.

In an attempt to convert *4-acetoxy-2-methylacetophenone*, b. p. 163°/15 mm. (I), into 5-acetyl-4-hydroxy-2-methylacetophenone (II), there were obtained only 4-hydroxy-2-methyl- (III) and 2-hydroxy-4-methyl-acetophenone (IV). That (II) is not first formed and then converted into (III) and (IV) is shown by the fact that *4-benzoyloxy-2-methylacetophenone*, m. p. 52—53°, passes, under similar conditions, into 2-hydroxy-4-methylacetophenone, no 2-hydroxy-4-methylbenzophenone being produced. The reactions involved are therefore (1) migration of the group in the *p*-position to the *o*-position, and (2) hydrolysis of the ester. That such migration is possible is shown by the conversion, by aluminium chloride at 170°, of (III) into (IV) and by an analogous conversion carried out with the corresponding benzoyl compound (at 180—190°).

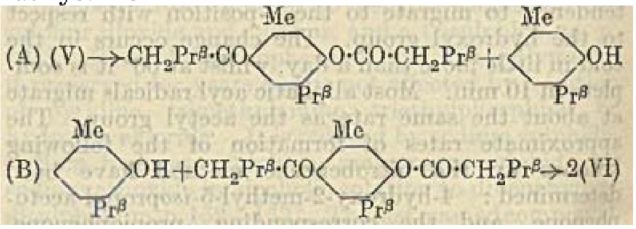
When slightly impure 4-hydroxy-2-methyl-5-*iso*-propyl*iso*valerophenone (V) is distilled in a vacuum, small quantities of thymyl *iso*valerate (VI) are formed. Although (V) is unaffected in this respect


(V.)


(VI.)

by a large number of acids etc. it is converted to a greater or less extent into (VI) when heated for 2—5 hrs. at 180—250° with sulphuric acid, sulphuryl chloride, phosphoric acid, or camphorsulphonic acid, the last-named being particularly effective. A number of ketones of type (V) have been heated at 150° for 1 hr. with a trace of camphorsulphonic acid. In general, 2-hydroxyphenyl alkyl ketones, 2-hydroxy-3-(4- or -5-)methylphenyl alkyl ketones, 2-hydroxy-5-methyl-3-ethyl-, 2-hydroxy-4-methyl-5-ethyl-, 3-chloro-2-hydroxy-5-methyl-, and 5-chloro-2-hydroxy-4-methyl-phenyl alkyl ketones are not subject to the (V) ⟶ (VI) type of change (*o*-hydroxy-ketones). Yet, whilst 4-hydroxyphenyl alkyl ketones and simply substituted 4-hydroxy-3-methylphenyl alkyl ketones are also stable under the conditions employed, 4-hydroxy-2-methyl-, 4-hydroxy-2-methyl-5-*iso*propyl-, and 4-hydroxy-5-methyl-2-*iso*propyl-phenyl alkyl ketones undergo conversion into esters. The actual cases described are the conversion of 4-hydroxy-2-methylacetophenone into *m*-tolyl acetate, that of 4-hydroxy-2-methylphenacetophenone into *m*-tolyl phenylacetate, those of 4-hydroxy-2-methyl-5-*iso*-propyl-aceto-, -propio-, -butyro-, -*iso*valero-, and -benzo-phenones into thymyl acetate, propionate, butyrate, *iso*valerate, and benzoate, respectively, those of 4-hydroxy-5-methyl-2-*iso*propyl-aceto-, -butyro-, and -benzo-phenones into carvacryl acetate, butyrate, and benzoate, respectively, and that of 4-hydroxy-2-methylbenzophenone into *m*-tolyl benzoate.

When (V) is heated for ½ hr. at 150° in presence of camphorsulphonic acid, thymol, thymyl *iso*valerate (VI), and the *isovalerate*, b. p. 200°/14 mm., of (V) are formed. If the reaction is carried out in a vacuum, so that the thymol is removed as fast as it is formed, the sole other product is the *iso*valerate of (V). If the latter is heated with more thymol and the catalyst, thymyl *iso*valerate results, so that the reactions involved in a normal heating of (V) with catalyst are :



with possibly a second (B′) stage involving interaction of a molecule each of ketone ester with (V).

When a mixture of phenol and *4-methoxy-2-methyl-5-isopropylbutyrophenone*, m. p. 50°, is heated with camphorsulphonic acid, the products are thymol methyl ether and phenyl butyrate, further evidence for stage (B) above. The migration of acyl groups from the nucleus to the phenolic oxygen is thus a bimolecular change.

The mechanism of the Fries transformation is discussed. It may be due to formation of acid chloride from the ester, followed by a Friedel–Crafts reaction (Skraup and Poller, A., 1925, i, 143), or it may be (von Auwers) an intramolecular change. That it is not of the latter type is suggested by the fact that simultaneous Fries treatment of 3-chloro-*p*-tolyl acetate and *p*-tolyl benzoate gives 3-chloro-2-hydroxy-5-methylbenzophenone and 2-hydroxy-5-methylacetophenone in addition to 3-chloro-2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone, whereas an intramolecular change should produce only the last two compounds. It appears probable, therefore, that in the Fries change 2 mols. of ester interact. This view is supported by the facts that (1) phenyl acetate reacts with chloroacetyl chloride in presence of aluminium chloride to give some *p*-hydroxyacetophenone chloroacetate, (2) *p*-tolyl acetate, nitrobenzene, and aluminium chloride afford only traces of 2-hydroxy-5-methylacetophenone, whilst (3) addition of thymol in (2) causes the formation of cresol and 4-hydroxy-2-methyl-5-*iso*propylacetophenone.

A similar explanation is given for the conversion of *o*- into -ketones (above). Thus, when 4-hydroxy-3-methylacetophenone and 3-chloro-*p*-cresol are "baked" together, 2-hydroxy-4-methylacetophenone and 3-chloro-2-hydroxy-5-methylacetophenone are formed, whereas on the intramolecular wandering theory only the former should be produced.

E. E. TURNER.

Mechanism of the Fries transformation. K. VON AUWERS and W. MAUSS (Annalen, 1928, 464, 293—311).—The claims of Rosenmund and Schnurr (preceding abstract) in connexion with the general improvement in methods of effecting the Fries transformation require some criticism, for although these authors have considerably improved those methods, some phenol esters, *e.g.*, the acetate and benzoate of 2-hydroxymesitylene, do not undergo the change under the conditions laid down by Rosenmund and Schnurr. Moreover, phenol benzoates and chloroacetates require more drastic treatment than do the corresponding acetates. Thus, phenyl chloroacetate and *m*-tolyl chloroacetate do not undergo the Fries change in 1 day in cold nitrobenzene solution in presence of aluminium chloride, whereas *m*-tolyl acetate and 2-*m*-xylyl acetate, under similar conditions, afford good yields of 2-hydroxy-4-methylacetophenone and 4-hydroxy-3 : 5-dimethylacetophenone, respectively; 4- and 5-*m*-xylyl acetates, the acetate and chloroacetate of 2 : 6-dimethyl-4-ethylphenol, and the *chloroacetate*, b. p. 138°/12 mm., of 3-chloro-*o*-cresol, are to a slight extent hydrolysed, but are otherwise unaffected under these conditions. 2 : 4 : 6-*Trichlorophenyl acetate*, m. p. 49—51°, is unaffected by aluminium chloride in $\frac{1}{4}$ hr. at 150°, whilst after 4 hrs. at 130—140° in presence of excess of chloride, tar, some trichlorophenol, and a trace of an *o*-hydroxyketone(?) are found present. When heated with aluminium chloride for 1 hr. at 100⟶140°, 3-chloro-*o*-tolyl chloroacetate gives, as main product, 3-*chloro-4-hydroxy-5-methylphenacyl chloride*, m. p. 98·5—99·5°; whether or not any *o*-displacement of chlorine occurs is uncertain.

Rosenmund and Schnurr's conclusion that the Fries transformation is bimolecular in type, *i.e.*, is a reaction of the Friedel–Crafts type between 2 mols. of a phenol ester, is open to criticism, if for no other reason than that whilst Fries changes lead to *o*- as well as to *p*-compounds, Friedel–Crafts reactions give exclusively the latter. Other evidence, as below, shows the untenability of Rosenmund's view. Meisenheimer and Hanssen (Diss., Tübingen, 1926) have shown that benzoyl chloride and 4-*m*-xylvl methyl ether under Friedel–Crafts conditions give mainly 5-hydroxy-2 : 4-dimethylbenzophenone, *i.e.*, the benzoyl radical goes *meta* to the methoxyl group. Were Rosenmund's contention correct, 4-*m*-xylyl acetate, under Fries conditions, should give 5-hydroxy-2 : 4-dimethylacetophenone, whilst in practice it gives, as the only recognisable product, 2-hydroxy-3 : 5-dimethvlacetophenone. Again, when a mixture of the acetate and the methyl ether of 4-*m*-xylenol is warmed with aluminium chloride in nitrobenzene, the ether is unaffected and the acetate gives 2-hydroxy-3 : 5-dimethylacetophenone, *i.e.*, no acetate reacts in the sense to be anticipated from Rosenmund's theory.

The main support for the latter theory is the formation from a mixture of 3-chloro-*p*-tolyl acetate and *p*-tolyl benzoate (Fries conditions) of 3-chloro-2-hydroxy-5-methylbenzophenone and 2-hydroxy-5-methylacetophenone in addition to the normal products, viz., 3-chloro-2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone. The present authors have obtained the same result, but have also isolated some 3-chloro-*p*-tolyl benzoate. It is shown that exchange of acyl groups frequently occurs when phenol esters of different acids are together submitted to Fries conditions, although this does not necessarily take place with every pair. Thus, a mixture of phenyl acetate and *p*-tolyl chloroacetate gives only 2- and 4-hydroxyacetophenone, and 2-hydroxy-5-methylphenacyl chloride, and, if mild conditions are employed, even the latter is not formed. Similarly, a mixture of *p*-tolyl acetate and 3-chloro-*p*-tolyl benzoate gives only traces of hydroxyketones derived from intermediate reciprocal exchange of acyl radicals. In short, the course of all such reactions is determined by the nature of the substances concerned (the benzoyl and chloroacetyl groups are more firmly attached to oxygen than is the acetyl group). A mixture of 2-*m*-xylyl acetate and *p*-tolyl benzoate gives xylenol and cresol, together with 2-hydroxy-5-methyl-acetophenone and -benzophenone, and 4-hydroxy-3 : 5-dimethylacetophenone. A mixture of the acetate of 2-hydroxymesitylene and *p*-tolyl chloroacetate gives cresol, 2-hydroxymesitylene, the acetate of the latter, and 2-hydroxy-3 : 4 : 5-trimethylacetophenone. The *chloroacetate*, m. p. 77—78°, b. p. 156°/12 mm., of 2 : 6-dimethyl-4-ethylphenol, gives a small quantity of 4-hydroxy-3 : 5-dimethylphenacyl chloride. A mixture of the same chloroacetate with *p*-tolyl acetate ($AlCl_3$; 150°) gives 2-hydroxy-5-methylacetophenone and unchanged chloroacetate, together with a trace of an *o*-hydroxyphenacyl chloride (?).

To determine whether in fact an acyl group attached to the oxygen atom of one phenol can enter the nucleus of another phenol molecule, mixtures of phenol ethers and esters have been heated with aluminium chloride. When 2-*m*-xylyl methyl ether and *p*-tolyl acetate are so taken, the products are xylenol, cresol, 2-hydroxy-5-methyl- and 4-hydroxy-3 : 5-dimethyl-acetophenone. With a mixture of 2-hydroxymesitylene methyl ether and *p*-tolvl chloroacetate, the two free phenols, chloroacetic acid, and unchanged ether are the sole products. Had Rosenmund substitution occurred, ketones derived from the ethers should have been formed.

Other evidence is obtained which shows that reciprocal exchange of acyl groups occurs in some cases under the conditions of a Fries change. 2-Hydroxymesitylene and *p*-tolyl benzoate, or the acetate of the former and *p*-cresol, do not interact in absence of a catalyst at 200°, whilst a mixture of the last two substances, when heated at 150° for $\frac{3}{4}$ hr. in presence of aluminium chloride, affords only 2-hydroxy-5-methylacetophenone and hydroxymesitylene. On the other hand, when a mixture of 2-hydroxymesitylene and *p*-tolyl benzoate is heated for $\frac{1}{2}$ hr. at 150° with aluminium chloride, the benzoate of 2-hydroxymesitylene is formed, together with the two free phenols and 2-hydroxy-5-methylbenzophenone, whilst under similar conditions a mixture of the acetate of 2-hydroxymesitylene and *p*-tolyl benzoate affords some of the benzoate of the mesitylenol, together with benzoic acid, 2-hydroxy-5-methylacetophenone, and 2-hydroxy-5-methylbenzophenone. A mixture of the acetate of 2-hydroxymesitylene with 3-chloro-*p*-tolyl benzoate gives free phenols, 3-chloro-2-hydroxy-

5-methyl-acetophenone, the corresponding -benzophenone, and the benzoate of 2-hydroxymesitylene.

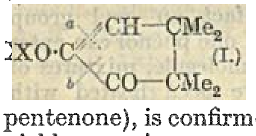
Since reciprocal esterification under Fries conditions would explain Rosenmund's test experiment, it is concluded that the Fries transformation is an intra- and not an inter-molecular change.

E. E. TURNER.

Course of the Friedel and Crafts synthesis of ketones with dialkyl [ethers of] resorcinol. F. MAUTHNER (J. pr. Chem., 1928, [ii], **119**, 311—314).—The "new resacetophenone" obtained by Claus and Huth (A., 1896, i, 227) by the Friedel–Crafts reaction with acetyl chloride and resorcinol diethyl ether was held by Eijkman to be a 4 : 6-diacetoresorcinol; this is confirmed. The action of 2 mols. of acetyl chloride and aluminium chloride on resorcinol dimethyl ether in carbon disulphide yields two products: the first, soluble in alkali, is 4 : 6-diacetoresorcinol monomethyl ether (Eijkman, Bergema, and Henrard, A., 1905, i, 360), and the second, insoluble in alkali, the corresponding dimethyl ether. Free resorcinol gives 4 : 6-diacetoresorcinol and (?) its dimethyl ether; resorcinol diethyl ether yields 4 : 6-diacetoresorcinol monoethyl ether.

E. W. WIGNALL.

Possibility of ring-chain valency tautomerism, and of a type of mobile hydrogen tautomerism analogous to the Wagner-Meerwein rearrangement. III. Orientation of some cyclic derivatives of phorone. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1928, 1868—1873).—The structure (I), previously assigned (this vol., 414) to the acetyl derivative (X=Ac) of hydroxyphorone (5-hydroxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone), is confirmed, since the dihydro-derivative yields an *oxime*, m. p. 93° (*hydrochloride*, m. p. 136—137°), which is reduced by sodium amalgam to 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. The formation of an oxime from 5-benzoyloxyphorone with extrusion of the benzoyl grouping as previously stated (*loc. cit.*) leaves doubtful the position in which the oximino-grouping has become attached to the ring. It is now shown that reduction of the oxime by sodium amalgam followed by phosphorus and hydriodic acid yields 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine; moreover, 5-benzoyloxyphorone is reduced by hydrogen and palladised barium sulphate to 5-benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanolone. The original benzoyloxy-compound must therefore have the structure (I) (X=Bz), and the oximino-group must enter the molecule in a position other than that from which the benzoyl group is expelled. 5-*p*-Bromobenzyloxyphorone is only very slightly affected by palladised barium sulphate and hydrogen, yielding a *compound*, m. p. 26—27°. Reduction of 5-*p*-bromobenzyloxy-2 : 2 : 3 : 3-Δ^4-*cyclo*pentenoneacetoxime with sodium amalgam and acetic acid yields 5-hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine, isolated as the picrate, and further reduction with phosphorus and hydriodic acid affords 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. It is shown that hydroxylamine can hydrolyse phenyl benzoate and 5-benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone, and that the methyl group of 5-methoxyphorone is removed by treatment with hydroxylamine, yielding the dioxime of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentan-1 : 2-dione. The normal mode of fission of hydroxyphorone or its derivatives by oxidation with potassium ferricyanide is at (*a*) (I), whilst fission with hydrogen peroxide occurs preferentially at (*b*) (I). Thus with potassium ferricyanide, 5-benzoyloxyphorone yields the lactonic acid of $\gamma\gamma$-dihydroxy-$\alpha\alpha\beta\beta$-tetramethylglutaric acid, whilst 5-acetoxyphorone and 5-hydroxyphorone yield tetramethylsuccinic acid. Benzoyloxyphorone and hydrogen peroxide yield $\alpha\alpha\beta\beta$-tetramethylglutaric acid.



M. CLARK.

Relative reactivity of methylene groups in 1 : 3-diketones. A. B. E. LOVETT and E. ROBERTS (J.C.S., 1928, 1975—1979).—ω-Phenylacetylacetophenone (I) condenses with salicylaldehyde in absolute alcohol solution in presence of piperidine, giving o-*hydroxybenzylidenephenylacetylacetophenone*, $OH\cdot C_6H_4\cdot CH{:}CPh\cdot CO\cdot CH_2\cdot CO_2Ph$, m. p. 171—174°. The constitution of this substance is fixed, since it is readily converted into acetophenone and 3-phenylcoumarin. The following substituted 3-phenylcoumarins in small yield are produced when the appropriate substituted salicylaldehydes are condensed with (I), but in these cases no intermediate product can be isolated: 6-*methyl*-, m. p. 146—147·5°: 6-*chloro*-, m. p. 199°; 6-*bromo*-, m. p. 189—191°; 6-*nitro*-, m. p. 251—253°; 8-*nitro*-, m. p. 236—239°; 6 : 8-*dichloro*-, m. p. 193—194·5°; 6 : 8-*dibromo*-, m. p. 186—187·5°; 6-*bromo*-8-*nitro*-, m. p. 228—230°; and 8-*nitro*-6-*methyl*-3-*phenylcoumarins*, m. p. 180—182°. 3 : 5-*Dinitrosalicylaldehyde* (II), m. p. 58—60°, is obtained by further nitration of the mixture of 3- and 5-nitrosalicylaldehydes produced by mononitration of salicylaldehyde; on oxidation it gives 3 : 5-dinitrosalicylic acid. 5-*Chloro*-3(?)-*nitrosalicylaldehyde* (III), m. p. 105—107°, is produced by nitration of 5-chlorosalicylaldehyde in glacial acetic acid. Its constitution is inferred from that of the analogous 5-bromo-3-nitrosalicylaldehyde. Aldehydes (II) and (III) fail to give substituted 3-phenylcoumarins with (I). Like 5-bromo-3-nitrosalicylaldehyde, from which only a trace of the corresponding coumarin is obtained, they react with piperidine to give stable piperidides of undetermined constitution. 6 : 8-*Dinitro*- and 6-*chloro* 8(?)-*nitro*-3-*phenylcoumarin*, synthesised by the Perkin reaction, have m. p. 244—246° and 212—214°. Ethyl phenylacetate and salicylaldehyde give some 3-phenylcoumarin when heated in presence of piperidine. 2-Hydroxy-α-naphthaldehyde and (I) react in alcoholic solution in presence of piperidine, giving a deep red *compound*, $C_{27}H_{18}O_2$, m. p. 155—156·5°. ω-Propionylacetophenone, b. p. 149°/17 mm., 151°/19 mm. (*copper* salt, m. p. 151—152°; p-*nitrophenylhydrazone*, m. p. 67—68°; *anil*, m. p. 48—49°), butyrylacetophenone, and propionylacetone yield resin-like products when treated with salicylaldehyde. It is deduced that the methylene group in (I) more reactive for condensation with aldehydes, is that adjacent to the phenyl group.

M. CLARK.

Syntheses of β-4-hydroxy-3-methoxystyryl n-propyl and n-amyl ketones. S. TSURUMI, S. MURAKOSHI, and R. YAMASAKI (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 703—705).—The condensation

of vanillin with methyl *n*-propyl and *n*-amyl ketones to yield β-4-hydroxy-3-methoxystyryl *n*-propyl and *n*-amyl ketones (cf. Nomura and Hotta, A., 1925, i, 1156; Murai, *ibid.*, 1157) takes place readily on boiling for 6 hrs. with aqueous-alcoholic potassium hydroxide. R. K. CALLOW.

Syntheses of β-4-hydroxy-3-methoxyphenylethyl *n*-pentenyl and *n*-hexenyl ketones. H. NOMURA and S. EL CHOI (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 707—710; cf. Nomura and Tsurumi, A. 1927, 1078).—Condensation of zingerone (β-4-hydroxy-3-methoxyphenylethyl methyl ketone) with *n*-butaldehyde and *n*-valeraldehyde in presence of aqueous potassium hydroxide yielded, respectively, β-4-*hydroxy-3-methoxyphenylethyl* n-*pentenyl ketone*, b. p. 198·5—200°/4·5 mm., and the n-*hexenyl ketone*, b. p. 203—206·5°/6 mm. The constitutions were confirmed by reduction with hydrogen in presence of platinum-black to the known saturated ketones (Murai, A., 1925, i, 1157; Nomura and Tsurumi, *loc. cit.*). R. K. CALLOW.

Chemical constitution and pungency. E. MARUI (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 695—702).—In view of the reported pungency of β-*o*-hydroxy- and β-2-hydroxy-3-methoxy-phenylethyl methyl ketones the author prepared other *o*-hydroxy-derivatives of this type. *o*-Hydroxystyryl ethyl ketone, m. p. 116—118° (cf. Auwers and Voss, A., 1910, i, 70), yields, on reduction by sodium amalgam, β-o-*hydroxyphenylethyl ethyl ketone*, m. p. 72° (I). *o*-Hydroxystyryl phenyl ketone (cf. Harries and Busse, A., 1896, i, 301) is reduced by hydrogen in the presence of platinum-black to β-*o*-hydroxyphenylethyl phenyl ketone, m. p. 91° (II) (cf. Borsche and Geyer, A., 1914, i, 711). β-*o*-Hydroxyphenylethyl methyl ketone is reduced by amalgamated zinc and hydrochloric acid to δ-o-*hydroxyphenylbutane*, b. p. 101—102°/11 mm. (III). The *sodium* ($+H_2O$), *potassium* ($+H_2O$), and *calcium* salts of hydro-*o*-coumaric acid (β-*o*-hydroxyphenylpropionic acid) (IV) (cf. Tiemann and Herzfeld, A., 1877, i, 708) were prepared. Compounds (I) and (III) are pungent. (II) is first sweet and then pungent. The salts of (IV) are pungent in proportion to their solubility. The anhydride, ethyl ester, and amide, m. p. 92° (lit. 70°), are all pungent. R. K. CALLOW.

Reduction of quinones by means of phenylhydrazine. A. GIACALONE (Gazzetta, 1928, **58**, 409—411).—Phenylhydrazine reduces quinones to quinols; with benzoquinone the reaction is so violent that benzene must be used as a diluent; thymoquinone is reduced in benzene, but with naphthaquinone [which with phenylhydrazine hydrochloride in acetic acid gives benzeneazo-α-naphthol (Zincke and Bindewald, A., 1885, 391)] reduction to the quinol occurs only in absence of solvent. Anthraquinone is not reduced. E. W. WIGNALL.

Reaction of malononitrile with α-naphthaquinone. W. KESTING (Z. angew. Chem., 1928, **41**, 745—748; cf. this vol., 606).—The intense blue coloration developed when neutral aqueous solutions (p_H greater than 2·5) of malononitrile and α-naphthaquinone are mixed is due to formation of β-*imino*-β-1 : 4-*naphthaquinonylpropionitrile*, $C_{10}H_5O_2\cdot C(NH)\cdot CH_2\cdot CN$, m. p. above 250° (decomp.; *silver* salt). The blue *ammonium* salt, obtained by passing ammonia into an ethereal solution of the components, dyes wool in bright violet shades, becoming black on exposure to light. The red *hydrochloride*, precipitated by hydrochloric acid from a solution of the ammonium salt, loses hydrogen chloride on exposure to moist air, giving the imino-nitrile, this being the only way in which the latter could be prepared in solid form. C. HOLLINS.

Course of the Friedel–Crafts reaction with anthraquinone-1 : 2-dicarboxylic anhydride. G. MACHEK and A. GRAT (Monatsh., 1928, **50**, 6—9).—The condensation of anthraquinone-1 : 2-dicarboxylic anhydride with benzene in presence of aluminium chloride gives, in place of the expected 1 : 2 : 3 : 4-diphthaloylbenzene (cf. Fairbourne, J.C.S., 1921, **119**, 1580), a *phthaloyldiphenylphthalide*,

$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2{<}{}^{CPh_2}_{CO}{>}O$, m. p. 180—182°, and the corresponding hydroxy-acid, $C_{28}H_{18}O_5$, m. p. 143—146°. C. HOLLINS.

Stereochemistry of aromatic compounds. VI. An optically active vat dye without an asymmetric carbon atom; *d*- and *l*-1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid. R. KUHN and O. ALBRECHT (Annalen, 1928, **464**, 91—100).—2 : 2′-Dimethyl-1 : 1′-dianthraquinonyl has been prepared by Scholl's method (A., 1924, i, 60). The intermediately used 1-iodo-2-methylanthraquinone has m. p. 172·5—173·5° (corr.), not 169—169·5° as given by Scholl. Oxidation of the dimethyl derivative with chromic anhydride in acetic anhydride and glacial acetic acid affords 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid in higher yield than that given by Scholl's method. The acid cannot be resolved through its brucine or morphine salts, but addition of light petroleum to a concentrated chloroform solution of the quinine salt effects partial resolution (see original for details). *Quinine* l-1 : 1′-*dianthraquinonyl-2 : 2′-dicarboxylate*, having $[\alpha]_D^{18}$ −110·7° (not optically pure), leads to the optically impure l-*acid*, $[\alpha]_D^{18}$ −237° in 0·1*N*-sodium hydroxide. The *quinine* salt of the *d*-acid, obtained optically pure, has m. p. 249—250°, $[\alpha]_D^{18}$ +369° in pyridine, and leads to the optically pure d-*acid* (m. p. phenomena indefinite, as with *l*-acid), $[\alpha]_D$ +346° in 0·1*N*-sodium hydroxide (rotatory dispersion measured). The *d*-acid does not undergo racemisation in 0·1*N*-sodium hydroxide during 6½ hrs. at 140—160°, nor in acetic anhydride during 7½ hrs. at 100°, but some racemisation occurs in acetic anhydride after 3½ hrs. at the b. p. of the solution. Conversion of the *d*-acid into a vat, using alkaline hyposulphite, and subsequent recovery of acid by oxidation appears to be without great effect on the activity. Some inconclusive experiments on dyeing viscose, hair, and wool have been made.

The non-co-planar configuration of the dianthraquinonyl molecule is demonstrated by the above resolution. E. E. TURNER.

Constitution of carotin. L. ZECHMEISTER and L. VON CHOLNOKY (Ber., 1928, **61**, [*B*], 1534—1539).—Catalytic hydrogenation of carotin in *cyclo*hexane in the presence of platinum shows that its double linkings

are divisible into two groups. At least two and probably three of them are distinguished by not being causative of colour; they become hydrogenated towards the end of the reaction after the double linkings of the second type have become almost completely saturated. The colour of carotin is due to a series of double linkings which readily absorb hydrogen. As long as hydrogenation mainly affects the latter type, the diminution in the intensity of the colour of the solution is proportional to the consumption of hydrogen. The colour appears to be lost completely after addition of 8 mols. of the gas. Partly hydrogenated solutions of carotin all exhibit the typical carotin spectrum and hence contain a mixture of unchanged material and decolorised products; coloured intermediate compounds do not appear to be formed. Carotin therefore appears to contain eight olefinic linkings conjugated with one another and three further double linkings. The optical inactivity of perhydrocarotin appears to ally it closely to perhydro-ψ-crocetin and to strengthen further the analogy between the safran dyes and the carotin group. Perhydrocarotin, $C_{40}H_{78}$, conveniently prepared by catalytic hydrogenation of carotin in chloroform in the presence of platinum, has normal mol. wt. in freezing benzene, indicating a C_{40} formula for carotin, which is supported by direct determinations of its mol. wt. in freezing benzene and camphor. H. WREN.

Crystalline carotin-like substances from meadow ranunculus and rose "hips." H. H. ESCHER (Helv. Chim. Acta, 1928, **11**, 752—754).—Details are given for the extraction of xanthophyll from the flowers of *Ranunculus Steveni*, Andrz., and of lycopin from rose "hips" (cf. Willstatter and Escher, A., 1910, i, 330; 1912, i, 125). H. BURTON.

Plant colouring matters. VII. Lycopin. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1928, **11**, 751—752).—Catalytic reduction of lycopin (Willstatter and Escher, A., 1910, i, 330) gives *perhydrolycopin*, $C_{40}H_{82}$, b. p. 238—240°/0·03 mm., thus demonstrating its aliphatic nature and its similarity to carotin and bixin (this vol., 869). H. BURTON.

Gossypol. IV. *apo*Gossypol. E. P. CLARK (J. Biol. Chem., 1928, **78**, 159—166; cf. this vol., 208, 426).—By heating gossypol with 40% sodium hydroxide at 100° and acidifying there was obtained apo*gossypol*, $C_{28}H_{30}O_6$ (*hexa-acetate*, m. p. 291°; *hexamethyl ether*, m. p. 259°); the mother-liquor yielded 2 mols. of formic acid which must have arisen from the two carbonyl groups of gossypol; as in gossypol hexa-acetate, two of the acetyl groups of *apo*gossypol hexa-acetate are more resistant to hydrolysis than the remaining four. *apo*Gossypol is considerably less toxic than gossypol, and causes acute effects only. C. R. HARINGTON.

Salep-mannan. H. PRINGSHEIM and G. LISS (Annalen, 1928, **460**, 32—42).—Salep-mannan is converted by acetic anhydride in presence of glacial acetic acid and pyridine, under certain prescribed conditions, into the *triacetate*, $[\alpha]_D^{19}$ −28·9°. This has *M* in acetic acid (f. p.) 293—717 and in nitrobenzene (f. p.) 518—1355. The degradation of the triacetate by heat in presence of naphthalene has been examined. E. E. TURNER.

Relation of lichosan to lichenin. II. H. PRINGSHEIM and H. BRAUN (Annalen, 1928, **460**, 42—56).—The viscosities of a number of lichenin solutions have been measured. The fermentative degradation of lichosan has been studied under various conditions. The different effects of ageing on aqueous solutions of lichosan and of lichenin is noted. The *product*, $C_6H_9O_4{\cdot}O{\cdot}PO_3H$, has been obtained by treating lichosan with phosphoryl chloride in presence of pyridine at −15°. E. E. TURNER.

Hypothetical combined pentose and so-called free pentose [in apples]; composition of pectin. R. B. MCKINNIS (J. Amer. Chem. Soc., 1928, **50**, 1911—1915).—A 95% alcoholic extract of apple pulp yields no furfuraldehyde when distilled with 12% hydrochloric acid. Free pentose is therefore absent, or present only in small amount. Determinations of the galacturonic acid content of the pulp from the amount of carbon dioxide liberated on hydrolysis, and of the yield of furfuraldehyde from Ehrlich's digalacturonic acid (A., 1917, i, 321) by distillation with hydrochloric acid, indicate that the furfuraldehyde formed when the whole apple pulp is distilled with acid is entirely accounted for by the galacturonic acid present. Pentoses, either free or combined, do not, therefore, occur in apples or in apple pectin (cf. Nanji, Paton, and Ling, J.S.C.I., 1925, **44**, 253T), although arabinose is probably an intermediate stage in the conversion of galacturonic acid into furfuraldehyde. H. E. F. NOTTON.

Acid constituents of sandarac resin. A. ROLLETT (Monatsh., 1928, **50**, 1—5).—At least three acids are probably present in sandarac resin. Sandaracic acid (*methyl* ester, m. p. 159°) and sandaricinolic acid, m. p. 199° [acetic anhydride isomerisation product (?), m. p. 223°]; are amorphous and labile (Wolf, Diss., Bern, 1906; Henry, Diss., London, 1901). A third acid, $C_{20}H_{30}O_3$, m. p. 263°, for which the old name "callitropic acid" is adopted, is now obtained pure and crystalline. C. HOLLINS.

Betulin. I. K. A. VESTERBERG and R. VESTERBERG. **II.** R. VESTERBERG (Arkiv Kemi, Min., Geol., 1928, **9**, No. 27, 1—17; No. 45, 1—11).—An amplified account of work already published (A., 1923, i, 590; 1927, 882). Dihydrobetulin diformate has m. p. 268°.

Oxidation of santonin. II. Rotatory power of some oxidation products of santonin. S. S. MEDVEDEV and E. N. ALEKSEEVA (Trans. Karpov Inst. Chem., 1926, No. 5, 57—61).—Santoninic, santonic, and santenonic acid have $[\alpha]_D$ −26·5°, −70·0°, and −125·5°, respectively, supporting the view that these acids have similar configurations. Santenonic acid, when heated in a vacuum, loses 2 mols. of water, yielding an unsaturated lactone, santonene, $C_{15}H_{16}O_3$, $[\alpha]_D$ −280·9° (acetyl derivative, $[\alpha]_D$ −1507° in alcohol, −1500° in chloroform, the high value indicating the formula

$$\begin{array}{l} CH_2{\cdot}CMe{:}C{\cdot}CH_2{\cdot}C{\cdot}O{\cdot}CO \\ CO{-}CMe{:}C{\cdot}CH_2{\cdot}C{-}CMeAc). \end{array}$$

CHEMICAL ABSTRACTS.

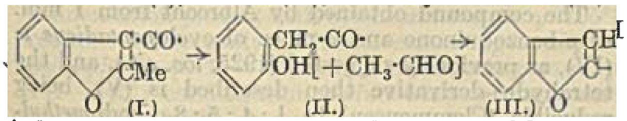
Cacao-red. II. A. HEIDUSCHKA and B. BIENERT (J. pr. Chem., 1928, [ii], **119**, 199—208; cf. B., 1928,

118).—Distillation of cacao-red with large excess of zinc dust in a stream of carbon dioxide gives mainly mesitylene. By acetylation of cacao-red in pyridine with acetyl chloride in chloroform below 0° between 8 and 9 acetyl groups are taken up, and a *compound*, decomp. 210—215°, is formed. Benzoylation gives similar results (*product*. decomp. 219—220°), but with methyl sulphate there are obtained a *heptamethyl ether*, decomp. 213—216°, and a mixture, decomp. 215°, of *tri-* and *penta-methyl ethers*. An impure phenylhydrazone of cacao-red is described, and the constitution further discussed. C. HOLLINS.

Rotenone, the physiologically active constituent of *Derris elliptica*. A. BUTENANDT [and, in part, O. LINSERT and D. BOTSCHWAR] (Annalen, 1928, **464**, 253—277).—Rotenone may be distilled in a high vacuum (b. p. 210—220°/0·5 mm.). Its hydrochloride has m. p. 194°, not 188° as given by Takei (this vol., 765). The presence of only one ethylenic linking in rotenone (Kariyone and co-workers, A., 1923, i, 477; 1924, i, 251) is confirmed, hydrogenation in presence of palladised barium sulphate giving dihydrorotenone, m. p. 214—216°, which with nitrous acid affords a *diketone*, m. p. 317° (decomp.). The carbonyl group in rotenone is also reduced if hydrogenation is carried out in presence of platinum, the resulting *dihydrodeoxyrotenone*, $C_{23}H_{26}O_5$, m. p. 168°, b. p. 220—230°/vac., having, however, little reactivity. Hydrogenation of rotenone in alcoholic ammonia in presence of platinum gives a *substance*, $C_{23}H_{26}O_6$, m. p. 206°.

In weakly acid solution rotenone gives an oxime (m. p. 249°; Takei gives 239°, Kariyone, 245°) and a hydrazone distinct from the iso*oxime*, m. p. 230°, and iso*hydrazone*, m. p. 229°, formed in presence of alkali (iso*phenylhydrazone* has m. p. 203°). The *iso*-derivatives may be formed as a result of scission of an oxide ring by the alkali, ring-closure subsequently occurring in a different position.

Rotenone contains the $\cdot CO\cdot CH_2\cdot$ grouping, since ethyl nitrite and acetic and hydrochloric acids afford a *diketone*, $C_{23}H_{20}O_7$, m. p. 298—300° (decomp.), $[\alpha]_D$ $-3{\cdot}5°$ in chloroform, possibly identical with Takei's rotenonone (A., 1925, i, 761). Treatment of rotenone with zinc dust and alcoholic potassium hydroxide produces *derritol*, $C_{21}H_{22}O_6$, m. p. 161° (a phenolic compound containing CO and 2OMe and giving, when distilled at 220—225°/0·06 mm., *anhydroderritol*, $C_{21}H_{20}O_5$, m. p. 157°, not reconvertible into derritol), together with *rotenol*, $C_{23}H_{24}O_6$, m. p. 115—120°, b. p. 200—210°/vac., which may be the secondary alcohol corresponding with the ketone, rotenone. Rotenol is hydrogenated in presence of platinum, giving *dihydrorotenol*, $C_{23}H_{26}O_6$, m. p. 131°, also obtained by the reduction of dihydrorotenone with zinc dust and alkali. Both rotenol and dihydrorotenol behave towards alkali as lactones. Possibly the annexed scheme represents the inter-relationship of rotenone (I), derritol (II), and anhydroderritol (II):



(I.) (II.) (III.)

Anhydroderritol contains no (detectable) CO group, but contains an ethylenic linking and a hydroxyl group, since it affords an *acetyl* derivative, m. p. 146°, which is hydrogenated in acetic acid in presence of platinum, giving a *dihydro*-derivative, m. p. 131°.

Treatment of rotenone with alkali affords tubaic acid, m. p. 129°, b. p. 130—140°/vac. (cf. Kariyone) (*acetate*, m. p. 133°; *methyl* ester, m. p. 48°, b. p. 120°/vac.), which on reduction gives *dihydrotubaic acid*, m. p. 166°. Since the latter is also obtainable from dihydrorotenone by a similar process, the alkali scission of rotenone involves the carbonyl group and not the ethylenic linking. Tubaic acid contains a hydroxyl group which, although acetylatable, is not methylated by diazomethane, so that the hydroxy-group may have two substituents *ortho* to it. Tubaic acid contains one methoxyl-free benzene ring, and to this benzene ring, in rotenone, at least one oxide ring must be attached (production of phenolic hydroxyl in presence of alkali). Moreover, the two benzene rings in rotenone are separated by a carbon chain. Further, since rotenone with alkali affords a phenol-carboxylic acid, rotenone and dihydrorotenone must contain a β-keto-acid lactone or a β-diketone grouping.

Oxidation of rotenone with chromic anhydride in acetic acid (Takei) gives rotenonone, whilst if the mother-liquor is freed from acid and then treated with diazomethane, a mixture of esters results, from which, by hydrolysis, tubaic acid is obtainable. Rotenonone forms a *dihydrazone*(?), m. p. 242°, and is hydrogenated in acetic acid (platinum) to *perhydrorotenonone*, $C_{23}H_{26}O_6$, m. p. 265—267° (decomp.) (*acetyl* derivative, m. p. 245°). Treatment of rotenonone (cf. Takei) with alcoholic potassium hydroxide at 100° produces a *hydroxy-acid*, $C_{23}H_{22}O_8$, m. p. 250° (*methyl* ester, m. p. 146—147°), possibly formed by a benzilic acid change from the diketone.

Rotenone is readily dehydrogenated to *dehydrorotenone*, m. p. 218°, b. p. 240—250°/vac., this change being effected by potassium permanganate in acetone containing alcoholic potassium hydroxide, by iodine and alcoholic potassium acetate, by potassium ferricyanide in aqueous methyl-alcoholic potassium hydroxide, by perbenzoic acid, or by alcoholic ammonia at 100°. Dehydrorotenone is possibly identical with the "crystalline yellow material" described by other workers as having m. p. ranging from 214° to 233°. It is converted by boiling alcoholic potassium hydroxide into a *hydroxyketo-acid*, $C_{23}H_{24}O_8$, m. p. 152°, which contains a methoxyl group and, when hydrogenated (acetic acid, platinum), passes into an *acid*, $C_{23}H_{26}O_8$, m. p. 168°. It therefore contains an ethylenic linking; it also contains a carbonyl group, for it gives an *oxime*, m. p. 200°.

The constitution of rotenone remains unsettled, but the author regards rotenone as possibly being not very different in general type from bergapten and xanthotoxin. E. E. TURNER.

Catalytic action. XXII. Catalytic action of reduced copper on unsaturated hydrocarbons. S. KOMATSU and M. KURATA (Mem. Coll. Sci. Kyoto, 1928, **11**, [*A*], 164—169; cf. A., 1925, i, 942).—When menthene is passed over reduced copper at 290—300°, menthane and *p*-cymene are produced. *d*-Limonene is converted completely into cymene at 280—300°, but

at 200° menthane, dipentene, and carvomenthene are formed also. Similar treatment of *d*-β-phellandrene at 300° gives cymene (82%) and menthane.

H. BURTON.

Transformation of aliphatic terpenes into monocyclic terpenes. Synthesis of menthol. R. HORIUCHI (Mem. Coll. Sci. Kyoto, 1928, **11**, [*A*], 171—197).—*d*-Citronellal is converted by 5% sulphuric acid at 25—30° into *iso*pulegol (7%), menthoglycol (75%), and an *ether* (3%), $C_{20}H_{36}O_2$, b. p. 191·5°/16 mm., d_4^{20} 0·9341, n_D^{20} 1·476, $[\alpha]_D$ −5° 30′, which is reduced catalytically to a *compound*, $C_{20}H_{38}O_2$, d_4^{20} 0·9155, n_D^{20} 1·4635, $[\alpha]_D$ −2° 52′ (cf. Barbier and Leser, A., 1897, i, 537). When 20% sulphuric acid is used, the corresponding percentage yields are 9, 39, and 21. The action of 50% sulphuric acid on citronellal is to form a *terpene* (I), $C_{10}H_{16}$, d_4^{20} 0·8535, n_D^{20} 1·4875, together with the above ether. Potassium hydrogen sulphate and citronellal react at 140°, yielding *iso*pulegol and di*iso*pulegyl ether, (II), $C_{20}H_{34}O$, b. p. 185°/12·5 mm., d_4^{20} 0·9120, n_D^{20} 1·4835, $[\alpha]_D$ +12° 15′, reduced catalytically to the saturated *ether*, d_4^{20} 0·8932, n_D^{20} 1·4678, $[\alpha]_D$ +6° 1′. Acetic acid, acetic anhydride, or acetic anhydride and sodium acetate convert citronellal at 150° into *iso*pulegyl acetate, although with the last reagents some citronellal mono- and di-enol-acetates are produced also. When *iso*pulegol is treated with 20% sulphuric acid, menthoglycol is formed, but with 50% acid a terpene similar to (I) is obtained. Menthoglycol is unaffected by 20% sulphuric acid, with 50% acid a partial transformation into (I) occurs, and with potassium hydrogen sulphate (I) and (II) are formed.

Citral is converted by 20% sulphuric acid into a *hydrocarbon*, $C_{10}H_{14}$, b. p. 183—186°, d_4^{20} 0·8886, n_D^{20} 1·5092, together with products which are decomposed by heat, whilst with 50% acid *p*-cymene is the main product. Potassium hydrogen sulphate and citral at 140° give *p*-cymene and a *hydrocarbon*, $C_{20}H_{28}$, b. p. 190—194°/14 mm., d_4^{20} 0·9244, n_D^{20} 1·528, whilst acetic acid at 150° yields cymene.

When *iso*pulegol is reduced by hydrogen in presence of platinum-black and glacial acetic acid *l*-menthol is obtained.

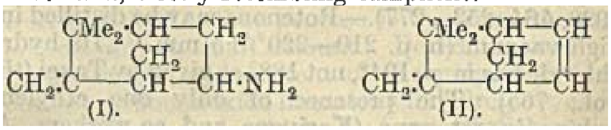
H. BURTON.

Production of inactive menthol (racemate of natural menthol). RHEINISCHE KAMPFER FABR. —See B., 1928, 547.

[Natural occurrence of inactive camphor.] Phenyl- and α-naphthyl-carbamylhydrazones [-semicarbazones] of inactive camphor. V. MORANI (Gazzetta, 1928, **58**, 404—409).—The essential oil of *Salvia officinale* contains *dl*-camphor. The oxime and semicarbazone of this are prepared and have the normal m. p., 176·5—177° and 236—238°; but when the semicarbazone is heated with aniline, dl-*camphor phenylsemicarbazone* is obtained, m. p. 171·5—172·5°. Synthetic *dl*-camphor gives a product of identical m. p., different from that of the *d*-camphor derivative, viz., 153—154° (Borsche, A., 1902, i, 186; Borsche and Merkwitz, A., 1904, i, 945). *dl*-Camphor can thus be characterised; there is also a difference in m. p. between d-*camphor* and dl-*camphor α-naphthylsemicarbazones*, m. p. 172·5° and 179—180° (from either natural or synthetic *dl*-camphor), respectively. These are prepared by heating with α-naphthylamine in quinoline, which is removed by dilute sulphuric acid; *acetophenone α-naphthylsemicarbazone* has m. p. 208°.

E. W. WIGNALL.

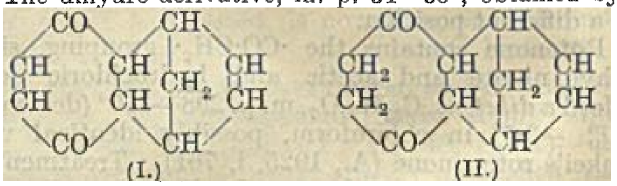
***iso*Camphodiene, a new dicyclic, doubly unsaturated hydrocarbon, and bornylenol, the product of its hydration.** S. NAMETKIN and A. ZABRODIN (Ber., 1928, **61**, [*B*], 1491—1494).—α-Aminocamphene (I) is converted by potassium hydroxide and methyl iodide into the corresponding *quaternary iodide*, transformed by silver oxide into the ammonium base which, when distilled, affords iso*camphodiene* (II), m. p. 41·5—42°, b. p. 149—150°/763 mm., closely resembling camphene.



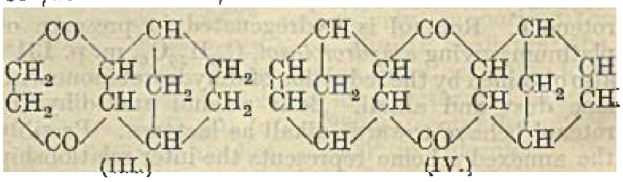
The hydrocarbon is transformed by glacial acetic and sulphuric acids into *bornylenyl acetate*, b. p. 106—107°/18 mm., d^{20} 1·0019, n^{20} 1·4662, hydrolysed by potassium hydroxide to *bornylenol* (III) or (IV), m. p. 60—61°.

H. WREN.

Syntheses in the hydroaromatic series. I. Additions of di-"en"-hydrocarbons. O. DIELS and K. ALDER (Annalen, 1928, **460**, 98—122).—The compound obtained by Albrecht (A., 1906, i, 674) by the combination of a molecule each of cyclo*pentadiene* and *p*-benzoquinone is shown to be (I), as already suggested by Diels, Blom, and Koll (A., 1925, i, 976). The dihydro-derivative, m. p. 34—35°, obtained by

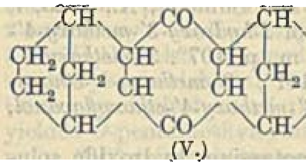
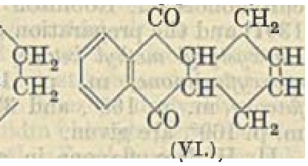


Albrecht, which must be (II), is hydrogenated, in alcohol, in presence of colloidal palladium, to 1 : 4-endo*methylene*-5 : 8-*diketodecahydronaphthalene* (III), m. p. 56—57° [*dioxime*, m. p. 217—218° (decomp.)], and this, by Clemmensen's method, is reducible to 1 : 4-endo*methylenedecahydronaphthalene*, b. p. 84—85°/15 mm. or 91°/22 mm.



The compound obtained by Albrecht from 1 mol. of *p*-benzoquinone and 2 mols. of cyclo*pentadiene* is (IV), as previously suggested (1925, *loc. cit.*), and the tetrahydro-derivative then described is (V), being reducible (Clemmensen) to 1 : 4 : 5 : 8-*di*endo*methylenetetradecahydroanthracene* (V, CO groups replaced

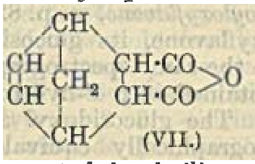
by CH_2), b. p. 157—159°/16 mm. This, when heated with selenium at 360—380°, affords 1 : 4 : 5 : 8-*di-*


(V.)

(VI.)

endo*methylene*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 157°.

Butadiene combines at 100° with α-naphthaquinone to give Δ^2-*tetrahydroanthraquinone* (VI), m. p. 102—103°, converted by chromic anhydride in acetic acid into anthraquinone.

Maleic anhydride and *cyclo*pentadiene combine in cold benzene solution to give cis-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride* (VII), m. p. 164—165°,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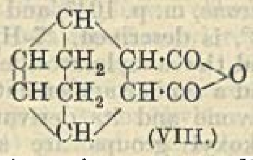
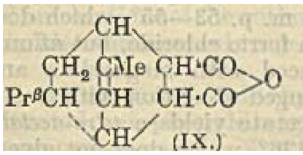

(VIII.)

converted by boiling water into the corresponding *acid*, m. p. 177—179°. Reduction of the *sodium* salt of the latter (hydrogen and palladium) gives cis-3 : 6-endo*methylenehexahydrophthalic* (cis-3 : 6-endo*methylene*cyclo*hexane*-1 : 2-*dicarboxylic*) *acid*, m. p. 160—161° (*anhydride*, m. p. 167—168°). The *trans*-acid, m. p. 194—195°, results when the *cis*-acid is heated with concentrated hydrochloric acid at 180—190°.

Butadiene combines with maleic anhydride to give cis-Δ^4-*tetrahydrophthalic anhydride*, m. p. 103—104°; the corresponding *acid*, m. p. 166°, is catalytically reducible to *cis*-hexahydrophthalic acid.

*cyclo*Hexadiene and maleic anhydride combine in cold benzene solution to give endo*dimethylene*-Δ^4-*tetrahydrophthalic anhydride* (VIII), m. p. 147°, not affected by boiling water. α-Phellandrene and maleic anhydride similarly afford the *anhydride* (IX), m. p. 126—127°.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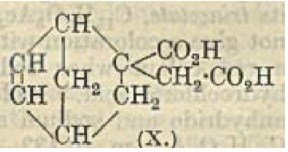

(X.)

Citraconic anhydride and *cyclo*pentadiene afford 1-*methyl*-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride*, m. p. 138°, whilst itaconic anhydride similarly produces the *anhydride*, m. p. 53—54°, of 2 : 5-endo*methylene*-Δ^3-cyclo*hexenylidenesuccinic acid* (X), m. p. 150—151°. Acrylic acid and *cyclo*pentadiene give 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzoic acid*, b. p. 132—134°/22 mm., reducible to the corresponding *hexahydro-acid*, m. p. 62—63°. Similarly, acraldehyde gives 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzaldehyde*, b. p. 70—72°/20 mm. (*semicarbazone*, m. p. 162°; condensation *product* with cylco*hexanone*, m. p. 105°), reduced catalytically to the corresponding *hexahydro-aldehyde*, b. p. 75—76°/25 mm. (*semicarbazone*, m. p. 141—142°; condensation *product* with *cyclo*hexanone, m. p. 101—102°).

Acraldehyde combines with butadiene at 100° to give Δ^3-*tetrahydrobenzaldehyde*, b. p. 51—52°/13 mm. (together with a glassy polymeride) (*semicarbazone*, m. p. 153—154°, reducible to hexahydrobenzaldehyde semicarbazone). E. E. TURNER.

Esters of tetrahydro-α-furfuryl alcohol. J. E. ZANETTI (J. Amer. Chem. Soc., 1928, **50**, 1821—1822).—The following esters, which, unlike the corresponding derivatives of α-furfuryl alcohol (A., 1925, i, 567, 953), are stable towards aerial oxidation, may be prepared by any of the usual methods: *tetrahydro-α-furfuryl acetate*, b. p. 194—195°/753 mm., d_0^{20} 1·061; *propionate*, b. p. 85—87°/3 mm., d_0^{20} 1·044; *butyrate*, b. p. 102—104°/4 mm., d_0^{20} 1·012; *valerate*, b. p. 97—99°/2 mm., d_0^{20} 0·999; *benzoate*, b. p. 138—140°/2 mm., d_0^{20} 1·137, and *furoate*, b. p. 136—138°/3 mm., d_0^{20} 1·194. H. E. F. NOTTON.

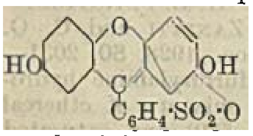
α-Furfuryl chloride (2-chloromethylfuran). α-Furfuryl ethers. I. W. R. KIRNER (J. Amer. Chem. Soc., 1928, **50**, 1955—1961).—*α-Furfuryl chloride*, b. p. 49·1—49·4°/26 mm., d_4^{20} 1·1783, n_D^{20} 1·4941, is prepared in 63% of the theoretical yield from α-furfuryl alcohol and thionyl chloride in pyridine at 0—15° (cf. Darzens, A., 1911, i, 513). It is more stable than the corresponding bromide (cf. Zanetti, A., 1927, 570; Gilman and Vernon, A., 1925, i, 53), remaining nearly colourless for several days after preparation. With alcohols and potassium hydroxide in ether it gives high yields of α-furfuryl ethers, for which the following new or revised data are given: methyl ether, d_4^{20} 1·0163, n_D^{20} 1·4570; ethyl, d_4^{20} 0·9844, n_D^{20} 1·4523; *n*-propyl, d_4^{20} 0·9656, n_D^{20} 1·4523; *n*-butyl, d_4^{20} 0·9516, n_D^{20} 1·4522; *allyl*, b. p. 173·5—174·5°/772 mm., 1·0025, n_D^{20} 1·4718; benzyl, b. p. 108—109°/1 mm., d_4^{20} 1·0865, n_D^{20} 1·5372; α-furfuryl, b. p. 88—89°/1 mm., d_4^{20} 1·1405, n^{20} 1·5088; and cinnamyl, d_4^{20} 1·0802, n_D^{20} 1·5661. H. E. F. NOTTON.

α-Furfurylamines. J. E. ZANETTI and C. O. BECKMANN (J. Amer. Chem. Soc., 1928, **50**, 2031—2033).—Mono-, di-, and tri-α-furfurylamine hydrobromides are formed when a mixture of ethereal α-furfuryl bromide (A., 1927, 570) and saturated alcoholic ammonia is kept for several days at the ordinary temperature. The free amines are distilled to remove α-furfurylamine, the residue is purified through its hydrochloride and fractionally redistilled, giving *di-α-furfurylamine*, b. p. 102—103°/1 mm. [*hydrochloride*, m. p. 186—187° (cf. Williams, this vol., 183); *chloroplatinate*; *chloroaurate*], and *tri-α-furfurylamine*, b. p. 136—138°/1 mm. (*hydrochloride*, m. p. 156—157°; *chloroplatinate*; *chloroaurate*). H. E. F. NOTTON.

Absorption spectra of sulphonefluorescein and some derivatives. R. C. GIBBS and C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, **50**, 1755—1762).—The absorption spectrum of 2 : 4-dihydroxybenzoylbenzene-*o*-sulphonic acid is similar to those of benzaldehyde, acetophenone, and 2 : 4-dihydroxybenzoyl-*o*-benzoic acid (cf. this vol., 526), which indicates a ketonic structure for this acid. The absorption spectra of sulphonefluorescein and dibromosulphonefluorescein in alcohol are unaffected by addition of hydrogen chloride; they differ from that of fluorescein, but correspond closely with that of fluorescein

hydrochloride. Accordingly, the sulphonefluoresceins probably exist in the free state as internal salts of *p*-quinonoid structure. A similar difference is shown to exist between the quinonoid curves for sulphonefluorescein and dibromosulphonefluorescein diacetates and the lactonoid curves for 3 : 6-dichlorosulphonefluoran and fluorescein diacetate. The absorption spectra of resorcinolbenzein, fluorescein, sulphonefluorescein, and dibromosulphonefluorescein in sulphuric acid show a remarkable similarity in type, as do those of the first three in alcoholic potassium hydroxide (4 mols.). The relative positions of corresponding bands are in accordance with the rule that increase in the mol. wt. displaces the band towards the red. With 1 mol. of alcoholic potassium hydroxide the curve for sulphonefluorescein partly resembles that for free fluorescein. In 33% aqueous potassium hydroxide sulphonefluorescein changes in the same way as fluorescein, the initially orange solution becoming purple (opening of the pyrone ring) after several days, and pale pink (irreversible decomposition) after 8 months. Opening of the pyrone ring does not greatly affect the position of the bands, but alters their relative intensity. H. E. F. Notton.

Quinolsulphonephthalein and some derivatives. W. R. Orndorff and C. V. Shapiro (J. Amer. Chem. Soc., 1928, **50**, 1730—1734).—When quinol and *o*-sulphobenzoic anhydride are fused together at 130° for 18—24 hrs., dark red *quinolsulphonephthalein* (20% yield), m. p. above 300°, is formed. The substance described by Sohon (A., 1898, i, 428) was probably an amorphous by-product. Addition of dehydrating agents lowers the yield. Quinolsulphonephthalein forms a bluish-purple *mono-* and bluish-black (?) *tri-ammonium* salt, a bluish-purple *disodium* salt, brown *barium* salt, and yellow *dibenzoate*. Unlike quinolphthalein, it does not yield

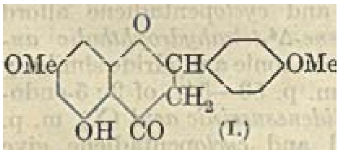


colourless lactonoid derivatives or combine with hydrogen chloride. These facts and the spectrochemical properties of quinolsulphonephthalein indicate that it is an internal salt of *m*-quinonoid structure (annexed formula). H. E. F. Notton.

Spectrographs of compounds of the flavone series. I. Derivatives of flavone, flavonol, and styrylchromonol. II. Synthesis of two new flavone glucosides. Spectrographical influence of sugar combination and acylation. S. Hattori (Acta Phytochim., 1928, **4**, 41—61, 63—75).—I. The spectrographs have been obtained of a number of flavones and related compounds, some of which were synthesised previously (A., 1927, 883). Introduction of a hydroxyl group into the benzopyrone nucleus of flavone has a much greater influence than introduction into the side benzene ring, except with 4′-hydroxyflavone, where the influence of the hydroxyl group is very marked. Methoxyl and ethoxyl groups are optically equivalent to the hydroxyl group, and a methylenedioxy-, two adjacent hydroxyl groups, and adjacent methoxyl and ethoxyl groups are equivalent. The auxochromic influence of hydroxyl is destroyed by acetylation. The introduction of methyl into the benzene ring of flavone (*e.g.*, 6-methylflavone) does not alter the absorption spectrum. The absorption spectra of some styrylchromonols and benzylchromonols (cf. Robinson and Shinoda, A., 1925, i, 1301) and the preparation of *2-hydroxy-3′-methoxy-4′-ethoxystyryl methyl ketone*, m. p. 107°, *3′-methoxy-4′-ethoxyflavanone*, m. p. 141°, *3′-methoxy-4′-ethoxyflavone*, m. p. 168°, and *3′-methoxy-4′-ethoxyflavanol*, m. p. 169°, are given.

II. Hydroxyflavone in potassium hydroxide solution treated with an acetone solution of acetobromoglucose yields *7-tetra-acetylglucosidoxyflavone*, m. p. 183°, which when dissolved in methyl alcohol and dry ammonia gas passed in, yields *7-glucosidoxyflavone*, m. p. 255°, $[\alpha]_D$ −160·42° (in methyl alcohol). 4′-Hydroxyflavone similarly yields *4′-tetra-acetylglucosidoxyflavone*, m. p. 216—217°, and *4′-glucosidoxyflavone*, m. p. 252—254° (lævorotatory but $[\alpha]_D$ not determined). The preparation of *7-propionyloxyflavone*, m. p. 104°, and *7-hexoyloxyflavone*, m. p. 82—83°, is described. 7-Hydroxyflavone, its glucoside, and the acetylglucoside have the same spectrographs and a similar agreement is obtained with 4′-hydroxyflavone and its derivatives. The glucosidoxyl and alkoxyl groups are spectrographically equivalent to the hydroxyl group, whereas an acyl group completely abolishes the effect of the hydroxyl group. It is suggested, therefore, that the position of the glucoside linking in compounds of this type may be determined by acetylating the glucoside and comparing the absorption curve with those of the acetates of the seven isomeric hydroxyflavones. A. Wormall.

Flavanone glucosides. II. Constitution of naringenin. Y. Asahina and M. Inubuse (Ber., 1928, **61**, [*B*], 1514—1516).—Naringin, m. p. 82°, $[\alpha]_D^{19}$ −82·11° in alcohol, is obtained by extracting the dried blossoms of *Citrus decumana* with hot alcohol, evaporation of the solution, and crystallisation of the residue from water. It is converted by boiling, dilute sulphuric acid into naringenin, m. p. 248°. The latter substance is converted by acetic anhydride containing a trace of sulphuric acid into its *triacetate*, $C_{15}H_9O_5Ac_3$, m. p. 53—55°, which does not give a coloration with ferric chloride, but affords a red colour when reduced with magnesium and hydrochloric acid. Prolonged ebullition with acetic anhydride and sodium acetate yields a *tetra-acetate*, $C_{15}H_8O_5Ac_4$, m. p. 133—136°, which does not give a



colour when reduced. Methylation with diazomethane transforms naringenin into its dimethyl ether, m. p. 116—117°, identical with sakuranetin monomethyl ether (I). Naringenin is therefore 5 : 7 : 4′-trihydroxyflavanone. H. Wren.

Synthesis of anthocyanins. IV. Constitution of *O*-benzoylphloroglucinaldehyde. A. Robertson, R. Robinson, and (Miss) A. M. Struthers (J.C.S., 1928, 1455—1459).—The constitution of the product of benzoylation of phloroglucinaldehyde by the Schotten–Baumann method (A., 1927, 974) was shown to be 2-benzoyloxy-4 : 6-dihydroxybenzaldehyde. It could be prepared by application of the

Gattermann synthesis to *O*-benzoylphloroglucinol, and it could be methylated by means of methyl iodide and potassium carbonate in acetone, giving 2-*benzoyloxy*-4 : 6-*dimethoxybenzaldehyde*, m. p. 148° ($+0{\cdot}5H_2O$), also obtained from 2-hydroxy-4 : 6-dimethoxybenzaldehyde. The last compound was obtained by hydrolysis of the benzoyl derivative and yielded *O*-pentamethylcyanidin chloride [*ferrichloride*, m. p. 210° (after softening)]. Further, the benzoylacacetinidin chloride (7-hydroxy-5-benzoyloxy-4′-methoxyflavylium chloride) [*picrate*, m. p. 230—231° (decomp., darkening at 215°)], obtained previously from *O*-benzoylphloroglucinaldehyde and *p*-acetylanisole (A., 1927, 1083), was also prepared from *O*-benzoylphloroglucinol and anisoylacetaldehyde. Moreover, benzoylacacetinidin chloride yields a red anhydro-base, whilst the anhydro-bases from 5-monohydroxylated flavylium salts are blue or violet. 5-*Hydroxy*-4′-*methoxy*-6 : 8-*dimethylflavylium chloride* ($+3H_2O$) was obtained by condensation of *m*-xylorcylaldehyde and *p*-acetylanisole in formic acid, and yielded a colour-base giving a blue solution in benzene. 5-Hydroxy-3 : 3′ : 4′-trimethoxy-6 : 8-dimethylflavylium chloride (A., 1927, 1064) yielded similarly a bluish-violet colour-base. Acetylation and reduction of 5-hydroxy-7-methoxy- and 7-hydroxy-4′-methoxy-flavones yielded violet and red colour-bases, respectively, supporting the general rule.

R. K. Callow.

Pigment of elderberry (*Sambucus nigra*, L.). T. J. Nolan and M. T. Casey (Proc. Roy. Irish Acad., 1928, **38**, 93—99; cf. Karrer and Widmer, A., 1927, 252).—The colouring matter of elderberry skins was extracted by ethyl-alcoholic hydrochloric acid. The *anthocyanin chloride* (*picrate*) so obtained is a brown powder (cf. *loc. cit.*), readily soluble in water (orange-red), methyl alcohol (violet-red), and dilute mineral acids. When hydrolysed with hot hydrochloric acid it yields an *anthocyanidin chloride* (*sulphate*; *picrate*) which is almost insoluble in cold water, is transformed by the action of warm water into an insoluble, violet product, and does not contain methoxyl. Colour reactions of the anthocyanin and anthocyanidin chlorides with several reagents are given.

H. Burton.

Condensation of aldehydes and phenols. III. Nitrated *ms*-phenyldinaphthaxanthens. O. Dischendorfer and E. Nesitka (Monatsh., 1928, **50**, 16—39).—M.-p. curves for mixtures of *p*-nitrobenzaldehyde and β-naphthol show the existence of an intensely yellow molecular *compound* (1 : 1), m. p. 76·5°, which is readily isolated and is stable for 24 hrs. at 0°, but rapidly becomes white at 15°, especially in presence of dilute acid, reverting to the yellow form above 55°. *o*-Nitrobenzaldehyde and β-naphthol give no molecular compound (eutectic, m. p. 31·5°, with 23% of β-naphthol). With 1-bromo-β-naphthol, *p*-nitrobenzaldehyde forms a stable, yellow molecular *compound* (1 : 1), m. p. 61°. *ms*-*p*-Nitrophenyl-β-dinaphthaxanthen (Zenoni, A., 1894, i, 136), m. p. 318°, prepared by warming β-naphthol (2 mols.) and *p*-nitrobenzaldehyde in hydrochloric–acetic acid, is oxidised with manganese dioxide, lead peroxide, or sulphuric acid to the *xanthhydrol*, m. p. 297° [*ferrichloride*, m. p. 290° (decomp.); *methyl ether*, m. p. 263° (decomp.); *ethyl ether*, m. p. 243—244° (decomp.)]. Werner's so-called ether of *ms*-phenyl-β-dinaphthaxanthhydrol is shown to be the xanthhydrol itself. By passing dry hydrogen chloride into a solution of the nitroxanthhydrol in chloroform containing a little acetyl chloride, ms-p-*nitrophenyl*-β-*dinaphthaxanthylium chloride hydrochloride* [*mercurichloride*, m. p. 253° (decomp.)] is obtained as red crystals rapidly becoming reddish-violet by loss of hydrogen chloride. The xanthylium *perbromide* and *perchlorate* (decomp. 299—301°) are described.

ms-*p*-Nitrophenyl-β-dinaphthaxanthen gives by reduction with zinc dust and acetic acid the p-*acetamidophenyl* compound, m. p. 170° (decomp., re-melting at 246°), from which are obtained by hydrolysis ms-p-*acetamidophenyl*-β-*dinaphthaxanthen*, m. p. 253—254° (decomp.), or by oxidation ms-p-*acetamidophenyl*-β-*dinaphthaxanthhydrol*, m. p. 270° [decomp.; *ferrichloride*, m. p. 243—245° (decomp.); *perchlorate*, m. p. 260° (decomp.); *mercurichloride*, m. p. 200—205° (decomp.)]. Nitration of the nitrophenylxanthen or of the xanthhydrol gives a *dinitro*-ms-p-*nitrophenyl*-β-*dinaphthaxanthhydrol*, darkening at 250° and not melted at 380°, in which, since it differs from the dinitrated *ms*-*o*-nitrophenyl compound (Dischendorfer, A., 1927, 1201), the new nitro-groups have not entered the phenyl nucleus. The corresponding *ferrichloride*, m. p. 325° (decomp.), *perbromide*, m. p. 260—270° (decomp.), and *perchlorate*, m. p. 301° (decomp.), are described. Nitration of *ms*-phenyl-β-dinaphthaxanthen or, better, of the xanthhydrol gives *dinitro*-ms-*phenyl*-β-*dinaphthaxanthhydrol*, m. p. 297—298° (decomp.), from which the xanthylium *ferrichloride*, m. p. 260° (decomp.), *perchlorate*, m. p. 288° (decomp.), and *perbromide* are prepared.

2 : 4 : 6-Trinitrobenzaldehyde forms with β-naphthol a molecular *compound* (1 : 1), m. p. 153°. Oxidation of *p*-dimethylaminophenyldi-(2-hydroxy-α-naphthyl)-methane (Hewitt, Turner, and Bradley, J.C.S., 1902, **81**, 1207) with hypobromite gives a *dehydro*-compound, $C_{29}H_{23}O_3N$, m. p. 245°.

C. Hollins.

Preparation and properties of selenophen and certain halogen derivatives of selenophen. H. V. A. Briscoe and J. B. Peel (J.C.S., 1928, 1741—1747).—When acetylene was passed over selenium at 400° (a solid deposit which appeared in the reaction-tube apparently exerted a catalytic effect), naphthalene, other hydrocarbons, and *selenophen*, b. p. 110°/752 mm., f. p. −38°, were obtained. The density, vapour density, and surface tension were determined over ranges of temperature: 1·5307, coefficient of expansion, 3α (15—50°) 0·001045, n_D^{15} 1·568, γ (15°) 36·49 dynes/cm. Vapour density and cryoscopic determinations agreed with the formula C_4H_4Se. The substance was stable and unaffected by oxidising or reducing agents, or by boiling with water, sodium hydroxide solution, or concentrated hydrochloric acid. With sulphuric acid and isatin an "indophenin" reaction was produced. Nitration and sulphonation yielded tarry products. Bromination in carbon disulphide yielded *tetrabromoselenophen*, m. p. 102°. Chlorination gave a small yield of *tetrachloroselenophen*, m. p. 87° (decomp.), which was markedly less stable than the bromo-derivative,

being decomposed by warming with water or on keeping. The "selenophen" described by Foa (A., 1910, i, 187) had entirely different properties.

R. K. CALLOW.

Synthesis of hydroxyamino-acids. S. KANAO and S. INAGAWA (J. Pharm. Soc. Japan, 1928, No. 554, 355—358; cf. *ibid.*, No. 553, 238—252).—α'-(2-Pyrrolidonyl)dialkylcarbinols, which were obtained from ethyl glutamate and organo-magnesium halides, can be readily hydrolysed into γ-amino-δ-hydroxy-δδ-dialkylvaleric acids, thus:

$$CO_2Et\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2Et \longrightarrow \begin{matrix} CH_2\cdot CH_2 \\ CO-NH \end{matrix}\!\!>\!CH\cdot CR_2\cdot OH \longrightarrow$$

$OH\cdot CR_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H$. *l*-α-(2-Pyrrolidonyl)diethylcarbinol, when boiled with 20% barium hydroxide solution, gives *γ-amino-δ-hydroxy-δδ-diethylvaleric acid*, m. p. 143°, $[\alpha]_D$ +3·4° (in water), $[\alpha]_D^{20}$ −14·5° (in 0·3*N*-hydrochloric acid). α-(2-Pyrrolidonyl)dibutylcarbinol is stable to baryta, but when hydrolysed with alcoholic potassium hydroxide, it gives *γ-amino-δ-hydroxy-δδ-dibutylvaleric acid*, m. p. 147°. α-(2-Pyrrolidonyl)diphenylcarbinol similarly gives *γ-amino-δ-hydroxy-δδ-diphenylvaleric acid*, m. p. 204—205°, $[\alpha]_D^{20}$ +48·5° (in 5*N*-acetic acid).

K. ISHIMURA.

Natural rotation of polarised light by optically active bases. I. Influence of solvent on the rotation of *d*-α-pipecoline and its hydrochloride. W. LEITHE (Monatsh., 1928, 50, 40—47).—Solvents may be grouped in three classes according as they have a very small, an appreciable, or a considerable influence on the rotatory power of *d*-α-pipecoline ($[\alpha]_D$ +36·0° in liquid state). In the first class are piperidine, hexane, and ether, and the absence of any appreciable effect is due to small associating power and to small effect of neighbouring solvent molecules on the field surrounding each molecule of solute. The influence is always markedly small in the case of solvents closely related to the solute, *e.g.*, piperidine in the present instance, and generally when racemics are the solvents for corresponding active compounds (cf. Ladenburg, A., 1910, i, 696). In the second class are benzene, ethyl acetate, acetone, pyridine, carbon tetrachloride, and chloroform, which do not (as judged by density determinations) form compounds with *d*-α-pipecoline, but probably have some tendency in that direction or influence the field by their residual affinity. The third class includes ethyl and methyl alcohols, water, and glacial acetic acid; these all produce marked effect also on the density, and their influence is due to formation of compounds.

C. HOLLINS.

Pentadecoyl-lutidine and pentadecoyl-lupetidine, a higher homologue of coniine. S. GOTTFRIED and F. ULZER (Wiss. Mitt. Oesterr. Heilmittelstelle, 1926, No. 1, 1—3, No. 2, 1—4; 1927, No. 3, 1—3, No. 4, 1—4; Chem. Zentr., 1928, i, 1192—1193).—A mixture of monomeric and trimeric palmitaldehyde, b. p. 170—172°/8 mm., 240—241° (corr.)/100 mm., m. p. 57·5—58·5°, was obtained from barium palmitate, formate, and carbonate; treatment with hydroxylamine in 80% alcohol yields palmitaldoxime, m. p. 87·5—88°, and leaves the trimeric aldehyde, m. p. 72·5°. The monomeric aldehyde has m. p. 33·5—34° (confirming Le Sueur's observation). The mixture, m. p. 58°, cannot be depolymerised by simple distillation; it was heated at 150°, 1—2 mg. of zinc chloride were added, and the mixture was rapidly distilled in a vacuum. When heated with ethyl acetate and alcoholic ammonia, the monomeric aldehyde affords *ethyl 4-pentadecoyl-2 : 6-dimethyl-1 : 4-dihydropyridine-3 : 5-carboxylate*, m. p. 50·5—51°. The crude product is treated with nitrogen trioxide, followed by treatment with hydrochloric acid and then sodium hydroxide, yielding *ethyl 4-pentadecoyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate*, b. p. 267—269°/10 mm. (*hydrochloride*, m. p. 88—89°; *chloroplatinate*, m. p. 119—120·5°). The free *acid* has m. p. 61° [*hydrochloride*, m. p. 123—124° (decomp.); *lead*, *silver*, and *copper* salts]. Distillation of the hydrochloride with soda-lime affords pentadecoyl-lutidine [*4-pentadecoyl-2 : 6-dimethylpyridine*], b. p. 240—242°/10 mm. (*hydrochloride*, m. p. 78—79°; *chloroplatinate*, m. p. 107—108°; *picrate*, m. p. 71°), which with sodium and alcohol gives pentadecoyl-lupetidine [*4-pentadecoyl-2 : 6-dimethylpiperidine*], an oil [*hydrochloride*, m. p. 126° (decomp.); *chloroplatinate*, m. p. 145·5—146·5°].

A. A. ELDRIDGE.

Manufacture of alkyl and aralkyl derivatives of diphenolisatins. F. HOFFMANN-LA ROCHE & Co.—See B., 1928, 548.

Decahydroquinolone derivatives. III. Hofmann degradation of decahydroquinoline. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 185—195; cf. this vol., 898).—*trans*-Decahydroquinoline, m. p. 45—45·5°, with methyl iodide and alkali yielded trans-*N-methyldecahydroquinolone methiodide*, m. p. 276° (*methochloroplatinate*, m. p. 255—256°; *methochloroaurate*, m. p. 172—173°), which when treated with silver hydroxide and distilled gave a 76% yield of a *base*, $C_{11}H_{21}N$, b. p. 204—205° (*picrate*, m. p. 101—102°). With platinum- or palladium-black and hydrogen the latter afforded trans-*2-dimethylamino*-n-*propyl*cyclo*hexane*, b. p. 206—208°, n_D^{20} 1·46036, 0·8551 (*picrate*, m. p. 114·5—115·5°; *chloroaurate*, m. p. 146—147°). Further degradation of the latter was effected by conversion into the *methiodide*, m. p. 185° (*methchloroaurate*, m. p. 94—95°), which gave (silver hydroxide; distillation) a *hydrocarbon*, C_9H_{16}, probably Δ^2-n-*propyl*cyclo*hexene*, b. p. 154·5—155·5°, d_4^{19} 0·8162, n_D^{19} 1·4541, and some 2-dimethylamino-*n*-propyl*cyclo*hexane. In a similar manner *cis*-decahydroquinoline, b. p. 205°, was converted into cis-*N-methyldecahydroquinoline methiodide*, m. p. 260° (*methochloroaurate*, m. p. 223°, *methochloroplatinate*, m. p. 254°), and the latter into an unsaturated *base* (60% yield), $C_{11}H_{21}N$, b. p. 213—214° (*picrate*, m. p. 135—138°), which when reduced with platinum-black and hydrogen gave cis-*2-dimethylamino*-n-*propyl*cyclo*hexane*, b. p. 214—216° (*picrate*, m. p. 173°; *chloroaurate*, m. p. 132°; *methiodide*, m. p. 186°; *methochloroaurate*, m. p. 130°).

I. VOGEL.

αγ-Diamino-β-phenylpropane and related compounds of pharmacological interest. J. G. JACKSON and J. KENNER (J.C.S., 1928, 1657—1662).—The pressor influence of β-phenylethylamine and the depressor influence of polymethylenediamines are

approximately balanced in derivatives of $\alpha\gamma$-diamino-β-phenylpropane, but in the 4-aminomethyldihydro*iso*quinoline derivatives obtained by intramolecular condensation the effect of the dihydro*iso*quinoline structure is preponderant, and they cause definite depression of the blood pressure of the cat.

Ethyl β-*phenylglutarate*, b. p. 180—184°/14 mm., was converted into β-*phenylglutardihydrazide*, m. p. 177°. The *diurethane*, m. p. 73—74°, was obtained by the action of amyl nitrite and hydrogen chloride, and converted by boiling hydrobromic acid into $\alpha\gamma$-*di-amino*-β-*phenylpropane hydrobromide*, m. p. 252° (decomp. 272°) [*base*, b. p. 150°/15 mm.; *carbonate*, m. p. 172° (decomp.); *picrate*, m. p. 247° (decomp.)]. The following derivatives were prepared: *diacetyl*-, m. p. 153—154°, *dibenzoyl*-, m. p. 179°, *di*-p-*toluene-sulphonyl*-, m. p. 91°, -*dimethyl*-NN'-*di*-p-*toluene-sulphonyl*-, m. p. 60°, *hydrochloride* of NN'-*dimethyl*-, m. p. 249°. γ-*Amino*-β-*phenylbutyric acid hydro-bromide*, m. p. 114°, obtained as a by-product in the preparation of $\alpha\gamma$-diamino-β-phenylpropane, yielded with alkali 4-*phenyl*-2-*pyrrolidone*, m. p. 60° (*acetyl* derivative; m. p. 63°, *benzoyl* derivative, m. p. 145°). $\alpha\gamma$-Diacetamido-β-phenylpropane, when boiled with phosphoric oxide in toluene, furnished 4-*aminomethyl*-1-*methyl*-3 : 4-*dihydro*isoquinoline, m. p. 182° (*dihydro-chloride*, m. p. 222°). $\alpha\gamma$-Dibenzamido-β-phenylprop-ane yielded the *benzoyl* derivative, m. p. 114°, of 4-*aminomethyl*-1-*phenyl*-3 : 4-*dihydroisoquinoline*, m. p. 169° (*dihydrochloride*, m. p. 291°). Condensation of ethyl *p*-methoxycinnamate with ethyl malonate furnished *ethyl* p-*methoxyphenylpropane*-$\alpha\alpha\gamma$-*tricarb-oxylate*, b. p. 225—240°/12 mm., which, on hydrolysis and heating, yielded β-p-*methoxyphenylglutaric acid*, m. p. 165° (*anhydride*, m. p. 152°; *methyl* ester, m. p. 42°, b. p. 205—210°/20 mm.; *ethyl* ester, b. p. 206—210°/14 mm.; *dihydrazide*, m. p. 190°; *diurethane*, m. p. 99—100°). Hydrolysis by hydrobromic acid yielded $\alpha\gamma$-*diamino*-β-p-*hydroxyphenylpropane dihydro-bromide*, m. p. 316° (*tribenzoyl* derivative of the base, m. p. 206—207°). The following are also described: 3 : 4-*dimethoxybenzylidenemalonic acid*, m. p. 208° (decomp.), *ethyl* β-3 : 4-*dimethoxyphenylglutaric acid*, m. p. 125—130° (+H_2O) (*anhydride*, m. p. 124°; *methyl* ester, m. p. 73°; *ethyl* ester, b. p. 226—229°/15 mm.; *dihydrazide*, m. p. 182°), $\alpha\gamma$-*diamino*-β-3 : 4-*dihydroxyphenylpropane dihydrobromide* (+H_2O), m. p. 294° (anhydrous) (*tetrabenzoyl* derivative, m. p. 217°).

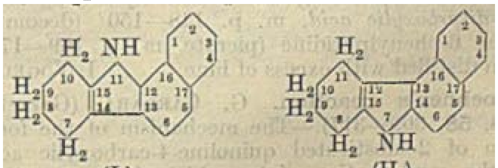
R. K. Callow.

Condensation of hexahydrocarbazole and of tetrahydropentindole with *cyclo*pentanone cyano-hydrin. S. G. P. Plant and (Miss) D. M. L. Rippon (J.C.S., 1928, 1906—1913).—An attempt was made to synthesise ring structures of the type present in 8 : 9-(1' : 2'-*cyclo*hexyl)hexahydrocarbazole (cf. Manjunath, A., 1927, 978) by a method analogous to the preparation of carbazole by fusion of 1-anilino*cyclo*-pentane-1-carboxylic acid with potassium hydroxide (Plant and Facer, A., 1925, i, 1271). The reactions did not, however, go in the expected directions. Treatment of hexahydrocarbazole with *cyclo*pentanone and potassium cyanide in glacial acetic acid yielded 1-*cyano*-1-(9'-*hexahydrocarbazyl*)cyclo*pentane*, m. p. 76°. Aqueous or alcoholic hydrochloric acid decomposed this into *cyclo*pentanone and hexahydrocarb-azole, but cold, concentrated sulphuric acid yielded 1-(9'-*hexahydrocarbazyl*)cyclo*pentane*-1-*carboxylamide*, m. p. 160°, which could not be hydrolysed to the acid by the action of aqueous-alcoholic potassium hydr-oxide or aqueous sulphuric acid. When boiled with hydrochloric acid or heated with solid potassium hydroxide the amide decomposed with the formation of hexahydrocarbazole. Reduction of the nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylic acid by zinc and acetic acid in the presence of *cyclo*hexanone yielded 1-(9'-*tetrahydrocarbazyl*)cyclo*pentane*-1-*carb-oxylic acid*, m. p. 184°, which, when warmed with 60% aqueous sulphuric acid, distilled, or heated with solid potassium hydroxide, yielded tetrahydrocarb-azole and Δ^1-*cyclo*pentene-1-carboxylic acid. It could not be reduced to the corresponding hexahydro-carbazole derivative.

Electrolytic reduction of dihydropentindole (Perkin and Plant, J.C.S., 1923, **123**, 3242) yielded *tetrahydro-pentindole*, b. p. 152°/16 mm., m. p. 21° (8-*acetyl* derivative, m. p. 78°; 8-*benzoyl* derivative, m. p. 86°; *picrate*, m. p. 159°), which was certainly the *cis*-form. Methyl iodide yielded the 8-*methyl* derivative, b. p. 136—137°/15 mm. (*picrate*, m. p. 116°; *meth-iodide*, m. p. 189°). 1-*Cyano*-1-(8'-*tetrahydro-pentindyl*)-cyclo*pentane*, m. p. 51° (*picrate*, m. p. 126°), and 1-(8'-*tetrahydropentindyl*)cyclo*pentane*-1-*carboxyl-amide*, m. p. 130°, were obtained in a similar way to the hexahydrocarbazole derivatives. They decom-posed under similar conditions to yield *cyclo*pentanone and tetrahydropentindole.

R. K. Callow.

Derivatives of 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole and of 8 : 9 : 10 : 11-tetra-hydro-α'β'-naphthacarbazole. S. H. Oakeshott and S. G. P. Plant (J.C.S., 1928, 1840—1847).—7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole ($\Delta^{1(6)}$-tetrahydrobenzo-α-naphthindole; cf. Borsche, Witte, and Bothe, A., 1908, i, 365) (I) (*picrate*, m. p. 172°) yielded αβ-naphthacarbazole on dehydrogenation with sulphur. Acetylation, which could be carried out only by the action of acetyl chloride on the Grignard compound, yielded the 11-*acetyl* derivative, m. p. 125°. The 11-*benzoyl* derivative, m. p. 146—147°, was obtained similarly, and on nitration gave a *trinitro*-11-*benzoyl* derivative, m. p. 255°. This was the only crystalline nitration product isolated from (I) or its derivatives. Electrolytic reduction of (I) yielded the 7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-compound, m. p. 88° (*dinitro*-derivative, m. p. 139—140°; 11-*acetyl* derivative, m. p. 132°, and 11-*benzoyl* deriv-ative, m. p. 148—149°, prepared by usual methods).



(I.) (II.)

8 : 9 : 10 : 11-Tetrahydro-α'β'-naphthacarbazole ($\Delta^{1(6)}$-tetrahydrobenzo-β-naphthindole) (II), m. p. 137° (Borsche, *loc. cit.*, gives 152°), yielded a *picrate*, m. p. 194° (decomp.). Dehydrogenation yielded α'β'-naphthacarbazole, confirming the constitution. Acetic anhydride and a trace of sulphuric acid yielded

first the 7-*acetyl* derivative, m. p. 162° (also prepared by way of the Grignard compound), and then a *C-acetyl-7-acetyl* derivative, m. p. 185°, which was hydrolysed by aqueous potassium hydroxide to a *C-acetyl* derivative, m. p. 213° (*oxime*, m. p. 213—216°). The following derivatives were also prepared: *mononitro-7-acetyl*, m. p. 222°; 7-*benzoyl*, m. p. 139°; *mononitro-7-benzoyl*, m. p. 208—209°. Reduction of (II) by red phosphorus and hydriodic acid yielded the 8 : 9 : 10 : 11 : 12 : 15-*hexahydro*-compound, b. p. 198—202°/10 mm. (*hydrochloride*, m. p. 265°; 7-*acetyl* derivative, m. p. 120°; 7-*benzoyl* derivative, m. p. 131°). From neither (I) nor (II) or their derivatives could any products resulting from the addition of ·OH and ·NO_2 or ·OH and ·OH to the double linking (as in the case of tetrahydrocarbazole) be isolated. The hexahydro-compounds are undoubtedly *cis*-forms.

R. K. CALLOW.

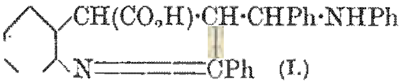
Chlorination of 2-aminopyridine. A. E. TSCHITSCHIBABIN and A. F. EGOROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 683—690).—Chlorination of 2-amino-pyridine with a large excess (97%) of chlorine gave an 80% yield of 3 : 5-dichloro-2-aminopyridine, m. p. 80—81°, and 68% of 5-chloro-2-aminopyridine, m. p. 134—135°. Treatment of the latter with a mixture of concentrated nitric and sulphuric acids at 0° yielded 5-chloro-2-nitroaminopyridine, m. p. 159—160°, which when warmed with concentrated sulphuric acid to 55° and treated with iced water isomerised to 5-chloro-3-nitro-2-aminopyridine, m. p. 195—196°. Diazotisation of the chloropyridine followed by hydrolysis gave 5-chloro-2-hydroxypyridine, m. p. 163°. Under similar conditions, the dichloro-compound yielded the corresponding 3 : 5-dichloro-2-hydroxypyridine. If hydrochloric acid was used in the above diazotisations instead of sulphuric acid, 2 : 5-dichloropyridine and 2 : 3 : 5-trichloropyridine were respectively obtained.

M. ZVEGINTZOV.

New synthesis of pyridine derivatives. E. SPATH and G. BURGER (Monatsh., 1928, **49**, 265—270).—Condensation of benzoylacetaldehyde and ethyl aminocrotonate in ethereal solution gave *ethyl 6-phenyl-2-methylpyridine-3-carboxylate* (I) (*chloroplatinate*, m. p. 201—203°) and none of the expected 4-phenyl-2-methyl derivative. Hydrolysis of (I) with aqueous potassium hydroxide led to *6-phenyl-2-methylpyridine-3-carboxylic acid* (II), m. p. 196° [*hydrochloride*, m. p. 288° (decomp.)], from which 6-phenyl-2-methylpyridine (cf. Scholtz, A., 1895, i, 562) was obtained by distillation with lime. Oxidation of (II) with alkaline permanganate led to *6-phenylpyridine-2 : 3-dicarboxylic acid*, m. p. 148—150° (decomp.), giving 6-phenylpyridine (picrate, m. p. 169—170°) when distilled with excess of lime.

I. VOGEL.

Doebner's reaction. G. CARRARA (Gazzetta, 1928, **58**, 309—317).—The mechanism of the formation of 2-substituted quinoline-4-carboxylic acids by the condensation of benzaldehyde, an aromatic amine, and pyruvic acid (cf. Doebner, A., 1887, 504; 1888, 299) is shown to be probably as follows. The pyruvic acid (1 mol.) and benzylideneaniline (1 mol.) combine, by condensation of aldol type, to form a disubstituted propionylformic acid, $CO_2H·CO·CH_2·CHPh·NHPh$, which in cold alcohol immediately yields the corresponding lactam, 4 : 5-diketo-1 : 2-diphenylpyrrolidine, but, when heated, is transformed into the acid, $CO_2H·CH(OH)·CH:CPh·NHPh$. This acid, with another molecule of benzylideneaniline, undergoes a double, cyclic-aldol condensation, yielding the unstable compound (I), which decomposes into benzylaniline and 2-phenylquinoline-4-carboxylic acid.



(I.)

That the reaction proceeds in this way is shown by the fact that, in definite conditions that render possible the rupture of the lactam ring and hence an equilibrium with the corresponding acid, $CO_2H·CO·CH_2·CHPh·NHPh$, 4 : 5-diketo-1 : 2-diphenylpyrrolidine is capable of reacting with benzylideneaniline to give 2-phenylquinoline-4-carboxylic acid.

T. H. POPE.

Synthesis of acridinic acid [quinoline-2 : 3-dicarboxylic acid]. G. KOLLER and E. STRANG (Monatsh., 1928, **50**, 48—50).—*o*-Aminobenzaldehyde is condensed with ethyl oxalacetate in absolute alcohol in presence of a little sodium hydroxide to give ethyl acridinate, m. p. 54—55°, which is hydrolysed with alkali to the acid.

C. HOLLINS.

Toxicity of an impurity in official cinchophen [2-phenylquinoline-4-carboxylic acid]. R. A. HATCHER (J. Amer. Pharm. Assoc., 1928, **17**, 557—563).—Cinchophen (U.S. Pharmacopœia) is contaminated with 3% of *γ-anilino-γ-phenylbutyric acid*, m. p. 193—194° (brominated *derivative*, m. p. 135°), with which it forms a *compound*, m. p. 183°. The impurity intravenously injected in large doses into cats causes increased reflex excitability, and convulsions (with probably stimulation of the vasomotor centre) and stoppage of the heart.

E. W. WIGNALL.

Carbazole-1-carboxylic acid. E. F. BRISCOE and S. G. P. PLANT (J.C.S., 1928, 1990—1991).—When a mixture of tetrahydrocarbazole-8-carboxylic acid (Collar and Plant, A., 1926, 735), sulphur, and pure quinoline is refluxed for 12 hrs. and the crude acid purified through its methyl ester, carbazole-1-carboxylic acid, identical with the acid obtained by Ciamician and Silber (A., 1882, 1103), is obtained.

J. W. BAKER.

Synthesis of acridone and acridine. G. KOLLER and E. KRAKAUER (Monatsh., 1928, **50**, 51—54).—Distillation of calcium anthranilate in a vacuum at 340° gives an *anhydro-bis-2 : 2'-diaminobenzophenone*, $NH_2·C_6H_4·CO·C_6H_4·N:C(C_6H_4·NH_2)_2$, m. p. 233°, which is hydrolysed by concentrated hydrochloric acid at 170° to acridone, or may be converted into acridine by distillation with zinc dust.

C. HOLLINS.

Derivatives of barbituric acid. A. W. DOX and E. G. JONES (J. Amer. Chem. Soc., 1928, **50**, 2033—2036).—The yield of "*tetrahydro-α-furanmethyl bromide*" [? tetrahydro-α-furfuryl bromide], b. p. 168—170°/744 mm., from tetrahydro-α-furfuryl alcohol by the usual methods is poor. With ethyl sodioethylmalonate the bromide forms *ethyl tetrahydrofuranmethylethylmalonate*, b. p. 155—157°/12 mm., which condenses with carbamide in presence of sodium ethoxide to *tetrahydrofuranmethylethylbarbituric acid*,

m. p. 190°. *n*-Amyl alcohol is converted by standard methods into *ethyl* n-*amylmalonate*, b. p. 134—136°/14 mm.; n-*amylmalonamide*, m. p. 206°; *chloro*-n-*amylmalonamide*, m. p. 134—135°, which is some 400 times as sweet as sucrose (cf. A., 1924, i, 716); n-*amylbarbituric acid*, m. p. 215°; *ethyl di*-n-*amylmalonate*, b. p. 158—161°/11 mm.; *di*-n-*amylbarbituric acid*, m. p. 118°; *ethyl ethyl*-n-*amylmalonate*, b. p. 139—141°/14 mm., and *ethyl*-n-*amylbarbituric acid*, m. p. 135°, which has a powerful hypnotic action.
H. E. F. Notton.

Action of carbonyl chloride on polypeptide derivatives of *p*-aminobenzoic acid. Formation of 1 : 3-substituted hydantoins. C. Tropp (Ber., 1928, **61**, [*B*], 1431—1439).—Carbamide derivatives do not appear to be formed when carbonyl chloride acts on peptide compounds in which a hydrogen atom of the amino-group is replaced by the phenyl radical. The latter group renders the residual hydrogen of the amino-complex so mobile that substituted hydantoins are readily produced under the influence of carbonyl chloride. This ring closure does not, however, occur when a carbonyl group attached to a molecule containing other negative substituents is vicinal to the amino-group.

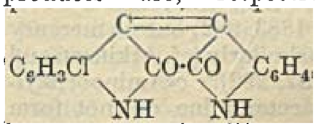
Carbonyldiglycylglycine is readily prepared in 55% yield by the action of carbonyl chloride in toluene on a solution of glycine anhydride in aqueous sodium hydroxide. *p*-Aminobenzoic acid in alkaline solution is transformed by chloroacetyl chloride in ether into p-*chloroacetamidobenzoic acid*, m. p. 257—258°, which with concentrated ammonia affords p-*aminoacetamidobenzoic acid* ($+H_2O$), m. p. 229°, with a small proportion of *imino*-p-*diacetamidobenzoic acid*, $NH(CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H)_2$, decomp. above 250°; the latter compound is the main product when a stiff paste of *p*-chloroacetamidobenzoic acid and water is mixed with concentrated ammonia. Treatment of *p*-aminoacetamidobenzoic acid dissolved in sodium hydroxide with carbonyl chloride in toluene yields 3-p-*carboxyphenylhydantoin*, m. p. 258—260° (decomp.). Under similar conditions, imino-*p*-diacetamidobenzoic acid affords 3-p-*carboxyphenyl*-1-*hydantoylacet*-p′-*carboxyphenylamide*,

$(C_6H_4{\cdot}CO_2H){\cdot}CO$
O——————CH_2 $>N{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, decomp. above 270°. A faintly alkaline solution of *p*-chloroacetamidobenzoic acid in sodium hydroxide is converted by *iso*amylamine into p-iso*amylaminoacetamidobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}CHMe_2$, m. p. 285°. Under similar conditions, diethylamine causes complete fission of the side-chain of p-*chloroacetylglycylamidobenzoic acid* (from chloroacetyl chloride and *p*-aminoacetamidobenzoic acid) with production of *p*-aminobenzoic acid. When di*iso*amylamine is gently warmed with *p*-chloroacetylglycylamidobenzoic acid in the presence of pyridine, p-*di*iso*amylaminoacetylglycylamidobenzoic acid*, m. p. 253°, results; if the acid is heated with pyridine in the absence of the base, p-*carboxyphenylamidoglycylacetylpyridinium chloride*, m. p. 258°, is produced. 3-*Carboxyphenyl*-1-isoamyl-*hydantoin*, m. p. 189°, is described. p-*Diglycylamidobenzoic acid*, m. p. 233°, from *p*-chloroacetylglycylamidobenzoic acid and ammonia, is converted by phenylcarbimide into p-N-*phenylureidoacetylglycylamidobenzoic acid*,
$CO_2H{\cdot}C_6H_4{\cdot}[NH{\cdot}CO{\cdot}CH_2]_2{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. 242°.
H. Wren.

Anhydrides of amino-acids. I. Molecular compounds of diketopiperazine with copper halides. T. Asahina and T. Dono (Bull. Chem. Soc. Japan, 1928, **3**, 151—156).—Interaction of 2 : 5-diketopiperazine and cupric chloride in aqueous solution gives (80% yield) the *compound*, $C_4H_6O_2N_2,CuCl_2,2H_2O$, decomposed by hot water and alcohol, partly by the cold solvents, and when heated at 110°. Cupric bromide gives the similar *compound*, $C_4H_6O_2N_2,CuBr_2,2H_2O$ (cf. Curtius and Gobel, A., 1888, 576). Spectroscopic determinations suggest that these compounds exist to some extent in solution when cupric salt is in excess.
R. Brightman.

Dipiperidyls. C. R. Smith (J. Amer. Chem. Soc., 1928, **50**, 1936—1938).—The isomeric dipiperidyls (cf. Ahrens, A., 1891, 1093; Blau, A., 1892, 1365) are conveniently obtained by hydrogenating the corresponding dipyridyls, using a platinum oxide–platinum-black catalyst in aqueous or alcoholic hydrochloric acid. Products of partial reduction were not formed. The following are described: 4 : 4′-dipiperidyl, m. p. 172° (dinitroso-derivative, m. p. 149°; *di-phenylthiourethane*, m. p. 225°); 2 : 2′-*dipiperidyl di-phenylthiourethane*, m. p. 178°; 2 : 3′-dipiperidyl picrate, m. p. 224°; 3 : 3′-*dipiperidyl*, m. p. 105°, b. p. 282° (*dinitroso*-derivative, m. p. 102°; *di-phenylthiourethane*, m. p. 200°), and 3 : 4′-*dipiperidyl*, m. p. 159°, b. p. 270° (*dinitroso*-derivative, m. p. 149°; *di-phenylthiourethane*, m. p. 202°; *picrate*, darkening from 200°; *chloroplatinate*, darkening from 235°).
H. E. F. Notton.

Chloro*iso*indigotins. A. Wahl and G. Fericean (Ann. Chim., 1928, [x], **9**, 277—315).—The condensation products of 5- and 7-chloroisatin with oxindole and dioxindole, various chlorinated disulphoisatides, and products derived from them have been investigated. 7-Chloro- and 5-chloroisatin [prepared by a slight modification of Sandmeyer's method (A., 1919, i, 318) by substituting hydroxylaminesulphonic acid for the free base] by heating with a slight excess of dioxindole in alcohol with a few drops of piperidine of a water-bath yield, respectively, 7-, m. p. 238°, and 5-, m. p. 256°, -*chloroisatide*. Similarly by condensation with oxindole they yield 7-, m. p. 182°, and 5-, m. p. 207°, -*chloroisatan* (cf. Wahl and Hansen, A., 1924, i, 322). When the latter condensation is effected in acetic acid–hydrochloric acid solution the products are, respectively, 7-*chloro*iso*indigotin*,

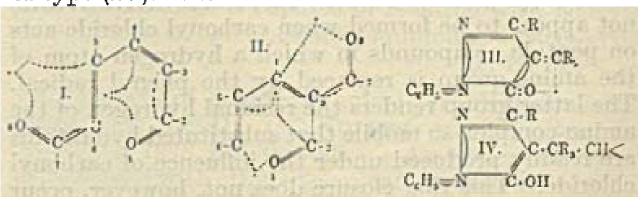


which is reduced to the *leuco*-compound with zinc and acetic acid, and 5-*chloro*iso*indigotin* (*leuco*-compound, m. p. 251). Sulphonation of these chloro*iso*indigotins with concentrated sulphuric acid at 100° and subsequent addition of sodium chloride yields *sodium 7-chloro*-, $+H_2O$, and *sodium 5-chloro*- $+4H_2O$ (*potassium* $+3H_2O$, and *barium* $+4H_2O$ salts) -iso*indigotin*-

sulphonates. Disulphoisatide is obtained crystalline in a 90% yield by passing dry hydrogen sulphide into a suspension of isatin in anhydrous methyl alcohol at the ordinary temperature. By analysis, mol. wt. determination of the product, and a determination of the sulphur liberated in the reaction, the formula assigned to this compound by Wahl and Hansen (*loc. cit*), is confirmed and Sander's view (A., 1925, i, 977) that it is 3-thio-oxindole is excluded, since the proportion of sulphur liberated in the latter case would be double that which is actually obtained. By boiling with pyridine it yields oxindole (*benzylidene* derivative, m. p. 174°). By similar methods of preparation the yields of 7 : 7′- and 5 : 5′-dimethyl-disulphoisatides (Wahl and Faivret, A., 1925, i, 588; 1926, 79) are increased to 80% and 81%, respectively, and 7 : 7′-*dichloro-* and 5 : 5′-*dichloro-* (yield 78%) *-disulphoisatides* are prepared. The action of boiling pyridine on these compounds yields, respectively, 7 : 7′-*dichloro*iso*indigotin* (*leuco*-compound by reduction) together with 7-*chloro-oxindole*, m. p. 215° (*benzylidene* derivative, m. p. 185°); and 5 : 5′-*dichloro*iso*indigotin* (*leuco*-compound) together with 5-*chloro-oxindole*, m. p. 192—195° (*benzylidene* derivative, m. p. 204—205°). By warming the 5 : 5′-dichloro-derivative with concentrated sulphuric acid the disulphonic acid is obtained from which the *disodium* $+6H_2O$, *dipotassium* $+4H_2O$, and *barium* salts are obtained. J. W. BAKER.

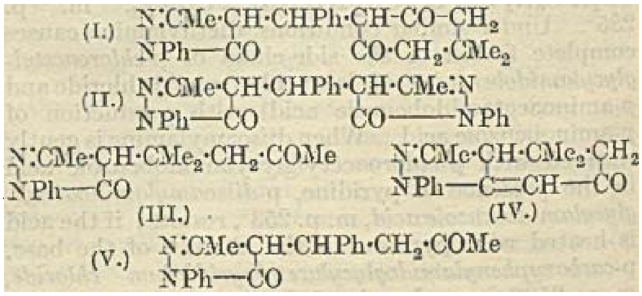
Relationship between atomic grouping and specific affinity. VII. Salt-formation capacity of glyoxaline derivatives. F. FEIGL and H. GLEICH (Monatsh., 1928, **49**, 385—400).—Benziminazole in alcoholic solution forms the following metallic *derivatives* when treated with ammoniacal solutions of the metallic derivatives; silver salt (cf. Bamberger and Lorenzen, A., 1893, i, 433): $C_7H_5N_2HgCl$; $4C_{14}H_{10}N_4Cu,NH_3,H_2O$; $C_{14}H_{10}N_4Cd$; $C_{14}H_{10}N_4Co$, and $4C_{14}H_{10}N_4Zn,NH_3,H_2O$. Methyl- and phenyl-benziminazole form only the analogous *silver* and *mercury* derivatives. 1-Phenylbenziminazole, 1-*benzylbenziminazole*, m. p. 105° [from benzyl-*o*-phenylenediamine (cf. Kehrmann, A., 1896, i, 508), anhydrous formic acid, and ammonia], and 1 : 6-dimethylbenziminazole do not form metallic derivatives. 2-*Phenoxymethylbenziminazole* (prepared from *o*-phenylenediamine and phenoxyacetic acid), m. p. 162°, 2-*ethoxymethylbenziminazole*, m. p. 152°, and 2-*methoxymethylbenziminazole*, m. p. 137°, give *silver* and *mercury* derivatives. *o*-Phenylenecarbamide and 2-chlorobenziminazole give no metallic derivatives, whilst anhydro-oxanilide yields *mercury* and *silver* derivatives only. Amarine forms a silver salt (cf. Claus and Elbs, A., 1883, 982) but no mercury derivative; lophine behaves similarly (cf. Atkinson and Gossmann, Annalen, 1856, **97**, 292). *o*-Aminobenzylaniline and *NN′*-diphenylacetamidine do not form metallic derivatives, whilst 6-methylbenziminazole and 6-*chloro-o-methylbenziminazole*, m. p. 191°, behave similarly to benziminazole. αβ-Naphthiminazole forms only *mercury* and *silver* derivatives. Glyoxaline yields metallic derivatives of silver (cf. Wyss, A., 1878, 25), *zinc*, and cobalt, but not of copper and cadmium. I. VOGEL.

Conjugated systems. Factors disturbing valency fields. III. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1927, **3**, 353—372; Chem. Zentr., 1928, i, 694; cf. this vol., 422).—A discussion of the author's results in the light of Stark's electron theory. New conjugated systems are considered: (I) in which 1 : 4- or 5 : 8-addition takes place; (II) in which 4 : 8-addition takes place. It has already been shown that αβ-unsaturated amides, unlike ketones and esters, do not add ethyl acetate or malonate. The disturbing action of the amino-group is greater than that of the alkoxyl group; the effect is annulled by suitable substitution in the amino-group. This is the case with compounds of type (III), which yield compounds of type (IV). Here the co-ordinative valencies of the



amino-group are concentrated on the phenyl group and the other nitrogen atom, an effect which is increased by cyclisation, so that conjugation of the carbonyl group with the ethylene group is no longer prevented. The difference between ethyl benzylidenemalonate and benzylideneacetate is also due to the disturbing influence of the phenoxy-group. It is concluded that (1) the additive character of the various carbo-indogenides is diminished as the disturbing effect of the chromogen attached to the phenyl nucleus increases, and (2) for the same conjugated system and disturbing factors the change in additive properties is influenced by the nature and structure of the addenda. A. A. ELDRIDGE.

Conjugated systems. Factors disturbing valency fields. IV. Action of substances with active methylene groups on alkylidene(or arylidene)phenylmethylpyrazolones. M. V. IONESCU (Bul. Soc. Stiinte Cluj, 1927, **3**, 381—393; Chem. Zentr., 1928, i, 694—695; cf. preceding abstract).—Benzylidene-1-phenyl-3-methylpyrazolone, m. p. 106°, with dimethyldihydroresorcinol in boiling absolute alcohol in presence of piperidine yields *benzylidene-1-phenyl-3-methylpyrazolonedimethyldihydroresorcinol*, (I), m. p. 220°; with indandione it yields benzylidene-bis-di-indone, m. p. 256°. Hence in the formation of known alkylidene(or arylidene)bis-1-phenyl-3-methylpyrazolones, *e.g.*, *benzylidenebis-1-phenyl-3-methyl-*



pyrazolone (II), m. p. 164—167°, from 1-phenyl-3-methylpyrazolone and aldehydes or ketones, the

compound, *e.g.*, benzylidene-1-phenyl-3-methylpyrazolone, is first formed. Also in certain cases the indogenide intermediate product is formed, and 1-phenyl-3-methylpyrazolone should add on to other substances with unsymmetrical heterogeneous conjugated systems. With mesityl oxide and styryl methyl ketone, it forms the *compounds* $C_{16}H_{20}O_2N_2$ (III), m. p. 142—144°, with some (IV), m. p. 117°, and $C_{20}H_{20}O_2N_2$ (V), m. p. 161—162°.

A. A. ELDRIDGE.

Behaviour of pyrazine compounds. I. C. GASTALDI and E. PRINCIVALLE (Gazzetta, 1928, **58**, 412—416).—The Rung–Behrend–Pinner reaction for glyoxalines is also given by pyrazines; the compound described by Pinner (A., 1905, i, 476) as 2-benzoyl-5-phenylglyoxaline, and by Gastaldi (A., 1921, i, 605) as 6-hydroxy-2 : 5-diphenylpyrazine, by methylation yields 2 : 5-diphenyl-1-methyl-6-keto-1 : 6-dihydropyrazine-4-methiodide, which when treated with potassium hydroxide loses methylamine. Similarly, 6-hydroxy-2 : 5-dimethylpyrazine (Gastaldi, *loc. cit.*) yields 1 : 2 : 5-*trimethyl*-6-*keto*-1 : 6-*dihydropyrazine*-4-*methiodide*, which also loses methylamine.

3 : 6-Dicyano-2 : 5-dimethylpyrazine (*loc. cit.*) is hydrolysed by sulphuric acid to the *diamide*, m. p. 290°, of 2 : 5-dimethylpyrazine-3 : 6-dicarboxylic acid, m. p. 194—195° (Wleugel, A., 1882, 949, gives 200°, but the observed value, 85—86°, for the m. p. of the ethyl ester).

E. W. WIGNALL.

Steric hindrance in reactions of substituted quinoxalines. G. M. BENNETT and G. H. WILLIS (J.C.S., 1928, 1960—1975).—A comparative study was made of the condensation of 2- and 2 : 3-substituted methyl and benzyl derivatives of quinoxaline with aromatic aldehydes and their reaction with bromine. The reactivity of 2 : 3-dimethylquinoxaline is of the same order as that of 2-methylquinoline, and is attributed to general and alternating polar influences. The polarisation may conceivably lead to tautomeric change, and it is pointed out that the possibility of such a change is a general accompaniment of reactivity of methyl groups. The usual products of condensation of 2 : 3-dimethylquinoxaline with aldehydes were distyrylquinoxalines, but monostyrylquinoxalines were isolated as well from *p*-methoxy- and *m*-nitro-benzaldehydes, and *o*-methoxybenzaldehyde yielded solely the monostyryl derivative. Nitrobenzaldehydes, particularly the *p*- and 2 : 4-derivatives, reacted readily, but methoxybenzaldehydes more slowly. It is suggested that these facts may be explained as an effect of steric hindrance due to the configuration of the monostyrylquinoxaline which is determined by the polarity of the groups present. Thus sufficient attraction exists between the nitrogen atoms of quinoxaline and nitro-groups for an additive *compound*, $C_{10}H_{10}N_2,2C_6H_3(NO_2)_2CHO$, m. p. 96—97°, to be formed from 2 : 3-dimethylquinoxaline and 2 : 4-dinitrobenzaldehyde. In a mono-*o*-nitrostyryl derivative the attraction between the quinoxaline nitrogen atom and the nitro-group will impose a configuration which leaves the second quinoxaline methyl group free, but the repulsion in the case of a mono-*o*-methoxystyryl derivative will impose a spatial arrangement which hinders reaction of the second methyl group. That pure steric hindrance is not the only factor is shown by the ready formation of a distyryl derivative with *o*-iodobenzaldehyde. The 6-methyl group in 2 : 3 : 6-trimethylquinoxaline is not reactive, but increases the reactivity of the 2- and 3-groups. None of the 2-phenyl-3-benzylquinoxalines prepared showed any reactivity of the methylene of the benzyl group, owing to the steric hindrance of the two phenyl groups.

2-*Benzylquinoxaline*, an oil (*picrate*, m. p. 117°), was prepared from benzylglyoxal and *o*-phenylenediamine. *Phenyl* β-*methoxy*-p-*chlorostyryl ketone*, b. p. 238°/16 mm., m. p. 45°, prepared from ω-methoxyacetophenone by condensation with *p*-chlorobenzaldehyde, was converted into *phenyl* p-*chlorobenzyl diketone*, m. p. 85°, by the action of hydrobromic acid, and 2-p-*chlorobenzyl*-3-*phenylquinoxaline*, m. p. 142°, was prepared by condensation with *o*-phenylenediamine. Hydrolysis of *phenyl* β : 3-*dimethoxystyryl ketone*, b. p. 245°/18 mm., yielded a *substance*, m. p. 175—180° (decomp.), which did not react with *o*-phenylenediamine.

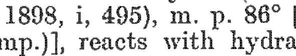
Condensation with aldehydes was generally carried out in boiling acetic anhydride. The yield in each case was determined. The following substituted *quinoxalines* were prepared: 2-(2 : 4-*dinitrostyryl*)-, m. p. 219—220° (decomp.); 2-o-*nitrostyryl*-, m. p. 156°; 2-m-*nitrostyryl*-, m. p. 199·5°; 2-p-*nitrostyryl*-, m. p. 200°; 2 : 3-*distyryl*-, m. p. 190·5° (*tetrabromide*, m. p. 190°); 2-*methylenedioxystyryl*-3-*methyl*-, m. p. 150°; 2 : 3-*di*(*methylenedioxystyryl*)-, m. p. 208°; 2-m-*nitrostyryl*-3-*methyl*-, m. p. 184°; 2 : 3-*di*-(m-*nitrostyryl*)-, m. p. 237°; 2-p-*methoxystyryl*-3-*methyl*-, m. p. 122·5°; 2 : 3-*di*-(p-*methoxystyryl*)-, m. p. 163°; 2 : 3-*di*-(m-*methoxystyryl*)-, m. p. 126°; 2-o-*methoxystyryl*-3-*methyl*-, m. p. 112°; 2 : 3-*di*-(3 : 4-*dimethoxystyryl*)-, m. p. 208°; 2 : 3-*di*-(β-*furylvinyl*)-, m. p. 169°; 2 : 3-*di*-(o-*nitrostyryl*)-, m. p. 194·5°; 2 : 3-*di*-(p-*nitrostyryl*)-, m. p. 288°; 2-(2 : 4-*dinitrostyryl*)-3-*methyl*-, m. p. 224—225° (decomp.); 2 : 3-*di*-(2 : 4-*dinitrostyryl*)-, m. p. 295—297° (decomp.); 2-(2 : 4 : 6-*trinitrostyryl*)-3-*methyl*-, m. p. 250—251° (decomp.); 2 : 3-*di*-(o-*chlorostyryl*)-, m. p. 189·5°; 2 : 3-*di*-(m-*chlorostyryl*)-, m. p. 149°; 2 : 3-*di*-(p-*chlorostyryl*)-, m. p. 218°; 2 : 3-*di*(o-*iodostyryl*)-, m. p. 179°; 2 : 3-*distyryl*-6-*methyl*-, m. p. 193°; 2 : 3-*di*-(*methylenedioxystyryl*)-6-*methyl*-, m. p. 168°; 2-p-*methoxystyryl*-3 : 6-*dimethyl*-, m. p. 116°; 2 : 3-*di*-(p-*methoxystyryl*)-6-*methyl*-, m. p. 136°; 2 : 3-*di*-(3 : 4-*dimethoxystyryl*)-6-*methyl*-, m. p. 205°; 2-m-*nitrostyryl*-3 : 6-*dimethyl*-, m. p. 165°; 2 : 3-*di*-(m-*nitrostyryl*)-6-*methyl*-, m. p. 244·5°; 2 : 3-*di*-(2 : 4-*dinitrostyryl*)-6-*methyl*-, m. p. 251—255° (decomp.); 2-*styryl*-3-*phenyl*-, m. p. 149°; 2-p-*nitrostyryl*-3-*phenyl*-, m. p. 233°; 2-(2 : 4-*dinitrostyryl*)-3-*phenyl*-, m. p. 215°; 2-(β-*phenyl*-p-*nitrostyryl*)-, m. p. 149°; 2-(β-*phenyl*-2 : 4-*dinitrostyryl*)-, m. p. 261—262°. Quinoxalino*cyclo*pentane yielded a *dibenzylidene* derivative, m. p. 213°, and a *di*-p-*nitrobenzylidene* derivative, decomp. 268—270°. By the condensation of quinoline bases with 2 : 4-dinitrobenzaldehyde, 2-(2 : 4-*dinitrostyryl*)*quinoline*, m. p. 200°, and the 8-*methyl*, m. p. 198°, and 3-*methyl* derivative, m. p. 257°, were obtained. 2 : 3-Dimethylquinoline and benzaldehyde yielded 2-*styryl*-3-*methylquinoline*, m. p. 102°. Condensation of 2 : 3-dimethyl-

quinoxaline with ethyl oxalate, preferably with potassium ethoxide, yielded *ethyl* 2-*methylquinoxaline*-3-*pyruvate*, m. p. 129° (p-*nitrophenylhydrazone*, m. p. 189°).

Bromination of the quinoxalines was carried out at 100° in acetic acid with bromine and acetic acid. 2-Methylquinoxaline yielded 2-ω-tribromomethylquinoxaline, m. p. 109°. In other cases steric hindrance supervened, 2 : 3-dimethylquinoxaline yielding only 2 : 3-*di*-(ω-*dibromomethyl*)*quinoxaline*, m. p. 228°, the symmetrical structure of which was shown by its hydrolysis by silver acetate to an unstable dialdehyde. 3-*Phenyl*-2-ω-*dibromomethylquinoxaline*, m. p. 148°, was similarly prepared. Phenylbenzyl- and phenyl-*p*-chlorobenzyl-quinoxalines yielded acetoxy-compounds, in which the reactive bromine of the intermediate monobromo-compound had reacted with the sodium acetate. 3-*Phenyl*-2-*phenylacetoxymethylquinoxaline*, m. p. 126°, and 3-*phenyl*-2-p-*chlorophenylacetoxymethylquinoxaline*, m. p. 119°, were obtained. 3-Phenyl-2-*p*-methoxybenzylquinoxaline did not react.

2 : 3-*Dimethylquinoxaline monomethiodide*, m. p. 192°, was prepared by heating the base with large excess of methyl iodide. It condensed with benzaldehyde or *p*-nitrosodimethylaniline to give black, insoluble products. 2 : 3-Dimethylquinoxaline did not react with amyl nitrite, Michler's hydrol, *p*-nitrosodimethylaniline, or a 2 : 4-dinitrobenzenediazonium salt. R. K. CALLOW.

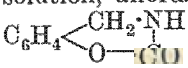
1 : 2 : 3-Triazoles. I. Reaction of aryl azides with hot alcoholic sodium alkoxides. A. BERTHO and F. HOLDER (J. pr. Chem., 1928, [ii], **119**, 173—188; cf. Bertho, A., 1925, i, 840).—The formation of 1-aryl-1 : 2 : 3-triazoles by heating aryl azides with an alcohol and the corresponding sodium alkoxide proceeds according to the equations (i) $CH_2R{\cdot}CH_2{\cdot}ONa = CHR{:}CH{\cdot}ONa + H_2$; (ii) $ArN_3 + H_2 = ArNH_2 + N_2$; (iii) $ArN_3 + CHR{:}CH{\cdot}ONa = (1)Ar{\cdot}C_2HN_3{\cdot}R(4) + NaOH$. It therefore depends on the ease of removal of hydrogen from the alkoxide, and hence ultimately on the "valency-need" of the group R, which occupies the 4-position in the resulting triazole. The yields of 4-substituted 1-*p*-xylyltriazoles, where R=Et, Pr^{β}, Me, Ph, are, respectively, 3, 2·5, 10, and 26%, and these figures are in accordance with the valency-need of these groups (Meerwein, A., 1920, i, 2). *p*-Xylyl azide, b. p. 90°/15 mm., reacts with sodium propoxide at 108° to give 1-p-*xylyl*-4-*methyl*-1 : 2 : 3-*triazole*, m. p. 57·5°, b. p. 165—170°; with sodium *iso*amyloxide at 130°, to give 1-p-*xylyl*-4-iso*propyl*-1 : 2 : 3-*triazole*, m. p. 118°; with sodium β-phenylethoxide at 120° to give 4-*phenyl*-1-p-*xylyl*-1 : 2 : 3-*triazole*, m. p. 129°. Sodium ethoxide and *n*-butoxide yield no isolable triazoles, and by prolonged action only *p*-xylenol. The constitution of the by-product from phenyl azide and any sodium alkoxide (*loc. cit.*), m. p. 282° (decomp.) when pure, mol. wt. 122—129 (not reconcilable with analysis), remains unknown; no corresponding substance is obtained with *p*-xylyl azide. C. HOLLINS.

1 : 2 : 3-Triazoles. II. Behaviour of 1-*p*-xylyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid in the Curtius reaction. A. BERTHO and F. HOLDER (J. pr. Chem., 1928, [ii], **119**, 189—198).—Methyl 1-*p*-xylyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate (Michael, Lühn, and Higbee, A., 1898, i, 495), m. p. 86° [free acid, m. p. 151° (decomp.)], reacts with hydrazine hydrate in alcohol to give a normal *dihydrazide*, m. p. 133·5° (*acetone* compound, m. p. 207°; *dibenzylidene* derivative, m. p. 186°), together with a cyclic *monohydrazide*, m. p. 286° (*silver* salt described). The dihydrazide is converted by nitrous acid into 5-*carbimido*-1-p-*xylyl*-1 : 2 : 3-*triazole*-4-*carboxylic azide*, decomp. 150°, which when boiled with absolute methyl alcohol yields, instead of the expected 4 : 5-diamine, 4 : 4′-*diazidocarbonyl*-1 : 1′-*di*-p-*xylyl*-1 : 2 : 3-*triazolyl*-5 : 5′-*carbamide*,  CO, m. p. 164°. Boiling with absolute ethyl alcohol gives only resinous products. C. HOLLINS.

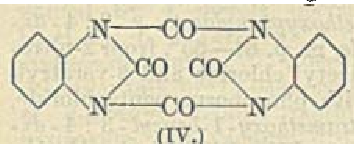
[Porphyrins and their syntheses.] H. FISCHER (Ber., 1928, **61**, [*B*], 1596).—A reply to Schumm (this vol., 776). H. WREN.

Degradation of *o*-substituted aromatic acid azides. H. LINDEMANN and W. SCHULTHEIS (Annalen, 1928, **464**, 237—253).—According to Stieglitz (A., 1914, i, 268), the thermal decomposition of azides gives, as a necessary intermediate, a free radical, R·CO·N⁚, but there is no experimental evidence for the existence of such compounds at any stage of the process. The thermal decomposition has now been effected of *o*-substituted aromatic acid azides, which, if they decomposed according to Stieglitz' view, should give one type of cyclic compound, but an entirely different one if intermediate carbimide formation took place. The conversion of *o*-hydroxybenzoyl azide into 2-hydroxyindoxazen and not into 1-hydroxybenz*iso*oxazole, reported previously (A., 1927, 262), is now regarded as evidence against the Stieglitz view, and the following facts point in the same direction.

o-Hydroxymethylbenzoyl azide,  m. p. 74—75° (decomp.), which, contrary to the statement of Wedel (A., 1900, i, 363), is readily obtained from the corresponding hydrazide, passes, when melted or when heated in benzene solution, into 3-*keto*-3 : 4-*dihydro*-2 : 4-*benzoxazine*,  and not into the isomeric compound,  which would result if a free radical were formed intermediately. The benzoxazine, m. p. 119—120°, is converted by boiling 50% sodium hydroxide into *o*-aminobenzyl alcohol.

Again, when the lactone of *o*-hydroxyphenylacetic acid is treated with alcoholic hydrazine hydrate it affords o-*hydroxyphenylacetylhydrazide*, m. p. 152°, normally convertible into o-*hydroxyphenylacetyl azide*, m. p. 51°. The latter, when heated in benzene solution, affords 2-*keto*-3 : 4-*dihydro*-1 : 3-*benzoxazine*,  m. p. 188°, converted by alkali and benzoyl chloride into ON-*dibenzoyl*-o-*hydroxybenzylamine*, m. p. 141·5°. The latter on partial hydrolysis affords N-*benzoyl*-o-*hydroxybenzylamine*, m. p. 144°.

Phthalyl diazide, from phthaloyl chloride and sodium azide in acetone solution, is highly explosive and cannot be manipulated at all readily. A less explosive *isomeride*, m. p. 56° (decomp.), is formed at the same time, and if the benzene solution of either is boiled, there results *o-carbimidobenzoyl azide*, $N_3CO{\cdot}C_6H_4{\cdot}NCO$, m. p. 60° (decomp.); at 100° the mass solidifies and melts again at 325°, when it consists of the *substance* (IV) (more readily obtained by boiling a freshly prepared toluene solution of phthalyl diazide), converted by boiling aniline into *s*-diphenylcarbamide, benzimazolone and *benziminazolone*-1-*carboxyanilide*, m. p. 197° (hydrolysed to benziminazolone by warm alkali).


(IV.)

Either diazide, when kept in methyl-alcoholic solution, yields *o-carbomethoxyaminobenzoyl azide*, $N_3CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Me$, which melts at 80° (decomp.), the fused mass then becoming solid and finally melting at 155°, owing to its conversion into *methyl benziminazolone*-1-*carboxylate*, m. p. 159°. The latter is also obtained by boiling a toluene solution of the last-named azide. *o-Carbethoxyaminobenzoyl azide*, m. p. 64—66° (decomp.), similarly passes into *ethyl benziminazolone*-1-*carboxylate*, m. p. 156°. This ester and the methyl analogue are converted into benziminazolone when a solution of either in alkali is acidified.

When aniline is added to a benzene solution of *o*-carbimidobenzoyl azide, *o-phenylcarbimidobenzoyl azide*, $N_3CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. 133°, is formed, the latter passing, in boiling toluene solution, into benziminazolone-1-carboxyanilide (above).

The more explosive and less explosive phthalyl diazides are possibly the symmetrical and unsymmetrical compounds, respectively, corresponding with the two phthalyl chlorides. E. E. TURNER.

Tautomerism of brilliant-cresyl-blue. W. C. HOLMES (J. Amer. Chem. Soc., 1928, **50**, 1989—1993; cf. B., 1924, 167).—Directly prepared chloroform solutions of this oxazine dye,

$$NH_2{\cdot}C_6H_3{<}^{N}_{O}{>}C_6H_2Me{:}NMe_2Cl,$$

contain principally a blue tautomeride which is also present in dilute aqueous solutions. On saturating the solution with ammonia this is converted with loss of one methyl group into a brown dye-base, which readily regenerates a blue dye with acids. When, however, the dye is extracted with chloroform from a solution in a 0·15*M*-acetate buffer which is 0·6*N* with regard to sodium chloride (p_H 3·42), the extract contains mainly a violet tautomeride which is also present in concentrated aqueous solutions. The absorption spectrum of the chloroform solution is only slightly altered by saturation with ammonia, most of the violet form remaining unattacked. Accordingly, the blue form is assigned the generally accepted formula (above), whilst the much less reactive violet form is represented as an additive product of the type, $R_2{:}N{<}^{Cl}_{Me}$.

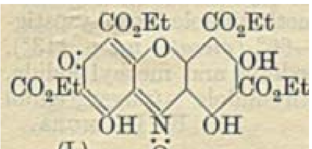
H. E. F. NOTTON.

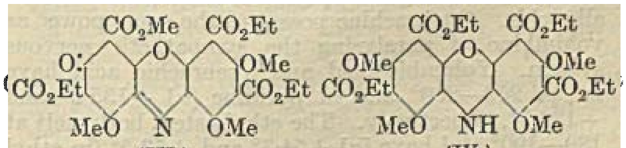
Action of diazomethane on ethyl phloroglucinoldicarboxylate and its derivatives; its reaction with nitrous acid. H. LEUCHS [with I. WALDORF, P. SANDER, and W. R. LEUCHS] (Annalen, 1928, **460**, 1—32).—Treatment of ethyl phloroglucinoldicarboxylate (cf. Annalen, 1924, **440**, 149), with benzoyl chloride in presence of light petroleum and ferric chloride gives the *O-benzoyl* derivative, m. p. 137—138°, converted by diazomethane into the *methyl*, m. p. varying between 102—103° and 116—118°, and *dimethyl ether*, m. p. 106°. The latter with cold alcoholic alkali gives the benzoyl-free *ester*, m. p. 146—147°, whilst the hot reagent produces the *dimethyl ether*, m. p. 186—188°, of the corresponding acid, converted by bromine in hydrobromic-acetic acid into the *compound*, $C_9H_9O_5Br$, m. p. 220° (decomp.). The ester, m. p. 146—147°, results when ethyl phloroglucinoldicarboxylate is treated with diazomethane.

Phloroglucinoldicarboxylic acid trimethyl ether (decomp. 260°), from the corresponding ester, is converted by the above brominating mixture into dibromophloroglucinol trimethyl ether. The *bromo*-derivatives of the trimethyl ethers of phloroglucinoldicarboxylic acid and ester melt, respectively, at 165—173° (decomp.) and 51°.

Diazomethane converts the nitro-derivative (A., 1909, i, 106) of ethyl phloroglucinoldicarboxylate into the *trimethyl ether*, hydrolysed to the corresponding *acid*, m. p. 132—135° (*methyl* ester, m. p. 70—71°). *Nitrophloroglucinol trimethyl ether* has m. p. 151—152°. *Ethyl* 1 : 2 : 3 : 5-*tetramethoxybenzene*-4 : 6-*dicarboxylate* has m. p. 64—65°. *Ethyl* N-*dimethylaminophloroglucinoldicarboxylate* has m. p. 151—152°. *Phloroacetophenonedicarboxylic acid trimethyl ether* has m. p. 142—144° (sinters 138°) (*ethyl* ester, oily; *methyl* ester, m. p. 74°).

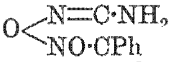
The compound, obtained from ethyl phloroglucinoldicarboxylate and nitric acid, previously regarded (*loc. cit.*) as $C_{22}H_{21}O_{13}N$, is now shown to be $C_{24}H_{23}O_{14}N$, and is called *ethyl phlorazurin*-1 : 3 : 6 : 8-*tetracarboxylate* (I). Diazomethane converts this into the *trimethyl ether*, m. p. 100—101°. When a solution of (I) in ethyl acetate is boiled for 1 day, the N:O group is reduced and one ester group is hydrolysed, giving the same substance, $C_{22}H_{19}O_{13}N$ (II), as is obtained when (I) is first reduced (by means of boiling alcohol, or by sulphurous acid) and then heated in ethyl acetate. When (II) is methylated, (III) results, and when it is reduced a substance, $C_{22}H_{21}O_{13}N$, is formed, m. p. 198—212° (decomp.), methylation of which produces (IV), which has m. p. 120—121°. The reduction of (I) with alcohol, referred to above, actually produces the corresponding *phenoxazone*, *i.e.*, the previously described compound, $C_{22}H_{21}O_{12}N$, the *trimethyl ether* of which has m. p. 112—113°. When the phenoxazone


(I.)


(III.) (IV.)

is heated with alcoholic hydroxylamine it gives two *oximes*, m. p. 141° and 138°, for which formulæ are proposed.

Other reactions of (I) and derived compounds are discussed. For these the original should be consulted. E. E. TURNER.

Dioximes. XLIX. A. VIANELLO (Gazzetta, 1928, **58**, 326—328; cf. Ponzio and Cerrina, this vol., 414).—When dissolved in 10% sulphuric acid and treated with bromine water, β-phenylaminoglyoxime decomposes with evolution of gas, but the α-compound yields *phenylaminoperoxide*,  or  or  m. p. 142°, which is neither hydrogenated by zinc and acetic acid nor deoxygenated by stannous chloride, but is slowly converted into phenylaminofurazan by tin and hydrochloric acid. The two forms of *p*-tolylaminoglyoxime exhibit similar difference in their behaviour towards bromine water. p-*Tolylaminoperoxide*, $C_9H_9O_2N_3$, m. p. 178°, is reduced by tin and concentrated hydrochloric acid to p-*tolylaminofurazan*, $C_{13}H_{15}O_4N_3$, m. p. 142°, which is also obtained by treatment of *diacetyl*-α-p-*tolylaminoglyoxime*, m. p. 168°, with 20% sodium hydroxide solution. T. H. POPE.

Synthesis of physostigmol ethyl ether. S. KEIMATSU and S. SUGANUMA (J. Pharm. Soc. Japan, 1928, No. 554, 348—355).—Physostigmol ethyl ether (Stedman, A., 1924, i, 981) is obtainable by the following method: *p*-Ethoxybenzenediazonium chloride and ethyl potassioacetoacetate give *ethyl* β-*methylpyruvate* p-*ethoxyphenylhydrazone*, m. p. 113—114°, which on boiling with 10% alcoholic sulphuric acid is converted into *ethyl 5-ethoxy-3-methylindole-2-carboxylate*, m. p. 168—169°. The corresponding *acid*, m. p. 183—184° (decomp.), loses carbon dioxide at 200° giving 5-ethoxy-3-methylindole (norphysostigmol ethyl ether), m. p. 65—66° (*picrate*, m. p. 113°), which, on treating with sodium and methyl iodide, gives 5-ethoxy-1:3-dimethylindole (physostigmol ethyl ether), m. p. 86°. K. ISHIMURA.

Identity of yohimbine and quebrachine. RAYMOND-HAMET (Compt. rend., 1928, **187**, 142—145).—Quebrachine obtained from the bark of *Aspidosperma Quebracho blanco* and yohimbine isolated from the bark of *Pausinystalia Yohimbe* or extracted from Gustrow's yohimbine hydrochloride give identical figures on analysis, have [α] +102·7° and +102·2° (in pyridine), respectively and as hydrochloride the lethal dose for guinea-pigs is the same for both alkaloids. Quebrachine possesses the same power as yohimbine of paralysing the sympathetic nervous system. Yohimbic acid and quebrachic acid have m. p. 259—260° and in pyridine [α] +135·9° and +136·7°, respectively. The ethyl esters both melt at 189—190° and have [α] +54·3° and +53·5° (in ethyl alcohol); similarly, the propyl esters, m. p. 136—137°, have [α] +48·1° and +47·8° (in ethyl alcohol). Yohimbine and quebrachine are therefore regarded as identical (cf. A., 1926, 1263; 1927, 471; this vol., 432). R. BRIGHTMAN.

Aporphine alkaloids. III. Synthesis of corytuberine dimethyl ether. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 1834—1838).—The method previously described (this vol., 532, 781) was applied to the synthesis of 3 : 4 : 5 : 6-tetramethoxyaporphine, the *d*-form of which was identical in properties with corytuberine dimethyl ether (Gadamer, A., 1912, i, 46).

2′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-3 : 4-*dimethoxyphenylethylamide*, m. p. 64—65°, from 2-nitro-3 : 4-dimethoxyphenylacetyl chloride and β-veratrylethylamine, yielded, with phosphorus pentachloride, 2′-*nitro*-6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline, m. p. 159—160° [*hydrochloride*, m. p. 227° (decomp.)]. Reduction of the *methiodide* of this base, m. p. 105—107° (+EtOH), decomp. 180—190°, with zinc dust and hydrochloric acid yielded 2′-*amino*-6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydro*isoquinoline (*dihydrochloride*, m. p. 188—190°), which could be diazotised and coupled with β-naphthol. Diazotisation in methyl alcohol and sulphuric acid and warming yielded 3 : 4 : 5 : 6-*tetramethoxyaporphine*, an oil (*hydrochloride*; *hydriodide*; *methiodide*, darkening at 220°, decomp. 248°). This *dl*-base yielded, with *d*-tartaric acid, l-*corytuberine dimethyl ether* d-*hydrogen tartrate*, m. p. 219—221° (decomp.), $[\alpha]_D$ −148·2° in water. The *d*-base was separated as the *l*-hydrogen tartrate. The properties of this, the reactions of the free *d*-base, and the properties of the methochloride, were in close agreement with those recorded by Gadamer (*loc. cit.*) for the base from natural sources. Carbethoxycorytuberine dimethyl ether also had properties identical with those of the compound from natural sources (Osada, A., 1925, i, 283). R. K. CALLOW.

Microchemical reactions of hyoscyamine. M. WAGENAAR (Pharm. Weekblad, 1928, **65**, 549—551).—The alkaloid sublimes when heated, forming droplets which can be caused to crystallise by sodium carbonate solution which has been shaken with the alkaloid itself or with atropine. The periodide and perbromide crystallise very readily, and are highly characteristic. The precipitates with gold chloride and picric acid, under suitable conditions, also crystallise well. S. I. LEVY.

Lupin alkaloids. I. G. R. CLEMO and G. C. LEITCH (J.C.S., 1928, 1811—1820).—A review of the literature is given. *i*-Lupanine, $C_{15}H_{24}ON_2$, from *Lupinus termis*, was found to be a diacidic base, yielding with hydrogen chloride in ether a *dihydrochloride*, m. p. 185° (decomp.), which decomposed to give the monohydrochloride when heated under reduced pressure. On the other hand, only a *monomethiodide*, m. p. 262—263°, and a *monomethosulphate*, m. p. 188°, decomp. 275°, could be obtained. Three methods of degradation were attempted: (*a*) decomposition of the methiodide with alkali hydroxides, (*b*) reduction, and (*c*) oxidation.

(*a*) Whilst the methiodide was unchanged by boiling methyl-alcoholic potassium hydroxide, and lupanine was recovered when the methiodide was distilled with solid sodium hydroxide, distillation with a mixture of sodium and potassium hydroxides yielded a mixture of α-*methyl-lupanine*, m. p. 123°,

insoluble in water [*hydrochloride*, m. p. 209° (decomp.)], and β-*methyl-lupanine*, a water-soluble oil [separated as the *methiodide*, m. p. 272° (decomp.)], with traces of simpler bases. These simpler bases formed the bulk of the distillate when fusion was carried out with potassium hydroxide alone. A fraction of b. p. 88—92°/1 mm., from which was obtained a *picrate*, $C_{18}H_{20}O_7N_4$ or $C_{17}H_{18}O_7N_4$, m. p. 130—131°, accompanied by a *picrate*, decomp. 225°, and a *base*, $C_{13}H_{22}N_2$, b. p. 127—132°/1 mm. (*picrate*, m. p. 137°; *dimethiodide*, m. p. 202°, decomp. 280°), were isolated. A similar mixture of bases was obtained by distillation of α-methyl-lupanine methiodide with potassium hydroxide, but vacuum distillation of the methylammonium hydroxide derived from it yielded a *base*, $C_{17}H_{30}O_2N_2$, b. p. 210—215°/1 mm., the formation of which was ascribed to a change from $\begin{matrix}-CH_2\\ \end{matrix}\!\!>\!NMe_2{\cdot}OH$ to $\begin{matrix}-CH_2OH\\ NMe_2\end{matrix}$.

(*b*) Heating lupanine with red phosphorus and hydriodic acid at 220° yielded *deoxylupanine*, $C_{15}H_{26}N_2$, b. p. 145°/1 mm. (*dihydrochloride*; *monopicrate*, m. p. 135°; *dipicrate*, m. p. 206—207°; *methiodide*, m. p. 226°). A comparison of the properties of deoxylupanine with those of sparteine, isomeric with it, indicated partial structural similarity for the compounds, including probably the presence of the quinuclidine ring-system, which is unaffected by this method of reduction. Deoxylupanine in an ethereal solution containing sulphur in suspension yielded an orange precipitate with hydrogen sulphide. Oxidation of deoxylupanine yielded iso*lupanine*, m. p. 113° (*monoethiodide*, m. p. 208°).

(*c*) Oxidation of lupanine with potassium permanganate in acetone yielded *oxylupanine*, b. p. 210°/1 mm., m. p. 123° [*chloroplatinate*, m. p. 232° (decomp.)], which had no reactive carbonyl, methylene, or hydroxyl group, or reactive tertiary nitrogen atom.

In the discussion of these results it is pointed out that the absence of carbonyl activity in any of the derivatives could be explained if they were α-quinuclidones, but the great stability to both acids and alkalis is against this hypothesis. R. K. CALLOW.

Salts of pelletierine. G. TANRET (J. Pharm. Chim., 1928, [viii], **8**, 112—120).—Analyses of commercial samples of pelletierine sulphate and tannate show wide divergencies both in the character and amounts of total alkaloid present and many are complex mixtures containing little or no pelletierine. An example is given of two preparations containing tannates and sulphates of only ψ-pelletierine and *iso*pelletierine. The optimum conditions for the preparation of the tannates of pelletierine and ψ-pelletierine are described and the properties and methods for the analysis of the salts are given.

E. H. SHARPLES.

Alkali [metal]-organic compounds. W. SCHLENK and E. BERGMANN (Annalen, 1928, **463**, 1—322; **464**, 1—42).—The results described previously (A., 1914, i, 396) have been extended and are now subjected to systematic classification. **I. Products of addition of alkali metals to olefinic compounds.** The addition of sodium to olefinic compounds may occur in one or other of two ways: (I) represented by the case of tetraphenylethylene: $CPh_2{:}CPh_2 \longrightarrow CPh_2Na{\cdot}CPh_2Na$, or (II) represented by *as*-diphenylethylene: $2CPh_2{:}CH_2+2Na \longrightarrow CPh_2Na{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2Na$. In order that either addition may take place, an aryl group must in general be attached to the carbon atoms concerned in the ethylenic linkings, only one exception to this rule being known, viz. that in the scheme:

$$2\,\begin{matrix}CMe_2{:}CH\\ CMe_2{:}CH\end{matrix}\!\!>\!C{:}CH_2 \xrightarrow{2Na} \left[\begin{matrix}CMe_2{:}CH\\ CMe_2{:}CH\end{matrix}\!\!>\!CNa{\cdot}CH_2{\cdot}\right]_2$$

In some cases sodium can be added to an ethylenic linking present in a benzene nucleus. Thus 4-phenyldiphenyl affords a substance of the formula:

Lithium may also be added to olefinic compounds. In general, it adds more rapidly than sodium and sometimes leads to compounds having configurations different from those derived from the sodium compounds (see II below). Potassium is difficult to manipulate and is not likely to give results very different from those obtained with sodium.

The alkali-metal additive compounds have been systematically studied from the point of view of their behaviour towards certain reagents, as follows: (*a*) *Water.* This substance (or alcohol) effects replacement of sodium (or lithium) by hydrogen. (*b*) *Carbon dioxide.* With this reagent, ·Na is replaced by $\cdot CO_2Na$. (*c*) *Alkyl iodides.* Methyl iodide converts a metal derivative formed by scheme I (above) into the original olefine (ethane formed), but one formed by scheme II into a saturated hydrocarbon in which methyl replaces sodium. (*d*) *Mercury.* This metal effects simple removal of sodium from compounds of an additive type, but does not affect compounds formed as a result of substitution of hydrogen by sodium. In a few cases mercury not only removes sodium, but also produces definite constitutional changes in the organic compound. This occurs with sodium compounds formed by scheme II. (*e*) *Thiocarbimides.* Compounds formed by scheme I undergo the reaction: $CR_2Na{\cdot}CR_2Na+2NR'{:}C{:}S \longrightarrow CR_2{:}CR_2+NR'Na{\cdot}CS{\cdot}CS{\cdot}NR'Na$, those formed by scheme II reacting analogously to the annexed process: $CPh_2Na{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2Na+2NEt{:}C{:}S \longrightarrow NEtNa{\cdot}CS{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2{\cdot}CS{\cdot}NEtNa$, water converting the latter compound into $(NHEt{\cdot}CS{\cdot}CPh_2{\cdot}CH_2{\cdot})_2$. (*f*) *Phenylcarbimide.* In general, the reagent undergoes conversion into its trimeride, no doubt owing to the action of traces of free sodium. Thus (cf. section V below) the sodium derivative of triphenylmethyl, the preparation of which does not involve the use of free sodium, is converted into triphenylacetanilide. (*g*) *Other reagents.* All organic compounds (save phorone, see below) capable of giving an enolic form behave towards the sodium derivatives as do water and alcohol (cf. Schlenk and Marcus, A., 1914, i, 823). Compounds derived by scheme I undergo this change simply, whilst those derived by scheme II behave more as Grignard reagents, the reaction being less rapid and sometimes more complicated.

[With H. WILLSTADT.]—Mercury converts disodiotetraphenylethane, from tetraphenylethylene, into

the latter substance; disodio- or dilithio-dihydroanthracene into anthracene; and αδ-disodio-ααδδ-tetraphenylbutane into *as*-diphenylethylene. Disodiotetraphenylethane is converted by ethylthiocarbimide into the *disodium* derivative of dithiooxethylamide [see (*e*) above], whilst phenylthiocarbimide regenerates tetraphenylethylene. Ethylthiocarbimide converts disodiotetraphenylbutane into the *dithioethylamide*, m. p. 223°, of ααδδ-tetraphenylbutane-αδ-dicarboxylic acid, formed from it by heating with hydrochloric acid at 160°. The disodio-compound with phenylthiocarbimide gives a *substance*, $C_{50}H_{41}N_2S_3$(?), m. p. above 280°, and a second *substance*, m. p. 140°, whilst with phenylcarbimide the latter undergoes trimerisation. Further reactions of disodiotetraphenylethane are as follows (tetraphenylethylene being formed in addition to the substance mentioned): with bromobenzene, some diphenyl; with benzaldehyde, some benzyl alcohol; with furfuraldehyde, some furfuryl alcohol; with trioxymethylene, some sodium formate and some ββγγ-*tetraphenylbutane-αδ-diol*, m. p. 187°; with methyl benzoate some ethane (?); with phenyl benzoate, diphenyl (general reaction with benzoic and other esters which do not enolise: $2Ph{\cdot}CO_2R' + CR_2Na{\cdot}CR_2Na \longrightarrow CR_2{:}CR_2 + 2Ph{\cdot}CO_2Na + R{\cdot}R'$) (benzyl benzoate gives dibenzyl; methyl formate and ethyl oxalate obey the rule); with benzoyl chloride, benzil; with α-naphthoyl chloride αα-*naphthil*, m. p. 187° ($CR_2Na{\cdot}CR_2Na + R'{\cdot}COCl \longrightarrow CR_2{:}CR_2 + NaCl + R'{\cdot}CNa{:}O$; $R'{\cdot}CNa{:}O + R'{\cdot}COCl \longrightarrow R'{\cdot}CO{\cdot}COR'$); with methyl chloroformate, methyl oxalate; with phorone, di*iso*butyl ketone. On the other hand, aniline converts disodiotetraphenylethane into tetraphenylethane and sodium-aniline, whilst ammonia is without action. Nitric oxide and the disodio-compound afford tetraphenylethane and sodium hyponitrite; carbon monoxide does not react, and sulphur dioxide produces tetraphenylethane and sodium tetraphenylethane-αβ-disulphinate.

Disodiotetraphenylbutane reacts as follows: Benzaldehyde gives αββεεζ-*hexaphenylhexane-αζ-diol*, m. p. 212° (sinters at 176°). Furfuraldehyde gives ββεε-*tetraphenyl-αζ-difurylhexane-αζ-diol*, m. p. 212—213°. Phenyl benzoate gives αδ-*dibenzoyl-ααδδ-tetraphenylbutane*, m. p. 195—196°. Benzoyl chloride gives 1 : 2 : 2 : 5 : 5-*pentaphenyl*cyclo*pentanol*, m. p. 179°, and its *benzoyl* derivative, m. p. 242°. Carbonyl chloride affords 2 : 2 : 5 : 5-*tetraphenyl*cyclo*pentanone*, m. p. 176°. Phorone gives tetraphenylbutane and the sodium derivative of enolic phorone. Nitrosyl chloride reacts according to the scheme, ⟶

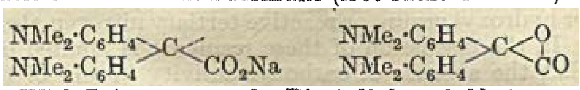
$$NO{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2Na \longrightarrow \underbrace{CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2}_{N(ONa)}$$

$\longrightarrow OH{\cdot}CPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2{\cdot}OH + NH_2OH$, the last stage occurring during the working-up process and thus affording ααδδ-tetraphenylbutane-αδ-diol.

αα-Diphenyl-β-methyl-, αα-diphenyl-ββ-dimethyl-, α-phenyl-ββ-dimethyl-, β-phenyl-ααβ-trimethyl-, and αα-diphenyl-ββ-dibenzyl-ethylene do not combine with sodium, although they (see above) apparently have the necessary phenyl radical attached to an unsaturated carbon atom. These substances are therefore regarded as possessing formulæ other than those corresponding with the above names (see below). This view is supported by the fact that αα-diphenyl-β-benzylethylene, instead of combining with sodium, reacts with it (below) [compare the reaction of sodium with 1 : 2 : 3-triphenylindene (section III)], and is established as correct, since αα-diphenyl-ββ-dimethylethylene gives, with lithium, γ-*lithio-γγ-diphenyl-β-methylpropylene*, $CPh_2Li{\cdot}CMe{:}CH_2$ (below), the reactions of which prove its constitution. Since on the new view β-phenyl-ααβ-trimethylethylene is actually βγγ-triphenylpropylene, the conversion of this substance into ααβ-tribromo-β-bromomethylethylene (γ-bromo-ααβ-triphenylpropylene) by bromine is more readily understood than on Meisenheimer's view (A., 1927, 957). The only discordant result is that with ααβ-triphenyl-β-methylethylene, which gives the disodio-derivative, $CPh_2Na{\cdot}CPhMeNa$. This apparent anomaly is explained by assuming that there is first formed the radical $CHPh_2{\cdot}CPhNa{\cdot}CH_2{\cdot}$, which changes into ${\cdot}CPh_2{\cdot}CPhMeNa$, the latter then combining with an atom of sodium.

Nitriles capable of the tautomeric change: $CH_2R{\cdot}C{:}N \quad CHR{:}C{:}NH$, behave towards sodium as if they possessed the second formula, and give ·NNa derivatives. Aromatic nitriles usually polymerise or condense in presence of sodium, but triphenylacrylonitrile combines additively with 2 atoms of sodium.

4 : 4′ : 4″ : 4‴-Tetra(dimethylamino)tetraphenylethylene and sodium afford the *disodio*-derivative of the corresponding ethane, since the latter is obtained by treating the product with alcohol, and since carbon dioxide converts the product into 4 : 4′ : 4″ : 4‴-tetra(dimethylamino)tetraphenylsuccinic acid. The *sodium* salt of the latter gives a deep blue aqueous solution which becomes colourless on warming. The blue and colourless solutions are explained on the basis of the annexed formulæ (free radical is blue):



[With J. Appenrodt.]—Bis-4-diphenylyl ketone and magnesium methyl iodide give *bis-4-diphenylylmethylcarbinol*, $(C_6H_4Ph)_2CMe{\cdot}OH$, m. p. 147°, converted by acetic and sulphuric acids at 100° into *as-bis-4-diphenylylethylene*, m. p. 211°. The latter reacts with sodium, giving the αδ-*disodio*-derivative of ααδδ-tetra-4-diphenylylbutane. Mercury converts this into the original ethylene, alcohol gives ααδδ-*tetra-4-diphenylylbutane*, m. p. 236°, and carbon dioxide gives ααα′α′-*tetra-4-diphenylyladipic acid*, m. p. above 300°.

Triphenylethylene and sodium give the *disodio*-derivative of ααβ-triphenylethane (m. p. 56°, lit. 54°). Carbon dioxide converts the disodio-derivative into *triphenylsuccinic anhydride*, m. p. 115°. ααβ-Triphenyl-β-methylethylene (see above) adds sodium or lithium, the *products* being decomposed by alcohol to ααβ-triphenylpropane. αα-Diphenyl-β-methylethylene does not combine with sodium (above), whilst potassium slowly reacts to give a product which on one occasion gave with carbon dioxide a *substance*, $C_{17}H_{14}O_3$(?), m. p. 164°, and on another an *acid*, $(C_{16}H_{15}O_2)_n$, m. p. 259 .

Methyl *iso*butyrate and magnesium phenyl bromide give *diphenyl*iso*propylcarbinol*, m. p. 47°, b. p. 169—170°/12 mm., converted by way of the corresponding

chloride (boiling pyridine) into αα-diphenyl-ββ-dimethylethylene, or, more probably, γγ-diphenyl-β-methylethylene, convertible into the above-described lithium compound, which with phenylthiocarbimide affords the *thioanilide*, m. p. 161°, of αα-diphenyl-β-methylvinylacetic acid. It is noted that Klages' supposed diphenyl-*n*-propylcarbinol (A., 1904, i, 487) is actually benzhydrol.

Interaction of ethyl dibenzylacetate and magnesium phenyl bromide produces *ααγ-triphenyl-β-benzylpropan-α-ol*, m. p. 100°, converted by way of the chloride into *αα-diphenyl-ββ-dibenzylethylene*, m. p. 78°, now regarded as *αγγ-triphenyl-β-benzylpropylene* (see above). β-Phenylpropionyl chloride and the Grignard reagent give *diphenyl-β-phenylethylcarbinol*, m. p. 87°, converted by acetic and sulphuric acids into *αα-diphenyl-β-benzylethylene*, b. p. 222°/10 mm., now regarded as *αγγ-triphenylpropylene*, slowly reacting with sodium to give a product affording the original hydrocarbon when decomposed with alcohol, and therefore probably possessing the formula $CPh_2Na\cdot CH{:}CHPh$.

Sodium reacts very slowly with ααγγ-tetraphenylpropylene, to give products of an indefinite nature, but lithium in a reasonable time affords a product which, when decomposed with alcohol, gives 1 : 2 : 3-*triphenylhydrindene*, m. p. 153°. No explanation of this result appears possible. The lithium compound reacts with carbon dioxide to give 1 : 2 : 3-*triphenylhydrindenecarboxylic acid*, m. p. 275°, which when heated with soda-lime affords a *stereoisomeride*, m. p. 126°, of 1 : 2 : 3-triphenylhydrindene. That the lithium compound is a monosubstitution product and not an additive compound is shown by the formation of the above acid, and from its conversion by ethylthiocarbimide into a *compound*, $C_{30}H_{27}NS$, m. p. 193° (transparent at 173°). With iodine the lithium compound gives diphenylmethane, ααδδ-tetraphenylbutadiene, and a (trace) third *substance*, m. p. 221°.

Triphenylacrylonitrile and sodium afford the *disodio*-derivative of αββ-triphenylpropionitrile. Benzonitrile gives, besides its trimeride (cyaphenine), a *substance* isolated as the *perchlorate*, $C_7H_7N,HClO_4$.

In fulvenes and diagrammatically similar compounds $\begin{matrix}C\text{—}C\\C\text{—}C\end{matrix}{>}\overset{1}{C}{=}\overset{2}{C}$, C_1 shows an exceptional tendency to combine with alkali metal. An example of a diagrammatically and chemically similar compound is the triolefine mentioned in the first paragraph above. The properties of C_2 depend largely on the nature of the groups attached to it. If it carries two aryl groups, it combines with sodium, but if it carries only one aryl group or alkyl groups, it reacts according to scheme II above. Thus benzylidenefluorene gives a disodio-derivative possessing the formula $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}CNa\cdot CHPh\cdot CHPh\cdot CNa{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, a rather striking fact in view of the behaviour of stilbene and triphenylethylene. Another important fact is that compounds containing more than one ethylenic linking seldom combine with more than two atoms of sodium. Addition of sodium to one centre of unsaturation therefore appears largely to destroy the unsaturated properties of other such centres (cf. Ziegler, A., 1924, i, 308). Two exceptional cases are those of 9 : 9′-dianthryl and 10 : 10′-diphenyl-9 : 9′-dianthryl, which each combine with 4 at. of sodium.

Diphenylfulvene (1-diphenylmethylene*cyclo*pentadiene) readily affords the *disodio*-compound $C_4H_4{:}CNa\cdot CPh_2Na$, for alcohol converts the product into 1-*diphenylmethyl*cyclo*pentadiene* (1-*benzhydryl*cyclo*pentadiene*), $C_4H_4{:}CH\cdot CHPh_2$, m. p. 36·5°, whilst carbon dioxide produces the *dicarboxylic acid*, m. p. 173—175° (decomp.). On the other hand, dimethylfulvene (1-*iso*propylidene*cyclo*pentadiene) gives a *disodio*-compound of the formula $C_4H_4{:}CNa\cdot CMe_2\cdot CMe_2\cdot CNa{:}C_4H_4$, converted by carbon dioxide into an acid isolated as the *methyl* ester, $[C_4H_4{:}C(CO_2Me)\cdot CMe_2\cdot]_2$, m. p. 194° (yield poor, owing to polymerisation, in first stage, produced by sodium).

1-Diphenylmethyleneindene affords the *disodio*-derivative, $\begin{matrix}C_6H_4\text{—}CNa\\ |\\ CH{:}CH\end{matrix}{>}CPh_2Na$, converted by alcohol into 3-benzhydrylindene, m. p. 114° (Courtot, A., 1915, i, 392), isomerisation occurring during hydrolysis, since treatment of the disodio-compound with carbon dioxide affords 1-*benzhydrylindene*-ω-1-*dicarboxylic acid*, m. p. 177° (decomp.). 1-*iso*Propylideneindene polymerises in presence of sodium, and does not combine with it. 4 : 4′-Bisdiphenylylene–ethylene, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$ gives the *disodio*-derivative of the corresponding ethane (m. p. 241—242°) [*dicarboxylic acid*, m. p. 240° (decomp.)]. Lithium gives similar results.

[With W. Schmidt-Nickels.]—Benzylidenefluorene reacts according to scheme II, the *disodio*-compound on decomposition (alcohol) affording *αβ-diphenyl-αβ-difluorenylethane*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}CH\cdot CHPh\cdot CHPh\cdot CH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, m. p. 321°, and on treatment with carbon dioxide giving *ββ′-diphenyl-ααα′α′-bisdiphenylyleneadipic acid*, decomp. 240°.

[With E. Müller.]—Furfurylidenefluorene behaves similarly, giving the *disodio*-derivative of *αβ-difuryl-αβ-difluorenylethane*, m. p. 238—242°. Cinnamylidenefluorene similarly affords the *disodio*-derivative of *αβ-difluorenyl-αβ-distyrenylethane*, m. p. 254—255°, together with a small amount of an *isomeride* (?), m. p. 204°. The latter compound is probably identical with a substance obtained by Thiele and Henle (A., 1906, i, 571); the other compound, m. p. 160—161°, obtained by reducing cinnamylidenefluorene, is probably a stereoisomeride of the above difluorenyldistyrenylethane.

Dixanthylene, $O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$, gives the *disodio*-derivative of dixanthyl, m. p. 209° (lit. 204—205°), the derived *dicarboxylic acid* having m. p. 189° (decomp.).

αα-Diphenyl-ββ-distyrenylethylene, $(CHPh{:}CH)_2C{:}CPh_2$, reacts rapidly with sodium, the product on decomposition giving *αβ-diphenyl-ββ-distyrenylethane*, m. p. 151—152°, or with carbon dioxide the *dicarboxylic acid*, m. p. 215° (decomp.), of the latter. *αα-Diphenyl-ββ-bis-ω-phenylbutadienylethylene*, $(CHPh{:}CH\cdot CH{:}CH)_2C{:}CPh_2$, m. p. 149° (from azibenzil and dicinnamylideneacetone), gives the *disodio*-derivative of *αα-diphenyl-ββ-bis-ω-phenylbuta-*

dienylethane, m. p. 140°. The expected *dicarboxylic acid* has m. p. 127° (decomp.).

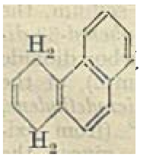
βζ-Dimethyl-δ-methylene-$\Delta^{\beta\epsilon}$-heptadiene is exceedingly readily converted by sodium into the *disodio*-derivative of *βι-dimethyl-δη-bis-ω-dimethylvinyl-$\Delta^{\beta\theta}$-decadiene*, b. p. 195—196°/58 mm. The *δη-dicarboxylic acid* of the latter results normally.

[With I. Rodloff.]—Tolane, which is most conveniently obtained by treating benzildihydrazone with mercuric oxide, gives ambiguous results with sodium, a *substance* (?), m. p. 295°, being the only product of the subsequent decomposition. On the other hand, lithium reacts fairly easily, and in a novel manner. It causes the combination of two molecules of tolane to give 1 : 2 : 3-*triphenylnaphthalene*, m. p. 151°, which reacts in two ways with the metal: (1) to give 4-*lithio*-1 : 2 : 3-*triphenylnaphthalene*, converted by alcohol into the above hydrocarbon, by carbon dioxide into 2 : 3 : 4-*triphenyl-α-naphthoic acid*, m. p. 258° (decomp.), and by phenylthiocarbimide into the *thioanilide*, m. p. 280—281°, of this acid, and (2) to give 1 : 2-*dilithio*-1 : 2 : 3-*triphenyl*-1 : 2-*dihydronaphthalene*, the presence of which is shown by the formation, in the above reaction with carbon dioxide, of the *anhydride*, m. p. 270°, of 1 : 2 : 3-*triphenyl*-1 : 2-*dihydronaphthalene*-1 : 2-*dicarboxylic acid* (not isolated). Mercury does not convert the mixture of lithio-derivatives into 1 : 2 : 3-triphenylnaphthalene, but into a *stereoisomeride*, $C_{28}H_{20}$ (? of the type already known in the diphenyl series), m. p. 227°, more readily produced by the action of iodine on the metal derivative. In one case where lithium and tolane remained together for several years, a third *isomeride*, $C_{28}H_{20}$, m. p. 192°, of the above hydrocarbon was obtained. The first-mentioned triphenylnaphthalene is not reduced by hydrogen in presence of palladised barium sulphate, but sodium and amyl alcohol afford a *hydrocarbon*, $C_{28}H_{21}$(?), m. p. about 75°.

[With O. Blum.]—When αα-dichloro- or αα-dibromo-ββ-diphenylethylene is treated with lithium and the product with alcohol, the triphenylnaphthalene, m. p. 152°, is formed. This when treated with lithium, with subsequent hydrolysis, gives the isomeride, m. p. 192°. Under different conditions the dihalogeno-compounds are converted by lithium into a *hydrocarbon*, $C_{28}H_{22}$, m. p. 184°, which when reduced catalytically, or when treated with lithium, followed by alcohol, is converted into a *hydrocarbon*, $C_{28}H_{24}$, m. p. 182°. The formation of triphenylnaphthalene is no doubt due to the intermediate formation of tolane.

4 : 4′-Dimethoxytolane (prepared by oxidising *anisildihydrazone*, m. p. 118°) reacts extremely slowly with lithium, whilst diphenyldiacetylene is mainly polymerised by the latter.

Phenanthrene does not combine with lithium in the 9 : 10-positions, but in the 1 : 4-positions. The 1 : 4-*dihydrophenanthrene*, b. p. 168—170°/15 mm. (annexed formula) obtained (alcohol), is converted by hydrogen and palladised barium sulphate into 1 : 2 : 3 : 4-*tetrahydrophenanthrene*, and an *isomeride*, b. p. 140—149° (two fractions obtainable, b. p. 140—145° and 145—149°).



From the residue obtained after distilling the dihydrophenanthrene, an *isomeride*, m. p. 71—73°, is obtained. Sodium reacts sluggishly with phenanthrene, the product being converted by carbon dioxide into 9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*diphenanthryl*-10 : 10′-*dicarboxylic acid*, m. p. 226° (cf. scheme II, above).

9 : 10-Diphenylphenanthrene combines with sodium or with lithium in the 9 : 10-positions. The so-obtained (alcohol) 9 : 10-*diphenyl*-9 : 10-*dihydrophenanthrene* has m. p. 130—131°, and the corresponding 9 : 10-*dicarboxylic anhydride* has m. p. 221°.

Ordinary naphthalene contains sufficient sulphur compounds to cause hindering of alkali-metal reactions, whilst Kahlbaum's "calorimetric" naphthalene, although reacting poorly with sodium for the same reason, is converted by lithium into 1 : 4-*dilithio*-1 : 4-*dihydronaphthalene* (identified by conversion into 1 : 4-dihydronaphthalene) and a lithium derivative of a *liquid*, b. p. 265—275°/14 mm. 1 : 4-*Dihydronaphthalene*-1 : 4-*dicarboxylic acid*, obtained normally, has m. p. 226—227°. Insufficiently long treatment of naphthalene with lithium gives rise, after alcohol treatment, to the known additive compound, m. p. 43—44°, of naphthalene and 1 : 4-dihydronaphthalene.

Diphenyl does not combine with sodium under the usual conditions, but lithium affords a dilithio-derivative, 

which with alcohol produces 1 : 4-*dihydrodiphenyl*, b. p. 110°/10 mm., and with carbon dioxide gives 1 : 4-*dihydrodiphenyl*-1 : 4-*dicarboxylic acid*, m. p. 266° (276° ?) (decomp.). That addition occurs 1 : 4 is shown by the reduction of the dihydrodiphenyl to phenyl*cyclo*hexane, and by the impossibility of obtaining the dicarboxylic anhydride using acetic anhydride.

[With E. Muller.]—4-Phenyldiphenyl combines with sodium slowly in ether, but more rapidly in dioxan, giving a product converted by carbon dioxide into 1 : 4-*diphenyl*-$\Delta^{2:5}$-cyclo*hexadiene*-1 : 4-*dicarboxylic acid*, m. p. 264° (decomp.) (sinters 240°). 1 : 2 : 4 : 5-Tetraphenylbenzene and sodium, followed by alcohol, give 1 : 2 : 4 : 5-*tetraphenyl*-1 : 2-*dihydrobenzene* (2 : 3 : 5 : 6-*tetraphenyl*-$\Delta^{1:3}$-cyclo*hexadiene*). The *sodium* salt of the derived *dicarboxylic acid* [m. p. 230° (decomp.)] readily undergoes autoxidation.

II. New facts in the stereochemistry of carbon. [With J. Appenrodt.]—*trans-trans*-αδ-Diphenylbutadiene combines with sodium or lithium to give *dialkali* derivatives of *αδ-diphenyl-Δ^{β}-butene*, b. p. 176°/13 mm., *i.e.*, an ethylene isomeride of the known butene, m. p. 45°. With carbon dioxide they give *αδ-diphenyl-Δ^{β}-butene-αδ-dicarboxylic acid*, m. p. 220°, and are converted by mercury into the original butadiene. ααδδ-Tetraphenylbutadiene similarly gives the *disodio*- or *dilithio*-derivatives of *ααδδ-tetraphenyl-Δ^{β}-butene*, m. p. 140·5° (reduced by sodium and amyl alcohol to tetraphenylbutane, but not decolorising bromine). The *αδ-dicarboxylic acid*, m. p. 262° (decomp.), of the butene, and the corresponding *methyl* ester, m. p. 148—148·5°, are described. Methyl iodide or mercury converts the dialkali compounds into the butadiene. Reduction of the latter with sodium amalgam and alcohol gives the above butene, so that this case differs stereochemically from that of diphenylbutadiene.

[With E. MÜLLER.]—*Mercury bis-ββ-diphenylvinyl*, $Hg(CH:CPh_2)_2$, m. p. 140·5°, from magnesium ββ-diphenylvinyl bromide and mercuric bromide (*mercury ββ-diphenylvinyl bromide* has m. p. 158—159°) reacts with sodium to give a disodio-derivative, which with carbon dioxide gives the dicarboxylic acid (m. p. 262°) of the above tetraphenylbutene, but with alcohol affords a *stereoisomeric* ααδδ-tetraphenyl-Δ^{β}-butene, m. p. 123—124°. The latter is converted into the butene, m. p. 140·5°, when warmed in glacial acetic acid in presence of a little sulphuric acid, and on reduction gives tetraphenylbutane. An explanation of these phenomena is put forward.

When addition of alkali metal to a poly-olefinic compound could theoretically give rise both to *cis-cis-* and to *cis-trans*-compounds, or to one of these, sodium and lithium may behave similarly or differently. Thus, when sodium (2 atoms) combines with stilbene, a meso-compound results, whilst lithium affords the corresponding *racemic* derivative. Assuming stilbene to possess the *cis-trans*-configuration, the sodium addition is *cis-trans*, the lithium *cis-cis*. The acid, m. p. 227°, previously obtained (1914, *loc. cit.*) from carbon dioxide and disodium stilbene, melts at 229—230° (decomp.) (*methyl* ester, m. p. 219°). The product of adding lithium to stilbene gives *s*-diphenylethane when treated with alcohol, and stilbene with mercury, whilst with carbon dioxide it gives a *diphenylsuccinic acid*, m. p. 241° (decomp.) (*methyl* ester, m. p. 169°, clearing at 191°). Addition of potassium to stilbene, followed by carbon dioxide treatment, gives the above meso-acid, m. p. 229—230° (decomp.) (cf. Wren and Still, J.C.S., 1915, **107**, 444).

*iso*Stilbene, prepared by the catalytic reduction of tolane, is so rapidly converted by alkali metals into stilbene that the products obtained are the same as from the latter.

s-Diphenyldimethylethylene combines with sodium to give a disodio-compound which is converted by alcohol into the *s*-diphenyldimethylethane (βγ-diphenylbutane) obtained by catalytic hydrogenation of the olefine, and with carbon dioxide affords the same *s-diphenyldimethylsuccinic acid*, m. p. 296° (decomp.), as is similarly derived from the more readily obtained *dilithium* compound. The latter gives the ethylene when treated with mercury.

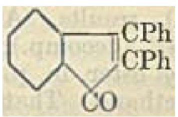
4-Benzoyldiphenyl (4-diphenylyl phenyl ketone) (preparation improved) is converted by phosphorus pentachloride into dichloro-4-diphenylylphenylmethane, $C_6H_5{\cdot}C_6H_4{\cdot}CPhCl_2$, m. p. 72° (lit. 45—47°), which, when heated in benzene solution with copper bronze, gives a mixture of the two, isomeric *s-diphenyl-bis-4-diphenylylethylenes*, m. p. 255° and 218°. Either isomeride combines with sodium or with lithium, the products of all four interactions giving, when treated with alcohol, two stereoisomeric *s-diphenylbis-4-diphenylylethanes*. m. p. 247° and 205—206°, respectively. This result is ascribed to the formation of a free radical (and consequent steric changes) during the decomposition with alcohol. The formation in all cases of the stabler of two isomerides in a mercury alkali-metal elimination is no doubt due to a similar cause.

4 : 4′-*Dimethoxy*iso*stilbene*, obtained together with the corresponding ethane from the above tolane by catalytic reduction, has m. p. 37°. Distillation at 217—219°/14 mm. gives considerable dimethoxystilbene, also produced when the new compound is treated with lithium and then with mercury.

Wizinger (A., 1927, 764) regards the intense colour of sodium additive compounds of the type under discussion as being due to their co-ordinative structure. The disodio-derivatives of bisdiphenylylene-ethane and of αα-diphenyl-ββ-distyrenylethane (above) give electrical conductivities agreeing with this theory. That of the second (intensely coloured) is 20 times as great as that of the less highly coloured, first compound.

1 : 1 : 3-Triphenylindene is converted by sodium into a compound which, when decomposed with alcohol, affords a 1 : 1 : 3-*triphenylhydrindene*, m. p. 133°, whilst a *stereoisomeride*, m. p. 111—112°, of the latter results when the indene is reduced with hydrogen and palladised barium sulphate or with phosphorus and hydriodic and acetic acids. Both isomerides are colourless and that melting at 112° fuses to a colourless liquid; that melting at 133° affords a yellowish-green liquid on fusion.

The existence of two stereoisomeric triphenylhydrindenes can be explained only on the assumption that the two rings of indene and its derivatives are not co-planar, at any rate under some conditions of substitution. The optical resolution of 2 : 3-diphenylindone (annexed formula) establishes this as the correct explanation.



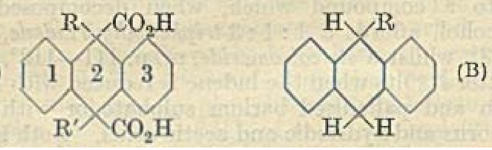
When diphenylindone is treated with phosphorus pentachloride, it affords the 2 : 3-*dichloro-2 : 3-dihydro*-derivative, m. p. 135—136°. Aniline and the indone condense at the b. p. in presence of aniline hydrobromide to give 1-*anilo-2 : 3-diphenylindene*, m. p. 201° (sinters at 160°), whilst *d*-bornylamine condenses with benzophenone to give N-*diphenylmethylenebornylamine*, m. p. 170°, [α] +7·57°, and with diphenylindone to give a small quantity of N-*diphenylindenylidenebornylamine*, m. p. 123°, [α] +124°. This, after being hydrolysed, gives rise to a 2 : 3-diphenylindone phenylhydrazone having [α] −1·85°, which establishes the resolution during the purification of the bornylamine anil.

2 : 3-Diphenylindone, when catalytically reduced, gives 1-*hydroxy-2 : 3-diphenylhydrindene*, m. p. 146°, (the phenylcarbamate of which, when crystallised from anisole, undergoes thermal decomposition into diphenylindone and *s*-diphenylcarbamide), together with 2 : 3-*diphenyl-1-hydrindone*, m. p. 100°. The phenylhydrazone of 2 : 3-diphenylindone has m. p. 179—180°; lit. 175—176°.

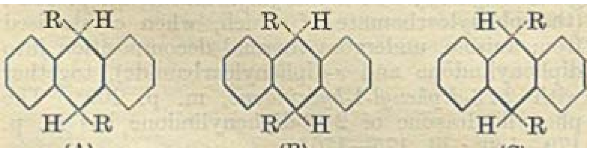
[With W. STOFFERS.]—When 3-phenyl-1-diphenylmethyleneindene is reduced with sodium and boiling amyl alcohol, 3-*phenyl-1-diphenylmethylhydrindene*, m. p. 137°, is formed, whilst when it is treated with sodium or lithium, followed by alcohol, there are formed 3-*phenyl-1-diphenylmethylindene*, m. p. 171° (giving the hydrindene, m. p. 137°, when reduced), and 1-*phenyl-3-diphenylmethylindene*, m. p. 131°. Sodium amalgam and alcohol convert 3-phenyl-1-diphenylmethyleneindene into the compound of m. p. 171°, together with an *isomeride*, m. p. 180°, which

is very readily dehydrogenated. Indene-1-carboxylic acid is formed when indene is treated with lithium ethyl followed by carbon dioxide.

Other new cases of stereoisomerism have been discovered. Compounds having the structure (A), where R—R′=H or R=R′=Ph, exist in three forms, only to be accounted for if, with ring 2 in the plane of the paper, rings 1 and 3 are inclined towards the latter (the assumption that both inclinations are downwards is sufficient to explain the new facts; one downward and one upward inclination give an unlikely, and for the present, an unnecessary, configuration). Compounds of the structure (B) (R—Ph or CO_2H) exist in two forms, as do 9 : 9′-dianthranyl and 9 : 10-diphenylanthracene.

(A)  (B)

[With O. Blum and K. Ehninger.]—The 9 : 10-dihydroanthracene-9 : 10-dicarboxylic acid previously described (1914, *loc. cit.*) as melting at 287—288° (decomp.) has m. p. 286° (decomp.) and is now called the α-acid. The β-*acid*, m. p. 294° (decomp.; sinters 264°) or 283° (+$1H_2O$) (indef.), is obtained by a slight modification of the method of preparation of the α-acid from the product of adding sodium to anthracene. When lithium is used, a third (γ) *acid*, m. p. 297° (decomp.; sinters 267°), results. A mixture of β- and γ-acids melts at 297° (decomp.), and both acids give the same (β) *methyl* ester, m. p. 163·5—165°, when treated with diazomethane. That the β- and γ-acids are distinct is shown, however, by the fact that the γ-acid may be caused to form a hydrate. This loses all water of crystallisation when kept for 1 day, whilst the β-hydrate is stable. Moreover, salts of the β-acid readily pass into α-salts, whilst, for the conversion into the latter of γ-acid, prolonged boiling with excess of alkali is necessary. The β- and γ-acids show similar luminescence colours under cathode rays, the α-acid showing different colours. The ease of conversion of β into α and the difficulty of conversion of γ into α are explained if in the annexed scheme (outer rings inclined downwards) ($R=CO_2H$), the β-acid is A, and the γ-acid is B or C


(A) (B) (C)

(α-acid, C or B), since β —— α involves one configurational change, whilst γ —— α requires two.

Hydrolysis of the β-ester (above) gives neither β- nor γ-acid, but α-acid. Moreover, if instead of esterifying the α-acid with diazomethane (giving the α-*methyl* ester, m. p. 162·5—163°) boiling methyl-alcoholic hydrogen chloride is used, some β-ester is also formed. The latter is almost quantitatively produced when the pure α-ester is heated for 7 hrs. at 200°.

[With O. Blum.]—If 9 : 10-disodio-9 : 10-dihydroanthracene is treated in benzene solution with anthracene, 9-sodio-9 : 10-dihydroanthracene results, so that by the action of carbon dioxide 9 : 10-dihydroanthracene-9-carboxylic acid (α-acid), m. p. 207°, (not 208—210°, *loc. cit.*) (*methyl* ester, m. p. 94—96°) is obtained. If higher concentrations are used in the first stage, the β-dicarboxylic acid (above) is formed together with 9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl*-10 : 10′-*dicarboxylic acid*, m. p. not below 370°, isolated as the *methyl* ester, m. p. 267°. Reduction of anthracene-9-carboxylic acid (catalytic) produces β-9 : 10-*dihydroanthracene*-9-*carboxylic acid*, m. p. 197° (sinters at 182°). Diazomethane converts the β-acid into the α-ester, m. p. 94—96°, which is also formed by the catalytic reduction of methyl anthracene-9-carboxylate. Three stereoisomeric 9 : 10-diphenyl-9 : 10-dihydroanthracene-9 : 10-dicarboxylic acids are obtained as follows: 9 : 10-Diphenylanthracene, prepared by heating 9-hydroxy-10-methoxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (m. p. 244°, not 274° as lit.) with formic acid, is reduced by sodium and amyl alcohol to 9 : 10-diphenyl-9 : 10-dihydroanthracene, m. p. 208° (sinters at 180°; lit. m. p. 218°) (the "diphenyldihydroanthracene," m. p. 164·2°, described by Linebarger, 1891, has another constitution), and gives a *disodium* additive compound. The latter with alcohol gives a mixture of two (polymorphic) diphenyldihydroanthracenes, m. p. 199° and 190°, respectively, which are distinct from the compound, m. p. 208°, above. The latter slowly reacts with bromine to give a *tetrabromodiphenylanthracene*, $C_{26}H_{14}Br_4$, m. p. not below 300°, also formed, with great vigour, from either of the lower-melting compounds. Treatment of the above disodium compound with carbon dioxide, followed by addition of water and immediate acidification, gives the β-*acid*, m. p. 277°, whilst if the alkaline solution is heated (100°; ¼ hr.) before acidification, the α-*acid*, m. p. 299°, results. The γ-*acid*, m. p. 282°, is obtained from the *dilithio*-compound (alcohol converts this into the mixture of hydrocarbons obtained from the disodio-compound). All three acids, with diazomethane, give the same *methyl* ester, m. p. 201°.

No stereoisomeric 9-methyldihydroanthracene derivatives could be obtained, but 9-phenyl-9 : 10-dihydroanthracene exists in two forms. Reduction of 10-methoxy-10-phenylanthrone with phosphorus and hydriodic and acetic acids gives phenylanthrone, also obtained from phenylphthalide. The 9-phenylanthracene, obtained from the anthrone by reduction, is reduced by sodium and boiling amyl alcohol to α-9-phenyldihydroanthracene (obtained by Baeyer, 1880, but regarded by him as a more fully hydrogenated compound), m. p. 87°. The latter passes unchanged through the usual sodium, followed by alcohol, process. When the product of interaction of anthrone and magnesium phenyl bromide is decomposed with water, a 9-phenylanthracene is obtained, which when reduced with sodium and boiling amyl alcohol gives β-9-phenyldihydroanthracene, m. p. 123°, converted by the sodium–alcohol process into the α-compound, m. p. 87°. The latter does not react with sodium, which converts the β-compound

into a *disodio*-derivative affording 9-phenylanthracene when treated with mercury.

9 : 9′-Dianthranyl, obtained by the method of Barnett and Matthews (J.C.S., 1923, **123**, 380), has m. p. 360° or higher, is reduced (sodium and amyl alcohol) to tetrahydro-9 : 9′-dianthranyl, m. p. 248—249°, and with sodium rapidly gives a product which gives indefinite results with carbon dioxide and is converted by alcohol into the latter hydrocarbon. When sodium diphenylmethyl, from benzhydryl methyl ether, reacts with 9-bromoanthracene, a second 9 : 9′-dianthranyl, m. p. 304°, results, its constitution following from its reduction (as above) to tetrahydrodianthranyl. It is clear, therefore, that the dianthranyl described by Liebermann and Gimbel in 1887 is an individual and not a mixture as stated by Barnett and Matthews (*loc. cit.*).

Two stereoisomeric 9 : 10-diphenylanthracenes are obtained as below: Phenylanthrone and magnesium phenyl bromide give 9-*hydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m. p. 202—203°, converted into the *methyl ether*, m. p. 226°, when treated with methyl iodide and potassium in xylene, but, when first heated with potassium and xylene and then treated with methyl iodide (ethyl iodide, or *iso*propyl, *tert.*-butyl, or benzyl chloride, or chloromethyl ether) affording the known (yellow) 9 : 10-diphenylanthracene, m. p. 247°, together with a colourless *isomeride*, m. p. 214°. Simultaneous interaction of sodium, methyl iodide, etc. gives only the yellow form. That the hydrocarbons are not simply dimorphic forms is established. Thus the compound, m. p. 247°, gives with sodium a product regenerating the original hydrocarbon when treated with mercury, whilst the hydrocarbon, m. p. 214°, similarly treated, is recovered unchanged. The two isomerides exhibit different colours in cathode rays. That they are not position isomerides is shown by their conversion by sodium and carbon dioxide into the same β-9 : 10-diphenyl-9 : 10-dihydroanthracene-9 : 10-dicarboxylic acid, and by lithium and carbon dioxide into the corresponding γ-acid. The sodium–mercury experiments appear to show that the isomerism is not that of *meso*- and *o*-quinonoid forms. Both forms give (free radicals?) yellow solutions in boiling ethyl benzoate.

Treatment of phenylanthrone with magnesium *o*-tolyl bromide gives 10-hydroxy-9-phenyl-10-*o*-tolyl-9 : 10-dihydroanthracene, m. p. 201°, which with potassium–*tert.*-butyl chloride–xylene gives a colourless *isomeride*, m. p. 172—173°, of the 9-*phenyl*-10-*o*-*tolylanthracene*, m. p. 257—258°, described below. 10-*Hydroxy*-9-*phenyl*-10-*methyl*-9 : 10-*dihydroanthracene*, m. p. 162° (decomp.), is converted by a similar process into the known 10-phenyl-9-methylanthracene, m. p. 116°.

1-Methylanthraquinone and magnesium phenyl bromide give 9 : 10-*dihydroxy*-9 : 10-*diphenyl*-1-*methyl*-9 : 10-*dihydroanthracene*, m. p. 236°, converted by formic acid and sodium formate at the b. p. into 1-*methyl*-9 : 10-*dihydroanthracene*, m. p. 194°. The similarly obtained pair of 2-methyl compounds have m. p. 238° and 214°, respectively (zinc and acetic acid reduction). Methoxyphenylanthrone (above), is converted by magnesium *o*-tolyl bromide into 10-*hydroxy*-9-*methoxy*-9-*phenyl*-10-*o*-*tolyl*-9 : 10-*dihydroanthracene*, m. p. 168°, whence the above-mentioned 9-phenyl-10-*o*-tolylanthracene, m. p. 257—258°, results. The corresponding pair of 10-m-*tolyl* compounds have m. p. 209—210° and 182—183°, respectively.

[With W. Stoffers.]—9-*Lithiofluorene* is obtained when lithium ethyl reacts with fluorene, and 9-*sodiofluorene* when sodium triphenylmethyl so reacts. Either compound is converted by carbon dioxide into β-*fluorene*-9-*carboxylic acid*, m. p. 232°. This, like the known (α-) acid, m. p. 222° (decomp.), affords fluorene when heated in aqueous-alkaline solution, a fact which establishes the chemical similarity of the acids, which with diazomethane give the same *methyl* ester, m. p. 63°, b. p. 193°/14 mm., together with some dimethyl bisdiphenylenesuccinate, m. p. 234°. The corresponding acid (see above) affords the ester, m. p. 63°, when kept in methyl-alcoholic sulphuric acid.

9-Lithiofluorene is converted by diphenylmethyl bromide into the known 9-benzhydrylfluorene (9-diphenylmethylfluorene), m. p. 217°, together with a *stereoisomeride*, m. p. 187° (9-sodiofluorene gives only the first isomeride), obtained as the main product (traces of isomeride, m. p. 217°) when sodium diphenylmethyl acts on 9-chlorofluorene. The identity of the lower-melting isomeride is shown by its conversion (potassium; carbon dioxide) into α-fluorene-9-carboxylic acid, together with a little diphenylacetic acid and diphenylmethane. The stereoisomerides appear distinct under cathode rays (absence of dimorphism).

Fluorenone dimethylacetal, m. p. 87—88°, from 9 : 9-dichlorofluorene, gives 9-sodio-9-methoxyfluorene (when treated with sodium), converted by carbon dioxide into 9-*methoxyfluorene*-9-*carboxylic acid*, m. p. 172—173°, and by methyl chloroformate into the corresponding methyl ester, m. p. 124° (also obtainable using diazomethane), which is identical with the ester obtained by Klinger (A., 1912, i, 701), and, when hydrolysed, gives the acid, m. p. 192° (decomp.), described by this author. Lithium may replace sodium in the above. Sodiomethoxyfluorene and methyl iodide give the known methoxymethylfluorene.

Treatment of lithiofluorene with iodine or with 9-chlorofluorene produces bisdiphenylylene-ethane. 9-Methoxy-9-phenylfluorene, from the corresponding chloro-compound, does not react at all readily with lithium, but with sodium, followed by carbon dioxide, produces 9-phenylfluorene-9-carboxylic acid. 9-Phenylfluorenol, benzyl alcohol, and hydrogen chloride give 9-*benzyloxy*-9-*phenylfluorene*, m. p. 141·5°, which may be used instead of the methoxy-compound.

Diphenylmethylene chloride converts disodiobenzophenone into α-benzpinacolin, yet with disodiofluorenone it gives 10-keto-9 : 9-diphenyl-9 : 10-dihydrophenanthrene, m. p. 193—194°. Similarly, 9 : 9-dichlorofluorene and disodiofluorenone afford 10-keto-9 : 9-diphenylylene-9 : 10-dihydrophenanthrene. On the other hand, disodiobenzophenone and dichlorofluorene give, besides the expected *diphenylylene diphenylethylene oxide*, m. p. 228°, two stereoisomeric 9-diphenylmethylenefluorenes, one, m. p. 225°, also obtained by heating 9-benzhydrylfluorenol with acetyl chloride, identical with that

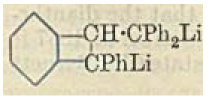
already known, the *isomeride* having m. p. 213°. Both on reduction afford 9-diphenylmethylfluorene, also formed by the action of sodium, followed by alcohol, on the isomeride, m. p. 225°. Mercury converts the sodium compounds of either isomeride into the hydrocarbon of higher m. p. When the above oxide, m. p. 228°, is heated with acetyl chloride it gives the two hydrocarbons, together with 9-benzoyl-9-phenylfluorene (proof of constitution).

Fluorenone is converted by magnesium *iso*propyl chloride into 9-*fluorenyl*iso*propylcarbinol*, m. p. 124°, transformed by way of the chloride (pyridine) into 9-iso*propylidenefluorene*, m. p. 113°, stereoisomeric with Courtot's compound, m. p. 89° (A., 1916, i, 475). 9-Fluorenyldiphenylcarbinol is converted by boiling acetyl chloride into the diphenylmethylenefluorene, m. p. 225°, which, together with its isomeride and the last-named carbinol, are formed when benzophenone acts on 9-lithiofluorene.

III. New type of compound with bivalent carbon. [With B. Benedikt and A. Wiegandt.]—Tetraphenylallene reacts readily with sodium (potassium also reacts) to give the *radical*, $CPh_2Na\cdot C\cdot CPh_2Na$, converted by alcohol into $\alpha\alpha\gamma\gamma$-tetraphenylpropylene, $CHPh_2\cdot CH{:}CPh_2$, no doubt by way of the free radical $CHPh_2\cdot C\cdot CHPh_2$. Carbon dioxide converts the sodium compound into the *sodium* salt, $CO_2Na\cdot CPh_2\cdot C\cdot CPh_2\cdot CO_2Na$, the aqueous solution of which soon deposits the *sodium* salt ($+3H_2O$) of *$\alpha\alpha\gamma\gamma$-tetraphenylvinylacetic acid*, $CPh_2{:}CH\cdot CPh_2\cdot CO_2H$, m. p. 179°. *Ethyl* β-*phenylcinnamate*, b. p. 207°/17 mm., from benzophenone and ethyl bromoacetate (Posner, A., 1911, i, 52), decomposing the intermediate hydroxy-ester by Rupe's method (cf. A., 1914, i, 281, and previous papers), is converted by magnesium phenyl bromide into $\alpha\alpha\gamma\gamma$-tetraphenylallyl alcohol, and the latter is converted into the ethyl ether (Ziegler, A., 1924, i, 308). Treatment of the ether with sodium, followed by carbon dioxide, gives the sodium salt ($+3H_2O$) and the acid, m. p. 179°, the constitution of which is thus proved.

The behaviour of various reagents towards the disodium compound (A) from tetraphenylallene and the monosodium compound, $CPh_2Na\cdot CH{:}CPh_2$ (B), obtained from the last-named ether and sodium has been compared. Methyl iodide converts A or B at the ordinary temperature into *$\alpha\alpha\gamma\gamma$-tetraphenyl-γ-methylpropylene* (*$\alpha\alpha\gamma\gamma$-tetraphenyl-Δ^{α}-butene*), $CPh_2Me\cdot CH{:}CPh_2$, m. p. 111°, which does not decolorise bromine nor undergo catalytic hydrogenation, whereas 9-ββ-diphenylvinyl-9-ethylxanthen, $O{<}{C_6H_4 \atop C_6H_4}{>}CEt\cdot CH{:}CPh_2$, is readily hydrogenated to 9-ββ-*diphenylethyl*-9-*ethylxanthen*, m. p. 118—119°. At temperatures not above −20°, A is converted by methyl iodide into tetraphenylallene (C), whilst B gives the above propylene. Both A and B react with chloromethyl ether to give *δ-methoxy-$\alpha\alpha\gamma\gamma$-tetraphenyl-Δ^{α}-butene*, m. p. 124—125°, readily hydrogenated to *methyl ββδδ-tetraphenylbutyl ether*, m. p. 87·5—89°. Methyl chloroformate reacts with A, giving *methyl $\alpha\alpha\gamma\gamma$-tetraphenylvinylacetate*, m. p. 117—118°, also obtained by treating the corresponding acid with diazomethane. Ethylthiocarbimide converts A or B into the *thioethylamide*, m. p. 171—173°, of the last acid. $\alpha\gamma$-Dibromopropane converts A into C, but B into *ζ-bromo-$\alpha\alpha\gamma\gamma$-tetraphenyl-Δ^{α}-hexene*, m. p. 120—121°. Iodine converts A into C, and B into a *hydrocarbon*, $C_{27}H_{22}$, m. p. 129—130°, possibly a triphenylhydrindene. Mercury has no action on A, further evidence in support of its assumed structure.

Lithium reacts with tetraphenylallene to give a product (annexed formula) which with alcohol affords



1-*phenyl*-2-*diphenylmethylbenz*cyclo*butene*, m. p. 184°, which exhibits interesting colour reactions with acids, and gives, as the main product of bromination, a *tribromo*-derivative, m. p. 212° (decomp.). The *cyclo*butene does not combine, but reacts, with sodium, the product giving, with carbon dioxide, an *acid*, $C_{27}H_{21}\cdot CO_2H$, m. p. not below 300°. Lithium ethyl converts the butene into its *lithio*-derivative, $C_{27}H_{21}Li$. The *cyclo*butene is readily hydrogenated to a *hexahydro*-derivative, $C_{27}H_{28}$, the fused benzene ring being the one reduced (reasons given). The original dilithium compound is converted by iodine in benzene or by mercury into a *hydrocarbon*, $C_{27}H_{20}$, m. p. 186°, not reducible catalytically, although converted by sodium and amyl alcohol or by phosphorus and hydriodic and acetic acids into a *hydrocarbon*, $C_{27}H_{22}$, m. p. 167—168°. The hydrocarbon, m. p. 186°, when treated first with sodium and then with alcohol, gives a *hydrocarbon*, $C_{27}H_{22}$, m. p. 103°.

2 : 3-Diphenylindone (preparation improved) with magnesium phenyl bromide affords 1-hydroxy-1 : 2 : 3-triphenylindene (Kohler, A., 1908, i, 777), reduced by phosphorus and hydriodic and acetic acids to 1 : 2 : 3-*triphenylhydrindene*, m. p. 153°. 1 : 2 : 3-Triphenylindene (Kohler) is obtainable by treating its 1-methoxy-derivative with sodium and the product with alcohol. *Diphenylbenzylacetyl chloride*, m. p. 90—91°, in presence of aluminium chloride and carbon disulphide, passes into a product which, after treatment with magnesium phenyl bromide, gives 1-*hydroxy*-1 : 2 : 2-*triphenylhydrindene*, m. p. 172—173°. The latter, when reduced (phosphorus method), affords 1 : 2 : 2-*triphenylhydrindene*, m. p. 142°, also obtained by the action at 140° of acetic anhydride and a little sulphuric acid on 1 : 2 : 2 : 3-*tetraphenylpropyl alcohol*, m. p. 141—142°, the latter being obtained by treating the product of the action of sodium on the methyl ether of diphenyldibenzylcarbinol with benzaldehyde:

$$CH_2Ph\cdot CPh_2\cdot OMe \longrightarrow CH_2Ph\cdot CPh_2Na \longrightarrow CH_2Ph\cdot CPh_2\cdot CHPh\cdot OH \longrightarrow \text{triphenylhydrindene.}$$

When $\alpha\alpha\beta\gamma$-tetraphenylpropane-$\alpha\beta$-diol is treated with acetyl chloride it gives benzyl triphenylmethyl ketone (obtained by Orekhov, A., 1919, i, 272, by treating the diol with sulphuric acid) together with 1 : 2 : 2 : 3-tetraphenylpropyl alcohol (obtained by a third process, see above, by treating with benzoyl chloride the product of the action of sodium on the methyl ether of diphenylbenzylcarbinol) and a *substance*, m. p. 126—127°, which may be 2-hydroxy-1 : 1 : 2-triphenylhydrindene.

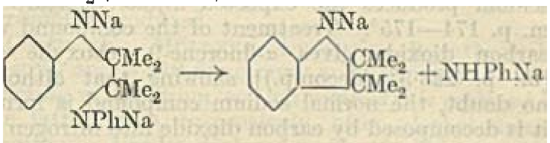
Diphenyl-*o*-tolylmethyl chloride, best obtained from the corresponding carbinol by passing hydrogen chloride into a benzene solution of the latter containing acetyl chloride, is converted by sodium amalgam into a sodio-compound, which with carbon dioxide affords *diphenyl*-o-*tolylacetic acid*, m. p. 240° (*ethyl* ester, from the sodio-compound and ethyl chloroformate, has m. p. 100—101°). The corresponding acid *chloride*, m. p. 86·5—87°, does not undergo ring-closure ($\cdot COCl + CH_3\cdot \longrightarrow \cdot CO\cdot CH_2\cdot$) when treated with boiling pyridine, but merely passes into the acid *anhydride*, m. p. 197°.

Methyl s-*diphenylethane*-2-*carboxylate*, b. p. 195—196°/25 mm., reacts with magnesium phenyl bromide to produce o-β-*phenylethylphenyldiphenylcarbinol*, $CH_2Ph\cdot CH_2\cdot C_6H_4\cdot CPh_2\cdot OH$, m. p. 103°, convertible into the corresponding *chloride*, m. p. 128—130°. When the latter is heated with quinoline at 150° it affords 1 : 1 : 2-*triphenylhydrindene*, m. p. 83°.

The following hydrocarbons were prepared during the investigation of the above *benzcyclobutene*. 9-*Diphenylmethyl*-9 : 10-*dihydroanthracene*, m. p. 207·5°, is formed by sodium–amyl alcohol reduction of 9-diphenylmethylanthrone. 9-ββ-*Diphenylethylfluorene*, m. p. 107°, is obtained by similar reduction of 9-ββ-*diphenylvinylfluorene*, m. p. 111—112°, which is formed by the action of boiling pyridine on the 9-β-chloro-compound corresponding with 9-β-*hydroxy*-ββ-*diphenylethylfluorene*, $C_{12}H_8\colon CH\cdot CH_2\cdot CPh_2\cdot OH$, m. p. 121°, the latter being prepared from magnesium phenyl bromide and ethyl fluorenylacetate. 9 : 10-*Diphenyl*-9-*methyl*-9 : 10-*dihydroanthracene*, m. p. 171°, is formed by reducing (phosphorus and hydriodic and acetic acids) 10-hydroxy-9 : 10-diphenyl-9-methyl-9 : 10-dihydroanthracene, m. p. 183—184°, this substance being prepared by treatment with methyl iodide of the sodio-compound formed by the action of sodium on 9-hydroxy-10-methoxy-9 : 10-diphenyldihydroanthracene. 9-Methoxy-9-phenylanthrone is reduced (sodium and amyl alcohol) to 9-phenyl-9 : 10-dihydroanthracene (m. p. 87°, above). The *hydrazone*, m. p. 142°, of the last-named anthrone is converted by sodium ethoxide into 9-phenylanthracene. 9-*Phenyl*-10-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 119° is formed by treating, first with sodium and then with alcohol, 9-phenyl-10-benzylanthracene (m. p. 151°; lit. 155°). The latter is obtained by phosphorus and hydriodic acid–acetic acid reduction of 10-*hydroxy*-9-*methoxy*-9-*phenyl*-10-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 151°, formed when magnesium benzyl chloride reacts with methoxyphenylanthrone.

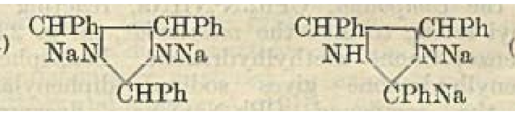
IV. Addition of sodium to carbon–nitrogen and to nitrogen–nitrogen double linkings. Acetophenone anil and sodium afford the *compound* CPhMeNa·NPhNa, converted by alcohol into phenyl-α-phenylethylamine, and by carbon dioxide into the *sodium* salt, $CO_2Na\cdot CPhMe\cdot NPh\cdot CO_2Na$. Fluorenone anil (9-anilofluorene) similarly gives rise to 9-anilinofluorene and 9-*anilinofluorene*-9-*carboxylic acid*, m. p. 217°. Benzylidene-ethylamine gives benzylethylamine, and acetophenone-benzylimide gives α-phenylethylbenzylamine. Fluorenoneimine (9-iminofluorene) gives a sodium compound decomposed by alcohol into iminofluorene and occasionally a little 9 : 9-difluorenylamine, and giving by the carbon dioxide process not the expected acid, which is very unstable, but 9-aminofluorene. Acetone anil affords (sodium, followed by alcohol) 2 : 2 : 3 : 3-tetramethylindoline (?), m. p. 39°, b. p. 148—149°/21 mm. (cf. Knoevenagel, A., 1922, i, 1060), and aniline, so that the original action of sodium is probably :

$2NPh\colon CMe_2 + 2Na \longrightarrow$



Similarly treated, the anil of methyl ethyl ketone gives aniline, methane, and 3-*methyl*-2 : 3-*diethyl*iso*indole*, b. p. 152—153°/12 mm. (*methiodide*. m. p. 242°).

[With R. Israel.]—Hydrobenzamide and sodium give the *compound* of formula (A), converted by alcohol into 2 : 4 : 5-*triphenyltetrahydroglyoxaline*, m. p. 270—271° (*hydrochloride*), also obtained from the

(A)  (B)

disodium compound (B) formed by amarine, or by the catalytic hydrogenation of the latter. Acridine and sodium give two compounds, the formulae of which follow from the fact that 5 : 10-dihydroacridine and *tetrahydro*-5 : 5′-*diacridyl*, m. p. 279°, result by treatment with alcohol. The diacridyl is apparently identical with that known to be formed when acridine is reduced with sodium amalgam and alcohol, which has hitherto been regarded as the 10 : 10′-compound. When the acridine–sodium compound is treated with benzoyl chloride, there is formed, as the least soluble product, NN′-*dibenzoyltetrahydro*-5 : 5′-*diacridyl*, m. p. 305°. Again, sodium–carbon dioxide treatment of acridine gives 5 : 10-*dihydroacridine*-5-*carboxylic acid*, m. p. 229° (decomp.), and evidently also the *NN*′-dicarboxylic acid of the diacridyl, for this substance is deposited shortly after the reaction product is dissolved in water.

5-Phenylacridine adds 2 atoms of sodium in the 5- and 10-positions, so that alcohol converts the product into 5 : 10-dihydroacridine, and carbon dioxide affords 5-*phenyl*-5 : 10-*dihydroacridine*-5-*carboxylic acid*, m. p. 225—227° (decomp.). Lophine (2 : 4 : 5-triphenylglyoxaline) reacts with sodium to give the 1-*sodio*-derivative and hydrogen. Treatment with carbon dioxide therefore regenerates lophine.

Phenazine reacts with sodium, but the product is unworkable. When the sodium ketyl prepared from phenyl diphenylyl ketone is added to phenazine in ether there is formed the additive *compound* of phenazine (1 mol.) with 5 : 10-disodio-5 : 10-dihydrophenazine (1 mol.). This, and the analogous *dipotassio*-additive compound, are converted by water into the known phenazine–dihydrophenazine additive compound (the so-called " quinhydrone ").

Acetophenone ketazine, CPhMe:N·N:CPhMe, combines with sodium to give the *compound* CPhMeNa·NNa·NNa·CPhMeNa. The similar *compound* from benzophenone ketazine, when decom-

posed with alcohol in an inert atmosphere, gives *s*-dibenzhydrylhydrazine, m. p. 138° (sinters 131°). Darapsky, who obtained only the impure hydrazine, gives m. p. 120—123° (A., 1903, i, 367). The normally derived *sodium* salt of the tetracarboxylic acid is described. Fluorenone ketazine and sodium give a compound the (alcohol) decomposition of which only seldom produces the expected *difluorenylhydrazine*, m. p. 174—175°. Treatment of the compound with carbon dioxide gives α-fluorene-9-carboxylic acid [m. p. 223·5° (decomp.)], showing that although, no doubt, the normal sodium compound is formed, it is decomposed by carbon dioxide into nitrogen and the above acid.

[With A. MICHAEL.]—Benzylideneazine forms the *disodium* compound, $(CHPh{:}N{\cdot}NNa{\cdot}CHPh{\cdot})_2$, converted by carbon dioxide into the *sodium* salt of the expected dicarboxylic acid and by alcohol into the expected *NN'-dibenzylidene-αβ-diphenylethane-αβ-dihydrazine*, m. p. 117—118°.

Benzophenone hydrazone is converted by sodium into the *compound*, $CPh_2{:}N{\cdot}NHNa$, reacting with methyl iodide to give the *methiodide*, m. p. 226·5°, of benzophenone methylhydrazone. Benzophenone diphenylhydrazone gives sodium diphenylamine and the *compound* $CPh_2Na{\cdot}NNa_2$, decomposed (alcohol) into benzhydrylamine. Benzophenone phenylhydrazone behaves similarly. The *anil* formed from benzophenone and benzhydrylamine has m. p. 153°. Decomposition of the original sodium compound–ether mixture with carbon dioxide gave aniline, the anil and *benzhydrylammonium carbonate*, which when heated in ethyl acetate (or alone at 56°) is converted into a substance, $(C_{15}H_{17}O_2N)_x$, m. p. 145°, evidently identical with the supposed tribenzhydrylamine obtained by decomposition of benzhydrylammonium carbamate. Benzophenone phenylmethylhydrazone behaves similarly to the phenylhydrazone.

Azomethane gives the *compound*, $NMeNa{\cdot}NMeNa$, convertible into hydrazomethane or into the *sodium* salt of hydrazomethane-NN'-dicarboxylic acid. Tetraphenyltetrazine and sodium give nitrogen and sodiodiphenylamine (2 mols.).

[With R. ISRAEL and H. WILLSTADT.]—The above product from sodium and benzophenone anil reacts with mercury, methyl iodide, benzoyl chloride, ethyl benzoate, or phenylthiocarbimide, giving the original anil. The product from sodium and benzylideneaniline is unaffected by mercury, is converted by phenylthiocarbimide into (the *disodium* derivative of) *αβ-bis-s-diphenylthiocarbamido-αβ-diphenylethane*, $(NHPh{\cdot}CS{\cdot}NPh{\cdot}CHPh{\cdot})_2$, m. p. 263°, by methyl iodide into *αβ-bismethylanilino-αβ-diphenylethane*, $(NPhMe{\cdot}CHPh{\cdot})_2$, m. p. 127°, by diphenylmethylene chloride into tetraphenylethylene, and by ethyl benzoate or benzaldehyde into the *compound*, $\begin{matrix}CHPh{\cdot}NPh\\ |\quad\ \ |\\ CHPh{\cdot}NPh\end{matrix}$, m. p. 153—154°.

V. Experiments with triphenylmethyl and sodium triphenylmethyl. [With C. BRESIEWICZ and H. ENDER.]—Sodium triphenylmethyl reacts with nitrous oxide in ethereal solution to give the red *sodium triphenylmethyl diazotate*, $CPh_3{\cdot}N{:}N{\cdot}ONa$. Continued action of nitrous oxide produces a yellow substance, which is being investigated. The diazotate is violently decomposed by alcohol, triphenylcarbinol being formed. Water produces a tar.

When nitric oxide is passed into an ethereal solution of sodium triphenylmethyl, a bluish-red *compound* separates (not more than 1 mol. of oxide must be used) which may be either $CPh_3{\cdot}N{\cdot}ONa$ or $CPh_3{\cdot}NNa{:}O$.

If more nitric oxide is passed into the suspension, the bluish-red compound is replaced by a bright yellow sodium salt, A. If sodium amalgam is present, the bluish-red compound is still produced, but passes later into a second bright yellow sodium salt, B, the solution then being bluish-green. Either A or B, when treated in ethereal suspension with sodium amalgam, affords sodium triphenylmethyl and sodium hyponitrite. Acidification of an aqueous solution of A produces triphenylcarbinol and nitrous oxide, whilst B under similar conditions affords the corresponding acid, which undergoes conversion into carbinol etc. only on long keeping or on warming. A and B are regarded as being the sodium salts of *syn-* and *anti*-forms of iso*nitrosotriphenylmethylhydroxylamine*, respectively:

$$\text{(A)}\ \begin{matrix}CPh_3{\cdot}N{:}O\\ \|\\ NaO{\cdot}N\end{matrix} \qquad \text{B)}\ \begin{matrix}CPh_3{\cdot}N{:}O\\ \quad\ \ N{\cdot}ONa\end{matrix},$$

whilst the true triphenylmethylnitrosohydroxylamine is probably present in the bluish-green solution mentioned above. A crystallises $+EtOH$ or $+C_6H_6$ and may be converted into the *silver*, *mercuric*, *cupric*, *ferric*, and *lead* salts. B crystallises $+EtOH$, and gives rise to salts (identical with the above ?) of other metals.

[With C. BRESIEWICZ and E. RUBENS.]—When an ethereal solution of triphenylacetyl chloride is added to one of sodium triphenylmethyl, *hexaphenylacetone* (*bistriphenylmethyl ketone*), $CPh_3{\cdot}CO{\cdot}CPh_3$, m. p. 80—81° results. In presence of excess of the sodium compound it passes into a brownish-red, crystalline *ketyl*, $CPh_3{\cdot}C(CPh_3){<}_{ONa}$, which may be decomposed into hexaphenylacetone and *hexaphenyl*iso*propyl alcohol* (not described).

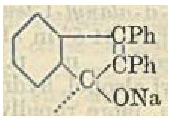
[With W. STOFFERS.]—Sodium triphenylmethyl undergoes the following reactions: (1) Ethylthiocarbimide gives the *ethylamide*, m. p. 143°, of triphenylthioacetic acid. (2) Phenylthiocarbimide gives *triphenylthioacetanilide*, m. p. 157°. (3) Allylthiocarbimide gives the *allylamide*, m. p. 131—132°, of trithioacetic acid. (4) Phenylcarbimide gives triphenylacetanilide. (5) Ethyl chloroformate gives ethyl triphenylacetate. (6) Acetyl, *iso*propyl, or *tert.*-butyl chloride gives triphenylmethane. (7) Chloromethyl ether gives *βββ-triphenylethyl methyl ether*, m. p. 137°.

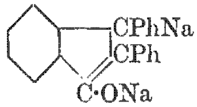
Sodium diphenylmethyl, readily obtained by treating benzhydryl methyl ether with powdered sodium in ether (cf. Ziegler and Thielmann, A., 1923, i, 921), gives the following reactions: (1) Phenylthiocarbimide gives diphenylthioacetanilide. (2) Benzophenone gives *ααββ-tetraphenylethyl alcohol*, m. p. 236°. (3) Fluorenone gives *9-hydroxy-9-diphenylmethylfluorene*, m. p. 183°.

[With T. KOHLER.]—Pure sodium diphenylmethyl is obtained if mercury dibenzyl is converted in benzene

into sodium benzyl, and this is digested with diphenylmethane.

VI. Diarylketone-alkali metal additive compounds. [With E. MÜLLER.]—2 : 3-Diphenylindone is converted by sodium in ether first into the *ketyl* and then into the *disodium* compound,





Alcohol converts the second compound into 2 : 3-diphenyl-1-hydrindone, methyl iodide affords 2 : 3-*diphenyl*-2 : 3-*dimethyl*-1-*hydrindone*, m. p. 166—167°, and carbon dioxide gives 2 : 3-*diphenyl*-1-*hydrindone*-3-*carboxylic acid*, m. p. 181° (decomp.).

[With H. WILLSTADT.]—Phenyl diphenylyl ketone sodium mono- and di-ketyls react with phenylthiocarbimide to give the compound, NPhNa·CS·CS·NPhNa (cf. I*e*, above).

[With A. KNORR.]—Benzyl chloride reacts with the disodium derivative of benzophenone according to the scheme : $CAr_2Na{\cdot}ONa(+R{\cdot}X) \longrightarrow CAr_2R{\cdot}ONa$, and with that of phenyl diphenylyl ketone thus: $CAr_2Na{\cdot}ONa(+2R{\cdot}X) \longrightarrow CAr_2R{\cdot}OR$. Diphenylbenzylcarbinol is the product of the first and the *benzyl ether*, m. p. 164—165°, of *phenyl*-4-*diphenylylbenzylcarbinol* that of the second reaction. This carbinol, formed by the interaction of magnesium benzyl chloride and phenyl diphenylyl ketone, has m. p. 129—130° and is converted by benzyl alcohol, benzene, and hydrogen chloride not into the above ether, but into αβ-*diphenyl*-α-4-*diphenylylethylene*, m. p. 134—135°. Methyl iodide reacts less simply with the disodium derivative of phenyl diphenylyl ketone, the products being : (1) *phenyldiphenylylmethylcarbinol*, (2) the corresponding methyl ether, (3) p-*tolyl* 4-*diphenylyl ketone*, m. p. 133—134°, converted by sodium, followed by alcohol, into 4-*phenyl*-4′-*methylbenzhydrol*, m. p. 110°, and also obtainable from diphenyl and *p*-toluoyl chloride in presence of aluminium chloride. The carbinol and ether (1 and 2) are not isolable, but their presence is shown by the conversion of the mixture into as-*phenyldiphenylylethylene*, m. p. 94°. The carbinol (1), m. p. 105—106°, is obtainable from phenyl diphenylyl ketone and magnesium methyl iodide, and readily affords the *methyl ether*, m. p. 117°. 2-*Phenylbenzophenone* (*phenyl* 2-*diphenylyl ketone*), synthesised for comparison purposes, has m. p. 90°, and results when magnesium phenyl bromide reacts with 2-*cyanodiphenyl*, m. p. 41°, b. p. 175°/13 mm. The latter is formed from phosphorus pentachloride and *diphenyl*-1-*carboxylamide*, m. p. 176°, obtained from the corresponding *chloride*, b. p. 169°/16 mm.

VII. Some scissions using alkali metals. [With H. WILLSTADT.]—When powdered sodium is used for the scission of benzophenone dimethylacetal in place of the potassium–sodium alloy used by Ziegler and Thielmann (*loc. cit.*) (these authors decomposed the product with carbon dioxide and obtained benzilic acid methyl ether), there is formed, after decomposition by alcohol, diphenylmethylcarbinol. Decomposition with carbon dioxide produces some benzilic acid and some of its methyl ether, whilst mercury produces diphenylmethylcarbinol. The scission reaction must therefore be : $CPh_2(OMe)_2 \longrightarrow CPh_2{\cdot}CNa{\cdot}OMe \longrightarrow CPh_2{\cdot}CMe{\cdot}ONa$, the intermediate compound accounting for the benzilic acid, etc.

Although it was expected that sodium would convert benzpinacolin diphenyl ether into benzpinacol diphenyl ether, the latter is not isolated, but passes into the compound $CPh_2{\cdot}CNa{\cdot}OPh$, so that triphenylcarbinol is produced.

[With E. MÜLLER.]—Similarly, 9-methoxy-10-phenyl- and 9 : 10-dimethoxy-anthracene, instead of reacting with sodium, so that methoxyl is replaced by the latter, give, respectively, after alcohol decomposition, 10 : 10′-*diphenyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl*, m. p. 260° (also obtained by the sodium–alcohol process from 10 : 10′-diphenyl-9 : 9′-dianthranyl), and 9-hydroxy-10-methoxyanthracene (isolated as the benzoate). Iodine converts the second sodium product into dimethoxydianthrone.

E. E. TURNER.

Quantitative analysis of organo-lead compounds. H. GILMAN and J. ROBINSON (J. Amer. Chem. Soc., 1928, **50**, 1714—1716).—Derivatives in which lead is directly attached to aryl groups cannot be satisfactorily analysed by existing methods (cf. Grüttner and Krause, A., 1916, i, 684 ; Calingaert, A., 1925, i, 798). Correct results are obtained by oxidising the sample (0·5 g.) by means of sulphuric and nitric acids (cf. Noyes and Bray, A., 1907, ii, 391), completely removing the nitric acid, and separating the lead sulphate in the usual way.

H. E. F. NOTTON.

Hydrolysis of polypeptides by *N*-alkali and by the enzymes of the pancreas. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1928, **9**, 430—438).—The *chloroacetyl*, m. p. 136—137° ; *glycyl*, m. p. 241—242° ; dl-α-*bromopropionyl*, m. p. 157—158° ; dl-*alanyl*, m. p. 254—255° (decomp.) ; *benzoyl*, m. p. 189—190° ; d-α-*bromo*-γ-*methylvaleryl*, m. p. 150—152° (decomp.), $[\alpha]_D^{20}$ −33·2° in alcohol, and l-*leucyl*, m. p. 240° (decomp.), derivatives of *dl*-α-aminobutyryl-*dl*-α-aminobutyric acid are prepared by the usual methods, also *chloroacetyl*-dl-*leucyl*-dl-α-*aminoheptoic acid*, m. p. 147·5°, and *glycyl*-dl-*leucyl*-dl-α-*aminoheptoic acid*, m. p. 240° (decomp.). The dipeptide and the *l*-leucyl tripeptide are not hydrolysed by *N*-sodium hydroxide in 123 hrs. at 37° (cf. this vol., 81) ; in the cases of the glycyl and alanyl derivatives, glycine and alanine are eliminated. The benzoyl derivative is hydrolysed slowly, without formation of free benzoic acid. Of glycyl- and *dl*-leucyl-*dl*-aminoheptoic acids, the former is hydrolysed but not the latter. Glycine is slowly eliminated from glycyl-*dl*-leucyl-*dl*-α-aminoheptoic acid. Since *dl*-α-aminobutyryl-*dl*-α-aminobutyric acid is decomposed in part by pancreas enzymes, it would appear to be a mixture of the *dd*- and *ll*-modifications, not of *dl*- and *ld*-forms. Pancreas enzymes do not hydrolyse the benzoyl derivative, but the glycyl- and alanyl-tripeptides are attacked, the former more slowly, the latter more rapidly than by alkali.

F. E. DAY.

Enzymic decomposition of polypeptides containing *l*-hydroxyproline. E. ABDERHALDEN and W. KOPPEL (Fermentforsch., 1928, **9**, 439—445).—The following substances have been prepared.

Chloroacetyl-l-*hydroxyproline*, m. p. 160°; *glycyl*-l-*hydroxyproline*, m. p. 215°, $[\alpha]_D^{20}$ −50·79° in water; dl-α-*bromo*-γ-*methylvaleryl*-l-*hydroxyproline*, m. p. 155°; dl-*leucyl*-l-*hydroxyproline*, m. p. 234°, $[\alpha]^{20}$ −36·97° in water. Glycyl-*l*-hydroxyproline is hydrolysed by erepsin, but not by pepsin or trypsin. None of these enzymes attacks *dl*-leucyl-*l*-hydroxyproline. *N*-Hydrochloric acid is practically without action on either dipeptide at 37°, at which temperature *N*-sodium hydroxide hydrolyses glycyl-*l*-hydroxyproline, but not the leucyl compound. During the preparation of *dl*-leucyl-*l*-hydroxyproline, a substance, m. p. 168°, was isolated, apparently *hydroxy*-γ-*methylvaleryl*-l-*hydroxyproline*. F. E. DAY.

Enzymic decomposition of polypeptides. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1928, 9, 446—461).—Improvements in the methods for preparing *d*-alanine, *d*-α-bromo-γ-methylvaleryl chloride, and *l*-α-bromopropionyl chloride are described, and from these the synthesis of *glycyl*-d-*alanyl*-l-*leucylglycyl*-d-*alanine* has been carried out. Chloroacetyl-*d*-alanine and its ammonium salt, from which glycyl-*d*-alanine is obtained by heating with alcoholic ammonia: *d*-α-bromo-γ-methylvalerylglycyl-*d*-alanine, m. p. 132—133°, $[\alpha]_D^{20}$ +31·2°±0·3° in alcohol; these constants are higher than those given by Fischer (A., 1909, i, 366) and *d*-α-bromo-γ-methylvaleramide was isolated as a by-product. Next *l*-leucylglycyl-*d*-alanine and its d-α-*bromoisopropionyl* derivative, m. p. 157—158°, $[\alpha]_D^{20}$ +12·9° in alcohol, −27·95° in water, d-*alanyl*-l-*leucylglycyl*-d-*alanine* (decomp. 240°), $[\alpha]_D^{17}$ −28·0° in water, *chloroacetyl*-d-*alanyl*-l-*leucylglycyl*-d-*alanine*, m. p. 143—147°, $[\alpha]_D^{20}$ −45·5° in alcohol, and finally glycyl-*d*-alanyl-*l*-leucylglycyl-*d*-alanine, decomp. 232°, $[\alpha]_D^{20}$ −70·6° in water. The pentapeptide is precipitated by saturated ammonium sulphate and gives a strong red biuret reaction. At 37° it is rapidly hydrolysed by trypsin (p_H 8·4) and by *N*-sodium hydroxide, less rapidly by erepsin (p_H 7·8), and only slightly by *N*-hydrochloric acid.

Trypsin is without action on *l*-leucylglycyl-*d*-alanine, which is rapidly hydrolysed by erepsin, mainly at the leucyl–glycyl linking; *d*-alanyl-*l*-leucylglycyl-*d*-alanine is hydrolysed by both enzymes at a moderate rate. The results may be to some extent vitiated by imperfect separation of the enzymes, but are confirmatory of the hydrolysis of pentapeptides by trypsin (cf. Waldschmidt-Leitz, Grassmann, and Schlatter, A., 1927, 1112). F. E. DAY.

Enzymic decomposition of polypeptides of various composition. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, 9, 462—484).—The preparation of the following substances and the action of erepsin and trypsin on the polypeptides are described: *d*-α-bromo-γ-methylvaleryl-*d*-valine; *l*-leucyl-*d*-valine, hydrolysed by erepsin but not by trypsin; *d*-α-*bromopropionyl*-l-*leucyl*-d-*valine*, m. p. 165°, $[\alpha]_D$ −34° in alcohol; *d*-*alanyl*-l-*leucyl*-d-*valine*, m. p. 243—245° (decomp.), $[\alpha]_D^{17}$ −60° in water, readily hydrolysed by erepsin, but not by trypsin; a second modification of this substance having similar physical properties, except that its solubility in water at 18° is 4·1 g. per 100 c.c., against 0·44 g. of the chief product, and probably a stable mixture of optical isomerides, unacted on by erepsin; *chloroacetyl*-l-*alanyl*-l-*leucyl*-d-*valine*, m. p. 204—205°, $[\alpha]_D^{20}$ −69·6° in alcohol; *glycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 240° (decomp.), $[\alpha]_D^{17}$ −98° in water (+$2H_2O$), hydrolysed by erepsin, little if at all by trypsin; d-α-*bromo*-γ-*methylvalerylglycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 187° (decomp.), $[\alpha]_D^{19}$ −34·5° in alcohol; l-*leucylglycyl*-d-*alanyl*-l-*leucyl*-d-*valine*, m. p. 205° (decomp.), $[\alpha]_D^{16}$ −60·4° in methyl alcohol, hydrolysed both by erepsin and by trypsin, more rapidly by a mixture of both enzymes. An attempt to deduce the point of enzymic attack by observation of change of α_D was unsuccessful. F. E. DAY.

Action of erepsin and trypsin on polypeptides containing *d*-glutamic acid. E. ABDERHALDEN and E. ROSSNER (Fermentforsch, 1928, 9, 494—500).—In preparing glycyl-*d*-glutamic acid, the intermediate chloroacetyl-*d*-glutamic acid is best purified as the ammonium salt. d-α-*Bromo*-γ-*methylvalerylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +24·6° in methyl alcohol, is converted into l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ 25·4° in water, by treatment with 25% aqueous ammonia, since alcoholic ammonia leads to anhydride formation. This compound gives a positive ninhydrin reaction, a bluish-violet biuret reaction, and is not precipitated by saturated ammonium sulphate. It is widely disintegrated by *N*-sodium hydroxide and by 5*N*-hydrochloric acid at 37°; one CO–NH linking is broken by erepsin, but trypsin has practically no action. *l*-Leucyl- and *dl*-leucyl-*d*-glutamic acids are only very slowly and slightly attacked by *N*-alkali, erepsin, or trypsin. Glycyl-*d*-glutamic acid is hydrolysed by *N*-alkali, 5*N*-hydrochloric acid, and erepsin, but not by trypsin. The action of extract of dried pancreas on *l*-leucyl- and glycyl-*d*-glutamic acids is similar to that of erepsin. F. E. DAY.

Enzymic decomposition of polypeptides by erepsin and by trypsin-kinase. Polypeptides containing *l*-cystine. E. ABDERHALDEN and W. KOPPEL (Fermentforsch., 1928, 9, 516—523).—By the usual methods the authors prepared di-(*d*-alanyl)-*l*-cystine, *di*-(d-α-*bromoisovaleryl*-d-*alanyl*)-l-*cystine*, m. p. 155°, $[\alpha]_D^{18}$ −18·6° in alcohol; *di*-(d-*valyl*-d-*alanyl*)-l-*cystine*, $[\alpha]_D^{19}$ −102·6° in *N*-hydrochloric acid; *di*-(d-α-*bromopropionyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, m. p. 163°, $[\alpha]_D^{20}$ +13·4° in alcohol; *di*-(d-*alanyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, $[\alpha]_D$ − 79·4° in *N*-hydrochloric acid, precipitated by ammonium sulphate; *di*-(d-α-*bromo*-γ-*methylvaleryl*-d-*alanyl*-d-*valyl*-d-*alanyl*)-l-*cystine*, m. p. 164°, $[\alpha]_D^{19}$ +34·3° in alcohol; di-(*l*-leucyl-*d*-alanyl-*d*-valyl-*d*-alanyl)-*l*-cystine, $[\alpha]_D^{18}$ −74·6 in *N*-hydrochloric acid. Erepsin acted rapidly on the tri- and penta-peptides, less strongly on the heptapeptide, not at all on the nonapeptide. The last was attacked readily by trypsin-kinase, the heptapeptide still more vigorously. The tripeptide was not affected, and the pentapeptide only comparatively slowly by trypsin-kinase. The action of these enzymes on di-(*l*-leucyl)-*l*-cystine, di-(*l*-leucylglycyl)-*l*-cystine, and di-(*l*-leucyl-*d*-alanine)*l*-cystine was similar to that on the above tri- and penta-peptides. F. E. DAY.

Specific adaptation of polypeptidases. E. Abderhalden and E. Schwab (Fermentforsch., 1928, **9**, 501—515).—In continuation of previous attempts to determine the molecular groupings attacked by different enzymes (cf. A., 1927, 1112), the phenylcarbamido-compounds of *dl*-leucylglycine, *glycyl*-dl-*α-aminoheptoic acid*, m. p. 181°, *glycyl*-dl-*α-amino*-n-*octoic acid*, m. p. 185°, *glycyl*-l-*tyrosine*, decomp. about 128°, glycyl-*dl*-serine, *dl*-leucylglycylglycine, and l-*leucylglycyl*-l-*leucine*, an oil, were submitted to the action of erepsin and of trypsin-kinase. All were hydrolysed by the latter, not by the former. Naphthalene-2-sulphonyl derivatives of glycyl-*dl*-leucine, *dl*-leucylglycine, glycyl-*l*-tyrosine, and *glycyl*-dl-*phenylalanine* were hydrolysed by trypsin-kinase, but not naphthalene-2-sulphonylglycylglycine. The latter, also the β-naphthalenesulphonyl derivativesof glycyl-*dl*-leucine and *dl*-leucylglycine, were not hydrolysed by erepsin. Neither enzyme acted on carbethoxyglycylglycine ester. By condensing 2-pyrrolidone-5-carboxyl chloride with *l*-tyrosine ester in chloroform, 2-pyrrolidone-5-carboxyltyrosine, decomp. 250°, and glutamyltyrosine, a syrup, were prepared. The latter was hydrolysed by erepsin and by trypsin. Of dl-*leucyltriglycyl*-dl-*serine* (decomp. above 175°; not precipitated by ammonium sulphate) and *dl*-leucyltriglycyltyrosine, the former was hydrolysed by erepsin, not by trypsin; the latter by trypsin, not by erepsin. Only polypeptides containing certain amino-acids are capable of hydrolysis by erepsin and then only if the amino-group is free (cf. Euler and Josephson, A., 1927, 696). The amino-group thus appears to be the point of attack by erepsin, but not by trypsin. The results suggest the composite nature of both enzymes.

F. E. Day.

Enzymic decomposition of polypeptides of various composition and their behaviour to *N*-alkali. Polypeptides containing mainly *l*-leucine. E. Abderhalden and R. Fleischmann (Fermentforsch., 1928, **9**, 524—533).—*dl*-Leucine was prepared from *iso*valeraldehyde and resolved by fractionation of the brucine salt of its formyl derivative. From it, *l*-leucyl-*l*-leucine; *benzoyl*-l-*leucyl*-l-*leucine*, m. p. 133°, $[\alpha]_D^{20}$ −49·14° in *N*-sodium hydroxide; *phenylcarbamido*-l-*leucyl*-l-*leucine*, m. p. 198°, $[\alpha]_D^{20}$ −68·66° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucine*, m. p. 180—182°, $[\alpha]_D^{20}$ −51·72° in alcohol; *glycyl*-l-*leucyl*-l-*leucine*, m. p. 232—234° (decomp.), $[\alpha]_D^{20}$ −67·01° in alcohol; d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucine*, m. p. 212°, $[\alpha]_D^{20}$ −38·04° in alcohol; l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −51·36° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, m. p. 193° (decomp.), $[\alpha]_D$ −76·19° in alcohol; *glycyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −78·63° in *N*-sodium hydroxide; d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucyl*-l-*leucine*, m. p. 224°, $[\alpha]_D$ −70·55° in alcohol; l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −89·95° in *N*-sodium hydroxide; *chloroacetyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −83·9° in alcohol; *glycyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −118° in *N*-sodium hydroxide, d-*α-bromo-γ-methylvaleryl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine*, $[\alpha]_D^{20}$ −94·5° in alcohol, and l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucyl*-l-*leucine* were prepared. The last pentapeptide was insoluble even in *N*-alkali. *l*-Leucyl-*l*-leucine and glycyl-*l*-leucyl-*l*-leucine were readily hydrolysed by erepsin, but only slightly by trypsin. None of the polypeptides containing only *l*-leucine was hydrolysed by *N*-sodium hydroxide at 37°, but the glycine was eliminated from the tri-, tetra-, and penta-peptides containing this as the end member of the chain. It is remarkable that in the case of phenylcarbamido-*l*-leucyl-*l*-leucine, *N*-sodium hydroxide yielded racemic phenylcarbamidoleucine and leucine. F. E. Day.

Colour reactions with lecithin. D. Migliacci Boll. chim. farm., 1928, **67**, 324—325).—The colour reactions obtained on the addition of a concentrated sulphuric acid to a mixture of a 2·5% solution of lecithin in alcohol with a 1% solution of each of the following aldehydes in alcohol is described: furfuraldehyde, benzaldehyde, salicylaldehyde, anisaldehyde, vanillin, and piperonal. E. A. Lunt.

Homogeneity of casein. K. Linderstrøm-Lang (Z. physiol. Chem., 1928, **176**, 76—78).—Casein, prepared from milk by precipitation with dilute hydrochloric acid, washed with water, and dried with alcohol and ether, has been extracted repeatedly with 60% alcoholic 0·001—0·002*N*-hydrochloric acid and the extracts have been treated with sodium hydroxide. The precipitates obtained were washed and dried with alcohol and ether, and these and other fractions have been analysed. Significant differences were observed in the phosphorus content (0·15—1·0%), tryptophan (1·4—2·3%), and tyrosine (3·8—6·1%), with smaller variations in arginine, monoaminodicarboxylic acids, and lysine. Treatment with the acid alcohol did not affect the casein in any way and the whole product is identical physically and chemically with the original preparation. The results indicate a non-homogeneity of casein.

A. Wormall.

Racemisation. VII. Action of alkali on casein. P. A. Levene and L. W. Bass (J. Biol. Chem., 1928, **78**, 145—157).—The mixture of amino-acids obtained by heating casein (4 hrs. at 125° with 5*N*-hydrochloric acid) has α_D^{25} +1·8°; treatment of casein with sodium hydroxide at 25° causes racemisation, the degree of which increases with the time and with the concentration of the alkali; heating at 125° with alkali causes complete racemisation. Casein therefore behaves differently from the polypeptides and diketopiperazines previously investigated, and also from gelatin. It is suggested that casein is composed either of exceptionally stable diketopiperazines or of amino-acids linked in a manner peculiarly favourable to racemisation.

C. R. Harington.

Analysis of mixtures of ethyl alcohol, ethyl acetate, acetic acid, and water. III. Determination of minute quantities of acetic acid. IV. General. S. Poznanski (Rocz. Chem., 1928, **8**, 263—271, 272—274).—A more detailed account of work already published (this vol., 784).

Colorimetric micro-determination of bile salts. O. Coquelet (Compt. rend. Soc. Biol., 1927, **97**, 1815—1818; Chem. Zentr., 1928, i, 1444).—An alcoholic solution (0·5 c.c.) of the pure salt or acid is treated with 1% alcoholic furfuraldehyde solution

(0·1 c.c.), and concentrated sulphuric acid (0·5 c.c.) is added so that the liquids do not mix. A comparison is similarly treated. The contents of the tubes are then rapidly mixed, 5 c.c. of a mixture of chloroform and alcohol (5 : 2) are added, and after 10 min. the tubes are examined colorimetrically. For the determination of bile salts in bile, two or three determinations are made on aliquot portions of a quantity of bile containing 0·5—2 mg. of salts. The bile is rendered alkaline by shaking with ether and 5% sodium hydroxide solution; the aqueous paste is decanted, and dried after being nearly neutralised with oxalic acid. The residue is extracted for 10 min. with chloroform, washed twice with chloroform, and the solution evaporated at a low temperature. The bile salts in an alcoholic solution of the residue are determined as above. CHEMICAL ABSTRACTS.

Determination of morphine in Codex preparations. L. MAGENDIE (Bull. Soc. Pharm. Bordeaux, 1927, **65**, 157—178; Chem. Zentr., 1928, i, 1444—1445).—Deniges' reaction (A., 1911, ii, 79) is applied quantitatively. The chief difficulty is the decolorisation of the solution; this is only partly effected by calcium hydroxide. Instead of copper sulphate solution, a mixture of copper sulphate and hydrochloric acid is employed as catalyst. The method is applied to various pharmaceutical preparations.

A. A. ELDRIDGE.

Alkalisation of ash at the expense of alkali chlorides, a source of error in determining organic acids by Hehner's method. P. FLEURY and P. AMBERT (J. Pharm. Chim., 1928, [viii], **8**, 5—11).—Hehner's method of determining organic acids in the presence of mineral acids uses the conversion by heat of their sodium salts into sodium carbonate which can then be titrated. Contrary to expectation, natural and synthetic gastric juices on incineration gave alkaline ashes. Determinations of the alkalinity of the ash obtained by incinerating in the presence of sodium chloride 21 members of the following groups: amino-acids, proteins, bases, alkaloids, purines, nitrogen-free aliphatic compounds, and nitrogen-free aromatic compounds, indicated that alkalisation with decomposition of sodium chloride occurs chiefly with certain nitrogenous substances, *e.g.*, uric acid, xanthine. It is thought that the substance responsible for the disappearance of hydrochloric acid in the course of incineration itself also disappeared. Hence Hehner's method for determining organic acids in gastric juice is limited to cases where such acids predominate. R. A. PRATT.

Biochemistry.

Hæmocyanin. V. Oxygen dissociation curve of hæmocyanin from the snail (*Helix pomatia*) in dialysed solution. E. STEDMAN and (MRS.) E. STEDMAN (Biochem. J., 1928, **22**, 889—901; cf. A., 1926, 1164; 1927, 689).—The oxygen dissociation curve of hæmocyanin from the snail has been determined at a temperature of 23° and at p_H values ranging from 4·04 to 9·04. No detectable change in the curve, which is hyperbolic, was observed with change in p_H. It is deduced from the results that one molecule of hæmocyanin combines with one molecule of oxygen and that each molecule of the pigment contains two atoms of copper. Hæmocyanin is molecularly dispersed in solution. S. S. ZILVA.

Changes in the oxygen capacity of rabbit's hæmoglobin following partial hepatectomy. B. B. STIMSON and M. C. HRUBETZ (J. Biol. Chem., 1928, **78**, 413—415).—As in the case of splenectomy (A., 1927, 1217) removal of 75—80% of the liver of rabbits causes conversion of part of the hæmoglobin into a non-oxygen-carrying pigment, not identical with methæmoglobin. C. R. HARINGTON.

Dependence of the catalytic and oxidative actions of iron on its condition of adsorption. R. KUHN and A. WASSERMANN (Ber., 1928, **61**, [*B*], 1550—1567).—The ability of hæmin to decompose hydrogen peroxide may be increased to more than 200% by adsorption on animal charcoal. Apart from the initial stages of the reaction, the activity of hæmin is restricted by adsorption by aluminium oxide; metastannic acid, as adsorbent, appears without influence. The transference of oxygen to linseed oil in the presence of hæmin is markedly inhibited by adsorption on charcoal and to a smaller extent by the use of aluminium oxide; metastannic acid exerts practically no influence. Separation of hæmin from the adsorbent is not observed in any case. The results, therefore, appear connected in some manner with the ease of elution of the individual adsorbates. The product when metastannic acid is used, which so closely resembles hæmin in catalytic activity, suffers elution with remarkable ease (2·5% of pyridine suffices), whereas the charcoal and aluminium oxide adsorbates are not thereby changed. Hæmin is removed from aluminium oxide by secondary phosphate, but decomposition of the charcoal adsorbates, in which the catalytic activity is most noticeably altered, cannot be effected.

The products obtained by the adsorption of iron on charcoal show enormously enhanced ability to decompose hydrogen peroxide catalytically, but restricted power of oxygen translation. If the iron is "bedded in" the charcoal (for example, by ignition of a mixture of iron salt and sugar), activation is caused in respect of catalysis and translation. If ferric chloride is adsorbed by aluminium hydroxide, its catalytic activity disappears, whereas great restriction is observed if metastannic acid is used. The opinion is expressed that hydrogen peroxide and ferrous iron can co-exist on charcoal in suitable circumstances. The activation of the catalytic decomposition of hydrogen peroxide by charcoal which has been allowed to adsorb ferric chloride is attributed to reduction to ferrous salt at the bounding surface. If a solution of ferric chloride is shaken with charcoal so that the iron is not quantitatively adsorbed, the liquid, after the adsorbate has been centrifuged, gives

a distinct Prussian-blue reaction with potassium ferricyanide. This behaviour has not, however, been observed in the simultaneous presence of hydrogen peroxide. Under these conditions the ferrous iron is present only in the limiting surface, not in solution.

H. WREN.

Transport numbers of fibrin. D. M. GREENBERG (J. Biol. Chem., 1928, **78**, 265—280).—Determination of the transport numbers of fibrin in dilute solutions of various acids and alkalis indicates that the protein forms completely ionisable salts with alkali hydroxide and with strong acids; in presence of weak acids such as formic, lactic, and phosphoric acids, positively charged ionic complexes of the protein with the acid are formed. The electrochemical equivalent of fibrin, measured by the rate of deposition of the protein on the anode, varied with different methods of preparation.

C. R. HARINGTON.

Precipitation of blood-proteins with tungstic acid. M. SOMOGYI (J. Lab. Clin. Med., 1927, **12**, 800—801).—The blood is preferably added to 8 vols. of $0·09N$-sulphuric acid; after laking, 1 mol. of 10% sodium tungstate solution is added, the mixture shaken, and filtered after 5 min.

CHEMICAL ABSTRACTS.

Sugars of blood and plasma. Protein-sugar. H. BIERRY (Bull. Soc. Chim. biol., 1928, **10**, 769—778).—A summary of previous work directing attention to the importance of protein-sugar in glycæmia (A., 1914, i, 218, 346, 454; 1918, ii, 416).

G. A. C. GOUGH.

Comparison of the Folin–Wu and new Benedict methods for the determination of blood-sugar. A. E. OSTERBERG (J. Lab. Clin. Med., 1926, **12**, 278—282).—Benedict's new method gives lower results than Folin and Wu's method.

CHEMICAL ABSTRACTS.

Ergosterol in human blood. L. H. DEJUST, (MLLE.) VAN STOLK, and E. DUREUIL (Compt. rend., 1928, **187**, 311—313).—The unsaponifiable fraction of the fats isolated from human blood-serum shows the three characteristic absorption bands of ergosterol in the ultra-violet region. A further absorption band at a wave-length shorter than 2700 Å. is observed.

G. A. C. GOUGH.

Cholesterol content of normal human plasma. III. So-called alimentary hypercholesterolæmia. J. A. GARDNER and H. GAINSBOROUGH (Biochem. J., 1928, **22**, 1048—1056).—The level of the cholesterol content of human plasma taken while fasting can be raised or lowered by sufficiently prolonged feeding with diets of high or low sterol content. Such changes are most marked as regards the cholesterol in ester form. As a result of a single meal, alimentary hypercholesterolæmia does not occur and there is no connexion between the amount of sterol ingested and the cholesterol level of the plasma during digestion. As compared with fasting values, the cholesterol content of the plasma fluctuates during digestion. This is probably due to an active endogenous metabolism, in which cholesterol takes part, during the process of digestion. In order to eliminate disturbing factors such as digestion or muscular work, it is important to use for comparative purposes bloods drawn while the subject is in a fasting condition.

S. S. ZILVA.

Calcium content of the serum of normal adults. I. ROSEN and F. KRASNOW (J. Lab. Clin. Med., 1926, **12**, 157—158).—The normal value (50 persons) is 10·7—13·2 mg. per 100 c.c.; in no case was less than 10 mg. per 100 c.c. present.

CHEMICAL ABSTRACTS.

Determination of calcium in whole blood. W. R. CAVEN and A. CANTAROW (J. Lab. Clin. Med., 1926, **12**, 76—77).—Blood (2 c.c.) is mixed with 4% ammonium oxalate solution (2 c.c.) in a graduated centrifuge tube, and after 1 hr. the mixture is centrifuged at a high speed for 10 min. The supernatant liquid is poured away, the tube inverted on filter-paper for 5 min., the precipitate washed once with distilled water (5 c.c.) and once with dilute ammonia solution (2 vol.-% of concentrated solution; 3 c.c.), and the mat is broken up with a spray of N-sulphuric acid (2 c.c.). After being kept at 100° for 1 min. the solution at 75° is titrated with $0·01N$-permanganate solution.

CHEMICAL ABSTRACTS.

Determination of chlorides in blood or urine. S. L. LIEBOFF (J. Lab. Clin. Med., 1927, **12**, 702—706).—The solution is neutralised with calcium carbonate and titrated with silver nitrate solution, using chromate as indicator; controls are used, and alkaline urine is first acidified.

CHEMICAL ABSTRACTS.

Determination of sodium in blood-serum or -plasma. M. D. ROURKE (J. Biol. Chem., 1928, **78**, 337—344).—A modification of the method of Kramer and Gittleman (A., 1925, i, 180) is described by which sodium may be determined in 0·3 g. of blood-serum or -plasma with an error of ±2%. The average sodium content of human blood-plasma is 0·339%.

C. R. HARINGTON.

Disappearance of hydrocyanic acid from blood. E. KOHN-ABREST and LUPU (Compt. rend., 1928, **187**, 362—364).—" Serum " free from reducing sugars, separated from hog's blood by adding 80 c.c. of 25% trichloroacetic acid per litre of blood, boiling, filtering, and addition of sodium hydroxide, was treated with hydrocyanic acid in the presence and absence of dextrose at 20° and at 37°. In the absence of dextrose there was no loss of hydrocyanic acid in 7 days at 20°; at 37° the loss was 17·2% in 2 days and this figure did not increase in 7 days. In the presence of an amount of dextrose corresponding with that normally present in human blood, 31% of the hydrocyanic acid disappeared in 2 days at 20° and 70% in 4—7 days; at 37° the loss was 68% in 2 days, 71% in 4 days, and 88·5% in 7 days. Similar experiments on the whole blood (with 2% of borax) showed losses of hydrocyanic acid amounting to 7·3%, 10·3%, and 10·8% in 2, 4, and 7 days, respectively, without dextrose, and 14·4%, 24·1%, and 21·1%, respectively, in presence of dextrose at 20°; at 37° the corresponding losses were 7·2, 43·8, and 26·2%, and 31·3, 51·5, and 82·7%, respectively. " Dissimulated " hydrocyanic acid, *i.e.*, as thiocyanate, was detected in the hog's blood at 20° only to the extent of 5% after 7 days at 20°. These results indicate that dextrose is less active in whole blood than in serum,

and are not in accordance with the observed absence of hydrocyanic acid from the blood of victims of hydrocyanic acid poisoning. R. BRIGHTMAN.

Blood stains. P. KARPOV (Bull. Univ. Asie Centrale, 1927, No. 16, 152—153).—The stain is extracted with Taraneck's reagent (physiological sodium chloride solution containing 0·25% of sodium carbonate) or Grigoviev's reagent (20% alcohol containing 0·1% of sodium carbonate). In a modification of van Deen's test the solution is mixed with 1—3 drops of guaiacum tincture and 1 drop of ozonised turpentine, and shaken with ammonia solution, which becomes blue. For the microscopical test, the formation of hæmin and hæmochromogen crystals by Bokarius' method is preferred. Halogenohæmatin crystals were best obtained in presence of halogen, chloroform, or iodoform; hæmochromogen crystals were best produced in presence of sodium sulphide and pyridine. CHEMICAL ABSTRACTS.

Benzidine test for blood. K. SCHERINGA (Pharm. Weekblad, 1928, **65**, 712—713).—The blue colour resulting from the action of oxidising substances on benzidine is produced by hydrogen peroxide only if a catalyst be present. Blood, even at a dilution of 1/10,000, is such a catalyst, as also, however, are numerous inorganic materials, iodides, and, after heating, substances of high protein content; the test is therefore less specific if the material to be tested has been strongly heated. H. F. GILLBE.

Precipitin test for blood. H. S. SHREWSBURY (Analyst, 1928, **53**, 380).—It is advisable to test the blood-stain solutions so that they may be within the p_H range for the precipitin reactions, and it was found that rolling the antiserum down the side of the tube inclined at 45° through the solution of the stain gave more definite zone reactions than layering. In Trinidad sera will remain potent only for 3 months even when kept on ice. D. G. HEWER.

Precipitin test for blood. G. R. LYNCH (Analyst, 1928, **53**, 435; cf. preceding abstract).—Factors such as temperature during transit, amount of agitation received, age, and other unknown influences render all purchased sera undesirable, and it is considered essential that every worker should make his own sera. D. G. HEWER.

Colloid-chemical significance of electrolytes for precipitation. N. HAYASHI (Sei-i-Kwai Med. J., 1927, **46**, 3—5).—Various salts can be substituted for sodium chloride in the agglutination reaction within various limits of concentration. The precipitation is mainly due to the cation, but the anion also has an effect. CHEMICAL ABSTRACTS.

Action of ultra-violet rays on complement. J. GORDON and A. WORMALL (Biochem. J., 1928, **22**, 909—919).—Complement of guinea-pig serum is readily inactivated by ultra-violet rays. When the serum is diluted with water or with 0·9% sodium chloride solution the process of inactivation proceeds more readily. This inactivation is primarily due to the inactivation or destruction of the heat-labile components. The relatively heat-stable components are not affected appreciably by irradiation. The separate irradiation of the isolated globulin and albumin fractions produced an inactive complement when recombined. Inactivation in these circumstances was more rapid owing to dilution. This deleterious effect of ultra-violet rays on the activity of the complement is not due to oxidation, although the rate of inactivation in a vacuum is slightly less than that in air. Irradiation of guinea-pigs with ultra-violet rays does not increase appreciably the complement activity of the serum, nor does the serum of guinea-pigs kept in the dark show any marked loss in this activity.
S. S. ZILVA.

Oxidases and peroxidases of the red bone-marrow, uncombined with hæmoglobin. I. A. NEUMANN. **II.** A. NEUMANN and E. GRATZL (Folia Hæmatol., 1927, **35**, 8 pp., 27 pp.; Chem. Zentr., 1928, i, 1198).—I. The term "oxone" is applied to substances which, owing to the presence of oxidases and peroxidases, have the character of a respiratory substance. The preparation of a hæmoglobin-free oxidative substance from the red bone-marrow of the horse, ox, and calf is described. It presumably originates in the leucocyte fraction.

II. The leucocyte value of dogs is increased by the injection of small amounts of "oxone."
A. A. ELDRIDGE.

Vital staining of normal and malignant cells. I. Vital staining with trypan-blue and the cytoplasmic inclusions of liver and kidney cells. R. J. LUDFORD (Proc. Roy. Soc., 1928, **B**, **103**, 288—301).—Dye droplets and mitochondria and dye droplets and Golgi apparatus have been demonstrated in the kidney and liver of animals stained intravitally with trypan-blue. There is no definite relationship between the dye droplets and mitochondria, but the former appear in relationship with the Golgi apparatus, from which they break away into the cytoplasm when formed. It is suggested that products synthesised enzymically at the mitochondrial-cytoplasmic surface diffuse into the cytoplasm and are concentrated at the surface of the Golgi apparatus into droplets preliminary to elimination.
S. S. ZILVA.

Ooplasmic intermicellar fluid. K. BIALASZEWICZ (Acta Biol. Exp., Warsaw, 1928, **1**, No. 11, 1—52).—The potassium content of the ash of eggs of birds, amphibiæ, fish, crustacea, molluscs, echinoderms, and annelids is comparatively constant, whilst the sodium, calcium, and magnesium contents, which are considerably lower, are more variable. 20—63% of the volume of the ooplasm is taken up by organic colloidal substances. The greater part of the alkali metals and chlorine present is to be found in the intermicellar fluid in a dialysable form, whilst the alkaline-earth metals and phosphoric acid are for the greater part adsorbed reversibly on the dispersed phase. The mineral content of the intermicellar fluid is fairly constant for the above-named species, 10 parts of sodium, and 7 each of calcium and magnesium being present for every 100 parts of potassium.
R. TRUSZKOWSKI.

Digestibility of white of egg. I. G. MACDONALD and E. G. YOUNG (Proc. Nova Scotian Inst. Sci., 1927, **16**, 197).—No difference exists in the rate of peptic digestion of egg-white coagulated for periods of 2—30 min. S. J. GREGG.

Chemical constitution and metabolism of fats in insects. J. Timon-David (Bull. Soc. Chim. biol., 1928, **10**, 784—795).—The oils or fats obtained from insect larvæ exhibit considerable differences in chemical character, some being of the non-drying type, whilst others show a tendency to oxidise in the air. The amounts of oils vary between 3·5 and 27·5% of the body-weight and are least in those larvæ which feed on substances of animal origin. The unsaponifiable fractions vary between 0·75 and 8·5% of the total fats. G. A. C. Gough.

Pigment of the fat of certain rabbits. S. G. Willimott (Biochem. J., 1928, **22**, 1057—1059).—The colouring matter in the adipose tissue of "pigmented" rabbits consists of xanthophyll pigments. S. S. Zilva.

Occurrence of glutathione in the animal kingdom. A. Blanchetière and L. Melon (Compt. rend. Soc. Biol., 1927, **97**, 1231—1232; Chem. Zentr., 1928, i, 709).—A study of cœlenterata, echinoderms, molluscs, annelids, arthropods, and fishes. A. A. Eldridge.

Accumulation of iodine in individual organs. T. von Fellenberg (Mitt. Lebensm. Hyg., 1926, **17**, 235—242).—See A., 1926, 1052.

Iodine metabolism. II. T. von Fellenberg (Mitt. Lebensm. Hyg., 1926, **17**, 223—234).—See A., 1926, 1056.

Colour of the peacock's "eye." (Lord) Rayleigh (Nature, 1928, **122**, 167).—On exposure to the light from a quartz mercury lamp, the dark colour of the centre zone is discharged, whilst that of the second zone is blue in the exposed and green in the unexposed portion. Sunlight has a definite, but less marked, effect. A. A. Eldridge.

Lipase in saliva. K. Scheer (Klin. Woch., 1928, **7**, 163—165; Chem. Zentr., 1928, i, 1428).—Saliva contains a lipase which is destroyed at 65°, and has optimal p_H 7. It is activated 300% by calcium chlorate and sodium oleate. A. A. Eldridge.

Thiocyanate content of serum and cerebrospinal fluid. R. Blum (Z. klin. Med., 1928, **107**, 61—71; Chem. Zentr., 1928, i, 1200—1201).—Normal serum contains 0·03—0·06 mg.-% of thiocyanate; smoking increases the value two- to four-fold. Oral administration of thiocyanate caused an increase to, but not above, 1·5 mg.-%. The average value for cerebrospinal fluid is equal to that for serum. A. A. Eldridge.

Organic phosphorus in cerebrospinal fluid. G. E. Youngburg (J. Lab. Clin. Med., 1927, **12**, 845—849).—*Post mortem* change of organic phosphorus is very slow. The organic phosphorus content of cerebrospinal fluid varies from 0·06 to 0·59 mg.%, and is generally 0·1—0·3 mg.%. The phosphorus is not present as lipins, but is probably combined with protein. Organic and inorganic phosphorus contents are independent. Chemical Abstracts.

Differences in chemical constitution, p_H, and digestive power of pancreatic secretion, according to the nature and intensity of the exciting factor. F. Czubalski (Acta Biol. Exp., Warsaw, 1928, **2**, 1—17).—The chloride content of pancreatic juice is inversely proportional to the velocity of secretion. When secretion is rapid, the p_H varies between 8·23 and 8·64, whilst the p_H of slowly secreted juice lies between 7·06 and 8·45. These differences are conditioned, not by the nature of the stimulus, but by its intensity. R. Truszkowski.

Mechanism of secretion of calcium and phosphorus in milk. N. C. Wright (J. Agric. Sci., 1928, **18**, 478—485).—In the presence of neutral caseinogenates colloidal calcium hydrogen phosphate is formed by the interaction of calcium chloride and disodium hydrogen phosphate. This colloidal calcium phosphate is non-diffusible across a membrane of cellophane. A mechanism is suggested explanatory of the secretion of high concentrations of calcium and phosphorus in milk from the low concentrations of these elements in the blood. H. J. G. Hines.

Colorimetric determination of free tryptophan in blood. C. A. Cary (J. Biol. Chem., 1928, **78**, 377—398).—Blood is boiled with acetic acid, treated with kaolin, and filtered; the filtrate is treated with sulphuric acid to 7% and the tryptophan precipitated with mercuric sulphate. The precipitate is separated, washed, and suspended in a solution of glyoxylic acid in slightly diluted sulphuric acid. After 48 hrs. at the ordinary temperature the solution is filtered and compared colorimetrically with one obtained by similar treatment of a known solution of tryptophan; a correction must be applied for losses of tryptophan in the process. The colour obtained from blood by this method compares well with that given by pure tryptophan, and tryptophan added to blood can be quantitatively recovered; spectrophotometric analysis, however, indicates that 15—25% of the colour is due to substances other than tryptophan. C. R. Harington.

Free tryptophan in cow's blood and its utilisation in milk secretion. C. A. Cary and E. B. Meigs (J. Biol. Chem., 1928, **78**, 399—407).—The average free tryptophan content of cow's blood is 1·12 mg. per 100 c.c.; the tryptophan content of the blood of the mammary vein is about 17% lower than that of the jugular vein in the lactating cow, whereas in the non-lactating cow the difference is negligible. The proportionate difference in the total amino-nitrogen in the two veins is similar to that between the tryptophan contents. The free tryptophan of the blood appears therefore to be utilised in milk secretion. C. R. Harington.

Urinary elimination of ammonia and nitrogen. Some urinary constants. R. Rafflin (Bull. Soc. Chim. biol., 1928, **10**, 812—821).—Seven equations, describing various functions of the p_H, the total nitrogen, the ammoniacal nitrogen, and the volume of the urine, are found to give constant values for normal subjects. Large variations are found to accompany pathological conditions and smaller differences occur after sleep and meals. G. A. C. Gough.

Nitrogen excretion of camels. H. W. Smith and H. Silvette (J. Biol. Chem., 1928, **78**, 409—411).—Contrary to the statement of Reid (A., 1928, 1204) the camel excretes amounts of carbamide and

ammonia comparable with those excreted by other herbivora. C. R. HARINGTON.

Determination of guanidine bases in urine. C. J. WEBER (J. Biol. Chem., 1928, **78**, 465—473).—Urine is cleared with lead acetate and sodium hydroxide; excess of lead is removed by treatment with sodium phosphate. The filtrate is treated with more sodium hydroxide and the guanidine bases are adsorbed on purified norit; the bases are recovered by treatment of the adsorbate with alcoholic hydrochloric acid, and are then determined colorimetrically by means of a reagent consisting of a mixture of sodium nitroprusside and potassium ferricyanide in alkaline solution. C. R. HARINGTON.

Determination of bismuth in urine. G. CIOGOLEA (Bul. Soc. Chim. Romania, 1928, **10**, 55—60).—The method of Cuny and Poirot (A., 1923, ii, 792) is most trustworthy for the micro-determination of bismuth. 100 c.c. of urine are evaporated almost to dryness and 2·5—3 g. of ammonium nitrate are added. The residue is ignited and treated with hot water to remove chlorides. The filter-paper used is returned to the dish and incinerated. About 1—1·5 g. of ammonium nitrate, dissolved in the minimum amount of water, is added and, after evaporation, the ignition is repeated. The residue is moistened with a few drops of concentrated nitric acid, evaporated, and again ignited. The resulting ash is dissolved in 4 c.c. of 10% nitric acid, the dish washed with water, and the whole made up to 10 c.c. Bismuth is determined in 5 c.c. of the filtered solution by the colorimetric method of Cuny and Poirot. J. S. CARTER.

Lipins of the blood-plasma in disease. J. FRIESZ and G. SZABÓ (Z. klin. Med., 1927, **106**, 701—716; Chem. Zentr., 1928, i, 1296).—Changes in the blood-cholesterol and -lecithin in pathological conditions are recorded. In general there is no relation between the blood-cholesterol, -lecithin, and -bilirubin. A. A. ELDRIDGE.

Mineral metabolism. IX. Phosphorus partition of blood in anæmia of cattle and sheep. A. I. MALAN (J. Agric. Sci., 1928, **18**, 401—405).—In cases of anæmia of cattle and sheep, the nucleoprotein-phosphorus fraction is present and associated with the appearance of nucleated red cells. H. J. G. HINES.

Calcium and carbohydrate metabolism. Calcium and dextrose tolerance in diabetes mellitus. M. WISHNOFSKY (J. Lab. Clin. Med., 1927, **13**, 133—137).—Intravenous administration of calcium chloride does not appear to influence the tolerance of diabetics for dextrose. CHEMICAL ABSTRACTS.

Hæmatoporphyrinuria. H. H. VAN DER Z. DE JONG (Nederl. Tijds. Geneeskunde, 1928, **72**, I, 165—168; Chem. Zentr., 1928, i, 1201)—Part of the porphyrin is present in non-toxic form combined with urofuscin; the name "porfuscin" is given to the compound. It slowly decomposes when the urine is kept, more rapidly when it is heated with dilute hydrochloric acid, producing a dark colour. In congenital porphyrinuria porfuscin is probably not formed. A. A. ELDRIDGE.

Change of the acid–base equilibrium in inflamed tissue. F. BRICKER and F. SUPONITZKAJA (Arch. exp. Path. Pharm., 1928, **133**, 103—106).—The acidosis associated with inflammation is a secondary result of the pathological process and not its cause. W. O. KERMACK.

Fat, lipin, and cholesterol constituents of adrenals and gonads in cases of mental disease. D. P. WOODHOUSE (Biochem. J., 1928, **22**, 1087—1096)—Analyses of the total alcohol–ether-soluble extractives of the adrenals and gonads of 38 mental patients for total fatty acids, lecithin, sphingomyelin, free and ester cholesterol, and free fatty acids have been performed. The results do not support the view that the lipoids of the gonad are elaborated by and transported directly to it from the adrenal cortex. The percentage of fatty extractives from the gonads shows much less variation than that from the adrenals. The lowest adrenal content was found in dementia præcox and the highest in senile dementia. Low values of phosphatide were obtained in the adrenals of the confusional group and high figures were found in the adrenals of epileptics. The relative proportions of the total cholesterol to the total phosphatide varied greatly in the cases examined and the ratio of these proportions in the pairs of glands differed from unity in a marked degree. S. S. ZILVA.

Phosphorus content of serum in renal disease. K. GRASSHEIM and E. LUCAS (Z. klin. Med., 1928, **107**, 172—180; Chem. Zentr., 1928, i, 1200).—The acid-soluble and organic phosphorus in the serum are normally 2—3·5 and 7—9 mg.-%, respectively. In hot weather the values, particularly the former, are higher. The increase of phosphorus runs parallel with the degree of renal disturbance. A. A. ELDRIDGE.

Standard for the Van den Bergh test. B. W. RHAMY and P. H. ADAMS (J. Lab. Clin. Med., 1927, **13**, 87—89).—A colour identical with azobilirubin solution equivalent to 5 in 10^6 of bilirubin is given by 0·7 c.c. of 0·1*N*-potassium permanganate solution diluted to 50 c.c. with water. CHEMICAL ABSTRACTS.

Serum in scarlet fever. E. TUDOS and A. EBEL (Z. ges. exp. Med., 1927, **57**, 709—714; Chem. Zentr., 1928, i, 1297).—In scarlet fever the electrolyte content and titratable sodium chloride of the blood-serum are subnormal. A. A. ELDRIDGE.

Increase in blood-sugar in experimental sunstroke of the rabbit. T. IMAZU (Proc. Imp. Acad. Tokyo, 1928, **4**, 252—253).—The blood of rabbits killed by exposure to the sun had a definitely higher sugar content than before exposure. Those rabbits which survived the exposure showed no hyperglycæmia. J. H. BIRKINSHAW.

Urinary elimination of iodine and goitre prophylaxis with sea fish. G. LUNDE (Ber. int. Kropfkonfer. Bern, 1927, 9 pp.; Chem. Zentr., 1928, i, 1298).—A study of the urinary elimination and intake (in sea fish) of iodine. A. A. ELDRIDGE.

Tissue respiration and endocrine function. I. Influence of thyroidectomy on the phenol oxidase content of animal tissues. II. Influence of thyroparathyroidectomy. J. A. DYE and

R. A. Waggener (Amer. J. Physiol., 1928, **85**, 1—13, 14—20).—I. Observations are reported on the comparative rates of formation of indophenol-blue from dimethyl-*p*-phenylenediamine and α-naphthol in the presence of air and of various tissues from normal and from thyroidectomised lambs and pups. The catalytic system in the tissues is active at 0°, has an optimum at 23—24°, and is destroyed in 30 min. at 55°. The activity of the tissues of animals deprived of their thyroid glands was 50—90% of the corresponding tissues of normal animals.

II. An increase in the oxidase activity of the tissues of the operated animals was found in the case of all the tissues examined except the kidney.

R. K. Cannan.

Sputum. II. H. Müller and H. Reinwein (Z. physiol. Chem., 1928, **176**, 200—206; cf. Reinwein, A., 1926, 1052).—From 2·5 litres of the sputum of a bronchial patient arginine and choline were isolated and identified. Carbamide was not found.

C. Hollins.

Cholesterol content of sputum. R. G. Kelly and M. Pinner (Amer. Rev. Tuberculosis, 1928, **17**, 430—433).—Extensive, acute, and tissue-destructive lesions are associated with an increase in sputum-cholesterol. Chemical Abstracts.

Cerebrospinal fluid in Meningitis tuberculosa. E. Tüdös and A. Ebel (Z. ges. exp. Med., 1927, **57**, 715—720; Chem. Zentr., 1928, i, 1297).—In children the conductivity of the cerebrospinal fluid is normally $1·3\times10^{-2}$ ohm^{-1}; in tubercular meningitis $1·26\times10^{-2}$ ohm^{-1}. That of the serum is $1·08\times10^{-2}$ ohm^{-1}. In meningitis the chlorine content of the fluid progressively diminishes. A. A. Eldridge.

p_H of normal, fœtal, and neoplastic tissues. H. Millet (J. Biol. Chem., 1928, **78**, 281—288).—The p_H of the Flexner rat carcinoma, and of both benign and malignant neoplastic tissue in man, as determined by the glass electrode, is about 6·9, whilst that of the normal tissues is about 7·1; no difference was observed in the p_H of the necrotic and non-necrotic portions of tumours. The p_H of fœtal tissues is low in the early stages of development, but increases steadily and reaches the normal value shortly after birth. C. R. Harington.

Effect of arsenic on some oxidation–reduction systems. G. Barry, E. Bunbury, and E. L. Kennaway (Biochem. J., 1928, **22**, 1102—1111).—Arsenic in the form of arsenite when in concentrations similar to those found in the skin in arsenical hyperkeratosis has a retarding action on the systems (1) hypoxanthine–xanthine oxidase of rat or mouse skin, (2) acetaldehyde–colloidal platinum, and (3) propaldehyde or acetaldehyde, glycine, and phosphate. Arsenates are comparatively inactive in this respect. The possible significance of these findings in connexion with the nature of arsenic cancer is discussed.

S. S. Zilva.

Gaseous metabolism of large wild birds under aviary life. F. G. Benedict and E. L. Fox (Proc. Amer. Phil. Soc., 1927, **66**, 511—534).—The birds examined represent two different heat-producing organisms in which the surface area is without significance. Chemical Abstracts.

Utilisation by the organism of energy liberated by oxidation processes and the food value of alcohol. E. F. Terroine and R. Bonnet (Compt. rend., 1928, **187**, 359—361).—Oxidation processes which take place in the organism are classified according to the utilisation of the energy liberated: (1) those, such as the oxidation of dextrose, in which the energy is used for any kind of work, mechanical or chemical, and (2) those in which the energy can be used only as heat. Alcohol falls into the second class, the energy liberated in its oxidation having no physiological value apart from its thermal effect.

R. Brightman.

Regulation of carbohydrate metabolism. Lactic acid as activator of liver prodiastase. A. Partos (Fermentforsch., 1928, **9**, 403—410).—1·0—1·5 c.c. of 0·7% lactic acid injected intravenously into dogs caused marked hyperglycæmia in 15 min. The assumption that this was due to activation of the liver prodiastase was supported by the observation that the production of dextrose by autolysis of minced liver is inhibited by excess of calcium carbonate or zinc oxide, and proceeds on removal of such excess.

F. E. Day.

Dextrose metabolism of kidney tissue *in vitro*. II. J. T. Irving (Biochem. J., 1928, **22**, 964—967).—Dextrose in phosphate buffer solution containing chopped kidney cortex is converted in large part into lactic acid; a slight fall in the inorganic phosphorus content is observed at the same time. In some cases the fall was sufficient to account for all the dextrose not turned into lactic acid, if it was assumed that hexosediphosphoric acid was formed. In other cases all the dextrose was still not accounted for. This might be due to the formation of a mixture of mono- and di-phosphoric esters. The utilisation of dextrose and the production of lactic acid are strongly inhibited in a vacuum or in the presence of hydrocyanic acid. No glycogen is synthesised by the tissue from the dextrose. S. S. Zilva.

Lactic acid formation in muscle contraction. II. G. Embden and E. Lehnartz (Z. physiol. Chem., 1928, **176**, 231—248).—The values previously obtained (Embden, Lehnartz, and Hentschel, A., 1927, 589) for the quotient (lactic acid excess in nitrogen-muscle)/(lactic acid burnt in oxygen-muscle) are confirmed, using frog's sartorius muscle, these values being much higher than the oxidation quotients of Meyerhof (Pflüger's Arch., 1927, **217**, 549). Certain criticisms by the latter are discussed.

J. H. Birkinshaw.

Pancreatic extracts in relation to lactic acid formation in muscle. E. M. Case and D. R. McCullagh (Biochem. J., 1928, **22**, 1060—1070).—The so-called pancreatic factor which inhibits lactic acid production by muscle enzyme is amylase. It is thermolabile, dialyses through membranes, is adsorbed with difficulty, and is inhibited by the presence of maltose. Its distribution in various animal tissues is also similar to that of amylase. The amylolytic power and the ability to inhibit esterification of phosphates and lactic acid formation correspond in different preparations and are destroyed by heat to the same extent. The presence of different con-

centrations of starch causes a variation in the inhibiting capacity of the pancreatic factor. Both animal and vegetable amylases act as inhibitors when starch or glycogen is used as substrate. The production of lactic acid from dextrose is not inhibited by the pancreas. The suppression of the esterification of phosphates in the presence of fluoride and starch (cf. McCullagh, this vol., 550) was the technique generally employed in the above experiments.

S. S. ZILVA.

Muscular activity. V. Changes and adaptations in running. J. H. TALBOT, A. FOLLING, L. J. HENDERSON, D. B. DILL, H. T. EDWARDS, and R. E. L. BERGGREN (J. Biol. Chem., 1928, **78**, 445—463).—Figures are given showing the changes in the blood (particularly in relation to respiratory metabolism) and in the urine during periods of work of varying severity in an untrained individual.

C. R. HARINGTON.

Heat of combustion of living muscle. H. RYCHLEWSKA (Acta Biol. Exp. Warsaw, 1928, **1**, No. 2, 1—6).—The heat of combustion of 1 g. of fresh frog gastrocnemius muscle is 1076·5 g.-cal.; after drying this value rises to 1094·4 g.-cal. The heat of imbibition of muscle is 12·51 g.-cal. per g. of dry substance. The processes taking place during the drying of muscle must be of an endothermic nature.

R. TRUSZKOWSKI.

Digestion of lignin by ruminants. F. ROGOZINSKI and M. STARZEWSKA (Acta Biol. Exp. Warsaw, 1928, **1**, [No. 8], 1—9).—Determinations of the methoxy-group content of the fæces of sheep indicates that the lignin contained in oat-straw and that prepared by Beckmann's method (B., 1921, 539) is not digested by these animals and cannot therefore serve as a source of nourishment. R. TRUSZKOWSKI.

Production of sugar from fat. Y. KOJIMA (Biochem. Z., 1928, **197**, 31—71).—Rats maintained practically free from carbohydrate with phloridzin could not produce sugar from the fatty acid components of fat. Two such series of rats did not tolerate the daily addition to their diet either of 2·0—4·0 g. of a mixture of 10 g. each of stearic and palmitic acids and 40 g. of oleic acid or of the same amount of the neutralised mixture, and died within 12—24 hrs. Moreover, the addition of 3—4 g. of butter to the diet of four such rats resulted in the average decrease of sugar in the urine of 35·2%, 19·3%, 11·8%, and 20·7%, showing that the formation of sugar from the glycerol of the fat was completely suppressed, the fatty acids of the fat being responsible for this marked inhibition. Comparison of the sugar in the urine of such rats fed on meat, fat, and a mixture of the two showed an excess of excreted sugar of 54% for flesh over fat, of 38% for flesh plus fat over fat, and of 26% for flesh over flesh plus fat. The excretion of sugar on a feeding day exceeds that on a starving day, for meat by 50% and for fat by 14·4%. Finally, the addition of 1 g. of sodium lactate to the diet of three rats resulted in an average increase of sugar production of 34·8%. L. C. BAKER.

Conversion of fat into carbohydrate. I. Metabolism of acetic acid. H. J. DEUEL, jun., and A. T. MILHORAT (J. Biol. Chem., 1928, **78**, 299—309).—After injection of sodium acetate into phloridzinised dogs the acetic acid was almost completely oxidised, but no significant change in the D : N ratio took place. Acetic acid cannot therefore readily give rise to dextrose, and this is further evidence against the supposed formation of carbohydrate from fat in the animal organism. C. R. HARINGTON.

Lipin and fat metabolism during fattening. H. KNAUER (Z. physiol. Chem., 1928, **176**, 151—172).—Plasma, serum, and erythrocyte fractions of blood from pigs slaughtered at various stages of fattening were analysed for phosphatides, cholesterol, and fatty acids. The lipin values of the pig are comparatively low; there is a definite decrease of all lipins during fattening, those of serum showing the greatest change and those of the erythrocytes the least. The rate of settling of the blood-corpuscles diminishes progressively.

In the case of geese, there is a similar steady decline in the lipins with increasing body-weight; when the fattening is intensive, the lipin values fall while fat is being accumulated, but rise considerably when weight equilibrium is reached. J. H. BIRKINSHAW.

Chemical composition of eels subjected to inanition. T. VIEWEGER (Acta Biol. Exp., Warsaw, 1928, **1**, No. 10, 1—19).—Eels weighing from 300 to 700 g. have a solid content of 50%, a nitrogen content of 2·35%, and a fatty acid content of 27·5%. Proteins represent 31·5% of the organic content, and fats 68·5%. Most of this fat is in the muscles and the adjacent subcutaneous layer, the skin and viscera accounting for only about 7% of the total fat content. After a period of inanition lasting up to 320 days and involving a loss of weight of up to 26%, the relative proportions of the organic constituents of these animals remain unchanged, indicating that no biological constituent is preferentially consumed under the above conditions. R. TRUSZKOWSKI.

Formation of organic bases during incubation of eggs. Y. NAKAMURA (Z. physiol. Chem., 1928, **177**, 34—41).—The free choline of hen's eggs is present only in the yolk. The quantity, originally 0·64 mg. per egg, decreases and reaches a minimum after 9 days' incubation; it then increases both in the yolk and in the embryo, reaching 2·27 mg. after 19 days. Combined choline is present in much greater amount and reaches a maximum (93·34 mg.) after 9 days, falling to 29·54 mg. at the 19th day. The increase in free choline is doubtless due to hydrolysis of combined choline, but most of the lecithin must undergo some other change, possibly into creatinine.

C. HOLLINS.

Cause of the specific dynamic action of albumin. II. III. R. LIEBESCHUTZ-PLAUT and H. SCHADOW (Pflüger's Archiv, 1927, **217**, 717—722, 723—727; Chem. Zentr., 1928, i, 714).—Following intravenous administration of amino-acids the usual specific dynamic effect is not observed. In intraduodenal administration of glycine the oxygen-consumption curve follows the blood-amino-nitrogen curve. A. A. ELDRIDGE.

Nutrition. I. Growth, reproduction, and lactation on diets with different proportions of cereals and vegetables. II. Effect of addition

of egg. M. S. Rose and E. L. McCollum (J. Biol. Chem., 1928, **78**, 535—547, 549—555).—I. Diets devised to imitate those consumed by normal children, ranging in the proportion of cereal (flour) and vegetables, were found adequate for growth and reproduction in rats, but lactation was unsatisfactory, owing, possibly, to deficiency in vitamin-*B*.

II. Addition of egg to such a diet caused improvement in growth of the young, fertility of the females, and lactation. C. R. Harington.

Mineral metabolism. IV. Determinations of phosphorus compounds in blood by dry combustion. H. H. Green (J. Agric. Sci., 1928, **18**, 372—375).—Dry combustion is combined with the coeruleomolybdate procedure of Deniges.

H. J. G. Hines.

Mineral metabolism. V. Composition of bovine blood on phosphorus-deficient pasture. A. I. Malan, H. H. Green, and P. J. du Toit (J. Agric. Sci., 1928, **18**, 376—383).—Examination of the phosphorus partition of the blood of cattle grazing on phosphorus-deficient pasture of South Africa showed that the outstanding characteristic is low inorganic phosphorus with a correlated reduction in total phosphorus. When a small ration of bone meal is given to the animals, comparatively normal figures are obtained. Colorimetric determination of inorganic phosphorus in the blood of the grazing animal provides a simple means of detecting deficiency in the pasture.

H. J. G. Hines.

Mineral metabolism. VI. Comparison of the blood of the cow and calf in respect to mineral constituents. H. H. Green and E. H. Macaskill (J. Agric. Sci., 1928, **18**, 384—390).—Total phosphorus of the blood of the new-born calf may be twice that of its mother. The red corpuscles contain all the organic acid-soluble phosphorus in both calf and cow, and in the case of the calf they contain also an unknown phosphorus fraction, probably of nuclear origin. An outstanding feature of calf blood is its high potassium content. H. J. G. Hines.

Mineral metabolism. VII. The unknown phosphorus fraction of calf blood. A. I. Malan and H. H. Green (J. Agric. Sci., 1928, **18**, 391—395).—This fraction is shown to be nucleoprotein and due to the presence of precursors of fully mature erythrocytes. This fraction may occur in small amounts in human and horse blood and always occurs in very large amount in the nucleated erythrocytes of birds. H. J. G. Hines.

Mineral metabolism. VIII. Comparison of phosphorus partition in the blood of calf fœtus, sheep fœtus, and lambs with corresponding maternal blood. A. I. Malan (J. Agric. Sci., 1928, **18**, 397—400).—A similar phosphorus partition in the blood of ewes and lambs to that obtaining in cows and calves was observed. H. J. G. Hines.

Normal deposition of mineral in the bones of dairy calves. J. H. Kruger and S. I. Bechdel (J. Dairy Sci., 1928, **11**, 24—34).—The phosphorus and calcium content of the bones of male calves at 90—180 days was constant; water decreased, whilst fat, ash, and organic matter increased, with age.

Chemical Abstracts.

Calcium fixation capacity of normal and rachitic cartilage. W. Schmidt (Z. Biol., 1928, **87**, 537—542).—The following specimens were examined for calcium fixation by placing the tissues in a calcium chloride solution for 24 hrs. Calf's epiphysis, cattle rib cartilage, cattle shoulder cartilage, proliferating and non-proliferating zones of calf's rib cartilage, rachitic and non-rachitic cartilage from children, and proliferating and non-proliferating zones of cartilage from rachitic children. There is no relationship between calcification and calcium fixation of these tissues. S. S. Zilva.

Biological significance of salt concentration in natural waters. C. Schlieper (Naturwiss., 1928, **16**, 229—237).—Both the number and the size of many marine animals decrease in regions where the salt concentration is less than that of the open sea. This is partly due to the difference in osmotic pressure between the body fluid and the external solution. In many cases the breathing apparatus of fresh-water animals is larger than that of closely related marine animals. It is suggested that the greater capacity for absorption of carbon dioxide possessed by sea-water is the reason why breathing is easier in sea-water than in fresh water. Rise of temperature increases the combination of carbon dioxide, and this explains why certain marine animals thrive in fresh water in warm climates. The effect of the carbonate/hydrogen carbonate equilibrium on the distribution of plankton is discussed. W. A. Richardson.

Oxidation of luciferin without luciferase; mechanism of bio-luminescence. E. N. Harvey (J. Biol. Chem., 1928, **78**, 369—375).—Luciferin in aqueous solution can be oxidised by a variety of oxidising agents, but in no case is luminescence produced unless luciferase be present; an alcoholic solution of luciferin luminesces slightly when heated or on treatment with certain oxidising agents. The presence of oxidising luciferin alone or of luciferase alone does not cause fluorescent dyes to luminesce, nor is luminescence shown by a solution of luciferase in electrical contact with one of luciferin. The previous hypothesis, that luminescence is due to activation of the luciferase molecules in the process of oxidising luciferin, is therefore confirmed.

C. R. Harington.

Salt action and diuresis. E. Bloch (Z. klin. Med., 1927, **106**, 733—744; Chem. Zentr., 1928, i, 1298).—A study of the elimination of salts after simultaneous administration of water and intravenous injection of potassium chloride.

A. A. Eldridge.

Phosphorus and calcium in blood after injection of brewer's yeast. C. I. Urechia and G. Popoviciu (Compt. rend. Soc. Biol., 1927, **97**, 1009—1011; Chem. Zentr., 1928, i, 371).—Injection of brewer's yeast causes fever; during rigor the phosphorus and calcium content of the blood is increased, falling to normal values during the fever.

A. A. Eldridge.

Pharmacological studies of the sterols. H. Seel (Arch. exp. Path. Pharm., 1928, **133**, 129—180).—The substances were employed in the non-irradiated as well as in the irradiated condition and colloidal

aqueous solutions were used. Oxycholesterol, which always accompanies cholesterol in the animal organism, was specially considered. All the sterols and derivatives used powerfully stimulated the activity of the normal isolated frog heart and oxycholesterol had the strongest effect. Fatigued and also injured (poisoned) frogs' hearts were frequently restored to normal by these sterols. Irradiation of the compounds by "artificial sunlight," except in a few cases where there was slight increase of stimulating effect on the heart, had scarcely any influence on that effect. The action of sterols on the heart is a specific effect, although adsorption phenomena may also be involved. The sterols, particularly oxycholesterol and oxysitosterol, acted powerfully on the smooth muscle of the uterus, raising the tonus and stimulating contraction. These sterols antagonised the influence of adrenaline on the activity of the uterus; they had only slight effect on the blood pressure. Oxycholesterol had a beneficial influence on metabolism and on growth. The oxygen requirements of rats were raised by it; the growth of their hair and the condition of their skin were greatly improved. Unirradiated oxycholesterol and oxysitosterol blackened the photographic plate, but the view that the photographic effect is related to antirachitic and antixerophthalmic properties could not be confirmed. Of the substances used, even when irradiated, only irradiated cholesterol had antirachitic effects. Unirradiated oxycholesterol prevented xerophthalmia, cured it in its initial stages, and favourably modified its effects in advanced stages. In "avitasterolosis"-*A* and -*D* there was a limitation of the oxidations in the organism. In xerophthalmia the diminution of the basal metabolic rate ran parallel with the retardation or stoppage of growth, but in rickets the limitation of oxygen consumption reached a much greater value than would correspond with the loss of weight.

W. McCartney.

[Action of] animal poisons [on lecithins and lysocithins]. A. Contardi and P. Latzer (Biochem. Z., 1928, **197**, 222—236).—The hæmolytic power of lysocithin prepared from egg yolk by the action of cobra venom was found to be slight at a dilution of 1/20,000, strong at 1/18,000, whilst that of its double salt with cadmium chloride was slight at 1/20,000, but strong at 1/15,000; of lysocithin–cadmium chloride prepared from lecithin from pancreas slight at 1/4000, strong at 1/2000, and obtained from brain slight at 1/6000 and strong at 1/5000. Wasp poison decomposed both lecithin– and lysocithin–cadmium chloride to cadmium chloride, glycerol, phosphoric acid, fatty acids, and choline; the lipase of castor seed acted similarly, but with octahydroanthracenesulphonic acid ("idrapid") a lysocithin was obtained which was strongly hæmolytic at a dilution of 1/4000, before undergoing similar decomposition. Calcium and sodium glycerophosphates were decomposed to give phosphoric acid by wasp poison and "idrapid," but not by cobra or bee poison or castor-seed lipase. Bee, cobra, and wasp poison and castor-seed lipase did not attack phytin. The nature of the fatty acids of lecithin was investigated by determining iodine values.

L. C. Baker.

Guanidine. II. Distribution of guanidines in acute guanidine and parathyroprivia tetanies. III. Water content of certain tissues during acute guanidine and parathyroprivia tetanies. IV. Changes in guanidine action and in parathyroprivia tetany produced by dextrose. M. M. Ellis (Biochem. J., 1928, **22**, 930—936, 937—940, 941—946).—II. Analyses of blood, voluntary muscle, liver, kidney, and brain of rabbits in acute guanidine tetany and in acute phenol tetany were made and compared with those of normal animals for guanidine and creatine content. The guanidine contents of the livers, kidneys, and brains of animals in acute guanidine tetany were high, whilst those of the blood and muscle even at the point of death were lower than in normal animals. There were relatively large amounts of guanidine in the brain of the guanidine tetany animals. No storage of guanidine was observed. The guanidine content of the brain of the untreated cat in acute parathyroprivia tetany is relatively high.

III. Brain, kidney, and striated muscle from animals (rabbit, cat, frog, and rat) in acute guanidine and parathyroprivia tetanies have a higher water content than the same tissues from normal animals. The ash : solids ratio in the respective tissues of both cases is, however, the same. Blood from rats in acute guanidine tetany has a lower water content than normal rat blood.

IV. From experiments on frogs it was found that dextrose–guanidine is less active both chemically and biologically than its equivalent of guanidine base. Combined injections of dextrose and guanidine carbonate are less toxic than injections of guanidine carbonate alone. Parathyroprivia tetany in cats is relieved by means of dextrose and adrenaline injections.

S. S. Zilva.

Chemical constitution and pharmacological properties of the methylglyoxalines. I. J. V. Supniewski (Acta Biol. Exp. Warsaw, 1928, **1**, No. 9, 1—19).—4-Methylglyoxaline has a depressor action, is a strong diuretic, and produces contractions in the isolated guinea-pig's uterus, but not of an intestinal loop. 2-Thion-4-methylglyoxaline and glyoxaline-4-carboxylic and -4 : 5-dicarboxylic acids are pharmacologically inactive, as is 4-hydroxymethylglyoxaline, except that the latter excites uterine and intestinal contractions. 5-Methyl-4-hydroxymethylglyoxaline has an action similar to that of methylglyoxaline. 4-Chloromethylglyoxaline has a powerful depressor action, inhibits the isolated frog's heart, and produces uterine contraction. 4-Aminomethylglyoxaline has an action similar to that of histamine, although weaker. 2-Thion-4-aminomethylglyoxaline has a feeble depressor action, and a slight inhibitive action on cardiac muscle. 4-Diethylaminomethylglyoxaline has an oxytocic and peristaltic action, inhibits the action of the heart, has an intense depressor action, and enhances both the rate and the amplitude of respiration. 4-Piperidylmethylglyoxaline is a powerful depressor, a cardiac inhibitor, a powerful diuretic, and an oxytocic agent, whilst having no action on other non-striated muscles.

R. Truszkowski.

Metabolism of animals after [administration of] synthalin. A. Moschini (Compt. rend. Soc.

Biol., 1927, **97**, 1199—1201; Chem. Zentr., 1928, i, 713).—The influence of synthalin on metabolism differs from that of insulin. Small doses (up to 2 mg. per kg.) of synthalin raise the blood-sugar; the hypoglycæmia following large doses (2·5—3 mg. per kg.), but not the other toxic symptoms, is affected by administration of dextrose. A. A. ELDRIDGE.

Hypoglycæmic properties of galegine sulphate. H. SIMONNET and G. TANRET (Bull. Soc. Chim. biol, 1928, **10**, 796—805).—See this vol., 199.

Action of some convulsion-producing poisons on blood-sugar, lactic acid, and alkali reserve. I. FUJII (Arch. exp. Path. Pharm., 1928, **133**, 242—256).—The substances used (picrotoxin and the sodium derivative of santonin) increase blood-lactic acid in two ways: If convulsions occur increased muscular activity leads to increase of lactic acid without change in the amount of blood-sugar. Without or before convulsions there is a second form of lactic acid increase which runs parallel with an increase in blood-sugar. These actions on lactic acid and blood-sugar are centrally conditioned and depend on the intactness of the splanchnic nerve. A connexion with adrenaline secretion may be assumed as far as increase of blood-lactic acid and of blood-sugar is concerned, for adrenaline produces simultaneous increases of both substances. Increase of lactic acid and consequent lowering of alkali reserve results in increased tendency to convulsions. If this lowering is prevented by section of the splanchnic nerve or if alkali is supplied the minimal dose required to produce spasms is raised not inconsiderably. Experiments with guanidine were inconclusive, but it seems that the convulsions produced by it are not analogous to those caused by insulin. W. MCCARTNEY.

Chronic morphine poisoning in dogs. I. General symptoms and behaviour during addiction and withdrawal. O. H. PLANT and I. H. PIERCE. **II. Changes in blood cells and hæmoglobin during addiction and withdrawal. III. Blood-sugar during tolerance and withdrawal.** J. H. PIERCE and O. H. PLANT (J. Pharm. Exp. Ther., 1928, **33**, 329—357, 359—370, 371—385).

Accumulation of arsenic in the brain following administration of neosalvarsan, arsenious and arsenic acids. B. ENGELMANN (Arch. exp. Path. Pharm., 1928, **133**, 181—191).—After intravenous injection of neosalvarsan a fairly definite accumulation of arsenic in the brain was observed, provided injections were continued for several weeks. When dextrose was injected at the same time as neosalvarsan increased amounts of arsenic accumulated in the brain. Considerable increase also took place when the drug was administered during fever. When injections were given during urethane narcosis there was partial or total suppression of the normal capability of the brain to accumulate arsenic. Deep ether narcosis acted similarly. The brain did not take up increased amounts of arsenic when the injections were preceded by administration of substances such as amyl nitrite, caffeine, and theophylline nor, apparently, in acute meningitis. Sodium arsenite and sodium arsenate when injected alone had effects similar to those produced by neosalvarsan alone. Rabbits were used, but the neosalvarsan was administered under conditions as similar as possible to those used for human beings. Arsenic was determined in the brain by Lockemann's modification of the method of Marsh and the determinations were checked, where possible, by Bang's process (A., 1926, 39). W. MCCARTNEY.

Toxicology of lead and its compounds. IV. Electrolytic detection of lead. V. Nephelometric determination of lead. P. W. DANCKWORTT and E. JURGENS.—See this vol., 981.

Urinary hæmatoporphyrin excretion in chronic lead poisoning. S. HIRSCHHORN and W. ROBITSCHEK (Z. klin. Med., 1927, **106**, 664—670; Chem. Zentr., 1928, i, 1298).—Hæmatoporphyrinuria, in which the spectrum of acid hæmatoporphyrin is visible with a 5 cm. layer of unacidified urine, is pathological; this was observed in 6 of 77 cases of lead poisoning. There is a close connexion between the disintegration of erythrocytes and the production of hæmatoporphyrin. A. A. ELDRIDGE.

Similarities in the catalytic action of enzymes and of definite organic substances. W. LANGENBECK (Z. angew. Chem., 1928, **41**, 740—745).—A review. A. DAVIDSON.

Toxic action of nascent tellurium and selenium on enzymes. R. LABES (Arch. exp. Path. Pharm., 1928, **133**, 57—62).—When saliva is incubated with hydrazine hydrate and telluric acid, the tellurium which is formed in a finely-divided condition is flocculated and at the same time the diastatic action of the saliva is destroyed. Hydrazine and telluric acid separately are without action, and if sufficient mucin is present so that precipitation of the colloidal tellurium does not occur, the diastase is not inactivated. It therefore appears that in order that inactivation should take place the nascent tellurium particles must come into direct contact with the enzyme. Nascent selenium behaves similarly. W. O. KERMACK.

Development of mutase action in germinating barley. Z. I. KERTÉSZ (Z. physiol. Chem., 1928, **176**, 144—150).—The enzymic mutation of acetaldehyde by germinating barley was found to vary directly with the time of germination. The mutase action decreased in the rootlets and increased in the shoots from the 12th to the 18th day. In comparative experiments with yeast, reaction coefficients showed no constancy, but a definite relation existed between the amount of yeast and the mutase action.

J. H. BIRKINSHAW.

Role of hexosemonophosphate in enzymic degradation of sugar. H. VON EULER and K. MYRBACK (Annalen, 1928, **464**, 56—69).—The mechanism of the fermentation of dextrose is probably as follows: (1) Under the influence of a synthetic enzyme, phosphatese, Robison's hexosemonophosphate (A., 1923, i, 86) is formed, but no free phosphate or carbon dioxide appears. (2) The monophosphate, under the influence of a " mutase " and the co-zymase, undergoes conversion, half into alcohol and carbon dioxide, and half into hexosediphosphate. (3) The latter is converted by a phosphatase into a hexose (lævulose ?), which (4) enters into the chain of processes

given above. The velocity of fermentation of monophosphate by dried yeast is the same as that of a mixture of equivalent quantities of dextrose and phosphate.

A method is described for the determination of mono- and di-phosphate during the course of fermentation (cf. Harden and Henley, A., 1927, 1113).

Most preparations of dextrose monophosphate using dried yeast give a product with $[\alpha]_D$ about $+26°$ (barium salt $+13°$), but when a very strongly phosphatising yeast was used, the product had $[\alpha]_D$ $+63°$ and is probably distinct from Robison's material.

E. E. TURNER.

Occurrence and decomposition of pyrophosphate in muscle. K. LOHMANN (Naturwiss., 1928, **16**, 298).—The increase of phosphate on digestion of muscle with sodium hydrogen carbonate solution is ascribed chiefly to enzymic hydrolysis of pyrophosphate to dipotassium hydrogen orthophosphate, and not to decomposition of lactacidogen.

CHEMICAL ABSTRACTS.

Dehydrogenation of malic acid. I. A. HAHN and W. HAARMANN (Z. Biol., 1928, **87**, 465—471).—In the presence of washed muscle reduction of methylene-blue is brought about by malic acid and the formation of carbon dioxide is also observed. The liberation of carbon dioxide appears to occur subsequent to the reduction of methylene-blue and it is suggested that by the dehydrogenation of malic acid oxalacetic acid is formed and that this compound then liberates carbon dioxide at a rate accelerated by the presence of the muscle tissue.

W. O. KERMACK.

Enzymic decomposition of starch. K. SJOBERG (Fermentforsch., 1928, **9**, 329—335).—A review.

F. E. DAY.

Lipase of the larva of *Galleria mellonella*. V. PERTZOV (Compt. rend., 1928, **187**, 253—255).—In solutions of p_H 8·2 ($\pm$1) and at 37—45°, the lipase of the larva hydrolyses emulsions of olive oil and of beeswax. The fat of tubercle bacilli, killed by heat, is also hydrolysed at 45°, with formation of acids. The lipase or lipases are equally soluble in 50% glycerol, *N*-sodium chloride solution, and in water made alkaline with ammonia. The presence of ethyl alcohol stops the action of the lipase. The extracts did not completely destroy living tubercle bacilli but produced very characteristic changes, the bacilli forming granules and losing their acid-fastness.

R. BRIGHTMAN.

Rennin coagulation of milk. Effect of hirudin, heparin, kephalin, and removal of fat. J. B. STONE and C. L. ALSBERG (J. Biol. Chem., 1928, **78**, 557—572).—Hirudin and kephalin were without effect on the coagulation of milk by rennin; various preparations of heparin, similar as regards their effect on blood coagulation, were variable in their effect on milk clotting. Extraction of a rennin solution with ether did not impair its coagulating properties. The presence of large amounts of ether, alcohol, or chloroform inhibits coagulation, whilst benzene, light petroleum, and saponin have little effect; soap solution delays coagulation, but the effect is neutralised by simultaneous addition of calcium chloride, and is probably due to precipitation of calcium. Milk skimmed in the centrifuge coagulates more slowly than milk skimmed by gravity; this may be partly due to the violent agitation of the milk in the former case.

C. R. HARINGTON.

Conductivity method and proteolysis. II. Interpretation of conductivity changes. H. D. BAERNSTEIN (J. Biol. Chem., 1928, **78**, 481—493; cf. A., 1927, 992).—At p_H 1·4 or less the rate of change of conductivity of a peptic digest of egg-albumin is coincident with the rate of change of amino-nitrogen; at more alkaline reactions there is divergence between the two. The change of conductivity calculated from the change in p_H is greater than the observed change when the conductivity is decreasing, and less when it is increasing; the discrepancy is to be ascribed to the dicarboxylic acids, since a similar phenomenon is observed on addition of glutamic or aspartic acid to a solution of hydrochloric acid, whilst on addition of glycine to such a solution the observed and calculated changes in conductivity show good agreement. It appears that the binding of hydrogen ions by amino-acids which takes place during peptic digestion is explicable on Bjerrum's theory (A., 1923, i, **444**) of ampholytic dissociation.

C. R. HARINGTON.

Action of pepsin of herbivora and carnivora on vegetable and animal proteins. H. W. VAHLTEICH (Z. physiol. Chem., 1928, **176**, 222—230).—No differences were observed in the digestion of various proteins by the pepsin derived from the horse and that from the dog. The number of carboxyl groups set free, determined by Willstätter's method, was consistently higher than the number of amino-groups determined according to Van Slyke; the ratio $CO_2H : NH_2$ varied according to the protein used.

J. H. BIRKINSHAW.

Alcohol. VI. Influence of alcohol on the action of pepsin. G. FRANZEN (Arch. exp. Path. Pharm., 1928, **133**, 111—120).—Up to concentrations of about 11%, ethyl alcohol promotes the proteolytic action of pepsin *in vitro*, but at higher concentrations it is inhibiting. White wine, red wine, and beer have a favourable effect on the activity of pepsin approximately corresponding with their content in ethyl alcohol, but this effect is most marked in the case of white wine. It appears to be partly neutralised in the case of beer by its action on the acid present in the digestion mixture and in the case of red wine by its content of tannic acid.

W. O. KERMACK.

Peptidases. H. VON EULER and Z. I. KERTECZ (Ber., 1928, **61**, [*B*], 1525—1529).—Fission of glycylglycine by a glycerol extract of pig intestine is greatly hindered by alcohol, boric acid, aniline, or glycine, but the effect of ethyl aminoacetate could not be investigated owing to the presence of lipase in the enzyme mixture. The effect of quinine sulphate or quinidine sulphate is not marked. Ammonia is without influence. The fission of alanylglycine is inhibited by glycine.

H. WREN.

Determination of trypsin in pancreatic juice. B. GOLDSTEIN (Fermentforsch., 1928, **9**, 322—328).—The Fuld–Gross method is modified by taking the first appearance of tryptophan as the end-point, instead of the absence of casein precipitate on acidifying.

F. E. DAY.

Effect of acidity and boiling on enterokinase. I. P. RASENKOW (Fermentforsch., 1928, 9, 382—388).—Working with material obtained from dogs it is found that 0·5% hydrochloric acid has no harmful effect on enterokinase, which can activate pancreatic secretion in presence of 0·3% of hydrochloric acid. Boiling destroys the activating power of enterokinase in neutral but not in such acid solutions.

F. E. DAY.

Influence of thyroxine, 3 : 5-di-iodotyrosine, and thyroid-substance on the course of autolysis and on the action of erepsin and trypsin. E. ABDERHALDEN and K. FRANKE (Fermentforsch., 1928, 9, 485—493).—The autolysis of 35—45 g. of pulped liver with 100 c.c. of water and 50 c.c. of phosphate buffer, p_H 8, is retarded by 1 mg. of thyroxine, but accelerated by 0·01 mg. and even by 0·001 mg. 3 : 5-Di-iodotyrosine and thyroid behave similarly, but not in proportion to their iodine content. The effect appears to be to some extent affected by the reaction of the medium. Similar results are obtained as regards the action of pancreas extract and erepsin on *dl*-leucylglycine and of trypsin-kinase on peptone and gelatin, although to a much less marked degree.

F. E. DAY.

Kinetics of the tyrosinase of potatoes. H. HAEHN and J. STERN (Fermentforsch., 1928, 9, 395—402).—The course of the oxidation of tyrosine under the influence of tyrosinase is unimolecular in presence of excess of oxygen. The coefficient is dependent on the concentration of the enzyme, not on that of the tyrosine. The ratio K/(weight of enzyme preparation) is therefore a measure of activity.

F. E. DAY.

Tyramine oxidase. I. An enzyme system in liver. M. L. C. HARE (Biochem. J., 1928, 22, 968—979).—A cell-free extract of liver is described which is capable of oxidising *p*-hydroxyphenylethylamine, one atom of oxygen being taken up per molecule of tyramine. Hydrogen peroxide is produced during the reaction, whilst methylene-blue is not reduced. The oxidation is not affected by the addition of 0·002M-potassium cyanide. Deamination of the compound occurs simultaneously, but only half the nitrogen in the tyramine molecule is accounted for as ammonia. The optimum reaction of the system is at p_H 10·0. The enzyme is inactive but not destroyed at p_H 4·4, but destruction occurs at p_H 11·5. Phenylethylamine and possibly also *p*-aminophenol are oxidised by the enzyme, but tyrosine and many other substances are not attacked. The enzyme is distinct from tyrosinase. The oxygen uptake was measured by the Barcroft differential manometer.

S. S. ZILVA.

Glycocyamase. J. KARASHIMA (Z. physiol. Chem., 1928, 177, 42—46).—Ox-liver preparations contain glycocyamase, since they convert guanidinoacetic acid into carbamide and glycine. The enzyme is absent from kidney, pancreas, spleen, and lung of cattle, and from liver and kidney of hens.

C. HOLLINS.

Specific action of salts in extraction of urease from amœbocytes of *Limulus*. L. LOEB, I. LORBERBLATT, and M. E. FIELD (J. Biol. Chem., 1928, 78, 417—431).—Magnesium and manganese chlorides show, in a smaller degree, the favourable effect previously observed (A., 1927, 484) for the salts of the alkaline earths in the extraction of urease; tervalent ions, on the other hand, have little or no effect on the extraction. Those salts which, in dilute solution, are most efficient in extracting urease are, in higher concentration, most toxic to the enzyme. An optimal extraction of the enzyme by sodium chloride solution is obtained in presence of 0·005N-sodium hydroxide and of 0·0005N-hydrochloric acid. Addition of calcium chloride to a sodium chloride extract does not affect the activity, but its addition to a magnesium chloride extract increases the activity in proportion to the calcium chloride added. Extractions with mixtures of salts give results intermediate between those obtained with the pure salts. It appears that the interactions of urease with salts may be divided into non-specific effects, *e.g.*, the injurious action of the heavy metals and osmotic effects, and specific effects consisting of formation of compounds with various cations; of these compounds, those with the alkaline earths are the most active, and those with the alkali metals are irreversible in character.

C. R. HARINGTON.

Influence of structure on the kinetics of desmolases. I. Systems uricase–uric acid–active and inactive charcoal or protein. S. J. PRZYŁECKI (Acta Biol. Exp. Warsaw, 1928, 1, No. 6, 1—26).—Uric acid and uricase are strongly adsorbed on iron-free charcoal, from which the former substance may to a great extent be eluted by the addition of alcohols. Adsorption does not inactivate uricase, but simultaneous adsorption of uric acid and uricase leads to a reduction in the total quantity of uric acid decomposed, although the percentage of that oxidised in solution, as opposed to that present in the system as a whole, is the same whether charcoal is present or not. Oxidation of uric acid is in all cases proportional to its concentration in solution, and for this reason is enhanced by the addition of elutive agents. Where active animal charcoal is used, both enzymic and catalytic oxidations occur; the action of these two factors is, however, independent, so that if allowance be made for the quantity of uric acid oxidised through the agency of the charcoal, the results obtained are similar to those of the first system. Restriction of access of oxygen does not affect these results. Coagulated egg-white has a very feeble adsorptive action on uric acid, but adsorbs uricase very strongly. Since simultaneous adsorption does not take place, the introduction of this adsorbent does not sensibly retard the reaction of uricolysis, and the same applies to soluble egg-white.

R. TRUSZKOWSKI.

Uricase and its action. I. Preparation. S. J. PRZYŁECKI (Biochem. J., 1928, 22, 1026—1034).—Frogs were ground, extracted with a mixture of water, chloroform, and glycerol, and the extract was precipitated with acetone. The precipitate when dissolved in a volume of 1% salt solution which was equivalent to the original volume of the glycerol extract yielded a solution more active than the original extract. This extract can be further purified by dialysis, ultra-filtration, or reprecipitation with alcohol or by a mixture of alcohol and acetone.

Uricase preparations from mammalian kidney and from wheat-seed were similarly prepared.
S. S. ZILVA.

Wildier's bios. Isolation and identification of "bios I." (MISS) E. V. EASTCOTT (J. Physical Chem., 1928, **32**, 1094—1111; cf. Tanner, Chem. Reviews, 1924, **1**, 399).—The crops of yeast obtained under standard conditions from 48 vegetable and 15 animal preparations are compared with those obtained by adding bios I or II (prepared from malt combings) or wort to the extracts. The results indicate that all the extracts examined contain bios I and II which are physiologically identical with those prepared from malt-combings. Bios I has been isolated from tea dust and is identical with *i*-inositol. The curves showing the rate of reproduction of yeast in solutions containing salts, sugar, inositol, and crude bios II have the same form as those obtained by Clark (A., 1922, i, 501) with solutions of salts, sugar, and wort. The inositol taken up by yeast can be quantitatively recovered by hydrolysis. Yeast grown in a solution containing only sugar and salts also yields inositol on hydrolysis, but in smaller amount.
L. S. THEOBALD.

Influence of various concentrations of phenol on the rate of alcoholic fermentation. E. ABDERHALDEN (Fermentforsch., 1928, **9**, 389—391).—In fermentations of 2·5 g. of dextrose dissolved in 25 c.c. of phosphate buffer solution (p_H 6), using 1·0 g. of yeast, the presence of 0·1—0·2 γ of phenol generally causes a distinct acceleration of the rate of fermentation.
F. E. DAY.

Liberation from yeast of substances giving the nitroprusside reaction. Y. POURBAIX and E. L. KENNAWAY (Biochem. J., 1928, **22**, 1112—1127).—A large number of agents have been examined for their power to liberate from yeast substances giving the nitroprusside reaction. Positive results were obtained by heating above a certain temperature, freezing, grinding, ultra-violet light, by exposure to certain saturated salt solutions or to many organic compounds of the phenol and amine classes. Many compounds inhibit the nitroprusside reaction, hence some of the negative results may be due to such suppression of the reaction. Some of the substances giving the reaction are liberated intracellularly and some extracellularly.
S. S. ZILVA.

Bacterial catalase. A. ITANO and S. ARAKAWA (Ber. Ohara Inst. landw. Forsch., 1928, **3**, 505—528).—The activity of the catalase of a thermophilic cellulose-fermenting organism is vigorous at 65° in cellulose medium, but is inhibited in dextrose broth. At 23° there is no inhibition in the latter medium, and since its hydrogen-ion concentration changes within 48 hrs. from p_H 6·75 to 4·98 at 65° but remains almost unchanged at 24°, it is concluded that the inhibition at the higher temperature is due, in part at least, to the increase in p_H. In determining the volume of oxygen liberated from hydrogen peroxide by the enzyme, the gas is collected for 10 min. from the time of starting the reaction. The potassium hydrogen phthalate of Clark's buffer solution has a marked disturbing influence on the results obtained when, in making the test, titration with permanganate of buffered solutions is substituted for the determination of the volume of oxygen liberated. Phosphate mixture has no such influence. The catalase shows greatest activity between p_H 8 and 9. At p_H less than 6·5 the activity diminishes rapidly, becoming almost nil at p_H 2·5, but it disappears more slowly on the alkaline side and is quite considerable at p_H 10. The vigour of catalase action increases with the age of the culture up to about 72 hrs., after which it decreases. The velocity of action is greatest at the end of 5 min. and diminishes thereafter. The reaction seems to be unimolecular. Activity of the catalase is at a minimum at 0° and at a maximum at 60°, but is quite considerable at 80° and is not destroyed altogether at 100°. Magnesium sulphate and copper sulphate have very slight depressive influence on the catalase action, but hydrochloric acid, mercuric chloride, and potassium cyanide have very marked effects, that of the last named being strongest.
W. MCCARTNEY.

Bacterial denitrification. M. P. KORSAKOVA (Bull. Acad. Sci. U.S.S.R., 1927, [vi], 1221—1250).—The results of experiments with *B. fluorescens liquefaciens* and *B. pyocyaneus* show that denitrification is a process of the reduction of nitrates in anaerobic conditions, the necessary energy being supplied by the oxidation of organic matter; when the latter is not present in sufficient amount, the normal course of the reduction of nitrates is disturbed. When denitrification proceeds in presence of dextrose, the p_H of the solution does not change during the whole process, and when citric acid is supplied as organic matter, the solution becomes alkaline and the quantity of carbon dioxide developed per unit quantity of free nitrogen is double that formed in presence of dextrose. The reduction process takes place in three phases, $2HNO_3 \longrightarrow 2HNO_2+O_2$, $2HNO_2 \longrightarrow$ intermediate product$+O_2$, intermediate product $\longrightarrow N_2+H_2O+O$. The fact that this intermediate product yields one molecule of nitrogen per atom of oxygen on reduction suggests that it may be Angeli's unstable nitrosyl, HNO. The dextrose present in the solution during denitrification is oxidised completely to carbon dioxide, and the ratios of the oxidised dextrose to the reduced nitrate on the one hand and to the carbon dioxide and nitrogen formed on the other are expressed by the equations $C_6H_{12}O_6+6O_2=6CO_2+6H_2O$ and $5C_6H_{12}O_6+24KNO_3=24KHCO_3+6CO_2+12N_2+18H_2O$.
T. H. POPE.

Nitrite test as applied to bacterial cultures. G. I. WALLACE and S. L. NEAVE (J. Bact., 1927, **14**, 377—384).—In high nitrite concentrations, favoured by peptones containing sulphur, the use of dimethyl-α-naphthylamine is preferred to that of α-naphthylamine.
CHEMICAL ABSTRACTS.

Composition of the active principle of tuberculin. IX. Fractional heat coagulation of the protein of tuberculin. X. Isolation in crystalline form and identification of the active principle of tuberculin. F. B. SEIBERT (Amer. Rev. Tuberculosis, 1928, **17**, 394—401, 402—421).—IX. Specific biological activity is associated with all the fractions obtained by coagulating the whole protein

of tuberculin at different temperatures, and a protein-free active fraction could not be thus obtained. All the fractions may be derivatives of the same protein in varying stages of chemical change.

X. The specifically active substance in tuberculin is an unstable, water-soluble coagulable protein, containing no carbohydrate, and crystallisable by Hopkins' method at p_H 4·9. CHEMICAL ABSTRACTS.

Active principle of tuberculin. XI. Preparation and assay of standard undenatured tuberculin. F. B. SEIBERT (J. Biol. Chem., 1928, **78**, 345—362).—A solution of tuberculin, obtained by growing tubercle bacilli on a synthetic protein-free medium, may be concentrated many times with negligible loss of activity by ultra-filtration through alundum shells impregnated with a 10—12% solution of guncotton in glacial acetic acid; further removal of diffusible impurities may be effected by addition of 0·5% phenol solution to the tuberculin solution during filtration. The purified tuberculin may be assayed chemically by determining the volume of the precipitate produced by addition of trichloroacetic acid; 0·2 mg. of the purified protein is a lethal dose for a 400—500 g. tuberculous guinea-pig.

C. R. HARINGTON.

Cultural separation of bacteria on the basis of triphenylmethane coefficients. J. W. CHURCHMAN and L. SIEGEL (Stain Tech., 1928, **3**, 73—80).—The crystal-violet coefficients of five Gram-positive and five Gram-negative organisms indicate that all known aerobic organisms, on the basis of their triphenylmethane coefficients, could probably be placed on a curve which would run parallel with the results of Gram staining. By making use of the differences in these coefficients cultural separations of organisms within the Gram groups may be effected.

H. W. DUDLEY.

Effect of chemical nature of a decoloriser on its action. I. The Gram classification. A. E. STEARN and E. W. STEARN. **II. Apparent isoelectric point.** E. W. STEARN and A. E. STEARN (Stain Tech., 1928, **3**, 81—86, 87—93).—I. Acidic decolorisers are more regular than basic substances in their action on the Gram stain.

II. The isoelectric point of a bacterial system is the hydrogen-ion concentration at which there is equal retention of anion and cation. This is determined by finding the point at which there is equal retention of acidic and basic stains when acetone is used as a decoloriser. Acidic decolorisers shift this point to a higher p_H, whilst basic decolorisers have the opposite effect. H. W. DUDLEY.

Factors influencing the staining properties of fluorescein derivatives. H. J. CONN and W. C. HOLMES (Stain Tech., 1928, **3**, 94—104).—The disodium salts of eosin, erythrosin, phloxin, and rose-Bengal are indifferent stains for bacteria in dried films of soil. If, however, 0·0001—0·1% of a salt of calcium, aluminium, magnesium, or lead be added to the solutions of the dyes they stain much more intensely. Practically identical staining can be obtained by using suspensions of the calcium, aluminium, or lead salts of these dyes, although their solubilities are very small. H. W. DUDLEY.

New circulation hormone and its action. III. E. K. FREY and H. KRAUT (Arch. exp. Path. Pharm., 1928, **133**, 1—56).—The heart stimulant previously described (A., 1926, 1168) as occurring in urine has been further purified and its physiological action on various organs has been investigated. The salts are dialysed away through parchment paper, through which the active substance passes only slowly, and concentration of the substance is then effected through adsorption on kaolin or alumina, from which it may be removed by elution with diammonium hydrogen phosphate. Precipitation with uranyl acetate in presence of alcohol is also a convenient means of purification. For further purification it may be adsorbed on finely-divided benzoic acid, which may then be removed by means of ether and alcohol. The active substance is highly unstable, being inactivated by acid or alkali or by boiling, and in its purified form is destroyed even by precipitation with alcohol. It is not yet possible to characterise the substance by chemical reactions. Its activity appears to be increased by cocaine and by calcium salts.

Blood and blood-serum contain some unknown substance capable of inactivating the active substance. Horse-serum inactivates strongly, pig-serum very little. The inactivating substance is very unstable, since, for example, blood loses its power of inactivation in a few days and also particularly rapidly when treated with acid. During inactivation by blood the substance is not destroyed but forms an inactive combination with the inactivating substance. The active substance is not choline, pituitrin, or histamine, although certain of its physiological effects are similar to those of the last-named substance. The compound appears to be present normally in the blood, but usually in the form of its inactive combination and only exceptionally in the free condition. It is considered to be a hormone and its physiological effects are in general such as facilitate muscular activity. W. O. KERMACK.

Influence of adrenaline on the protein metabolism of isolated organs. B. S. SENTJURIN (Arch. exp. Path. Pharm., 1928, **133**, 233—241).—The influence of adrenaline and. in the first place also, of Ringer–Locke solution on the secretion of proteins by isolated organs has been examined. Determinations of total nitrogen and of residual nitrogen were made and the amount of protein nitrogen was obtained by difference. Prolonged action of Ringer–Locke solution produces gradual but continuous decrease in the amount of residual nitrogen and an initial decrease followed by increase in that of protein nitrogen. Ordinarily the absolute amount of protein nitrogen is greater than that of residual nitrogen and the difference increases continuously in course of time. Adrenaline causes the amount of residual nitrogen to increase, but its effect on protein nitrogen is variable. The ratio of residual nitrogen to protein nitrogen increases. Although the experiments were made for the most part on testicles, the behaviour of other organs is the same. W. MCCARTNEY.

Action of adrenaline on the mobilisation of sugar in muscle. W. GRUNKE and A. KAIRIES (Arch. exp. Path. Pharm., 1928, **133**, 63—68).—Per-

fusion of the muscle of the frog with Ringer's solution containing adrenaline causes the removal of a greater quantity of sugar than when adrenaline is absent, although the effect of adrenaline on the muscle is less marked than on liver when similarly perfused.

W. O. KERMACK.

Effect of insulin on protein metabolism. V. C. KIECH and J. M. LUCK (J. Biol. Chem., 1928, **78**, 257—264).—Administration of insulin to normal rats caused an increase in the carbamide content and a decrease in the amino-acid nitrogen content of the whole animal, indicating an increase in the rate of catabolism of amino-acids together with a decrease in the rate of formation of the latter by degradation of protein. C. R. HARINGTON.

Effect of insulin on sugar content of erythrocytes. H. C. TRIMBLE and S. J. MADDOCK (J. Biol. Chem., 1928, **78**, 323—336).—The sugar content of erythrocytes is better determined by direct analysis of the separated cells than indirectly by determination of the sugar content of whole blood and plasma and calculation from the cell-volume. Administration of insulin to diabetic patients and to depancreatised dogs causes an almost parallel decrease of sugar in red blood-corpuscles and plasma, no signs of a sudden preliminary drop in the former being observed.

C. R. HARINGTON.

Effect of insulin on the metabolism of striped muscle. K. KIMURA and H. TAKAHASHI (Tohoku J. Exp. Med., 1928, **10**, 215—247).—Injection of insulin lowers the oxygen consumption of the dog's gastrocnemius and diminishes the sugar content of the blood circulating through the muscle through the arrest of cell activity. Insulin increases the hæmoglobin content of the blood, and diminishes the serum-globulin. The changes in serum sodium chloride are irregular. CHEMICAL ABSTRACTS.

Insulin hypoglycæmia and insulin shock in man. O. KLEIN and H. HOLZER (Z. klin. Med., 1928, **107**, 94—112; Chem. Zentr., 1928, i, 1200).—An examination of the relation between insulin (hypoglycæmic) shock, the reserve carbohydrate, the formation of carbohydrate, and the alkali reserve.

A. A. ELDRIDGE.

Insulin, folliculin, and glycæmia in normal dogs. F. RATHERY, R. KOURILSKY, and (MLLE.) Y. LAURENT (Compt. rend., 1928, **187**, 255—257).—Folliculin and insulin exert opposing influences on glycæmia in dogs. In the simultaneous injection of folliculin (10 units) and insulin (20 units) into animals of either sex, folliculin prevents insulin from exerting its normal effect on the initial hyperglycæmia produced by the ingestion of dextrose, and retards the later hypoglycæmia due to insulin. In starving animals the hypoglycæmic effect of insulin is decreased.

R. BRIGHTMAN.

Hormones and vitamins. New definitions of vitamins. L. RANDOIN and H. SIMONNET (Bull. Soc. Chim. biol., 1928, **10**, 745—756).—Vitamins may be considered to be hormones which are produced from sources other than the organism on which they eventually exert their influence (exohormones as distinct from endohormones, formed by internal secretion). G. A. C. GOUGH.

Assay of vitamin-*A*. K. H. COWARD and K. M. KEY (Biochem. J., 1928, **22**, 1019—1025).—Tests are described in which subnormal growth of rats on a deficient diet graded quantitatively to the dose has been obtained without being followed by premature slackening. Rats apparently in a similar physiological or pathological condition may react by resumption of rapid growth, by immediate resumption of subnormal growth, or by a long latent period followed by a resumption of normal growth, on the same dose. S. S. ZILVA.

Absorption spectrum of vitamin-*A*. R. A. MORTON and I. M. HEILBRON (Biochem. J., 1928, **22**, 987—996).—From spectroscopic examination of various oils and preparations it is concluded that the presence of vitamin-*A* is characterised by an absorption band with a maximum at 328 $\mu\mu$. Sometimes, as in the case of dog-fish oil, this characteristic band may be masked by superimposition of a neighbouring band. The destruction of the vitamin-*A* of an oil is accompanied by the disappearance of the band at 328 $\mu\mu$. It is probable that one of the decomposition products of vitamin-*A* has an absorption band near 275—285 $\mu\mu$. S. S. ZILVA.

Colour tests for sterols and for vitamin-*A*. II. Spectroscopic study of the colorations attributed to vitamin-*A*. F. WOKES (Biochem. J., 1928, **22**, 997—1006).—From the spectroscopic studies of the colours produced by arsenic or antimony trichlorides on a number of cod-liver oils and concentrates, the vitamin-*A* potency of which has previously been assessed biologically, it has been ascertained that in the case of the former reagents bands at about 587 and 475 $\mu\mu$ were discernible, whilst antimony trichloride gave bands at about 614 and 530 $\mu\mu$. There is a gradual loss in the blue and a gain in the red colour when the chromogen remains in contact with either reagent. This is accompanied spectroscopically by a gradual transition from the stage giving the "initial" band (at about 587 or 615 $\mu\mu$) to the stage giving the "second" band (at about 475 or 530 $\mu\mu$). S. S. ZILVA.

Vitamin-*A* formation. The feeding of etiolated wheat shoots to rats kept in darkness. T. MOORE (Biochem. J., 1928, **22**, 1097—1101).—These shoots were found to be an effective source of vitamin-*A* when tested on rats under conditions involving the use of the minimum of red light illumination. S. S. ZILVA.

Relative stability of vitamin-*A* from plant sources. H. C. SHERMAN, E. J. QUINN, P. L. DAY, and E. H. MILLER (J. Biol. Chem., 1928, **78**, 293—298).—Heating of tomato juice at 95—99° for 4 hrs. in presence or absence of oxygen destroyed about 17% of the vitamin-*A*; the rate of destruction of the vitamin during anaerobic heating was not affected by altering the p_H of the juice from its natural value (4·2) to 9·2. Anaerobic heating of an olive oil extract of dried spinach caused 20% destruction of vitamin-*A*, whilst similar treatment of a solution of butter in olive oil destroyed 33% of the vitamin.

C. R. HARINGTON.

Tripartite nature of vitamin-*B*. R. R. WILLIAMS and R. E. WATERMAN (J. Biol. Chem., 1928,

78, 311—322).—Pigeons were kept on a synthetic diet in which vitamin-B_1 was supplied in the form of a fuller's earth adsorbate of a dialysed yeast extract, and -B_2 as autoclaved yeast. Such birds showed a marked improvement on the addition of air-dried brewer's yeast to the diet. The factor thus supplied could not be any known vitamin, and is thought to be a third, heat-labile component of vitamin-*B*.

C. R. HARINGTON.

Multiple nature of vitamin-*B*. A. G. HOGAN and J. E. HUNTER (J. Biol. Chem., 1928, **78**, 433—444).—Irradiation with ultra-violet light destroys the growth-promoting properties of yeast and of vitamin-*B* preparations derived therefrom, while leaving the antineuritic properties unimpaired.

C. R. HARINGTON.

Glutathione and reducing power of muscle in vitamin-*B* deficiency. H. YAOI (Proc. Imp. Acad. Tokyo, 1928, **4**, 233—235).—The muscle of pigeons fed on a diet deficient in vitamin-*B* has a weaker reducing action on methylene-blue than normal pigeon muscle. No material difference is detectable in the glutathione content in the two cases. J. H. BIRKINSHAW.

Comparative variations in the content of water, fatty acids, and cholesterol in the liver and spleen of guinea-pigs on a normal diet and on one deprived of antiscorbutic vitamin. (MLLE.) L. RANDOIN and (MLLE.) A. MICHAUX (Compt. rend., 1928, **187**, 146—149).—The fresh liver of normal guinea-pigs contains 0·21% of cholesterol, 1·81—2·26% of fatty acids, and 72·5—74·6% of water. When fed on diets deficient in vitamin-*C*, the fatty acids increase gradually to 3·0% in the final stages, the cholesterol tending to increase slightly but within the limits of variations with individual animals. The lipocytic coefficient (ratio of cholesterol to fatty acids) thus decreases with the progress of scorbutic symptoms. The weight of the spleen is very variable, but on an average the normal spleen contains 78·3% of water, 0·4% of cholesterol, and 1·4% of fatty acids. In acute scurvy the spleen increases in volume and weight after some time. In the final stages the cholesterol decreases sharply, the fatty acids to a slight extent, and the water content tends to increase. In all these variations the lipocytic coefficient is lower than in the case of animals fed on a complete artificial diet (cf. A., 1926, 1181; 1927, 282).

R. BRIGHTMAN.

Biological assay of cod-liver oil. G. ADAMS and E. V. McCOLLUM (J. Biol. Chem., 1928, **78**, 495—524).—No biological method has been devised for the evaluation of the absolute antirachitic potency of cod-liver oil. For the comparison of different samples of oil determination of the ash content of the bones of the experimental animals is of little value. Of greater utility is the determination of the product of the ionic concentrations of calcium and phosphorus in the blood; the results of such determinations can be correlated with those obtained by histological observations. The conclusion of Holt (A., 1925, i, 1209), that the value of the above-mentioned ionic product is less than 8×10^{-25} in active rickets, is confirmed. C. R. HARINGTON.

Examination of irradiated zymosterol for the presence of vitamin-*D*. E. M. HUME, H. H. SMITH, and I. SMEDLEY-MACLEAN (Biochem. J., 1928, **22**, 980—986; cf. Smedley-MacLean, this vol., 329).—Zymosterol is not capable of being activated by ultra-violet irradiation. This was ascertained by biological tests in which four different diets were employed, namely, a diet deficient in both fat-soluble vitamins, the same containing wheat germ (this vol., 556), McCollum's diet 3143, and Sherman and Pappenheimer's diet. Comparisons have also been obtained for the minimum doses of irradiated ergosterol necessary to produce an effect when the different diets are employed. S. S. ZILVA.

Variations in the process of photosynthesis. N. A. MAXIMOV and T. A. KRASSNOSSELSKI-MAXIMOV (Ber. deut. bot. Ges., 1928, **46**, 383—391).—The process of photosynthesis does not take place at a uniform rate, but varies widely in its intensity within periods of a few minutes. When measured over longer periods the total amount of carbon dioxide involved in the process shows a fair regularity. A possible connexion is suggested between this phenomenon, the rhythmic motion of the stoma, and the periodicity of transpiration. A. G. POLLARD.

Application of the Donnan equilibrium to the ionic relations of plant tissues. G. E. BRIGGS and A. H. K. PETRIE (Biochem. J., 1928, **22**, 1071—1082).—The conception of a simple Donnan membrane equilibrium operating between two homogeneous phases is inadequate to explain the phenomena of ionic intake by plants. S. S. ZILVA.

Cell phosphatides of plants. II. B. H. CRANNER (Meld. Norges Landbruks, 1927, **7**, 611—643). —A study of the reactions of phosphatide extracts with solutions of acid and alkaline dyes.

CHEMICAL ABSTRACTS.

Water content of leaves in relation to the wilting of plants. R. KÔKETSU (Proc. Imp. Acad. Tokyo, 1928, **4**, 229—230).—The ratio between the water content at the time of critical wilting and that at full turgidity is probably specific for a given plant when cultivated in a given soil.

J. H. BIRKINSHAW.

Chemical composition of vegetable seed fats in relation to the natural order of plants. T. P. HILDITCH (Proc. Roy. Soc., 1928, **B**, **103**, 111—117). —The existing data on the chemical nature of various seed fats are discussed with reference to botanical order. It is shown that, although other acids always exist in fair to considerable proportions, the four acids lauric, myristic, erucic, and petroselic are specific in the respective cases of the four orders, *Palmæ*, *Myristiceæ*, *Cruciferæ*, and *Umbelliferæ*.

E. A. LUNT.

Potassium and sodium in sea-weeds. G. BERTRAND and M. ROSENBLATT (Compt. rend., 1928, **187**, 266—270).—Immersion of sea-weeds in distilled water results first in a decrease and then in an increase of the sodium : potassium ratio in some cases but has little effect in others. All the species examined contained potassium. For plants washed twice in water the ratio (Na : K) varies from 1 : 4·20 to 1 : 0·58. G. A. C. GOUGH.

Occurrence of manganese in trees. M. KLEINSTUCK (Chem.-Ztg., 1928, **52**, 598—599).—The manganese content of different parts of various trees growing in the valley of the Elbe is recorded. The bark and leaves have in general a higher manganese content than the wood, and the manganese content of the leaves increases rapidly during the season. It is suggested that the manganese acts as a catalyst in the organs of assimilation and that its catalytic activity is destroyed by sulphur dioxide; this would explain the serious effect of sulphur dioxide on vegetation. A. R. POWELL.

Manganese in plants: its importance in plant metabolism. W. B. S. BISHOP (Austral. J. Exp. Biol. Med. Sci., 1928, **5**, 125—141).—Manganese is present in many varieties of seeds, plants, and fruits; it is not evenly distributed throughout the plant and is at its highest concentration in those parts where there is most intense chemical activity. Manganese is essential for plant development. Experiments were made with plants grown in neutral and in acid media, with the addition of manganese sulphate in amounts similar to those present in a water-soluble condition in average soil, as well as in much larger amount. Results showed that within rather narrowly-defined limits manganese has beneficial effects on plant growth and that calcium reduces the toxicity of high concentrations of the element. The effect of manganese is not due to reduced absorption of iron by the plant, but there is some relation between the presence of manganese and carbon assimilation. The determinations of manganese were made colorimetrically by the persulphate method. W. MCCARTNEY.

Determination of the salt content from the p_H value of apple juice. Mineral content of the juice and whole apple. D. HAYNES and J. W. BROWN (Biochem. J., 1928, **22**, 947—963).—It is possible to obtain an assessment of the salt content of the apple as "equivalent potash" by comparing the p_H and titratable acidity of the juice with the acidity and p_H of mixtures of malic acid and potassium malate of known concentration. Acidity titrations, p_H, and "equivalent potash" are given for samples of Lane's Prince Albert and Cox's Orange Pippin picked at the normal season and also earlier and later. Similar measurements on samples from a single picking of other kinds of apple are also given. The same percentage of potash was found in the expressed juice as in the whole apple. Larger percentages of magnesia and lime, some of which was most probably of cell-wall origin, were found in the juice than in the whole apple. There is some evidence that this dissolution of cell-wall material by the juice varies with the acidity of the juice. S. S. ZILVA.

Chemical composition of juices of American apples. J. S. CALDWELL (J. Agric. Res., 1928, **36**, 407—417).—Data extending over a period of 3 years relating to the total sugar, astringency, and acid content of the juice of 98 varieties of apple are in agreement with the previous conclusions of the authors that climatic conditions during the period of development and maturity of the fruit produce consistent effects on its chemical composition, the character of these effects being similar in large groups of trees of dissimilar origin. E. A. LUNT.

Composition of American-grown French cider apples and other apples of like character. J. S. CALDWELL (J. Agric. Res., 1928, **36**, 391—406).—Data are given for the total astringency, sugar, and acid values of the juice of 82 varieties of apple of French, American, and Siberian origin, with a view to the preparation of a non-fermented beverage juice. The results indicate that the composition of the French cider apples remains unaltered after 23 years' growth in America either at an elevation of 2170 ft. or at sea-level. E. A. LUNT.

Changes produced in apples by the use of cleaning and oil-coating processes. J. R. WELLER (J. Agric. Res., 1928, **36**, 429—436).—The application of a coating of paraffin to apples causes a reduction in the respiratory rate of the fruit even after 8 months of cold storage, and the oiled fruit subsequently loses weight and shrinks less rapidly at market temperature than the unoiled fruit. The dessert quality of the fruit is unaffected. E. A. LUNT.

Nitrogen metabolism of *Pyrus malus*, L. I. Influence of temperature of desiccation on water-soluble nitrogenous constituents and separation of water-soluble protein from non-protein constituents. II. Distribution of nitrogen in the insoluble cytoplasmic proteins. W. THOMAS (Plant Physiol., 1927, **2**, 55—66, 67—70).—In respect of coagulation and proteolysis, the optimal temperature for desiccation is 60°. Direct extraction with water produces less disturbance in the protein and non-protein fractions due to *post mortem* changes than methods employing cytolytic agents. The proteins are best separated by means of colloidal ferric hydroxide. Little qualitative change in the nature of the insoluble leaf proteins occurs during development; the presence of a single protein is assumed. The carbohydrate–nitrogen relations of plants are discussed. CHEMICAL ABSTRACTS.

Development of the wheat kernel. C. E. SAUNDERS (Sci. Agric., 1928, **8**, 524—531).—The rate of deposition of protein is greatest when the kernel is gaining in weight most rapidly. During the first few days of the experiment the deposition of non-protein material was more rapid than that of protein. CHEMICAL ABSTRACTS.

Quantitative variations of enzymes in grains of wheat in the course of ripening, resting, and germinating. A. N. BACH, A. I. OPARIN, and R. A. VENER (Trans. Karpov Inst. Chem., 1926, No. 5, 62—70).—During ripening, two opposing processes occur simultaneously: formation of active enzymes and their transition into inactive zymogens; the latter become transformed into enzymes in the course of germinating. Catalase and peroxidase decrease little, whilst amylase and protease disappear, during ripening; all increase largely during germination. CHEMICAL ABSTRACTS.

Development of cotton bolls and the rate of formation of gossypol in the cotton seed. W. D. GALLUP (J. Agric. Res., 1928, **36**, 471—480).—The

chemical composition of cotton bolls with reference to ash, nitrogen, carbohydrate, ether-soluble material, and fibre content has been determined as a function of the age of the boll. The development of oil and gossypol occurs simultaneously in the cotton seed during a short and well-defined period between the 24th and 32nd days of growth. E. A. LUNT.

Transport of carbohydrates in the cotton plant. II. Factors determining the rate and direction of movement of sugars. T. G. MASON and E. J. MASKELL (Ann. Bot., 1928, **42**, 571—636).—The movement of sugar from leaf to root in the cotton plant was examined by regional analysis of the plant-tissue and shown to follow a definite concentration gradient. This occurred when the normal direction of sugar movement was artificially reversed, although the change in concentration gradient lagged behind the directional change. The amount of sugar passing down the stem was decreased by the removal of portions of bark, but the sugar passing unit sectional area of the restricted channel increased proportionally with the increased concentration gradient. Within the bark the concentration of sucrose increases from outside to inside, and that of reducing sugars in the opposite direction. The radial concentration gradient of sucrose varied considerably, but that of reducing sugars was fairly stable. In a given area of bark there is a high positive correlation between the percentage of sieve tubes and the sucrose concentration and a correspondingly high negative correlation for reducing sugars. Generally speaking, longitudinal transport of sugars takes place through the sieve tubes at rates varying with the concentration gradient and the process is akin to, but far more rapid than, simple diffusion. Lateral movement of sugar, *e.g.*, from bark to wood, is similar in nature and rate to physical diffusion. A. G. POLLARD.

Phosphorus compounds in plants. I. Exosmosis of phosphorus compounds from plants. W. ZALESKI and W. MORDKIN (Biochem. Z., 1928, **195**, 415—420).—The functional permeability of different organs of the plant is different and changes during the various stages of growth. Resting seeds permit of the diffusion of a greater amount of organic phosphorus compounds than germinating and unripe seeds. The amount of phosphatide passing into water can scarcely be regarded as arising merely from the limiting surface of the cells. P. W. CLUTTERBUCK.

Influence of sodium carbonate and calcium chloride on the acidity of the sap of the maize plant. II. S. KARASIEWICZ (Bull. Soc. Chim. biol., 1928, **10**, 702—713; cf. A., 1927, 798, 908).—The predominant effect of media containing calcium chloride on the total acidity of the plant, as distinct from the effect of sodium carbonate, is largely due to the fact that the soluble sodium salts are easily excreted by the roots. Water containing even small amounts of the two salts (0·2% of calcium chloride and 0·01% of sodium carbonate) increases the growth. G. A. C. GOUGH.

Action of mixed reagents on the viscosity of protoplasm. H. TIMMEL (Protoplasma, 1927, **3**, 197—212; Chem. Zentr., 1928, i, 1049—1050).—Centrifuge experiments were carried out with the chloroplast of various plants and single or mixed salts, particularly potassium, and organic compounds. A. A. ELDRIDGE.

Liberation of the free iodine of *Laminaria flexicaulis*. P. DANGEARD (Compt. rend., 1928, **186**, 1371—1373).—Slow liberation of iodine from the thallus of *L. flexicaulis* takes place continuously in all except very young plants. The output of iodine is increased temporarily by damaging the tissue either by incisions or by acids. There is evidence that the iodine cells lie near the surface of the thallus. E. A. LUNT.

Mechanism of fruit-ester formation by *Willia anomala*. M. YAMADA (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 73—76).—The following mechanism for the production of ethyl acetate is proposed

$$\text{Sugar} \longrightarrow \text{Me·CHO} \longleftarrow \text{EtOH}$$

$$\text{Me·CO}_2\text{H} \longrightarrow \text{Me·CO}_2\text{Et}.$$

CHEMICAL ABSTRACTS.

Formation of starch in the haricot. H. COLIN and R. FRANQUET (Compt. rend., 1928, **187**, 309—311).—Little starch is found in the stalks, stems, roots, leaves, or the young seeds of haricot; the ripened seeds contain 35·66%, which almost completely disappears on germination. G. A. C. GOUGH.

Theory of starch formation. K. JOSEPHSON (Z. physiol. Chem., 1928, **174**, 179—190).—It is assumed that there is a single parent substance (an anhydroglucose) which gives rise to the different constituents of starch (amylose and amylopectin). Two molecules of anhydroglucose unite to give a disaccharide anhydride which contains both α- and β-glucoside linkings. The union of the 2 mols. of anhydroglucose is complete in the amylose fraction, but not in the amylopectin fraction; when native starch is converted into the so-called soluble starch of Zulkowsky, the reaction in the amylopectin fraction is completed. Amylopectin consists of the anhydroglucose or the disaccharide anhydride combined with some other grouping, perhaps a hexosephosphate or similar compound. A. WORMALL.

Composition of aquatic plants of Lake Mendota. II. *Vallisneria* and *Potamogeton*. H. A. SCHUETTE and H. ALDER (Trans. Wis. Acad. Sci., 1928, 23, 249—254). CHEMICAL ABSTRACTS.

Influence of geographical factors on the chemical composition of plants. N. N. IVANOV (Ann. State Inst. Exp. Agron. [Russia], 1926, **4**, 23—32).—The protein content of wheat grown at the same longitude is greater for more southerly latitudes (46° 25′, 55° 48′); at the same latitude it is greater for a more easterly longitude (30° 38′, 100° 22′). The water regime influences the protein content of wheat. Similar results were obtained with barley, oats, and rye. CHEMICAL ABSTRACTS.

Spectrum and pharmacology of chlorophyll. F. GRILL (J. Amer. Pharm. Assoc., 1928, **17**, 422—427).—The spectrum of chlorophyll dissolved in different solvents is described. Heat seems to have no appreciable effect on the spectrum, but the intensity is reduced with age. Chlorophyll extracts, but not the chlorophyll granules themselves, have a general

stimulating action on all the tissues and organs of animals. Earthworms are very susceptible to the action of chlorophyll extract, and their use is suggested for the biological examination of commercial preparations. E. H. SHARPLES.

Digitalic acid. P. BOURCET and A. FOURTON (Compt. rend., 1928, **186**, 1577—1578).—The impure digitalic acid described by Kolipinski (Interstate Med. J., 1913, **20**, 1117) as being without physiological activity is impure succinic acid. The unstable, active acids are found in larger amounts in the fresh plant. G. A. C. GOUGH.

Corolla of *Monarda punctata*, L. H. G. HEWITT (J. Amer. Pharm. Assoc., 1928, **17**, 457—458).—The florets on distillation with xylene gave 68—70% of water. Neither the aqueous nor the hydrocarbon distillate gave a positive test for thymol or carvacrol. The air-dried florets (6% of water) contained 10·49—10·92% of ash (insoluble 5·52—6·11%) and on steam distillation gave 3·45% of oil (d^{22} 0·9652) containing little, if any, thymoquinol. E. H. SHARPLES.

Principles of two types of *Combretum* seeds. V. HASENFRATZ and R. SUTRA (Compt. rend., 1928, **186**, 1860—1862).—The pulverised seeds of *C. Bernierianum* when extracted with carbon disulphide yielded 10% of a light yellow oil, consisting chiefly of palmitin and olein with a small quantity of other glycerides. The seeds also contained sucrose. *C. subumbellatum* yielded the same products. No trace of a glucoside was found. J. D. FULTON.

Mannan of iris seed. H. COLIN and A. AUGEM (Bull. Soc. Chim. biol., 1928, **10**, 822—825).—The mannan of iris seed yields mannose (82%) and arabinose (18%) on hydrolysis with boiling 3% sulphuric acid. The sugar reserve of the seed is present probably as a mannoaraban. Sucrose, but no free mannose is found in the young seeds. G. A. C. GOUGH.

Enzymic hydrolysis of melezitose and turanose. T. AAGAARD (Tidsskr. Kjem. Bergv., 1928, **8**, 5—9, 16—20, 35—39).—Bourquelot's method has been utilised in an attempt to determine the constitution of the above sugars. Melezitose was prepared by Tanret's method from Abyssinian manna. The pure product had m. p. 152°, and had a rotation $[\alpha]_D$ +88·4°. Turanose could not be satisfactorily prepared from this by Tanret's method (cf. A., 1906, i, 560), but was finally obtained by carefully heating a 10% solution of melezitose on the water-bath for 45 min. with 1% sulphuric acid. The dextrose simultaneously produced was removed by subsequent fermentation, which does not affect the turanose. The product had $[\alpha]_D$ +73°, and a reducing power of 0·566 referred to dextrose as unity. A 1% solution of turanose alcoholate, $C_{12}H_{22}O_{11},0\cdot5EtOH$, treated with brewer's yeast and kept at 30°, was rapidly hydrolysed, the decomposition into dextrose and lævulose being practically complete after 2 hrs. Similar experiments with emulsin, rhamnodiastase, and autolysed yeast containing invertase had no effect. The hydrolysis in the first case is ascribed to the α-glucosidase present in the yeast, this view being confirmed by an experiment using yeast which had been precipitated and washed with alcohol, and dried in a vacuum. This treatment destroys α-glucosidase, and the resulting product had no action on turanose. Turanose is consequently to be regarded as an α-glucoside of lævulose, just as maltose can be regarded as an α-glucoside of dextrose. Melezitose is regarded as having the composition

$$\overbrace{\text{dextrose}<\text{lævulose}}^{\text{turanose}}\underbrace{<>\text{dextrose}}_{\text{sucrose}};$$

this view is supported by the fact that the disaccharide turanose formed from it on hydrolysis does not reduce a hypoiodite solution, and must consequently be regarded as having a ketonic structure. *Aspergillus niger* partly hydrolyses melezitose into turanose and dextrose, but owing to the presence of other enzymes in the extract, secondary reactions take place, a part of the turanose being decomposed, so that no definite conclusions can be reached from the results. The presence of a specific enzyme "melezitase" in the extract is suggested. Melezitose is not acted on by invertase; with methylemulsin a slow decomposition takes place. α-Glucosidase yields lævulose and dextrose, but the results throw no light on the composition of the original sugar. The above experiments do not support the view of Kuhn and van Grundherr (cf. A., 1926, 1127) that there is a "glucoinvertase" present in the extract of *A. niger* which causes the hydrolysis of melezitose, and that ordinary invertase is a fructoinvertase.

A series of tables showing the effect of various enzymes on sugars of known composition is also given. H. F. HARWOOD.

Carotin; a pigment of honey. H. A. SCHUETTE and P. A. BOTT (J. Amer. Chem. Soc., 1928, **50**, 1998—2000).—Carotin (0·01%) was separated from a highly pigmented honey by the method of Palmer and Eckles (A., 1914, i, 624). H. E. F. NOTTON.

Chemical constitution of chondriosomes and protoplasts of plants. P. MILOVIDOV (Compt. rend., 1928, **187**, 140—142).—The mycelium of *Saprolegnia* gives positive tests with the following reagents: Derrien and Furchini's, Zacharias', Millon's, xanthoprotein, quinol, phosphomolybdic acid, biuret, eosin, and iodine–iodide. The spherical protoplasts of the epidermis of *Tradescantia* and the shoots of *Elodea canadensis* give positive results with the same reagents (only feebly with eosin), and the protein reactions thus appear to be the same for the chondriosomes of these different types of plant. It is concluded that there is no essential chemical difference between animal and plant chondriosomes. R. BRIGHTMAN.

Protein content of grass, chiefly meadow foxtail (*Alopecurus pratensis*), as influenced by frequency of cutting. F. T. SHUTT, S. N. HAMILTON, and H. H. SELWYN (J. Agric. Sci., 1928, **18**, 411—420).—From analyses of the produce of plots cut at frequent intervals and those cut for hay, it is concluded that in a season's growth a larger amount of digestible protein was produced on the plot cut every third week than on the plot cut as hay. H. J. G. HINES.

Does the pea plant fix atmospheric nitrogen? D. Burk (Plant Physiol., 1927, 2, 83—90).—When grown in culture solutions under sterile conditions, *Pisum sativum* (dwarf variety) showed, statistically, a loss of nitrogen large enough to hide evidence of fixation. Chemical Abstracts.

Tabacin, the toxic principle of tobacco. N. A. Barbieri (Atti R. Accad. Lincei, 1928, [vi], 7, 764—768).—Treatment of unfermented Kentucky tobacco, dried either by direct heat or in the sun, with a series of organic and aqueous solvents yields nine distinct fractions, comprising xanthophyll, chlorophyll, cellulose, fats, etc., together with *tabacin*, which is a yellow, waxy, hygroscopic substance of irritating, caustic taste and acid reaction, and with an odour resembling that of methylamine. Tabacin, which is composed of a glucoside with a nitrogen-containing acid, emits irritant vapours of tabacol at about 110°, and is rapidly transformed into its components, tabacol, tabacinic acid (non-toxic), and a sugar, by cold 2% potassium hydroxide solution. Tabacol, like tabacin, loses ammonia and yields nicotine on protracted heating with concentrated potassium hydroxide; it has an irritating acrid odour. Both tabacin and nicotine, whether obtained commercially or prepared from tabacol, are fatal to guinea-pigs in doses of 9 mg. per 100 g. of body-weight. Tabacol is a very powerful, convulsant poison, with an effect, when injected, resembling those of hydrocyanic acid and strychnine together. Scafatin, the yellow colouring matter of tobacco, is neutral and is insoluble in all known neutral solvents except water.

T. H. Pope.

Constituents of *Typha angustata*, Bory. et Chaub. M. Fukuda (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 711—717).—See this vol., 560.

Glutelins. IV. Glutelins of maize (*Zea mays*). D. B. Jones and F. A. Csonka (J. Biol. Chem., 1928, 78, 289—292).—Maize meal was extracted with 60% alcohol containing sodium hydroxide, and the crude glutelin obtained by acidification of the extract; dissolution of the precipitate in aqueous sodium hydroxide and treatment with ammonium sulphate to 3% saturation gave a precipitate of α-glutelin, figures for the nitrogen distribution of which are given; treatment of the mother-liquor with ammonium sulphate to 16% saturation gave a small amount of β-glutelin. C. R. Harington.

Metabolism of *Aspergillus oryzæ*. II. H. Tamiya (Acta Phytochim., 1928, 4, 77—213; cf. A., 1927, 906).—The effect of various metallic ions on the growth and metabolism of *A. oryzæ* in media of different p_H has been examined. The p_H-growth curves show no marked alteration from the normal when salts of the alkali metals are added, whereas calcium, strontium, and barium ions increase growth at lower p_H values and have a retarding action in more alkaline solutions. Aluminium, iron, cobalt, and nickel ions have an action similar to that of the alkaline-earths, whereas small amounts of zinc, copper, mercury, and silver ions promote growth at about p_H 4—5 and inhibit at higher or lower p_H. Double-peaked growth–p_H curves, similar to the normal curve and having a middle minimum at p_H 5—6, are obtained with the usual culture method (spore cultures), when these salts, except those of copper, mercury, silver, and zinc, are added. These characteristic curves are due to the young mycelia and no double-peaked curves are obtained with well-grown surface cultures, which are also more resistant than spore cultures to alkalis. Growth stimulated by the salts of heavy metals, and to a smaller extent that promoted by the salts of the alkaline-earth metals, is often accompanied by a diminished kojic acid production, whilst a deficiency of nitrogen in the medium favours the formation of this acid. In the absence of oxygen the conidia do not germinate, and instead of growth of the fungus an alcoholic fermentation occurs, this fermentation being greatest with young mycelia and at p_H 5—6; the fermentation is accompanied by autolysis of the fungus, but at p_H 5—6 this autolysis is not very marked and the ratio alcohol : carbon dioxide is approximately 1. Aerobic respiration is more marked in earlier stages of the development of the fungus and has an optimum reaction of p_H 6—7. Deprivation of nutrient salts leads to a diminution of growth under aerobic conditions, but has no marked effect on anaerobic culture. Growth under aerobic conditions is promoted by oxalic acid, zinc sulphate, and lactic acid, the effect decreasing in this order, whilst ferrous chloride and calcium carbonate have an inhibitory influence; anaerobically, calcium carbonate only has any influence, and the inhibition observed with this salt is attributed to its alkalinity.

The relationship between aerobic and anaerobic respiration has been studied. Admission of oxygen after a period of anaerobiosis results in normal growth and respiration, and anaerobiosis exerts no influence on the subsequent aerobiosis. The ratio of anaerobically produced alcohol to aerobically produced carbon dioxide is somewhat smaller than that found by various authors for other plants, and the value decreases with the ageing of the culture; if corrections are made for the increase in weight of the fungus during aerobiosis, however, the ratio is approximately 1/6 and is independent of the age of the culture. The energy production in anaerobiosis is therefore about 1/50 of that in aerobiosis. With surface cultures, nitrates are better sources of nitrogen than ammonium salts at lower p_H values, but the converse is found for p_H 7—8. A. Wormall.

Cytochrome in fungi. H. Tamiya (Acta Phytochim., 1928, 4, 215—218).—Cytochrome has been detected spectroscopically in surface cultures of *Aspergillus oryzæ*. Older cultures give the characteristic absorption bands to a smaller extent or not at all, and there is a parallelism between cytochrome content and intensity of respiration. Anaerobiosis leads to a disappearance of the cytochrome, which reappears, however, when aerobiosis follows. Mycelia cultivated anaerobically by shake culture or anaerobic surface cultures of the fungus, which give therefore no cytochrome bands, yield more marked hæmochromogen–pyridine reactions than do aerobic cultures. A. Wormall.

Stimulating effect [of sugars] on the invertase of *Penicillium glaucum*. Z. I. Kertesz (Ferment-

forsch., 1928, **9**, 300—305).—*Penicillium glaucum*, grown in a medium containing mineral salts and glycerol, produced invertase only when sucrose or raffinose was also present. Invert-sugar and lactose caused no invertase formation. With sucrose, the optimum concentration for invertase production was about 30—40%. F. E. DAY.

Mechanism of degradation of fatty acids by mould fungi. II. P. D. COPPOCK, V. SUBRAMANIAM, and T. K. WALKER (J.C.S., 1928, 1422—1427).—In continuation of previous work (this vol., 804) the action of *Aspergillus niger* on calcium *n*-butyrate, *n*-valerate, and *iso*valerate has been investigated. With calcium butyrate, butyric acid, β-hydroxybutyric acid, acetoacetic acid, and acetone are successively produced. No formation of crotonic acid could be detected. With the *n*-valerate, β-hydroxyvaleric acid and methyl ethyl ketone are produced. With the *iso*valerate β-oxidation again occurs, first yielding β-hydroxy*iso*valeric acid, which is then degraded to acetoacetic acid and finally acetone, this result being in agreement with the observed physiological degradation of this acid (cf. Dakin, "Oxidation and Degradation in the Animal Body," 1922) and contrary to Meyer's results obtained by permanganate oxidation *in vitro* (A., 1883, 983). The authors thus differ from Stokoe (this vol., 335) and Derx (A., 1924, i, 1119), who presume that a β-keto-acid is the first product of oxidation of a straight-chain acid. J. W. BAKER.

Grey speck disease of oats. G. SAMUEL and G. S. PIPER (J. Agric. S. Australia, 1928, **31**, 696—705, 789—799).—A disease of oats grown on certain alkaline soils, and identified as grey speck disease (Dorrfleckenkrankheit), is shown to be due to manganese deficiency in the plant and may be cured by treatment of the soil with manganese sulphate. Soil sterilisation by heat, which increased the solubility of manganese, completely prevents, addition of ammonium sulphate or chloride partly cures, whilst addition of lime increases, the disease. E. A. LUNT.

Determination of the reaction of swamp waters. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1928, **10**, 806—811).—The values obtained by the use of hydrogen and quinhydrone electrodes in the absence of buffer solutions often show wide variations (up to 0·597 p_H). Colorimetric determinations using buffer solutions and nitrophenol indicators are satisfactory and permit distinction between waters from *Sphagnum* (p_H 3·82—5·6) and those from *Carex* (p_H 7·4—8·47).
G. A. C. GOUGH.

Colorimetric determination of lactic acid. A. HANSEN, O. RIESSER, and T. NAGAYA (Biochem. Z., 1928, **196**, 301—308).—The colorimetric method of Mendel and Goldscheider (A., 1926, 212) is successfully applied to the determination of lactic acid in muscle, brain, and other physiological substances.
P. W. CLUTTERBUCK.

Absorption paper used in the micro-analytical methods of Bang. F. NEPVEUX and A. THÉPENIER (Bull. Soc. Chim. biol., 1928, **10**, 699—701).—Asbestos paper cannot be used in these analyses, since it does not absorb the blood efficiently. The best absorption paper is fairly thin, pure cotton-cellulose paper, which has been boiled with 10% aqueous acetic acid for 1 hr. and washed with water. G. A. C. GOUGH.

Determination of the total bases of the serum and other liquids by electrodialysis, and other applications of the method. R. WERNICKE (Rev. inst. bacteriol., 1926, **4**, 7—13; Chem. Zentr., 1927, ii, 613).—A three-cell apparatus with two permanganate membranes was employed; the *P.D.* of 260 volts available between the platinum electrodes was regulated to give a current density of 0·04 amp./cm.^{2} With this apparatus cations were completely removed as hydroxides from solutions of their salts. The precipitation of proteins is also complete, and the method can be applied to anions containing oxygen.
A. A. ELDRIDGE.

Rapid determination of organic iodine in body fluids. P. KUHN and A. LOESER (Arch. exp. Path. Pharm., 1928, **131**, 262—267).—A measured quantity of the organic material is heated in an iron crucible with sodium carbonate [(?) hydroxide] 1 part and potassium nitrate 2 parts. The mass after cooling is extracted with hot water, filtered, and the filtrate is carefully acidified. The iodine thus set free is extracted with chloroform, solid sodium hydrogen carbonate is added with vigorous shaking until the reaction is alkaline to litmus, and the iodine is then titrated with sodium thiosulphate.
W. O. KERMACK.

Determination of carbamide as dixanthylcarbamide. A. BOIVIN (Bull. Soc. Chim. biol., 1928, **10**, 684—698).—Carbamide, isolated from biological fluids as the dixanthyl derivative (A., 1927, 1067), may be determined by carbon analysis by the method of Nicloux (*ibid.*, 436). Silver chromate, originally employed in the analysis, is omitted, since its use leads to the formation of carbon monoxide. G. A. C. GOUGH.

Extraction of liquids. E. P. WIDMARK (Bull. Soc. Chim. biol., 1928, **10**, 669—674).—A new extraction funnel, consisting of two ordinary funnels joined some distance above the taps by a short wide glass tube, is described. Quantitative experiments show the advantages of this device, which is claimed to avoid the formation of emulsions in the extraction of fluids such as blood. G. A. C. GOUGH.

Ultrafiltration. A. AUGSBERGER (Biochem. Z., 1928, **196**, 276—288).—The technique and theory of ultrafiltration of biological fluids are investigated and a method of preparing the membrane and of avoiding membrane and evaporation errors is given. The formation of a filtrate of constant composition is demonstrated with mixtures of gelatin or serum with sodium chloride. For gelatin and serum solutions of changing colloid content, a filtrate–time law is given according to which the filtration velocity is inversely proportional to the amount of filtrate.
P. W. CLUTTERBUCK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1928.

General, Physical, and Inorganic Chemistry.

Measurement of the life period of metastable mercury atoms. T. ASADA, R. LADENBURG, and W. TIETZE (Physikal. Z., 1928, 29, 549—550).—The life period of the metastable $^3P_0$ atom in the presence of a few millimetres of nitrogen is 15×10^{-4} sec. The measurements, being based on optical excitation, are free from objections such as can be made to data from electrical excitation. Absorption of the resonance line 2537 Å. excites the unstable $^3P_1$ atom, and this state or the neighbouring metastable $^3P_0$ and $^3P_2$ atoms formed by collisions can be raised to the higher 2^3P_1 state by absorption of visible wave-lengths, only to fall back spontaneously with the accompaniment of fluorescent emission of the 5461 line. By means of a rotating disc equipped with filters this line can be photographed and from the intensity the life period can be calculated. The method has possibilities for further applications.

R. A. MORTON.

Colouring [of band spectra] and [electron] exchange. H. LUDLOFF (Naturwiss., 1928, 16, 611—612).—The two ways in which molecules can be formed out of atoms, *i.e.*, on the basis of the space distribution of their charges and on the basis of electron exchange, can be distinguished by observing the band spectra of the compounds. Two examples are taken and examined by quantum mechanics. The first, that of the combination of two hydrogen atoms to form a molecule, would give red colouring of the band spectrum. The second is the combination of hydrogen with a metal such as calcium or zinc. This should give violet colouring. A. J. MEE.

Spark spectra of sulphur, selenium, and tellurium in the Schumann region. P. LACROUTE (J. Phys. Radium, 1928, [vi], 9, 180—184).—The source of light used was a discharge tube with external electrodes. A fluorite window was used and limited the measurements to the region greater than 1235 Å. A vacuum grating spectrograph was employed. Tables of wave-lengths of lines found are given.

W. E. DOWNEY.

Width of the lines of the Balmer series. (MLLE.) M. HANOT (J. Phys. Radium, 1928, [vi], 9, 156—169).—See this vol., 209.

Colour temperature of the magnesium flame. W. DZIOBEK (Z. wiss. Phot., 1928, 25, 287—290).—Measurement of the colour temperature of a magnesium flame gave the value 3700°±75°. W. CLARK.

Factors governing the appearance of the forbidden line 2656 in the optical excitation of mercury. R. W. WOOD and E. GAVIOLA (Phil. Mag., 1928, [vii], 6, 271—276).—The presence of water vapour, for enhancing the forbidden line of mercury, has the disadvantage that under illumination it liberates free hydrogen, which is known to be very efficient in shortening the life of the metastable atoms necessary for the appearance of the line, as well as decreasing the intensity of the resonance line. With water vapour it is necessary always to neutralise the effect of the hydrogen by admitting small quantities of air or oxygen. These difficulties are reduced by employing a mixture of 2—3 mm. of nitrogen and 0·1—0·4 mm. of water vapour and introducing a small quantity of mercuric oxide into the tube. This serves to remove the hydrogen as fast as it is formed. A. E. MITCHELL.

Active nitrogen. A. E. RUARK (Phil. Mag., 1928, [vii], 6, 335—336).—A discussion of certain discrepancies between the results of Okubo and Hamada (this vol., 210) and those of Ruark, Foote, Rudnick, and Chenault (A., 1927, 395). The differences in the spectra obtained from thallium, cadmium, and mercury in contact with active nitrogen can be attributed to the different pressures at which the observations were made. The Geissler type of discharge tube employed by Okubo and Hamada introduces possible secondary effects such as collisions of the second kind, so that their observation of the $2^3P-2^3P'$ lines of magnesium cannot be accepted as conclusive proof that two electrons can be displaced simultaneously to higher energy levels by the primary process giving rise to metallic spectra at much lower pressure. The criticism of the observation of the second positive bands of nitrogen in the afterglow spectrum is shown to be invalid. A. E. MITCHELL.

Power relation of the intensities of the lines in the optical excitation of mercury. R. W. WOOD and E. GAVIOLA (Phil. Mag., 1928, [vii], 6, 352—356).—The previous work of Wood (A., 1925, ii, 1015) in which it was shown that the relative intensity of the line 3650 Å. of mercury could be varied over a large range by changing the conditions of excitation has been extended to the case where the intensity of the exciting radiation has been diminished to a known extent by interposition of a wire gauze screen. The intensities of the lines that appear in fluorescence are shown to be proportional to the square of the intensity of the exciting radiation with the exception of 3650 and 3021 Å., which change with the third power, and of 2537 and 2656 Å., which

are directly proportional to the intensity of the exciting radiation. These results form the basis of an explanation of the previous observations (*loc. cit.*).

A. E. MITCHELL.

Continuous spectrum of hydrogen. Y. TAKAHASHI and Y. HUKUMOTO (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 675—678).—The spectra emitted by a hydrogen discharge tube at the ordinary temperature and when cooled in liquid air were compared. The continuous spectrum, particularly in the region of wave-lengths greater than 2300 Å., was enhanced by cooling, whilst the intensities of the lines of the secondary spectrum and Balmer's series were reduced.

C. J. SMITHELLS.

Stark effect of the second order in hydrogen. H. R. VON TRAUBENBERG (Naturwiss., 1928, **16**, 655—656).—An apparatus is described with which it was found possible to investigate the Stark effect of the second order (displacement towards the red of the resolved components) in hydrogen in a field of 420,000 volts/cm. The results obtained agree well with the values calculated by Schrodinger's theory, but not so well with those obtained by Epstein. The displacement is proportional to the square of the field strength, as theory indicates.

A. J. MEE.

Fine structure of the sodium *D* lines. L. DOBREZOV and A. TERENIN (Naturwiss., 1928, **16**, 656).—The structure of the sodium *D* lines was investigated using a Lummer–Gehrcke plate perpendicular to the rays. Without resolution of the D_1 and D_2 lines, the interference pattern appeared as a series of fine triplets, which on resolution of the *D* lines were resolved into two series of fine doublets, the separation of the components being of the order of 0·01 Å.

A. J. MEE.

A fine quantum analysis of certain terms of thallium I. M. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 51—56).—Using the data of Mohammad and Mathur (this vol., 677), the term separations and the fine quantum numbers of each of the sub-terms of $2p_1$, $2p_2$, $3d_1$, $3d_2$, and $2s$ terms of the thallium I spectrum have been calculated.

R. A. MORTON.

Series relations of the neon spectrum. Y. ISHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 1—3).—Stark effect patterns of the neon spectrum are not in complete agreement with Paschen's series classification. In *p–d* combinations the predominating patterns are (1) an unsymmetrical type, consisting of three lines, the centre component being slightly bent to the positive side; the right component is an ordinary line, whereas the other two components are combination lines; (2) a symmetrical type consisting of four lines, the inner pair being deflected about one half as much as the outer pair; the two positive lines are ordinary lines, whereas the two negative lines are combination lines.

R. A. MORTON.

Zeeman effect in the band spectrum of helium. W. E. CURTIS and W. JEVONS (Proc. Roy. Soc., 1928, **A**, **120**, 110—127; cf. A., 1925, ii, 1103).—Observations have been made of the Zeeman effects in two regions of the helium band spectrum, in fields up to 20,000 gauss, using (i) an Eagle spectrograph with an 8 ft. concave grating, giving a dispersion of about 2·35 Å./mm. in the third order, and (ii) a 1 cm. Fabry–Perot étalon in conjunction with a glass prism spectrograph. The ranges of wave-lengths investigated with the grating were 4758—4365 Å. and 4161—3626 Å., and with the étalon spectrograph, 5000—4300 Å. Special H-shaped discharge tubes were employed, with copper strip electrodes sealed into the upper ends of the vertical limbs, which were of circular section, the horizontal limb being of elliptical cross-section. Resolution of the magnetic components has been effected only in one case (the band near λ 4648), but many instances of broadening have been observed, and some information as to the polarisation of the components has been obtained by means of a double-image prism. The results for the bands due to transitions between *S* and *P* electronic states are in complete accordance with theoretical predictions. The effects decrease in amount with increase of rotation, and the polarisation of the outer components is opposite in character for *Q* and *PR* type branches. A totally different behaviour has been observed in the case of the band near λ 4472; the effects are relatively large throughout both *Q* and *R* branches (the *P* branch being too weak for observation), and they show similar polarisations. They have a common set of initial levels, and the final levels are the *B* and *A* rotational sub-levels of the 2*P* electronic state of the ortho-helium molecule. It is termed 4*Z*, and shows certain other unusual characteristics besides the exceptional magnetic behaviour. A table is given of unallocated lines which show well-marked broadenings in the field.

L. L. BIRCUMSHAW.

Energy distribution in the continuous spectrum [of radiation emitted] from aluminium electrodes sparking under water. I. WYNEKEN (Ann. Physik, 1928, [iv], **86**, 1071—1088).—The distribution of energy was determined by comparison with that in the spectrum of the carbon arc, which is already known. A rotating-sector photometer was used in conjunction with a camera, the velocity of rotation of the sector being so arranged that the frequency of extinction was the same as the spark frequency. The photograph of the spectrum of light emitted from a copper arc was taken on the same plate for calibration purposes. The photometric comparison of intermittent and continuous light sources is discussed. The energy of radiation was calculated and plotted against the wave-length. There is a clear energy maximum at a wave-length of about 2850 Å. On the basis of Wien's law this would correspond with a temperature of 10,000° Abs. By extrapolating the curve to zero intensity it is found that the energy of radiation is zero at approximately 2000 Å. This decrease in energy is not due to absorption by the water or colloidal particles present.

A. J. MEE.

Stark effect of Balmer series at high field. Y. ISHIDA and S. HIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 1—14).—By employing a high electrical field, measurements have been made of the Stark effect of the Balmer series of hydrogen

up to the third order. The results obtained generally support the theoretical conclusions reached from wave mechanics, both as regards intensity and deflexion. J. W. SMITH.

Zeeman resolution of the oxygen spectral line at λ 5577 A., the auroral green line. J. C. McLENNAN, J. H. McLEOD, and R. RUEDY (Phil. Mag., 1928, [vii], 6, 558—567; cf. A., 1927, 910).—The oxygen green line at λ 5577 Å. is resolvable magnetically into a normal triplet and must originate in electronic transitions from the $^1S_0$ to the $^1D_2$ metastable levels of oxygen atoms. S. K. TWEEDY.

New bands in the secondary spectrum of hydrogen. D. B. DEODHAR (Phil. Mag., 1928, [vii], 6, 466—479).—Data relating to seven new bands in the secondary spectrum of hydrogen, situated in the yellow region, are recorded. These bands, which are not of the half quantum type, are emitted by an excited hydrogen molecule. S. K. TWEEDY.

Ultra-violet radiations emitted by point discharges. J. THOMSON (Phil. Mag., 1928, [vii], 6, 526—546).—A preliminary investigation is recorded of the variation with pressure (up to 1 atm.) of the ionising and photo-electric radiations from hydrogen and nitrogen excited by spark discharge, and of the intensity variations of these radiations when the discharge current is varied at constant gas pressure. The radiations are probably molecular in origin and the observed variations are made up of both absorption and emission variations. The effects in carbon dioxide are exceedingly small, whilst oxygen exhibits a spontaneous ionisation probably due to the gradual change of ozone molecules formed during discharge into normal oxygen molecules (cf. Wynn-Williams, A., 1926, 331). S. K. TWEEDY.

Transition probabilities in the lithium atom II. B. TRUMPY (Z. Physik, 1928, 50, 228—233).—The transition probabilities of the $2_2—2_1$ and $3_2—2_1$ energy changes in the lithium atom have been calculated according to the method of Schrödinger and Sugiura as $f=0·7230$ and 0·0642, respectively. Combining these values with those previously deduced (A., 1927, 998) the value of Σf for the region of continuous absorption is calculated to be 0·171. J. W. SMITH.

Interpretation of band spectra. II. R. DE L. KRONIG (Z. Physik, 1928, 50, 347—362; cf. this vol., 456).—Using an approximate method, the two-atom molecule is examined by means of wave mechanics. An expression is obtained for the dependence of the doublet separation on the rotation quantum number in terms of the direction of the impulse of rotation of the electrons; also, an explanation of "disturbances" or variations of some terms from the calculated values. Henri's concept of pre-dissociation is used to obtain an estimate of the life of the "predissociated" molecule. W. E. DOWNEY.

Widening of spectral lines by the thickness of the vapour of the absorbing atoms. E. VOGT (Z. Physik, 1928, 50, 395—396).—The measurements of Schütz (A., 1927, 1117) and of Trumpy (*ibid.*, 179) yield results which differ from one another in their order of magnitude. W. E. DOWNEY.

Magneto-optical determination of the intensity of the first two members of the principal series of potassium and the vapour pressure of potassium. J. WEILER (Z. Physik, 1928, 50, 436—439).—The intensity ratio of the doublets of the first member of the principal series of potassium for temperatures between 155° and 265° is 1·96+0·07. Similarly, the ratio for the second member between 240° and 353° is 1·94±0·09. The ratio of the first to the second member, in the temperature interval 253—265°, is 96±4. The vapour pressure of potassium should obey the formula $\log pT = 20{,}000/4·571T + 9·866$, giving as the heat of vaporisation of potassium 20,000 g.-cal. W. E. DOWNEY.

Series spectra of Hg-like atoms—Tl II and Pb III. K. R. RAO, A. L. NARAYAN, and A. S. RAO (Indian J. Physics, 1928, 2, 467—476).—A preliminary report of series regularities discovered in the spectra of singly-ionised thallium and doubly-ionised lead, which are homologous with the neutral mercury atom. The first members in each of the triplet series of these spectra have been identified. The resonance potential of thallium is 6·47 volts and the ionisation potential about 20·3 volts. In the case of lead these are 7·95 and 31·5 volts, respectively. J. W. SMITH.

Series spectra of Sn IV and In III. K. R. RAO, A. L. NARAYAN, and A. S. RAO (Indian J. Physics, 1928, 2, 477—483; cf. A., 1927, 911).—Further experiments support the observations of Rao in the identification of the $1^2D—1^2F$ member of the first fundamental series of Sn IV. It is suggested that the large ^2F term obtained by Lang (A., 1927, 911) has its origin in the N_4 orbit, whilst the smaller term found by Rao arises from the O_4 orbit. The results of Lang on the In III spectrum have also been extended. The ionisation potential of indium is 27·91 volts. J. W. SMITH.

Extreme ultra-violet spectrum of argon excited by controlled electron impacts. K. T. COMPTON, J. C. BOYCE, and H. N. RUSSELL (Physical Rev., 1928, [ii], 32, 179—185).—In the wave-length region 1066—461 Å. 20 arc lines and 68 spark lines (attributed to A II) are recorded; 37 of the spark lines have been classified. The ionisation potential is 27·82±0·05 volts, whence 43·51 volts is the minimum potential for double ionisation with reference to the $^3P_2$ limit. A. A. ELDRIDGE.

Assignment of quantum numbers for electrons in molecules. I. R. S. MULLIKEN (Physical Rev., 1928, [ii], 32, 186—222).—Tentative formal assignments (based on band spectra, ionisation potentials, and positive ray data) of quantum numbers for most of the known electronic states of diatomic molecules composed of elements of the first short period of the periodic classification have been made and tabulated. A notation for designation of the state of each electron and the molecule as a whole is proposed. The possible molecular states corresponding with various electron configurations are deduced. The electrons in a molecule may be classified accord-

ing to their "bonding power." Rules expressing the relations of the electronic states of a molecule to those of its dissociation products are discussed, together with selection rules for electronic transitions and certain of Hund's rules. Nearly all the observed ionisation potentials of the molecules discussed can be accounted for by the removal of a single electron from one or other of the various closed shells supposed to be present. A. A. ELDRIDGE.

Spectrum of sulphur, S II. S. B. INGRAM (Physical Rev., 1928, [ii], **32**, 172—178).—In the spectrum of S II 183 lines have been classified. The ionisation potential of the S II ion is 23·3±0·1 volts. A. A. ELDRIDGE.

Rotational structure of the blue-green bands of Na_2. F. W. LOOMIS and R. W. WOOD (Physical Rev., 1928, [ii], **32**, 223—236).—Measurement of the bands in absorption shows that they consist of only one *P*, one *Q*, and one *R* branch. The combination relations hold rigorously except for a small *PQR* defect. Constants of the band system are recorded; the large internuclear distances correspond with weak molecular binding, which accords with the low heat of dissociation. No alternation in intensity of the absorption lines was observed. A. A. ELDRIDGE.

Spark potential curve of a pure gas at low pressures. K. ZUBER (Naturwiss., 1928, **16**, 615—616).—An expression for the spark potential is calculated which gives, within certain limits, values in agreement with experiment. A. J. MEE.

New photo-electric phenomenon with thin sheets of alkali metals. R. SUHRMANN (Naturwiss., 1928, **16**, 616—617; cf. this vol., 680).—Gudden's explanation of the phenomenon (this vol., 808), viz. that there are local differences of potential of the order of 0·1 volt on the metal film, is in contrast with the hypothesis of surface ionisation. It should be possible to decide between the two by investigating the influence of temperature on the effect. A. J. MEE.

Multiple valency. A. F. RICHTER (Z. physikal. Chem., 1928, **135**, 444—460).—The effect of the ratio of the stabilities of opposing configurations of electrons on the work necessary to detach electrons is examined. W. E. DOWNEY.

Photo-electric thresholds of potassium. (MISS) J. BUTTERWORTH (Phil. Mag., 1928, [vii], **6**, 352).—A correction to the previous paper (this vol., 931) in which centigrade temperatures were inadvertently used instead of absolute temperatures. The corrected calculations show that potassium has photo-electric thresholds at 7100 and 21,000 Å., with a possible threshold at 10,000 Å. Previous observations have been confirmed by modification of the method. A. E. MITCHELL.

Photo-electric effect of soft *X*-rays. G. B. BANDOPADHYAYA (Proc. Roy. Soc., 1928, **A**, **120**, 46—58).—An investigation of the yield of photo-electrons, due to the same beam of soft *X*-rays, from different elements under similar conditions. Twelve elements (carbon, aluminium, iron, cobalt, nickel, copper, molybdenum, silver, tantalum, tungsten, platinum, and gold) were used, and the photo-electric currents were measured with an electrometer by the ordinary timing method, all the readings being taken at a pressure of the order of 10^{-7} mm. Values of the photo-electric efficiency i_p/i_t (photo-electric current/thermionic current) observed with different elements by the action of *X*-rays from a copper anticathode at voltages from 200 to 500 are tabulated, readings for both thoroughly degassed and undegassed photo-electric plates being recorded. The latter values are in general higher, except for aluminium, and it is found that degassing affects the relative values. On plotting i_p/i_t against atomic number for the different elements, it appears that there is no simple relation between the two properties. The sensitiveness of different elements under soft *X*-rays is very similar to that under ultra-violet light. Assuming that the law governing the ejection of photo-electrons under soft *X*-rays is similar to that for ejection under ultra-violet light, a formula is deduced indicating that the number of photo-electrons liberated should be proportional to the voltage. This is found to be approximately true. L. L. BIRCUMSHAW.

Critical potentials of metallic vapours. I. Copper. H. B. WAHLIN (Physical Rev., 1928, [ii], **32**, 277—286).—A number of critical potentials in copper vapour in the region 0—20 volts have been found, and their significance is discussed. A. A. ELDRIDGE.

Thermionic emission. L. TONKS (Physical Rev., 1928, [ii], **32**, 284—286).—It is proved thermodynamically that the work function in the exponent of the Richardson equation is the same whether emission takes place at constant total charge or constant surface charge. A. A. ELDRIDGE.

Diffraction of electrons at an optical grating. E. RUPP (Naturwiss., 1928, **16**, 656).—It was found possible to diffract electrons at an optical grating by using the method of grazing reflexion. For the success of the experiment it is necessary to use a metal grating, to focus the electron beam by means of a magnetic field, and to bombard the grating repeatedly with rapid electrons during an exposure. Estimation of the "wave-length" of electrons by this method can be carried out with an accuracy of ±5%. A. J. MEE.

Cathodic sputtering. IV. Effect of material and state of cathode on sputtering. E. BLECHSCHMIDT and A. VON HIPPEL (Ann. Physik, 1928, [iv], **86**, 1006—1024; cf. A., 1926, 1013; 1927, 118).—The simple theory to explain cathodic sputtering put forward in previous papers is extended, and the influence of surface layers of adsorbed gas on the cathode is discussed. A new and better method is described by means of which the extent of sputtering of pure metallic surfaces can be measured. Experiments carried out with cadmium, antimony, bismuth, lead, zinc, silver, copper, magnesium, and aluminium gave results in agreement with theory. A. J. MEE.

Single scattering of hydrogen nuclei at solid bodies. C. GERTHSEN (Ann. Physik, 1928, [iv], **86**, 1025—1036; cf. this vol., 683).—Experiments were made to test the accuracy of Rutherford's

scattering formula when applied to the single scattering of hydrogen nuclei by solid bodies. In order to overcome the difficulty, hitherto experienced, of measuring the scattering at large angles of scattering, a Geiger counter was employed. By this means it was found possible to determine the number of particles scattered through an angle range of 20—135°. Within this range the number of hydrogen particles scattered is inversely proportional to the fourth power of the sine of half the angle of scattering, *i.e.*, Rutherford's formula holds. The effect of recoil of the atomic nuclei on the observed angular distribution is investigated and the ratio of scattered to incident particles is calculated. A. J. MEE.

At. wt. of cæsium. T. W. RICHARDS and M. FRANÇON (J. Amer. Chem. Soc., 1928, **50**, 2162—2166).—Analysis of cæsium chloride confirms the accepted at. wt. of cæsium, viz., 132·81 (Ag=107·880). This corresponds with a "packing fraction" of -14×10^{-4}, greater than would be inferred from Aston's curve (A., 1927, 914), indicating that cæsium may be a mixture of isotopes. S. K. TWEEDY.

Constitution of zinc. F. W. ASTON (Nature, 1928, **122**, 345).—The mass spectra of zinc indicate that the following isotopes (in lettered order of intensity) are present: 64 (*a*), 65 (*e*), 66 (*b*), 67 (*d*), 68 (*c*), 69 (*g*), 70 (*f*). A. A. ELDRIDGE.

Electron counter for the measurement of very weak activities. H. GEIGER and W. MÜLLER (Naturwiss., 1928, **16**, 617—618).—A very sensitive electron counter is described which will measure activities of the order of the β- and γ-radiations of potassium. A. J. MEE.

Condensation of water vapour on charged atoms of actinium-*A*. M. AKIYAMA (Compt. rend., 1928, **187**, 341—342).—The origins of the paths of the α-particles emitted by the atoms of actinon and actinium-*A* demonstrated by Wilson's method are often different. Since the calculated value of the ratio of the number of charged atoms removed in a given period, measured from the moment of their production, to the total number of charged atoms of actinium-*A* is always twice the experimental value, it seems that about 50% of the charged recoil atoms are not utilised as nuclei for condensation. The number and lives of the displaced atoms of actinium-*A* are in approximate agreement with radioactive data. The charged recoil atoms probably require a higher degree of saturation than the positive ions. J. GRANT.

Purely electronic amplification method for counting corpuscular rays. E. RAMELET (Ann. Physik, 1928, [iv], **86**, 871—913).—Greinacher's method for measuring ionising radiations such as α- and β-particles (A., 1926, 553) has been studied from the quantitative aspect, and details are given of an arrangement for securing accuracy. The variations in the ionising power of α-particles have been studied using the following gases in the chamber: hydrogen, nitrogen, oxygen, air, hydrogen–nitrogen 1 : 1, carbon dioxide. The results are discussed in detail. R. A. MORTON.

γ-Ray spectrum of protoactinium and the energies of the γ-rays arising from α- and β-ray changes. L. MEITNER (Z. Physik, 1928, **50**, 15—23).—By photographing the β-rays emitted by protoactinium in a magnetic field it has been shown that there are three γ-radiations of wave-length 130, 41·9, and $38\cdot2\times10^{-11}$ cm., respectively. It is pointed out that the shortest wave-length of the γ-rays associated with various α-ray changes is of the same order in all cases so far investigated, but in the case of the β-ray changes variations are found of more than 1 : 50. Hence it is concluded that the disarrangement of the nucleus produced is of the same order for all α-ray emissions but varies widely for different β-ray emissions. This is parallel to the relative energies of α-rays and primary β-rays. For α-ray changes in the same disintegration series, the energy associated with the γ-line of shortest wave-length is the greater the longer is the life period of the emitting element. The reverse is shown by β-ray changes. J. W. SMITH.

Radon content of the atmosphere as measured during aeroplane ascents. A. WIGAND and F. WENK (Ann. Physik, 1928, [iv], **86**, 657—686).—An apparatus for the condensation of radon at the temperature of liquid oxygen has been used during aeroplane flights for the determination of the radon content of the atmosphere at different heights. The results indicate a falling off to quite small values as the height increases. The reading obtained at a given height depends on the origin, previous history, and stratification of the air, but it seems clear that all the radon comes from the earth's surface and that the vertical distribution arises only from the normal processes of air motion. Data obtained in a tower 30 m. high show that the radon content of smoke-laden town air may be strikingly high. R. A. MORTON.

Ionisation curve in pure hydrogen for the α-rays of polonium. F. JOLIOT and T. ONODA (J. Phys. Radium, 1928, [vi], 9, 175—179).—The length of the path of α-rays from polonium in pure hydrogen is 17·30±0·03 cm. at 15° and 760 mm. Hg. The ratio of the stopping power of hydrogen to that of air is 0·223. The length of path in air is found to be 3·87±0·01 cm. at 15° and 760 mm. Hg. W. E. DOWNEY.

Recoil-diffusion and secondary emission of moderately rapid cathode rays from metals. K. H. STEHBERGER (Ann. Physik, 1928, [iv], **86**, 825—863).—An improved experimental arrangement is described for determining the velocity distribution of electrons from a conductor bombarded with cathode particles at definite velocities. By extrapolation on the distribution curves a distinction can be made between recoil-diffusion (*R*) and secondary emission (*S*). The secondary velocity distribution for gold, lead, copper, and aluminium at different primary velocities (V_p) between 2000 and 10,000 volts has been studied. The distribution range of secondary emission extends from 0 to 36 volts, and the results are not dependent on V_p or the radiator. The maximum velocity cannot be fixed exactly, but is certainly very small. Another arrangement permits the normal emission to be studied and here also velocities very much smaller than those of the impinging electrons are recorded. It is shown that the

recoil-diffusion can be measured in this way, and when determinations of the total effect are also made and taken in conjunction with the ratio S/R, it is concluded that over the V_p range used the incident secondary radiation arises entirely from recoiling primary electrons. It is also possible to evaluate the recoil-diffusion constant for gold and aluminium. Control experiments on gold leaf showing the variation in S/R with thickness confirm the views as to the origin of the secondary effect. The back-diffusion layer for sputtered platinum over the V_p range 4000—9000 volts is 80—120 $\mu\mu$ thick. R. A. MORTON.

Hall-effect in the experiments of Corbino. W. W. SLEATOR (Physikal. Z., 1928, **29**, 584—585; cf. *ibid.*, 1911, **12**, 561).—Corbino's experimental results are theoretically examined in the light of Sommerfeld's electron theory of metallic conduction. W. E. DOWNEY.

Hall-effect in the experiments of Corbino. W. W. SLEATOR (Physikal. Z., 1928, **29**, 628—629; cf. preceding abstract).—A theoretical investigation of the work of Corbino on the action on a disc carrying a current of a perpendicular magnetic field. It is shown that this arrangement with a circular plate gives the same value for the Hall constant as is obtained by the usual rectangular foil method. The question is attacked both by the classical method and by Fermi's statistics, and equations are derived which are in agreement with those of Sommerfeld (cf. this vol., 467). A. J. MEE.

Absorption in lead, secondary rays, and wave-length of penetrating radiation. L. MYSSOVSKI and L. TUVIM (Z. Physik, 1928, **50**, 273—292).—The absorption of penetrating radiation by lead has been investigated in a similar manner to the absorption by water (A., 1926, 221). The absorption coefficient obtained agrees with the value calculated from the water experiments. For the investigation of the upper part of the absorption curve, the electroscope was placed in the centre of a large block of ice, the lead absorbing sheets being placed either within or outside the ice. Some secondary radiation is produced under these conditions, and the photoelectric effect resulting from their absorption in the lead is of importance. It is pointed out that this method of determining the wave-length of penetrating radiation is qualified by the assumption that the absorption coefficient is equal to the scattering coefficient. J. W. SMITH.

Negatively modified scattering. M. N. SAHA, D. S. KOTHARI, and G. R. TOSHNIWAL (Nature, 1928, **122**, 398).—A discussion of the bearing of the theory of modified scattering on the phenomena of resonance spectra of the vapours of sodium, potassium, and the halogens. A. A. ELDRIDGE.

Scattering of light by free electrons according to Dirac's new relativistic dynamics. O. KLEIN and Y. NISHINA (Nature, 1928, **122**, 398—399).

Atomic synthesis occurring during atomic scattering and the theory of the building up of atoms from hydrogen and helium. W. D. HARKINS and H. A. SHADDUCK (Z. Physik, 1928, **50**, 97—122).—See A., 1927, 183. J. W. SMITH.

Deductions from the atomistic constitution of light energy. J. STARK (Ann. Physik, 1928, [iv], **86**, 1037—1040).—The theory is applied to the time of emission of light and to the emission of light from a moving atom. A. J. MEE.

Application of the Pauli–Fermi electronic gas theory to the problem of cohesive force. J. FRENKEL (Z. Physik, 1928, **50**, 234—248).—Mathematical. The kinetic repulsive force between atoms is calculated from the point of view of relativistic mechanics, and the condition of equilibrium deduced. The Thomas–Fermi atom model, the structure of atomic nuclei, and the structure of the very dense stars are also discussed from the point of view of this theory. J. W. SMITH.

General relativity quantum theory of the electron. H. TETRODE (Z. Physik, 1928, **50**, 336—346; cf. this vol., 933).—Dirac's theory is extended from the point of view of the general theory of relativity. A direct derivation of the impulse-energy principle is obtained. W. E. DOWNEY.

Transmutation of an element by cathode rays. A. KOENIG and F. VON KOROSY (Z. Elektrochem., 1928, **34**, 305—311).—An amplification of a previous paper (this vol., 216). L. F. GILBERT.

Absorption spectra of sulphonefluorescein and some derivatives. R. C. GIBBS and C. V. SHAPIRO.—See this vol., 1019.

Valency. IX. Molecular structure of thallium salts. (*a*) Thallium tri-iodide; (*b*) alkyl derivatives. A. J. BERRY and T. M. LOWRY [with (MRS.) R. R. GOLDSTEIN and F. L. GILBERT] (J.C.S., 1928, 1748—1768).—The evidence for regarding thallium tri-iodide as thallic iodide or thallous polyiodide is conflicting. Solutions in methyl alcohol or acetonitrile form additive compounds with pyridine and chloropyridines, and complex ions with potassium iodide, and exhibit the general reactions of a thallic salt, but the reactions of thallous ions could not be detected with certainty. The following *compounds* are described: $(C_5H_5N)_2HTlI_4$, dark red crystals from acetone; $(C_5H_5N)_2TlI_3$, orange, soluble in many organic solvents; $TlI_3(C_5H_3NCl_2)_2$, golden-yellow crystals; $TlI_3(C_5H_2NCl_3)_5$.

Investigation of absorption spectra obtained with solutions in methyl alcohol shows that thallium tri-iodide alone and with iodine, the complex compound, $KTlI_4$, and also the above-mentioned compounds with pyridine or chloropyridines, all exhibit two absorption bands near 4000 and 2550—2600 Å., log ε being of the order 4. The fact that the two maxima are about 1400 units apart whereas the maxima given by $\overset{+}{K}\overset{-}{I_3}$ and by $C_6H_4Br{\cdot}\overset{+}{N}Me_3\overset{-}{I_3}$ are separated only by 650 and 720 units, respectively, indicates that the iodine atoms in thallium tri-iodide are not present as a tri-iodide ion, but are joined, at least in part, by covalent linkings directly to the metal. The view that the compound is a simple aggregate of tervalent thallium and univalent iodine atoms is ruled out because these ions do not give rise to absorption bands.

The molecular conductivities of the thallium trihalides in methyl alcohol and in acetonitrile are

less than those of potassium iodide; the salts therefore behave only as binary electrolytes, in which some of the halogen is linked to the metal, even in the most dilute alcoholic solutions.

Dimethylthallonium iodide is hydrolysed in dilute aqueous solutions and is derived from a base which is much weaker than thallous hydroxide. The molecular conductivity of thallic bromide is less than that of a binary electrolyte except in dilute aqueous solutions, where it is hydrolysed progressively. Absorption spectra indicate that the tribromide is not a mere aggregate of thallium and halogen ions, nor can the bromine be present as a perbromide ion.

The hypothesis that thallium is related to mercury as nitrogen is to carbon is used as a basis for explaining peculiarities in the properties of thallium.

R. A. MORTON.

Ultra-violet emanations of some organic phosphatides after irradiation. C. SERONO and A. CRUTO (Gazzetta, 1928, **58**, 402—404).—Organic phosphatides present in impure cholesterol, after ultra-violet irradiation, possess the property of affecting a photographic film. It is shown that this is due to the re-emission of ultra-violet light by the phosphatides. Similar results are obtained with pure cerebrin and with chlorophyll, but not with pure cholesterol.

F. G. TRYHORN.

Absorption spectrum of iodine in ethyl alcohol. A. BATLEY (Trans. Faraday Soc., 1928, **24**, 438—452).—The maxima at 360 and 290 $\mu\mu$ recorded by previous workers in the ultra-violet absorption spectrum of alcoholic solutions of iodine have been proved to be due to the formation of hydrogen tri-iodide. Precise measurements of the true absorption curve between 250 $\mu\mu$ and 720 $\mu\mu$ have been made in the presence of ozone, which decomposes the iodides of hydrogen as they are formed. The true curve shows one maximum only, of wave-length 477 $\mu\mu$ ($e_{max.} = 9{\cdot}45 \times 10^5$), with general absorption in the far ultra-violet region. The hydrogen tri-iodide was isolated as a brown film by allowing an alcoholic solution of iodine to evaporate on a gelatin film and brushing off the layer of iodine crystals. The absorption of this film showed no traces of the characteristic iodine maximum in the neighbourhood of 444 $\mu\mu$, but gave a definite maximum at 368 $\mu\mu$ of the nature expected from the examination of the iodine solution. The mechanism of the formation of the hydrogen tri-iodide was studied spectrophotometrically, and was shown to be represented by the equations $EtOH+I_2=Me{\cdot}CHO+2HI$; $I_2+HI \rightleftharpoons HI_3$. The former reaction is slow and photochemical, the latter practically instantaneous and thermal. In general, there are in solutions of iodine in alcohol opposing reactions, viz., the photochemical one given above and the photochemical oxidation of hydrogen iodides by dissolved oxygen. The factors influencing the velocities of these reactions were considered, including the purity of the solvent, the light source used, and the concentration of the iodine.

F. G. TRYHORN.

Absorption of ultra-violet light by organic compounds. IX. L. KWIECIŃSKI and L. MARCHLEWSKI (Bull. Soc. chim., 1928, [iv], **43**, 725—743).—See this vol., 346. Like dextrose and lactose, *d*-galactose shows no selective absorption.

Infra-red adsorption by the S–H linking. J. W. ELLIS (J. Amer. Chem. Soc., 1928, **50**, 2113—2118).—The absorption spectra between 0·59 μ and 2·80 μ are investigated for ethyl, *n*-propyl, *n*-butyl, *iso*amyl, phenyl, and benzyl mercaptans and the corresponding sulphides. The main bands which occur in the two series are also found in the spectra of the corresponding primary, secondary, and tertiary amines (cf. this vol., 458). The spectrum of a mercaptan differs from that of the corresponding sulphide by a single band at 1·99—2·00 μ, which may be regarded as the first harmonic of the band at 3·8—3·9 μ. Both these bands probably originate with the sulphur–hydrogen linking. The spectrum of *iso*amyl disulphide reveals no characteristics not shown by the monosulphide. Solid and liquid benzyl sulphide show identical absorption bands, indicating that the energy associated with the carbon–hydrogen linking probably remains unchanged during crystallisation. A small systematic error may be present in Bell's work (A., 1927, 1052).

S. K. TWEEDY.

Structure and stages of excitation of the molecules of some nitriles, determined from the ultra-violet absorption spectra of the vapours. (FRL.) H. E. ACLY (Z. physikal. Chem., 1928, **135**, 251—290).—The absorption spectra of benzonitrile and and *p*-toluonitriles have been studied for the vapours, and the data interpreted according to the methods of Henri. In each case the absorption is of two kinds, a banded structure and a region of continuous absorption. Equations are given which cover the data with considerable accuracy and show the occurrence of doublet series throughout. Comparison of these with earlier analyses of the spectra of benzene and benzene derivatives discloses the dominance of the benzene ring, a conclusion which is confirmed by the investigation of the absorption spectrum of cyanogen. The latter is a vibration–rotation spectrum situated in the far ultra-violet, and the oscillation periods are different from those of the nitriles and from the bands shown in the emission spectrum of nitrogen and the carbon arc.

From the data on nitriles it is shown that the molecules exhibit high deformability; indeed the distances between oscillating atoms are increased by about 3% on excitation. The moment of inertia of benzonitrile is approximately $J=38{\cdot}8 \times 10^{-40}$ from the structure of the bands. The predissociation phenomena (Henri) occur with the toluonitriles after the first excitation and with benzonitrile after the second. Two electron states of activation have been ascertained for each of the substances studied, one deduced from the banded spectrum and the other from the continuous absorption. Numerical values for the different states are calculated.

R. A. MORTON.

Optical examination of perylene and its derivatives. I. Visible absorption spectrum of some simple derivatives. A. DADIEU (Z. physikal. Chem., 1928, **135**, 347—361).—The influence of the groups Cl, Br, Ac, CO_2Et, Bz, $CO{\cdot}C_6H_4Cl$ on the absorption spectrum, in the visible region, of perylene has been studied. Three effects were observed:

movement of the bands towards the red, broadening of the bands, and lowering of the intensity of the bands. A proportionality was observed between the broadening of the bands and the number of electrons in the outer sheath of the substituent. The lowering of intensity runs parallel with the broadening of the bands. W. E. DOWNEY.

Anti-Stokes radiation of fluorescent liquids. R. W. WOOD (Phil. Mag., 1928, [vii], **6**, 310—312).—It is suggested that for the phenomenon of anti-Stokes radiation the absorbing molecule may be in states of vibration and rotation higher than the zero state and after excitation may revert to the zero state, when the excess energy requisite for the anti-Stokes term or terms was stored in the molecule before it absorbed the exciting radiation. Alternatively, when the molecule is in the excited state, it may, by collision with another molecule, be carried to a higher vibrational and rotational state and thus on reversion to the lower initial state release more energy than it absorbed. Both processes should be enhanced by rise of temperature. It is found that some solutions of dyes are non-fluorescent at 100° but fluoresce strongly at the ordinary temperature, and at the same time the absorption band increases in wave-length with rise of temperature. In this case it is suggested that at the higher temperature the molecules were in a partly excited state and that consequently less energy from the radiation of longer wave-length would be necessary to carry them to a definite upper level. A. E. MITCHELL.

Band system in the spectrum of iodine vapour. P. PRINGSHEIM and B. ROSEN (Z. Physik, 1928, **50**, 1—14).—A new series of bands which occurs only at temperatures above 500° has been discovered in the absorption spectrum of iodine vapour. Their fine structure has been investigated and the arrangement of the band heads deduced. A number of new bands were also found in the infra-red region at high temperatures. All the known data concerning the iodine spectrum are discussed with reference to the various electronic excitation terms of the iodine molecule. J. W. SMITH.

Extinction of photoluminescence in uranyl salt solutions. S. J. VAVILOV (Z. Physik, 1928, **50**, 52—57).—Mathematical. Employing an approximate method of calculation and the equation derived by Leontovitsch (cf. following abstract), an expression is deduced for the mean time between the activation of a uranyl salt molecule and its collision with another solute molecule. The calculated values, however, are about fifty times as great as those found experimentally (Vavilov and Levschin, this vol., 814). This discrepancy is attributed to either the solvation of the molecule or the possibility that every collision may not cause extinction. J. W. SMITH.

Theory of extinguishing collisions between dissolved molecules in viscous liquids. M. LEONTOVITSCH (Z. Physik, 1928, **50**, 58—63).—Mathematical. An expression is developed for the mean time between the activation and first collision of an active molecule with another molecule. This is equally applicable to liquids or gases.
J. W. SMITH.

Change of colour of crystals at low temperature. I. OBREIMOW and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 353—356).—A preliminary investigation of the absorption spectra of crystals of potassium dichromate, iodine, and azobenzene in sheets 0·1—0·2 mm. thick at the temperature of liquid hydrogen is described. At the ordinary temperature potassium dichromate exhibits general absorption from 5500 Å. to the extreme ultra-violet, but at 20° Abs. it is pleochroic and the absorption band is split up into sharp lines. Thin plates of iodine which are opaque down to the temperature of liquid air transmit red light (>6700 Å.) at 20° Abs. and exhibit weak periodical bands. Azobenzene is pleochroic, transmitting orange light parallel to the *b* axis of the crystal and lemon-yellow at right angles to this. At −180° the colours change respectively to lemon-yellow and pale green. Spectroscopical examination of the former component shows general absorption at the ordinary temperature which breaks up at −196° into a series of narrow but still diffuse bands. At 20° Abs. a sharp absorption line spectrum appears in which a certain periodicity has been traced. Change of colour with lowering of temperature therefore depends on the narrowing of the absorption bands. J. W. BAKER.

Principal vibration quanta of alkali halide vapours. K. SOMMERMEYER (Naturwiss., 1928, **16**, 653—654)—Absorption experiments with alkali halide vapours yield continuous spectra only. Using an excitation method, certain bands can be observed. Their separation is less at the longer wave-lengths, whilst in the ultra-violet they become progressively feebler and finally disappear. They correspond with the vibration quantum of the normal state of the molecule, which would be strongly excited at the high temperature of the experiment (750—1100°). By measuring the greatest separation, which occurs in the farthest ultra-violet, the value of the quantum number can be obtained, and agrees well with that calculated by Born and Heisenberg. In the case of cæsium iodide, higher quantum numbers of the normal state can be calculated, again with good agreement. Since, at least with small dispersion, only the structure corresponding with the principal quantum number appears, the indication is that all electron switches take place between states of equal excitation. This can be explained on the assumption that the combination is very weak. A fine structure of the bands is visible only with very high dispersion. From the position of the band of shortest wave-length the dissociation energy of the normal atom can be calculated, with certain reservations. The values so derived show fair agreement with those obtained by chemical methods. A. J. MEE.

Theory of the Raman effect. M. BORN (Naturwiss., 1928, **16**, 673).—Raman's discovery is not incompatible with quantum mechanics.
R. A. MORTON.

Ultra-violet, visible, and infra-red reflectivities of snow, sand, and other substances. E. O. HULBERT (J. Opt. Soc. Amer., 1928, **17**, 23—25).—The diffuse reflectivities in the region 0·3—7 μ have been measured for snow, sand, crushed quartz,

plaster of Paris, white paper, white cotton cloth, sodium carbonate, and sodium chloride, using a small quartz–mercury lamp, a thermocouple, and absorbing screens for separating out various spectral regions. The ultra-violet reflectivity of snow is relatively high, being two to four times that of sand. This gives a physical basis for the current idea that ultra-violet glare is an important factor in snow-blindness.

L. L. BIRCUMSHAW.

Temperature of the under-water spark as computed from distribution of intensity in OH absorption bands. E. D. WILSON (J. Opt. Soc. Amer., 1928, **17**, 37—46).—Measurements of the wave-lengths of the OH bands absorbed in the under-water spark show that the bands at λ 2811, 2875, 3064, and 3126 are developed nearly as completely as in emission. Measurement of intensity in branches of the bands at λ 3064 gives a maximum at about $m = 10{\cdot}2$, and from this the effective temperature of the under-water spark has been calculated. From Birge's formula this is found to be 5115° under the conditions of the experiment. Details are given of the experimental methods: the electrical circuits employed, the spectrographic and photometric procedure, and the measurement of the wave-lengths.

L. L. BIRCUMSHAW.

Penetration of ultra-violet light into pure water and sea-water. E. O. HULBURT (J. Opt. Soc. Amer., 1928, **17**, 15—25).—An apparatus consisting of a quartz spectrograph, a sodium hydride quartz photo-electric cell, and a quadrant electrometer is described. With this arrangement measurements have been made of the molecular absorption coefficient of sea-water and aqueous solutions of the principal salts in the sea. The coefficient A is defined by $(\alpha-\alpha_0)/C$, where α is the absorption coefficient of the solution, α_0 that of the pure solvent (water), and c is the concentration in g.-mol. per litre of solution. Measurements were made in the region λ 4000—2500, and the salts investigated were potassium chloride, sodium chloride, magnesium chloride, magnesium sulphate, and calcium sulphate. It was found that the transparency decreases rapidly with decreasing wave-length in the ultra-violet and becomes quite small below λ 3000; that from λ 3400 to 3000 calcium sulphate contributes about one half to the absorption of sea-water, water about one quarter, and the other salts the rest. From λ 3000 to 2500 magnesium chloride, calcium sulphate, and water each contribute roughly one third, the other salts giving but little absorption. A close analogy is traced between the decrease of the transparency of the sea with decreasing wave-length in the ultra-violet and the spectral energy curve of sunlight. A possible function of the part played by the actinic effects of sunlight on the concentration of the sea and the air is suggested by these facts.

L. L. BIRCUMSHAW.

Limits of ultra-violet transmission of certain inorganic compounds. M. KIMURA and M. TAKEWAKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 57—64).—The spectrum of the light transmitted by a 0·5 mm. layer of finely-powdered crystals has been photographed for a large number of inorganic compounds. Colourless compounds of alkali and alkaline-earth metals are more transparent to ultra-violet light than the compounds of other metals. For halides, the limits of transparency are displaced towards the red in the order chlorides, bromides, iodides; *e.g.*, cadmium chloride, bromide, and iodide cease to transmit at 240, 300, and 385 μμ, respectively. Colourless chlorides usually transmit well into the ultra-violet, as do some sulphates and phosphates. All nitrates absorb beyond 320 μμ owing to the selective absorption of the nitrate ion. The only oxides (among the large number tested) which transmitted ultra-violet light at all well were those of magnesium, calcium, and aluminium. All the sulphides studied absorbed strongly. Considering the chlorides, the ultra-violet limits of transparency are shifted towards the red as the at. wt. of the metal increases in the series lithium, sodium, potassium; magnesium, zinc, cadmium; tin, lead; but the reverse is true for the series calcium, strontium, barium. R. A. MORTON.

Infra-red region of the spectrum. I. Prism spectrometer and apparatus. II. Calibration of prism spectrometer; general procedure; preparation of pure ammonia, phosphine, and arsine. III. Infra-red absorption spectra of ammonia, phosphine, and arsine. IV. Discussion of absorption bands of ammonia, phosphine, and arsine. (SIR) R. ROBERTSON and J. J. FOX (Proc. Roy. Soc., 1928, A, **120**, 128—148, 149—160, 161—189, 189—210).—I. A very detailed account is given of the apparatus adopted for the investigation of the infra-red absorption by ammonia, phosphine, and arsine. Attention is directed to the necessity for keeping the source of energy constant, for calibrating the mechanism for reading wave-lengths, for shielding the thermopile from variations in air pressure, for keeping a close watch on the temperature of the prism, especially when made of rock-salt, on account of the high temperature coefficient of its refractive index, for accurate alinement of the observation tubes containing the gas, and for obtaining a galvanometer of great sensitiveness and freedom from external perturbations. The work was carried out as near 18° as possible. A current of 1 amp. and 110 volts from a battery of accumulators was supplied to a Nernst filament, backed by a concave mirror and enclosed in an asbestos housing. The radiation passed through a rock-salt lens of 21 cm. focus and 0·5 cm. aperture and thence through an observation tube, two being used (one empty, one containing gas) mounted on a rocking arrangement for throwing them alternately into the optical path. Two lengths of observation tube were used, according as strong or faint bands were being explored; the shorter tubes were of Pyrex glass, 50 mm. in diameter and 100 mm. long, and the longer tubes of soda glass, 50 mm. in diameter and 450 mm. long. After leaving the observation tube the beam was focussed on the collimator slit of the infra-red spectrometer, furnished with either a 60° rock-salt prism, a quartz or a fluorite prism, and having a Wadsworth mirror for securing minimum deviation. On emerging from the second slit of the spectrometer the radiation was received by a 20-junction bismuth–silver thermopile housed in an air-tight holder, whilst the current

generated here was carried by glass-encased leads to a Downing galvanometer of the Paschen type. A mercury lamp was used for calibration of the instrument as set up. Directions are given for correcting the observation tubes and for the transference of gas from the holders to the observation tubes.

II. [With E. S. Hiscocks.]—Details are given for the calibration of the wave-length drum in terms of the angle of rotation of the prism table, for prisms of rock-salt, quartz, and fluorite. Paschen's values for the refractive indices were used, corrected to 18° (in the case of rock-salt and fluorite) by means of Liebreich's temperature coefficient determinations (Verh. Phys. Ges., 1911, **13**, 1). The general procedure used in the setting up of the apparatus and the method of conducting an experiment are described, and details are given for the preparation of pure ammonia (from synthetic ammonium chloride and 50% potassium hydroxide solution), phosphine (from phosphonium iodide and 50% potassium hydroxide solution), and arsine (from zinc–arsenic alloy and 30% sulphuric acid).

III. A general description is given of the absorption bands found in the three gases, together with curves showing their occurrence in the region 1—17 μ, and evaluations of the maxima of the absorption bands. The quality of resolution was as follows: Bands were unresolved below 2·2 μ (quartz prism); bands were partly resolved from 2·2 μ (quartz), from 4 μ (fluorite), and from 5 μ (rock-salt); and bands were resolved to show fine structure from 3 μ (quartz), from 6 μ (fluorite), and from 8 μ (rock-salt). Unresolved bands show one peak, the centre near the top being taken as the position of the oscillation band; partly resolved bands show three peaks, the centre one being taken for calculation of the oscillation frequency; whilst for resolved bands, the positions of the maxima of rotation imposed on the oscillation band are recorded. All the readings have been converted into wave-numbers per cm. for purposes of calculation and comparison, and the figures are given to show percentage absorption/wave number. Graphs of the absorption bands found in the three gases are set out to show a general comparison. Whilst ammonia exhibits a more complicated spectrum, all three gases have in common a main sequence of harmonic bands (I, II, . . .); ammonia has a second sequence (C, D, . . .), not represented in phosphine or arsine, also a faint sequence (a, b, . . .) of which the farthest band measured is a member, and a band at 4·05 μ and a well-defined and resolved band at 10·55 μ; phosphine and arsine have also a second sequence (A′, B′ . . and A″, B″ . . .) and a sequence (α, β, . . .) not represented in ammonia. The bands I—VI form a nearly harmonic sequence, and are all of the same type, characterised by an intense zero branch with less intense side branches. Fine structure has been found superimposed on this general contour in bands I and II of ammonia, and in band I of phosphine and arsine. The ammonia band at 10·55 μ has been resolved and has the unique feature of having two *Q* branches close to one another. Tables are given showing data for the oscillation bands of the three gases, the structure of bands I, II, and 10·55 μ of ammonia, the intermediate region between bands I and 10·55 μ of ammonia, the structure of bands I, II, and α of phosphine, the structure of bands 1 and α of arsine, the effect of pressure (varying from 1 to 1/16 or 1/32 atm.) on the maxima of the absorption bands, and the effect of pressure on the area under the absorption bands. The values for ammonia are in good agreement with those of Schierkolk from the visible to 14 μ (cf. A., 1925, ii, 180), and the data obtained by Spence for the ammonia band at 3 μ have also been confirmed (cf. *ibid.*, 350).

IV. The types of absorption bands in the near infra-red which are partly or completely resolved are described. It is found that there are nearly constant ratios between the vibration numbers of the members of the main sequence common to the three gases, and that the second sequence found in phosphine and arsine has a ratio similar to that in the main series. There are thus certain degrees of freedom common to these gases. Tables are given showing the harmonic relations of the oscillation bands in the three gases, and it is seen that, whilst the bands of the main sequences are approximately multiples of the fundamental, in none of the gases does Kratzer's relation hold (Z. Physik, 1920, **3**, 289). In all cases the value for the fundamental is low when compared with the values for the other bands divided by their ordinal number. The structure of the rotation–oscillation bands is discussed. Consideration of the effect of pressure on the intensity of the bands shows that, whilst no generalisation can be made on the intensities of the central frequencies, in the resolved bands, Beer's law holds at the lower pressures for the bands of fine structure. This is shown well for the bands of the fine structure of ammonia band I and band 10·55 μ. The results obtained on evaluating the area under the contour of the same bands are in close agreement with those obtained from a consideration of the central frequencies alone. The moments of inertia of the molecules of the gases, calculated from the average spacing differences determined from the fine structure of bands I, II, and 10·55 μ (ammonia), I and α (phosphine), and I and α (arsine) are found to be $2{\cdot}78\times10^{-40}$, $4{\cdot}78\times10^{-40}$, and 5·53 or $6{\cdot}51\times10^{-40}$ g. cm.^{2}, respectively, for ammonia, phosphine, and arsine. The values are compared with those derived from the energy relation for three degrees of freedom. Evidence in favour of the tetrahedral model for the molecules of the gases is discussed. The existence of oscillation bands of various frequencies in the infra-red spectrum of ammonia shows that the ions are separating, and one of the modes of vibration may be considered to be the oscillation of nitrogen against the plane of the hydrogen atoms. In such a case, Hund's condition (Z. Physik, 1925, **31**, 99) is fulfilled, and a tetrahedral structure is required for the model. The large temperature effect on the dielectric constant of gaseous ammonia, together with its high electric moment (cf. Watson, this vol., 107), is in favour of this view. The considerations leading to a tetrahedral structure for ammonia apply likewise to phosphine and arsine. L. L. Bircumshaw.

Short-wave infra-red absorption of artificial and natural sylvite. C. Schaefer and C. Bormuth

(Z. Physik, 1928, **50**, 363—365).—Artificial sylvite does not exhibit the infra-red absorption bands given by natural sylvite (cf. Coblentz, Bull. Bur. Standards, 1912, **7**, 653). It is probable that the bands are due to traces of ammonium chloride.

W. E. DOWNEY.

Band spectrum of water vapour. III. D. JACK (Proc. Roy. Soc., 1928, **A**, **120**, 222—233; cf. A., 1927, 808; this vol., 571).—The structure of the bands in the spectrum of water vapour has been investigated, using the new notation proposed by Mulliken (cf. this vol., 105). The connexion between the old and new notation is shown by means of a table. The water-vapour bands can be interpreted as arising from transitions between ^2S and ^2P levels. The ^2P levels are subject to σ-type doubling (A, B), whilst the ^2S levels are probably rotationally single. For the P and R branches the transitions are between 1A and 1B, or 2A and 2B states, whilst the Q branches show "crossing over," 1A to 1A, and 2A to 2A. The σ-type doubling and crossing over are capable of accounting for the failure of the combination principle, $R(j-1)-Q(j)-Q(\gamma-1)-P(\gamma)$, when applied to the main branches. The P, R, and Q satellites are considered; in some of the Q satellites the transitions violate the σ-selection rule in that they arise from transitions from A to B states whilst at the same time $\Delta j_k=\sigma$. The most remarkable feature shown by these bands is the presence of a singlet series for which the combination principle definitely indicates a transition of two units in γ_k. It is concluded that the only selection rule which holds rigidly is $\Delta j=\pm1, 0$. The most probable transition of any momentum component is ±1 or 0, but this rule cannot be taken as final. L. L. BIRCUMSHAW.

Quartz rod or sphere for condenser in spectroscopy. H. NAGOAKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8** [Suppl.], 1—3).—The different methods of using quartz rods or spheres as condensing lenses in spectroscopy, especially for investigations in the ultra-violet region, and their respective advantages for this purpose are discussed. J. W. SMITH.

Absorption of light by iron pentacarbonyl. J. DRECHSLER (Z. Elektrochem., 1928, **34**, 320—323).—The absorption of visible light by iron pentacarbonyl in various solvents follows Beer's law at all concentrations between 99 and 0·5%, and is independent of the solvents employed (acetone, chloroform, carbon tetrachloride, benzene, toluene, *o*- and *m*-xylene). Qualitative experiments show, however, that the rate of decomposition of the carbonyl is influenced by the solvent. No connexion could be observed between the dielectric constant of the solvent and the rate of decomposition. L. F. GILBERT.

Band spectrum of mercury hydride. E. HULTHEN (Z. Physik, 1928, **50**, 319—335; cf. A., 1925, ii, 470).—The band spectrum of mercury hydride has been studied in detail using an intense source of light and higher dispersion than in the previous work. New bands have been discovered and the $^2P-^2S$ system has been completed. In the region 3100—2900 Å. some bands, degraded towards the red, were observed and classified in a $^2S-^2S$ system. An isolated feeble band at 2700 Å. probably arises from a more strongly excited $^2S-^2S$ system. The theoretical bearings of the results are discussed. The energy of dissociation, calculated from the rotational terms, is found to be 0·369 volt.

W. E. DOWNEY.

Light emitted by the recombination of halogens. V. KONDRATEEV and A. LEIPUNSKI (Z. Physik, 1928, **50**, 366—371).—The light emitted by halogens heated at 1000—1100° has been spectroscopically examined. The spectrum coincides with the absorption spectrum of the halogen in question. The emission is explained as due to a reversed photodissociation according to the equation $X+X'-X_2+h\nu$. W. E. DOWNEY.

New class of spectra due to secondary radiation. I. C. V. RAMAN and K. S. KRISHNAN (Indian J. Physics, 1928, **2**, 399—419).—When light from a quartz-mercury lamp is diffused within a liquid and the scattered light spectroscopically analysed, a large number of new lines are observed in the scattered spectrum which are not present in the incident spectrum. These spectra have been photographed in the cases of benzene, toluene, pentane, ether, methyl alcohol, and water; each liquid shows a distinctive scattered spectrum, but certain general similarities are shown by liquids having chemically similar groups in their composition. In the case of benzene it has been shown that corresponding with each unmodified line in the spectrum there are seven modified lines observable, two being especially prominent. The frequency differences between the unmodified and modified lines are independent of the wave-length of the incident line; six of the modified lines have frequencies lower than the exciting line, the other having a higher frequency, the increase in wave number in this case being numerically equal to the decrease in the case of one of the other six lines. The shift in frequency of the modified lines is found to agree with certain characteristic infra-red frequencies of the molecule. Hence the observations are explained by supposing the incident quantum to be absorbed in part and scattered in part by the molecule, the former portion causing a change in energy level. The modified line of higher frequency is supposed to be due to the radiation inducing a return from a higher energy state to the normal state. The comparative feebleness of this line is explained thermodynamically.

J. W. SMITH.

Wave-length shifts in scattered light. A. E. RUARK (Nature, 1928, **122**, 312—313).

[Lamp] to obtain the maximum short-wave ultra-violet radiation. N. IAROTZKY (Compt. rend., 1928, **187**, 459—461).—A mercury-vapour lamp working at 80,000 volts is described which gives the ray 253 $\mu\mu$, and may be brought close to the subject without the use of filters to absorb thermal radiations. J. GRANT.

NH-Band and the dissociation energy of nitrogen. E. GAVIOLA (Nature, 1928, **122**, 313—314).—An explanation for the appearance of the band at 3360—3670 Å., with intensity proportional to the square of that of the exciting light, is sought. It is assumed that the atomic nitrogen is formed by

three-body collisions of N_2 molecules with two excited mercury atoms, and it appears probable that the dissociation energy of nitrogen is less than, or about, 9·8 volts. A. A. ELDRIDGE.

Measurement of ultra-violet quanta by fluorescence photometry. W. T. ANDERSON, jun., and L. F. BIRD (Physical Rev., 1928, [ii], **32**, 293—297).—Equally accurate results are obtained by the use of photometric and thermopile methods. A. A. ELDRIDGE.

Wave-length shifts in scattered light. R. W. WOOD (Nature, 1928, **122**, 349).

Approximation method and application to some HCl bands. D. G. BOURGIN (Physical Rev., 1928, [ii], **32**, 237—249).—Theoretical. A. A. ELDRIDGE.

Quantum mechanics of the rotational distortion of multiplets in molecular spectra. E. HILL and J. H. VAN VLECK (Physical Rev., 1928, [ii], **32**, 250—272).—A study of the effect of molecular rotation on spin multiplets, and the development of an elementary theory of σ-type doubling. The authors consider Hund's limiting cases (*a*) and (*b*), the general intermediate case, the doublet case, and simple special cases of the doublet intensity formulæ. A. A. ELDRIDGE.

Influence of deformation on the interior photoelectric effect for rock-salt. M. N. PODASCHEWSKY (Naturwiss., 1928, **16**, 653).—Plastic deformation of rock-salt crystals exerts a noticeable effect on the primary photo-electric current. This falls rapidly at first, then more slowly, finally reaching a constant value. The photo-electric sensitivity may even be reduced to zero by this treatment, but may be restored by repeated exposure to *X*-rays. A. J. MEE.

Dipole moment of symmetrical compounds and *cis–trans*-isomerism at "single" linkings. R. ENGELAND (Physikal. Z., 1928, **29**, 626; cf. Weissberger, this vol., 689).—The question of *cis–trans*-isomerism and its connexion with valency discussed by Weissberger has already been decided by Schlesinger through his experiments with the copper salts of certain bis-α-imino-acids (cf. A., 1925, i, 1249). Final proof is furnished by the fact that α-aminoacetic acid, which itself forms no optical antipodes, forms two different copper salts, one of which corresponds in colour and in water content with the optically active and the other with the racemic form of the higher homologues. The copper salt corresponding with the optically active acids can be prepared only from glycine which has been made by the hydrolysis of albumin. A. J. MEE.

Dispersion of conductivity. H. SACK (Physikal. Z., 1928, **29**, 627—628).—A method is described for the determination of the change of conductivity of a solution with the frequency of the current traversing it (cf. Debye and Falkenhagen, this vol., 596). The method depends on the fact that in a tuned circuit consisting of a self-inductance and a capacity with parallel resistance (in this case a condenser with a conducting liquid), any change in the resistance will produce a change in the current strength at resonance which can be measured. The results obtained are of the order of magnitude required by the theory. A. J. MEE.

Dielectric constant of air at radio frequencies. A. B. BRYAN and I. C. SANDERS (Physical Rev., 1928, [ii], **32**, 302—310).—The value obtained for $\varepsilon-1$ at *N.T.P.* is 0·0005893. A. A. ELDRIDGE.

Applicability of Fresnel's law in deducing evidence in favour of surface structure from surface reflectivity. S. S. BHATNAGAR, D. L. SHRIVASTAVA, and N. C. MITRA (J. Indian Chem. Soc., 1928, **5**, 329—342).—Measurements have been made of the intensity of the reflected beam of unpolarised light, incident at various angles on to surfaces of a number of liquids, in order to ascertain whether deviations from Fresnel's law exist on account of molecular orientation in the surface. No such deviation has, however, been observed, although some evidence has been obtained of differences between the optical properties of polar and non-polar liquids. H. F. GILLBE.

Quantum theory of scattering and dispersion. A. SMEKAL (Naturwiss., 1928, **16**, 612—613).—When radiation is scattered by atoms, the energy of an electron in the atom can be changed by an amount corresponding with the quantum switch. There should thus be a frequency change, the scattered radiation consisting of one of the primary frequency and others above and below it. The effect should be obtained with visible light. Raman has succeeded in observing the effect using light from a mercury-vapour lamp and passing it through various liquids, *e.g.*, benzene. In benzene, the frequency differences are constant with varying primary frequency, and correspond with the switch producing an observed infra-red radiation. This can be described in terms of the analogy between quanta and electrons. The change of an energy level of an electron in the scattering atom can take place through collisions of the first or second kind with light quanta of any primary frequency, just as with electrons of any original velocity. A. J. MEE.

Theory of the Ramsauer effect. J. HOLTSMARK (Naturwiss., 1928, **16**, 614—615).—Ehrenfest and Rutgers sought to identify the Ramsauer effect with the disappearance of zero-order optical diffraction. On this view the scattering would vanish for electrons other than those corresponding with long wave-lengths. The application is doubtful, because inside the atom the electron wave-length becomes greatly changed owing to the high refractive index; however long the wave-length is outside, it will be short inside the atom. Thus the wave-length for disappearance of scattering will depend on the atomic field. The Ramsauer effect is treated as the analogue of Rayleigh's diffraction theorem. In place of Fourier coefficients there are coefficients of the expanded characteristic function, account being taken of the change of wave-length in the atomic field. Thus, contrary to Wentzel's view, there is no need to treat the problem in three dimensions. The calculation of scattering for argon on this theory is in good agreement with experimental values; with neon, the agreement is not so good. A. J. MEE.

New phenomenon in the scattering of light in crystals. H. Kornfeld (Naturwiss., 1928, **16**, 653).—The change of wave-length occurring on scattering which was determined quantitatively for quartz by Landsberg and Mandelstam (this vol., 936) has been found to occur with calcite. The measured change of wave-length corresponds with the excitation of an infra-red oscillation of the wave-length 9·1 μ. In this region there lies a series of combination oscillations of CO_3 ions. A. J. Mee.

Polychroism and the orientation of the ions in the crystals of the rare earths. R. Brunetti (Physikal. Z., 1928, **29**, 571—575).—The polychroism of the crystalline salts of certain rare-earth metals can be correlated with an axis connected with the structure of the ions in relation to the axes of symmetry of the crystal. W. E. Downey.

Rotatory dispersion of certain isomeric butyl esters of *l*-mandelic acid. C. E. Wood, A. E. Chrisman, and S. D. Nicholas (J.C.S., 1928, 2180—2190).—The rotatory dispersions of the isomeric butyl esters of *l*-mandelic acid have been measured at a large number of temperatures between 0° and 100°. Mandelic acid was resolved by a modification of McKensie's method (*ibid.*, 1899, **75**, 966) and from the morphine *l*-mandelate, m. p. 223—224° (McKensie, *loc. cit.*, gives 202°), *l*-mandelic acid, m. p. 133·5°, was obtained. From this its *n*-butyl, m. p. 38·5° (corr.), d_4^{30} 1·0443, $[M]_D^{30}$ −186·99° (cf. Smiles and Walker, A., 1909, ii, 846), *iso*butyl, m. p. 35·5° (corr.), $d_4^{38.5}$ 1·0536, $[\alpha]_D^{42}$ −102·65° (cf. Walden, A., 1896, ii, 135), tert.-*butyl*, m. p. 65°, d_4^{21} 1·0665, $[\alpha]_D^{21}$ −82·70°, and d-sec.-*butyl*, b. p. 88°/0·05 mm., d_4^{19} 1·0623, $[\alpha]^{20}$ −77·50°, esters were prepared. All the esters exhibit complex and normal rotatory dispersion. The *iso*butyl ester shows an increase and the *tert.*-butyl a decrease of negative rotation compared with the normal ester. Pronounced decrease in rotation occurs, especially in the violet end of the spectrum, when two asymmetric centres of opposite sign are present in the molecule, as in *d-sec.*-butyl *l*-mandelate, but the effect is not sufficiently marked to cause visual anomaly, since the mandelic acid radical dominates the rotatory power. For visual anomaly the two asymmetric centres must be of comparable magnitude, as in *d-sec.*-butyl *d*-lactate. The dispersion ratios of the *n*-, *iso*-, and *tert.*-butyl esters are sensibly constant, but the curve for the tertiary ester tends to diverge from those of the *n*- and *iso*-esters, the divergence becoming more marked at the violet end of the spectrum. Rise of temperature causes a decrease in rotation in each case, the change being more pronounced in the blue region. For the longer wave-lengths the temperature–rotation curves are nearly linear, but as the wave-length decreases the curvature increases uniformly. Comparison of the rotation data of the three esters affords no generalisation for the determination of the relative configuration. Acylation of both ethyl and methyl mandelates causes a displacement of the rotations, without change of order, further into the negative region. The rotational displacements of the esters of *l*-mandelic, *l*-lactic, *d*-tartaric, *d*-malic, *d*-α-hydroxybutyric, *l*-glyceric acids, and certain of their acetyl and benzoyl derivatives are discussed as a guide to configuration, but no general rule could be formulated. J. W. Baker.

Optical anisotropy of atoms and molecules. I. R. Rao (Indian J. Physics, 1928, **2**, 435—465).—The fact that the distances between the optical centres of atoms in molecules calculated from scattering data show large discrepancies from the values obtained by *X*-ray measurements is held to indicate that the assumption of the isotropy of atoms is untenable. The depolarisation of light scattered by rare gases leads to the same conclusion. The values of the anisotropy of several ions are calculated in the various compounds of which the scattering data are accurately known. The results indicate that of all similar ions the rare-gas atoms exhibit the least anisotropy and that heavier atoms show less anisotropy than lighter ones. The anisotropy of an ion increases, but the ionic deformability diminishes, with increasing opposite charge on the adjacent ion. The deformability of the heavier elements changes less with increasing adjacent charge than that of lighter ones. The theoretical basis of atomic anisotropy is also discussed. J. W. Smith.

Optically active copper compounds. W. Wahl (Comm. Phys.-Math., 1927, IV, No. 14, 5 pp.; Chem. Zentr., 1928, i, 1377).—Diethylenediaminediaquocupric sulphate must possess an octahedral arrangement of the co-ordinatively linked groups, as well as two ring planes. By means of barium *d*-tartrate the salt was obtained in two optical antipodes. *l*-Diethylenediaminediaquocopper iodide is considered to have $[M]_D$ −190°. Diethylenediaminediaquonickel sulphate was also resolved. A. A. Eldridge.

Quantum mechanics of homopolar valency. F. London (Z. Physik, 1928, **50**, 24—51).—Mathematical (cf. Heitler and London, A., 1927, 923; London, this vol., 344). J. W. Smith.

Is the molecule of gaseous hydrogen chloride polar or non-polar? F. I. G. Rawlins (Z. Physik, 1928, **50**, 440—442).—Polemical against Kondratéev (this vol., 688). It is insisted that gaseous hydrogen chloride has a polar molecule. W. E. Downey.

Problem of Brownian molecular motion. (Frl.) F. Stadie (Ann. Physik, 1928, [iv], **86**, 751—797).—Mathematical. R. A. Morton.

***X*-Rays do not always give the true structure of crystals.** C. Mauguin (Compt. rend., 1928, **187**, 303—304; cf. Friedel, this vol., 817).—An attempt is made to show that for biotite and the chlorites the *X*-ray method does not always give the true crystal structure, and a scheme is outlined for the approximate determination of the extent to which it is masked. J. Grant.

***X*-Ray analysis of Heusler's alloy.** E. Persson (Naturwiss., 1928, **16**, 613).—Heusler's alloy (a copper–manganese–aluminium alloy) consists of three phases. It is the second, or β-phase, which has been reinvestigated. The fundamental lattice is body-centred cubic, and the aluminium atoms are situated in a face-centred cubic lattice with double the para-

meter of the fundamental lattice. The elementary cell contains 16 atoms, 12 of which are copper and manganese, and the remaining 4 aluminium. The formula $(Cu,Mn)_3Al$, which had previously been supposed to represent the constitution of this solid solution, is confirmed. The magnetic properties of this alloy are due to the presence of this β-phase. It is possible, however, for an alloy of copper, manganese, and aluminium to consist almost entirely of this β-phase and yet be non-magnetic. The concentration of manganese influences the magnetic properties; it must reach a definite value for the alloy to be magnetic. The *X*-ray observations also show the presence of a fourth phase, but it is improbable that this can account for the magnetic properties of the alloy.
A. J. MEE.

***X*-Ray examination of liquids by the rotating-crystal method.** D. COSTER and J. A. PRINS (J. Phys. Radium, 1928, [vi], 9, 153—155).—Apparatus is described whereby an *X*-ray tube and spectrograph can be rotated with respect to a horizontal liquid surface. Mercury has been examined with the apparatus and three bands have been obtained.
W. E. DOWNEY.

Physical purity and powder rontgenograms. N. H. KOLKMEIJER (Z. physikal. Chem., 1928, **136**, 45—48).—See this vol., 692.

***X*-Ray spectrography of alloys.** H. WEISS (Bull. Soc. chim., 1928, [iv], **43**, 697—711).—A lecture.

***X*-Ray analysis of silver–aluminium alloys.** A. F. WESTGREN and A. J. BRADLEY (Phil. Mag., 1928, [vii], **6**, 280—288).—The existence, at the ordinary temperature, of two intermediate phases in the Ag–Al system, both formed through transformation in the solid state, has been shown by *X*-ray analysis, thus confirming the previous result of Petrenko (A., 1905, ii, 635). The Ag_3Al phase is shown to be cubic, the edge of the unit cell, containing 20 atoms, measuring 6·920 Å. The other intermediate phase, stable over the range 27—40 at.-% aluminium, is a solid solution of close-packed hexagonal structure. The lattice dimensions change continuously from $a_1=2\cdot865$ Å., $a_3=4\cdot653$ Å., and $a_3/a_1=1\cdot625$ when saturated with silver to $a_1=2\cdot879$ Å., $a_3=4\cdot573$ Å., and $a_3/a_1=1\cdot588$ when saturated with aluminium.
A. E. MITCHELL.

***X*-Ray investigation of the changes in the alloy CuAu.** W. GORSKY (Z. Physik, 1928, **50**, 64—81).—An alloy consisting of equal atomic proportions of copper and gold was heated to various known temperatures, quenched, and examined by Debye's *X*-ray method. Below 385°, the stable form is a tetragonal lattice, but with no systematic distribution of copper and gold atoms. The axis ratio a/c changes from 1·07 at 380° to 1·08 at 300°, and $\sqrt[3]{a^2c}=3\cdot860$ Å. The transition from cubic into tetragonal forms and *vice versa* occurs through a process of recrystallisation. The gradual change in the axis ratio brought about by a sudden change in temperature occurs according to an exponential equation. The observed phenomena are explained by thermodynamic and statistical methods.
J. W. SMITH.

***X*-Ray spectroscopic measurements of the *M*-series of the elements uranium to gadolinium.** E. LINDBERG (Z. Physik, 1928, **50**, 82—96).—Using an accurate *X*-ray spectroscope of the Siegbahn type, new measurements have been made of the *M*-series lines of a number of elements between uranium (92) and gadolinium (66), a large number of new lines being observed. Several of the lines were traced systematically down the series of elements and constant intensity ratios found. Observations of the $M_{\alpha_1\alpha_2\beta}$ doublet confirmed the results of van der Tuuk (A., 1927, 999).
J. W. SMITH.

Oven for *X*-ray investigations at high temperatures and preliminary results with pentaerythritol and quartz. W. M. COHN (Z. Physik, 1928, **50**, 123—136).—A camera is described in which the fine structure of the *X*-ray spectrum of solid, non-conducting bodies may be determined, the preparation being brought to a known high temperature for long periods. Both in the cases of pentaerythritol and quartz the effect of rising temperature was to cause a general weakening of the intensity of the bands with equal times of exposure and a falling off of the higher interference bands. On the other hand, the broadening of the lines which was anticipated on theoretical grounds was observed only in the case of pentaerythritol.
J. W. SMITH.

Absolute intensity of *X*-rays. T. E. AUREN (Medd. K. Vetens. Nobel Inst., 1927, **6**, No. 13).—The absolute intensity of *X*-rays has been measured by the heat excited in metals on absorption of the rays. No difference in the energy measurements was found using plates of copper, silver, and lead. Up to 100 kilovolts, the intensity is exactly proportional to the current through the tube. The relationship between the total intensity of the energy radiated as *X*-rays and the voltage applied to the tube has been determined. The effect of an aluminium filter also was studied. The energy necessary to produce a pair of ions is not found to increase with decreasing wave-length.
W. E. DOWNEY.

Determination of the absorption coefficient of various metals and organic compounds in the short-wave *X*-ray region. H. STUMPEN (Z. Physik, 1928, **50**, 215—227).—A new method has been devised for the measurement of *X*-ray absorption. The results obtained with the metals and organic compounds investigated confirm those of previous workers.
J. W. SMITH.

***X*-Ray diffraction and its bearing on molecular complexity in the liquid state.** P. KRISHNAMURTI (Indian J. Physics, 1928, **2**, 491—500).—The *X*-ray diffraction of 26 pure organic liquids has been investigated. In all cases where the surface-tension method indicates association the inner ring is very prominent. By substituting the spacing obtained by the *X*-ray method for the value of $\sqrt[3]{m/d}$ in Ramsay and Shields' relationship, more probable values have been obtained for the degree of association and some anomalous values have been rectified. It is suggested that all liquids can be dealt with as solutions of double molecules in a solvent composed of single molecules, or of triple molecules in a solvent of

double molecules, and that the ideas derived from a study of aqueous solutions containing small and large molecules of solute at different concentrations can be applied equally well to this case in explaining the intensity and extent of the inner ring.

J. W. SMITH.

X-Ray diffraction in aqueous solutions and liquid mixtures. I. P. KRISHNAMURTI (Indian J. Physics, 1928, 2, 501—507).—The X-ray diffraction of ammonium nitrate and acetamide both in powder form and in their aqueous solutions at various concentrations has been investigated. The concentrated aqueous solutions tend to develop an inner ring, which is in favour of the existence of a regular arrangement of atoms as in the liquid or solid state. The general scattering which occurs in concentrated ammonium nitrate solutions but not in acetamide is attributed to a portion of the ions being distributed at random in the liquid. In both cases the two rings which appear in the solid state persist in the liquid state and in very concentrated solutions, both rings undergoing some contraction. As dilution increases the inner ring contracts and tends to disappear as a general halation, whilst the outer ring expands and merges with the water ring. Hence it is deduced that the outer ring is a superposition effect due to the water and solute taken in their proper proportions.

J. W. SMITH.

X-Ray diffraction in liquids. Comparison of isomerides of n-heptane and of certain carbon chains. G. W. STEWART (Physical Rev., 1928, [ii], **32**, 153—161).—Diffraction ionisation curves for the $K\alpha$ doublet of molybdenum were obtained for synthetic *n*-decane, ββδ-trimethylpentane, β-methyl-Δ^{β}-hexene, ββγ-trimethylbutane, γγ-, βγ-, ββ-, and βδ-dimethylpentane, γ-ethylpentane, γ-methylhexane, and β-methylhexane. The diameter of the normal paraffin chain throughout the range C_5—C_{15} is 4·64 Å.; the length is given by $L=1{\cdot}24n+2{\cdot}70$ Å., where n is the number of carbon atoms, it being assumed that the molecules are longitudinally parallel and in square array in the plane normal to their lengths. It is tentatively concluded that the attachment of two methyl groups to the same atom does not necessarily increase the diameter by the same amount, the effect depending on whether a third methyl branch is attached to an adjacent atom or to the next but one. Attachment of a methyl group to the penultimate carbon atom seems to produce two symmetrical branches of one methyl group each.

A. A. ELDRIDGE.

Crystallographic identity of the two forms of mercuric oxide. G. R. LEVI (Gazzetta, 1928, **58**, 417—418; cf. A., 1924, ii, 860).—A reply to the criticisms of Kolkmeijer (this vol., 692).

F. G. TRYHORN.

Dehydrated gibbsite. J. DE LAPPARENT and E. STEMPFEL (Compt. rend., 1928, **187**, 305—306).—The changes in optical properties shown by crystalline gibbsite during dehydration at gradually rising temperatures (up to 1000°) indicate that the final product is also crystalline, the structure having changed from clinorhombic to orthorhombic at 600°.

J. GRANT.

X-Ray observations with cellulose. R. O. HERZOG and W. JANCKE (Naturwiss., 1928, **16**, 618).—The Röntgen diagram of natural cellulose shows a blackening at a point corresponding with $\sin\theta/2=0{\cdot}0218\pm0{\cdot}0003$. This also appears if mercerised ramie is used, but not so definitely. If it is due to the cellulose lattice, it corresponds with a lattice space of 35·3 Å. There is also a weak point which indicates a period perpendicular to the axis of 16 Å.

A. J. MEE.

Crystal structures of the compounds RuS_2, OsS_2, $MnTe_2$, and $AuSb_2$. I. OFTEDAL (Z. physikal. Chem., 1928, **139**, 291—299).—Powder photographs show that the compounds RuS_2, OsS_2, $MnTe_2$, and $AuSb_2$ exhibit the pyrites structure. Parameters of about 1/8 are found. The following lattice constants are given: pyrites (Kongsberg) $a=5{\cdot}414$ ($\pm0{\cdot}003$) Å., $MnTe_2$, $a=6{\cdot}943(\pm0{\cdot}002)$ Å.; $AuSb_2$, $a=6{\cdot}636(\pm0{\cdot}010)$ Å.

R. A. MORTON.

Crystal structure of tetraethylammonium iodide. I. NITTA (Proc. Imp. Acad. Tokyo, 1928, **4**, 292—296).—The structure of tetraethylammonium iodide has been examined by means of the Laue and ionisation methods. The lattice is found to be tetragonal body-centred, the unit cell consisting of two molecules. It is not possible to decide whether the structure is that of sodium chloride or that of cæsium chloride.

W. E. DOWNEY.

Slip-bands produced when crystals of aluminium are stretched. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 289—317).—The plastic strain produced in pieces of aluminium when stretched has been found to be a simple shear on the slip plane and along the direction of slip, so far, at least, as general external form is concerned. The directions of the slip bands are in accordance with the predictions of Taylor (A., 1927, 1017), although some of the quantitative observations are not in agreement with those of the latter investigator.

J. W. SMITH.

Anisotropy of the carbon atom. (MRS.) K. LONSDALE (Phil. Mag., 1928, [vii], **6**, 433—446).—From a consideration of the X-ray data for hexachloroethane and isomorphous compounds a structure is suggested for the carbon atom in which two of the valencies differ geometrically from the other two. This is in agreement with the Main Smith and Stoner configurations of the carbon atom. Evidence is adduced in favour of the non-tetrahedral carbon atom. A critical discussion of the structures of symmetrically substituted methane derivatives shows that the existence of the pyramidal carbon atom has not been established. The structure suggested agrees with crystallographic data and explains the non-symmetry of many simple carbon compounds.

S. K. TWEEDY.

Oxides and hydroxides of cobalt. G. NATTA and M. STRADA (Gazzetta, 1928, **58**, 419—433).—Chemical and X-ray crystallographic analyses have been made of cobalt oxide and hydroxide preparations to determine which of those described in the literature may be accepted as definite compounds. Three oxides of cobalt with definite chemical and crystalline structures are recognised. Cobaltous oxide, with a

cubic face-centred lattice, has an elementary cell of edge 4·22 Å., containing four molecules of the sodium chloride type. The oxide Co_3O_4 (cobaltous cobaltate) has a cubic structure with a lattice of the spinel type, with an elementary cell of edge 8·05 Å. containing eight molecules. Cobaltic oxide has probably an hexagonal or a rhombohedral structure with a cell of edge $a=4·64$ Å., $c/a=1·24$, containing two molecules. The calculated density is 5·34. Cobaltic hydroxide may be prepared satisfactorily by drying the hydrate at 250°. Above this temperature the oxide Co_3O_4 is obtained. Products described previously as cobalt suboxide, Co_2O, are mixtures of the metal and cobaltous oxide. Of the hydroxides of cobalt recorded only cobaltous hydroxide has a definite composition and crystalline structure. The crystals are of rhombohedral form (type brucite) with an orthorhombic elementary cell ($a=3·19$ Å., $c/a=1·46$) containing one molecule of cobaltous hydroxide. Cobaltic hydroxide could not be obtained in a definite crystalline form, but in *X*-ray photograms exhibits the lines of cobaltic oxide, which it forms on dehydration. Other oxides and hydroxides lower than Co_2O_3 and $Co(OH)_3$ cannot be obtained as chemical individuals, and must be represented as mixtures of the above compounds. No oxide higher than Co_2O_3 could be obtained in the dry state. F. G. TRYHORN.

Isomorphism, polymorphism, and monotropy. I. Compounds of the type ABX_3. G. NATTA and L. PASSERINI (Gazzetta, 1928, **58**, 472—484).—*X*-Ray crystallographic analyses by the powder, Laue, and rotating-crystal methods have been made of some complex halides of cæsium and mercury and of cæsium and cadmium. The cubic modifications of cæsium trichloromercuriate and of cæsium tribromomercuriate possess elementary cells of edges 5·44 and 5·77 Å., respectively, each containing one molecule; $d_{calc.}$ 4·53 and 4·97, respectively. These compounds are isomorphous and form a complete series of solid solutions. Cæsium monochlorodibromomercuriate and cæsium monobromodichloromercuriate do not exist as chemical individuals, but belong to the continuous series of solid solutions formed by the above two halogenomercuriates. They have the same lattice as these latter, but deformed. The dimensions of the cells of the mixed crystals follow closely Vegard's rule. Isomorphous with the preceding compounds are cæsium tribromocadmiate and cæsium trichlorocadmiate. The bromo-compound has an elementary cell of edge 5·33 Å. with a calculated density 5·38. Cæsium tri-iodomercuriate and cæsium tri-iodocadmiate are not isomorphous with the corresponding chloro- and bromo-derivatives and have a lower crystalline symmetry. The latter, $Cs[CdI_3]$, (d 5·48, m. p. 193°) was prepared by the dehydration of the monohydrate. The relations which must exist among the atoms A, B, and X in the compounds ABX_3 in order that certain types of structure may be possible have been determined. The values of $t=(R_a+R_x)/\sqrt{2}(R_b+R_x)$, where R_a, R_b, and R_x are respectively the atomic radii of the ions A, B, and X, have been calculated for various series of compounds. For oxygen compounds, t is less than 0·8 for the rhombohedral structure (type corindon and ilmenite); between 0·8 and 1·0 for cubic crystals (type cæsium chloromercuriate); between 1·0 and 1·2 for rhombohedral crystals of the calcite and sodium nitrate types, and between 1·20 and 1·30 for rhombic crystals of the aragonite type. Analogous relationships exist, within certain limits, among double halides of the type ABX_3. For the cubic modifications of compounds of the cæsium chloromercuriate type the value of t is greater than 0·830. Compounds having values of t near 0·830 are dimorphous. When the value of t is less than 0·825 the compounds possess lower crystalline symmetry and belong to the rhombic or monoclinic systems. Iodo-derivatives alone form exceptions to these limitations; cæsium tri-iodocadmiate with $t=0·840$ is not isomorphous with the other halogenocadmiates of cæsium, and, owing to the presence of the iodine ion, shows strong polarisation. F. G. TRYHORN.

Mechanical properties of brass crystals. M. MASIMA and G. SACHS (Z. Physik, 1928, **50**, 161—186).—It has been found that the electrical conductivity in brass crystals containing about 72% of copper is an isotropic property, whereas the elastic properties are strongly anisotropic. The directions of the slip-planes determined and the elasticity in different directions have been investigated. The shear along the slip plane at the elastic limit is constant and independent of the direction of the stress. The distortion produced by stretching beyond the elastic limit and breaking strain has also been investigated and the conditions required for the establishment of secondary slip-planes deduced. J. W. SMITH.

Method of crystal class determination. A. HETTICH and A. SCHLEEDE (Z. Physik, 1928, **50**, 249—265).—The piezo-electric methods of Giebe and Scheibe (*ibid.*, 1925, **33**, 760) and of Meissner (A., 1927, 1014) have been applied to the determination of the structure of a large number of crystalline substances. The results indicate that the present classification of some of these crystal types requires modification. J. W. SMITH.

Structure of Tl-α and Tl-β. H. PERLITZ (Z. Physik, 1928, **50**, 433—435).—The data of the resistance and volume changes of thallium at its conversion and m. p. are examined. α-Thallium has a hexagonal structure with close packing and β-thallium a face-centred cubic structure. W. E. DOWNEY.

Space-filling forms in crystal lattices. H. TERTSCH (Fortsch. Min. Kryst. Petr., 1927, **12**, 89—90; Chem. Zentr., 1928, i, 1358).—The alkali halides exhibit two types, cubic and octahedral; sodium chloride belongs to the former, and cæsium chloride to the latter, type, whilst rubidium chloride is partly intermediate. Metal ions do not vary from their type, as do negative ions. The change from cubic to octahedral type is considered to be associated with the number and distribution of the electronic orbits. A. A. ELDRIDGE.

Formula and crystal structure of tetrahedrite. F. MACHATSCHKI (Norsk geol. Tidsskr., 1928, **10**, No. 1, 10 pp.; Chem. Zentr., 1928, i, 1359).—Debye-Scherrer diagrams for tetrahedrite are very similar

to those for zinc blende; the bivalent metals are supposed to be present as admixed isomorphous sulphides, and the ratio $R^I:R^{III}:S$ is $3:1:3$. Silver fahl ore from Colquechaca, Bolivia, has a_0 10·41 Å., and fahl ore from Felsobanya has a_0 10·29 Å. The unit cell contains 8 mols. $R_3{}^IR^{III}S_3$ (56 atoms), whilst in a zinc sulphide cell 64 atoms are present. The following densities are computed: Cu_3SbS_3 4·88, Cu_3AsS_3 4·34, $75Cu_3SbS_3+25Ag_3SbS_3$ 5·28, $75Cu_3AsS_3+25Ag_3AsS_3$ 4·74. Tetrahedrite is hexakistetrahedral, space-group T_d^3; distance Sb—S 2·45 Å., Cu—S 2·24 Å.; shortest distance Cu—Sb 3·25 Å., Cu—Cu 3·65 Å. A. A. ELDRIDGE.

Crystal structure of solid mercury. M. WOLF (Nature, 1928, **122**, 314).—Debye–Scherrer analysis of the product of reduction of mercurous oxide by formic acid in gelatin supports McKeehan and Cioffi's result that solid mercury has a simple rhombohedral structure. A. A. ELDRIDGE.

X-Ray studies on iron nitrides. G. HÄGG (Nature, 1928, **122**, 314).—Previous conclusions (this vol., 605) are modified; the nitrogen atoms have definite places in the lattice of the cubic γ-phase, for which the formula Fe_4N is given. A. A. ELDRIDGE.

Crystalline structure of benzene. E. G. COX (Nature, 1928, **122**, 401).—The unit cell is simple orthorhombic, a 7·44, b 9·65, c 6·81 Å. at $-22°$, and contains four molecules; the space-group is Q_h^{15}. In the crystal the molecule has a centre, but no planes, of symmetry. A. A. ELDRIDGE.

Iron-containing rings of smaller effective permeability. U. RETZOW (Physikal. Z., 1928, **29**, 534—538).—The order of magnitude of the effective maximal permeability for alloys, wires, and "mass cores" has been determined as follows: iron–nickel alloys (copper and manganese as minor constituents), $\chi\times10^4$; Elmen bronzes (nickel, cobalt, iron, manganese), $\chi\times10^3$; Heusler bronzes (copper, aluminium, manganese), $\chi\times10^1-\chi\times10^2$; ring wire cores of iron and steel wires, $\chi\times10^2$; "mass cores" of pressed powdered iron enclosed by an insulating material, $\chi\times10^{-1}-\chi\times10^2$; iron and steel wires, $\chi\times10^1$. R. A. MORTON.

Magnetic properties of cobalt. (FRL.) M. SAMUEL (Ann. Physik, 1928, [iv], **86**, 798—824).—The magnetic properties of two specimens of cobalt have been studied, but although both samples received the same heat treatment before the experiments, the results are not in agreement. The normal and ideal magnetisation curves, the reversible permeability, and the coercive force as a function of temperature differ for the two samples. No marked change in magnetic properties occurs on heating to 1000°. As in the cases of iron, steel, and nickel, the reversible susceptibility is clearly a function of the magnetisation, but the Gans law of magnetic corresponding states is not here valid. The coercive force is a definite function of the temperature, between $-185°$ and $+400°$, but the function is not that observed by Gans for iron, steel, and nickel. R. A. MORTON.

Magnetisation of single crystals of nickel. S. KAYA (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 639—663).—Oblate ellipsoids with equatorial planes coinciding with the (100), (110), and (111) planes, respectively, were prepared from large single crystals of nickel, and their magnetic properties measured. Magnetisation curves in the direction of the principal axes showed the isotropic properties of the crystal up to an intensity of magnetisation of 205, but above this value magnetisation varies in different directions, the trigonal, digonal, and tetragonal axes being in decreasing order of magnetisability. This is the reverse of the order found for iron (cf. A., 1927, 298). The parallel and perpendicular components of magnetisation for a constant field vary periodically according to the space lattice in the three principal planes. C. J. SMITHELLS.

Principal susceptibilities of manganese ammonium sulphate crystals at low temperatures. L. C. JACKSON and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 346—349; cf. Jackson and Onnes, A., 1924, ii, 90).—The magnetic susceptibilities of small cylinders of manganese ammonium sulphate cut with their axes (a) parallel to the axis of symmetry of the crystal, (b) perpendicular to the 001 plane, and (c) perpendicular to the 110 plane, have been separately determined at 20·3°, 18·9°, 16·9°, and 15·0° Abs. The curves obtained by plotting $1/\chi'_m$ against T (where is the molecular susceptibility) are straight lines, all of which pass through the origin. Hence each of the principal susceptibilities of the crystal powder follows the simple Curie law $\chi T-C$, but with different values of C in each case. J. W. BAKER.

Electric explosions. H. NAGAOKA and T. FUTAGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **8**, 269—288).—Photographs have been taken of the explosions resulting from the discharge of a large battery of condensers (capacity 1·7 microfarads) charged to 40 kilovolts through fine pieces of metallic wire. These indicate the projection of charged particles at right angles to the wire, the appearance of the explosion being considerably modified by the presence of a strong magnetic field. In the case of long and thick wires where the explosion is incomplete, a pole-effect is evident, the wire being more vaporised at the positive than at the negative pole. Cinematographic photographs have also been taken to show the progress of the explosion. Similar explosions carried out in oil, in an attempt to effect the transmutation of elements, yielded negative results. J. W. SMITH.

Magnetic studies on salts, particularly those with complex ions. L. A. WELO (Phil. Mag., 1928, [vii], **6**, 481—509).—A descriptive paper in which magnetic data for 124 compounds are recorded. In connexion with salts having negative values of θ [Curie's law: g.-atomic susceptibility=const.$\times(T-\theta)^{-1}$] it is suggested that organic groups are probably permanent electric dipoles and, following Debye, the elementary magnets in the molecule have permanent electric moments also; these dipoles provide the fields which resist magnetisation. On this view the negative values of θ have a different origin from the positive values. Rosenbohm's conclusion that geometrical and co-ordination isomerides cannot be distinguished

by magnetic measurements is confirmed for chromium and cobalt compounds (A., 1920, ii, 160). The low moment in potassium ferricyanide is practically unaltered by substitution of other groups for the cyanogen radical. Evidence against paramagnetism in iron in the $Fe(CN)_6$ ion is recorded.

S. K. TWEEDY.

Iron crystals. IV. Dependence of magnetisation on temperature. E. DUSSLER (Z. Physik, 1928, **50**, 195—214).—The dependence of the magnetisation of iron crystals on temperature has been investigated along both the diagonal and tetragonal axes between the temperature of liquid air and the Curie point. At all temperatures the *B–H* curve is initially linear and inflects suddenly, slowly attaining saturation (cf. A., 1927, 924). The linear portion of this curve is independent of temperature, but the higher the temperature the smaller is the field at which saturation is attained and the lower the saturation magnetisation. The variation with temperature of the magnetisation at the point of inflexion and the saturation value both follow an exponential law.

J. W. SMITH.

Magnetic susceptibility of ozonides. V. I. VAIDYANATHAN (Indian J. Physics, 1928, **2**, 421—433).—The magnetic susceptibilities of a few typical ozonides have been measured, a modified form of Curie balance being employed. All were found to be diamagnetic, but, owing to their superior stability, the most trustworthy measurements were those on phenanthrene and naphthalene diozonides. Assuming magnetic susceptibility to be an additive property, it is deduced from the data obtained that the susceptibility of ozone is about -25×10^{-6} per g.-mol. The structure of the ozone molecule and the electron arrangements within it are discussed in relation with this result.

J. W. SMITH.

Theory of forced double refraction (photo-elasticity). K. F. HERZFELD (J. Opt. Soc. Amer., 1928, **17**, 26—36).—Mathematical. The double refraction of crystals is discussed, and it is pointed out that it may be due to (*a*) the anisotropy of the ions taken separately, (*b*) the anisotropic arrangement of the ions in the lattice which results in an anisotropic force even if the ions are undisturbed, or (*c*) an anisotropic "Lorentz–Lorenz force" due to the anisotropic arrangement of the ions. Calculations are made to determine the magnitude of (*c*) in cubic crystals of rock-salt and sylvine under stress (forced double refraction, photo-elasticity), and it is concluded that the double refraction cannot be explained entirely by this means. It is also shown how the Lorentz–Lorenz force is built up in the unstrained crystal.

L. L. BIRCUMSHAW.

Conductivity of powdered salts. J. CICHOCHI (Compt. rend., 1928, **187**, 287—289).—Measurements of the conductivity of dry powdered barium chloride heated electrically in a copper tube by means of an axial copper wire support Peczalski's theory (A., 1927, 634, 710) that the increased conductivity of salts in the powdered state is due, not only to the conductivity of the solid particles, but also to that of the vapours of the salt and to dispersed metallic copper.

J. GRANT.

Influence of the solvent on the mobility of electrolytic ions. R. T. LATTEY (Phil. Mag., 1928, [vii], **6**, 258—270).—It is shown that the mobility, l, of an ion in solution should be represented by the expression $l-Fe/\eta\sigma\,.\,\phi(3k\theta D\sigma/2e^2)$, where F is the Faraday charge, e ionic charge, η viscosity of solvent, σ ionic radius, $(3k\theta/2)$ thermal energy of the molecule at the temperature of the experiment, D dielectric constant of the solvent, and ϕ an unspecified function. Examination of a large number of data shows $l\eta=\alpha+\beta(\theta D)^2$, where α and β are constants characteristic of the ion, which from dimensional analysis is equivalent to $FeA/\sigma_1+9Fk^2\sigma_2B(\theta D)^2/4e^3$, where A and B are constants and σ_1 and σ_2 are functions of the dimensions of the ion and in the case of elementary ions approximate to the radii.

A. E. MITCHELL.

Superconductivity according to the Schrödinger wave-equations and the Fermi statistics. E. KRETZSCHMANN (Ann. Physik, 1928, [iv], **86**, 914—928).—In an earlier paper (*ibid.*, 1926, [iv], **80**, 109—136) it was shown that on the basis of the Maxwell–Boltzmann statistics and classical mechanics the conditions for absence of electrical resistance were, in classical terms, no interpenetration of elementary charges, or, in quantum terms, no interchanges of bound and free electrons. It is now shown that the condition for superconductivity may be restated thus: only Coulomb forces shall operate between elementary charges, and the movement of free electrons must be determined solely by the Schrödinger equation, and the velocity and energy distribution by the Fermi statistics.

R. A. MORTON.

Does grey tin become superconductive? W. J. DE HAAS, G. J. SIZOO, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 350—352).—Measurements of the conductivity of grey tin pressed into the form of a bar at very low temperatures show that it does not become superconductive even at the lowest temperature used, 1·8° Abs.

J. W. BAKER.

Investigation of Tammann's theory of "resistance limits" for the gold–copper system. M. LE BLANC, K. RICHTER, and E. SCHIEBOLD (Ann. Physik, 1928, [iv], **86**, 929—1005).—Tammann's work on the limiting composition of gold–copper alloys such that when the gold content exceeds this limit the alloys are unattacked by various reagents has been repeated and his theory to account for the phenomenon has been criticised (cf. A., 1919, ii, 398, 406). Alloys of gold and copper were prepared of various compositions, and the action of nitric acid on them was investigated, the amount of copper dissolved being determined. The results do not agree with those of Tammann. The problem is also attacked by determining the crystal structure of the alloys by the *X*-ray method. The types of distribution of two atoms in a space lattice which Tammann has distinguished (cf. A., 1919, ii, 406) are discussed, and it is shown from the *X*-ray experiments that Tammann's "normal" distribution does not hold for alloys of copper content between 0·375 and 0·625 molar concentration, as Tammann supposed it would. Hence Tammann's theory to account for the "resistance limit" of the alloys is untenable. Indeed, it

is shown that there is no absolute "resistance limit" in the quantitative sense independent of temperature and of the solvent used. A new theory which will explain many of the phenomena is put forward and discussed. A. J. MEE.

Electrometric titration curves of dibasic acids. II. β-Substituted glutaric acids. R. GANE and C. K. INGOLD (J.C.S., 1928, 2267—2272).—The first and second dissociation constants of the following β-substituted glutaric acids have been measured by the potentiometric method (cf. this vol., 846) and the apparent distance (r) between the two carboxyl groups has been calculated in accordance with the Bjerrum theory. The values of k_1, k_2, and r (Ångstrom units) for the cases studied are, respectively, unsubstituted, $4{\cdot}60\times10^{-5}$, $5{\cdot}34\times10^{-6}$, 9·22; β-methyl, $5{\cdot}77\times10^{-5}$, $6{\cdot}28\times10^{-7}$, 2·27; β-*n*-propyl, $4{\cdot}97\times10^{-5}$, $4{\cdot}32\times10^{-7}$, 2·12; ββ-dimethyl, $2{\cdot}03\times10^{-4}$, $5{\cdot}51\times10^{-7}$, 1·57; ββ-diethyl, $3{\cdot}40\times10^{-4}$, $7{\cdot}85\times10^{-8}$, 1·02; ββ-di-*n*-propyl, $2{\cdot}03\times10^{-4}$, $5{\cdot}42\times10^{-8}$, 1·01; *cyclo*pentane-1 : 1-diacetic acid, $1{\cdot}68\times10^{-4}$, $2{\cdot}63\times10^{-7}$, 1·40; *cyclo*hexane-1 : 1-diacetic acid, $3{\cdot}36\times10^{-4}$, $1{\cdot}02\times10^{-7}$, 1·04; *cyclo*heptane-1 : 1-diacetic acid, $2{\cdot}78\times10^{-4}$, $1{\cdot}09\times10^{-7}$, 1·10. The values are in general agreement with the predictions of the Thorpe–Ingold valency deflexion hypothesis, the anomalous position of the *cyclo*heptane compound owing to its multiplanar strain-free configuration (cf. Baker and Ingold, J.C.S., 1923, **123**, 122; Baker, A., 1925, i, 1277) again being evident. The much greater value for r in the unsubstituted acid suggests that whilst in this acid the carbon atoms form a straight (zigzag) chain, the presence of a β-substituent causes the molecule to assume a coiled configuration. J. W. BAKER.

Electrical resistance of pure molten metals. Y. MATSUYAMA (Kinzoku no Kenku, 1926, **3**, 254—261).—The specific resistance of mercury, tin, antimony, cadmium, lead, bismuth, aluminium, and silver increases with rise of temperature, whilst that of zinc decreases slightly. The specific resistances of the molten metals at the m. p. are, respectively, 93·1, 48·1, 115·0, 32·2, 95·8, 126·7, 25·5, 17·3, 37·0. CHEMICAL ABSTRACTS.

Theory of the electrical conductivity of metals. P. LAPINSKY (Ukrain. physikal. Abhandl., 1926, **1**, 70—74).—Thomson's and Borelius' formulæ can be deduced from the laws of thermodynamics if it is assumed that the condition of the conducting electrons as a thermodynamic system in the metal depends on the composition and on the temperature and other physical magnitudes. At low temperatures the relation between the electrical conductivity and the absolute temperature is expressed by: $(\sigma+\alpha/T^2)(T-T_0)-(dpeT_0)/k$, where T_0 is the original temperature, d the distance between two atoms, p the number of electrons passing per sec. from one atom to its neighbour, e the charge on the electron, and k and α are constants. CHEMICAL ABSTRACTS.

Physical properties of salicylaldehyde. T. S. CARSWELL and C. E. PFEIFER.—See this vol., 1009.

Influence of constitution on the stability of racemates. A. FINDLAY and A. N. CAMPBELL (J. (J.C.S., 1928, 1768—1775).—The f.-p. and solubility curves of active and racemic forms of tartaric acid, of its methyl ester, and of the methyl esters of diacetyl-, dipropionyl-, and dibenzoyl-tartaric acids and of the ethyl esters of diacetyl- and dibenzoyl-tartaric acids have been studied. Introduction of an acyl group into the methyl or ethyl ester of tartaric acid lowers the m. p. of the racemic form relatively to that of the active form, and reduces the range of stability of the racemic form. The acetyl group is much more effective in this respect than the propionyl or benzoyl group. The transition point of methyl diacetylracemate lies at about 23°. R. A. MORTON.

Heat capacity of hydrogen bromide from 15° Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and R. WIEBE (J. Amer. Chem. Soc., 1928, **50**, 2193—2202).—The heat capacities of solid and liquid hydrogen bromide are recorded; the results disagree somewhat with those of Eucken and Karwat. The heat of fusion is 575·1 g.-cal./mol.; m. p. 186·24° ±0·05; b. p. 206·38°±0·05; heat of vaporisation, 4210±4 g.-cal./mol. The entropy at the b. p. is 44·9±0·1 g.-cal./1° per molecule, in agreement with the value calculated from the Sackur equation with the Tetrode constant enlarged by the entropy due to the rotational–vibrational energy, which is calculated from the band spectra (this vol., 228). S. K. TWEEDY.

Volume change of manganese during solidification. Y. MATSUYAMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 731—733).—Manganese contracts 1·7% of its volume on solidification. C. W. GIBBY.

Heat of fusion and heat of the new transformation in tellurium. S. UMINO (Kinzoku no Kenku, 1926, **3**, 498—501).—The latent heat of fusion of tellurium at 446° is 33·50 g.-cal., and that of a new transformation at 348° is 0·63 g.-cal. CHEMICAL ABSTRACTS.

Precise determination of thermal capacities. Molybdenum. T. E. STERN (Physical Rev., 1928, [ii], **32**, 298—301).—The specific heat of molybdenum, determined with a Bunsen ice calorimeter provided with a silvered vacuum jacket, is $c_p=0{\cdot}05973+0{\cdot}00001619t$ mean g.-cal./g. per 1° between 0° and 444·5°. A. A. ELDRIDGE.

Simple relation between thermal conductivity, specific heat, and absolute temperature. C. C. BIDWELL (Physical Rev., 1928, [ii], **32**, 311—314).—A relation of the form $k/aC=K_1/T+K_2$, where k is the thermal conductivity, aC the atomic heat, and T the temperature (absolute), is valid for zinc, sodium, lithium, copper, lead, aluminium, and mercury. The relation is considered in application to the theory of the double mechanism of heat conduction. A. A. ELDRIDGE.

Gases with molecular attraction. K. SHIBA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 740—747).—Theoretical. The expression $e^{-(3m/4\epsilon)(u^2+v^2+w^2)}$, in which ϵ is the mean kinetic energy, is suggested as a correction to Maxwell's distribution law. C. W. GIBBY.

Saturated vapour pressure and latent heat of vaporisation of liquids. M. LEVALT-JEZERSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 743—763).—For

all liquids the relation between saturated vapour pressure and temperature may be expressed by the equation (i); $p=p_0\times10^{\alpha\tau}$, where p_0 is the vapour pressure at the f. p. of the solution, α is a constant, characteristic of the given liquid, and $\tau=\delta/T$, where δ is the temperature above the m. p. and T is the absolute temperature. The value of α can be calculated from the equation $\alpha=(\log p_2-\log p_1)/(\tau_2-\tau_1)$. Equation (i) may be substituted in the Clapeyron–Clausius equation, $d\log_e p/dT=\lambda/RT^2$, whence the equation $\lambda=m\alpha RT_0$ is derived, m being the conversion factor to natural logarithms, α the above constant, and T_0 the f. p. of the given liquid. Values of λ calculated from this equation are in good agreement with experiment, except in those cases where the vapour contains associated molecules.

R. TRUSZKOWSKI.

Vapour density and other properties of formic acid. A. S. COOLIDGE (J. Amer. Chem. Soc., 1928, **50**, 2166—2178).—Pure formic acid, d^0 1·2456, d^{20} 1·2206, f. p. 8·26°, is prepared by vacuum sublimation of Kahlbaum's purest acid. The vapour pressures of aqueous solutions of the acid are recorded; that of the pure acid is 8·67 mm. for the solid and 11·16 mm. for the liquid at 0°. Decomposition of the pure acid may be prevented by keeping the latter frozen. The vapour densities of the pure acid are recorded between 10° and 156°, corrections being applied for wall adsorption. The results may be interpreted on the assumption that the vapour is an ideal mixture of two gases, containing single and double molecules, respectively, each deviating from the perfect gas laws in the same way as a unimolecular vapour of the same mol. wt. The heat of dissociation of the double molecules is approximately 14,125 g.-cal./mol.

S. K. TWEEDY.

Critical isotherms and Wohl's equation of state. R. WEGSCHEIDER (Z. physikal. Chem., 1928, **135**, 362—367).—Polemical against Wohl (this vol., 827). The conditions which a critical isotherm must fulfil are discussed in relation to the author's views (A., 1922, ii, 192). W. E. DOWNEY.

[Critical isotherms and Wohl's equation of state.] K. WOHL (Z. physikal. Chem., 1928, **135**, 368).—Polemical against Wegscheider (cf. preceding abstract). W. E. DOWNEY.

Method of determining the absolute zero of temperature. J. R. POTTER (Phil. Mag., 1928, [vii], **6**, 318—320).—An electro-calorimetric modification of Kelvin's vapour-pressure thermometer is described. Electrical energy is used to cause a mixture of a liquid and its vapour to undergo an isothermal expansion from an initial to a final measured volume, the initial and final pressures at the unknown constant temperature being measured. The latent heat of vaporisation at constant temperature is thus found as a function of the pressure and the result employed in the integration of Clapeyron's equation $dT/T=(v_2-v_1)dp/Q$. A. E. MITCHELL.

Physical properties of liquids as functions of the temperature. G. ANTONOV (J. Chim. phys., 1928, **25**, 497—500).—The graphs expressing the variation with temperature of the latent heat, density, and mean of the densities in the liquid and vapour states of pure benzene show slight discontinuities of a systematic character which are too high (0·5—2%) to be due to experimental errors or impurities, and may be explained by the author's hypothesis that the elementary constituents of matter at relatively low temperatures are highly complex molecular aggregates (A., 1926, 786). J. GRANT.

Surface tension of liquid metals. III. Surface tension of mercury. L. L. BIRCUMSHAW (Phil. Mag., 1928, [vii], **6**, 510—525; cf. A., 1927, 719).—The surface tension of mercury was measured by the method of maximum bubble pressure. Glass tubes gave slightly higher results than silica tubes; the latter gave consistent results only when the tips were roughened. With the exception of oxygen, the nature of the gas used for blowing the bubbles is practically without influence. Allowing the bubble to hang for various lengths of time resulted in a lower surface tension with one glass tip, but with another produced no effect. The time of formation of the bubbles had no influence between 35 and 150 sec., and the depth of immersion of the tip could be varied within wide limits without effect. The results of Stöckle (Ann. Physik, 1898, **66**, 499) and of Popesco (A., 1925, ii, 952) are discussed from the point of view of Bancroft's explanation ("Applied Colloid Chemistry," 1921, 134). It is deduced that the square of the time required for the surface tension to fall to the vacuum value is proportional to the density of the superincumbent gas, but this is not in agreement with Popesco's results. S. K. TWEEDY.

Coefficient of expansion of zirconium oxide. W. M. COHN (Ber. deut. keram. Ges., 1928, **9**, 16—18; Chem. Zentr., 1928, i, 1515).—The coefficient of expansion of rods of zirconium oxide (containing 1—3% of other oxides) ignited at 2100° is $8\cdot0\times10^{-6}$ at 40° or $8\cdot7\times10^{-6}$ at 200°; values for rods ignited at 1250° are 3·85 and 3·9, respectively. A. A. ELDRIDGE.

Free path of molecules and the coefficient of inner friction in fluids. N. GERASIMOV (Physikal. Z., 1928, **29**, 575—584).—The internal friction of fluids is treated mathematically by means of the kinetic theory of gases. W. E. DOWNEY.

Viscosities of the rare gases. A. NASINI and C. ROSSI (Gazzetta, 1928, **58**, 433—442).—The viscosities of helium, krypton, and xenon have been redetermined by Rankine's method. The values obtained agree closely with Rankine's figures, except in the case of xenon. For this gas the new values are higher than the old: η_0 2122×10^{-7}, $\eta_{16\cdot5}$ 2250×10^{-7}, and $\eta_{99\cdot4}$ 2871×10^{-7}. F. G. TRYHORN.

Mixtures of ethyl and amyl alcohols and water. B. LAMPE and W. KILP (Z. Spiritusind., 1928, **51**, 250).—The expansion and fall in temperature produced when amyl alcohol is mixed with aqueous ethyl alcohol are due to the affinity of the former for the ethyl alcohol. In the analysis of such mixtures by density determinations with an ordinary alcoholometer the correct proportion of water is obtained, for the amyl alcohol in the mixture produces the same effect as if it were ethyl alcohol. J. GRANT.

Physical properties of heterogeneous ternary mixtures. P. MONDAIN-MONVAL (Compt. rend.,

1928, **187**, 444—447).—Accurate determinations of the refractive indices of mixtures of ethyl and *iso*amyl alcohol and water have failed to confirm the anomalies recorded by Brun (this vol., 844) in the neighbourhood of the critical point (cf. Barbaudy, A., 1926, 671).

J. GRANT.

Solutions. I. F.-p. diagrams and latent heats of evaporation of binary mixtures of volatile liquids. W. F. WYATT (Trans. Faraday Soc., **24**, 1928, 429—438).—On recalculation of Tyrer's results for the latent heats of evaporation of binary mixtures (J.C.S., 1911, **99**, 1633) it was found that characteristically irregular curves were obtained when molal latent heats were plotted against the composition of the mixtures. To investigate the origin of these irregularities the f.-p. curves have been determined for the systems acetone–chloroform, ethyl alcohol–carbon tetrachloride, ethyl alcohol–benzene, and benzene–chloroform. A compound, $CHCl_3,COMe_2$ (m. p. —99·5°), was found in the first system. In the system ethyl alcohol–carbon tetrachloride there is a transition point on the liquidus at —47·6°, corresponding with a mixture containing 44·6% of carbon tetrachloride. Simple eutectic curves were found for the other two systems. Analysis of the solids separating from these mixed liquids revealed the existence of extensive systems of mixed crystals, the transition point in the system ethyl alcohol–carbon tetrachloride being due to conjugate solid solutions. The probable nature of the forces acting among the molecules in these systems is discussed in the light of these results and with reference to other physical properties of the mixtures.

F. G. TRYHORN.

Partition of light between two absorbing media. J. PLOTNIKOV and K. WEBER (Z. Elektrochem., 1928, **34**, 316—320).—The partition of the absorption of light between two media forming a homogeneous mixture is discussed.

L. F. GILBERT.

Diffusion of hydrogen through nickel. V. LOMBARD (J. Chim. phys., 1928, **25**, 501—530; cf. A., 1923, ii, 570).—The number of c.c. of hydrogen (measured at 0° and 760 mm. of mercury) passing per hr. through a nickel plate 1 cm.² in area is proportional to the square root of the pressure, or of the partial pressure if the hydrogen is mixed with another gas (*e.g.*, nitrogen) having a negligible power of diffusion. Between 350° and 750° the permeability (d) is related to the temperature (t) by the expression $d=Ka^{\alpha t}$, where K is a function of the pressure of the gas and of the thickness (for 0·16—2 mm.) and structure of the membrane, and α is a constant characteristic of the metal (cf. Deming and Hendricks, A., 1924, ii, 94). The permeability is inversely proportional to the thickness of the metal between 408° and 555° (cf. Johnson and Larose, A., 1924, ii, 750), and two membranes in contact behave as a single membrane having the thickness of the two combined. The values obtained were dependent on the structure of the metal, and even when membranes of the same origin were used variations of 15—20% were observable. The values are not affected by the presence of moisture or oxygen (of the order of 1%) in the hydrogen and are reproducible to within 6—7%, the sources of error being considerable, but for the most part compensatory.

J. GRANT.

Lead–antimony alloys. W. BRONIEVSKI and L. SLIVOVSKI (Rev. Mét., 1928, **25**, 397—404).—Observations on the hardness, electrical conductivity, potential, thermo-electric power, coefficient of expansion, and microstructure of lead–antimony alloys after prolonged annealing have failed to disclose the existence of any definite compound of the two metals. The alloys form two series of limited solid solutions which form a eutectic with one another containing 13% Sb (m. p. 250°). The saturated solid solution of lead in antimony contains about 11% Pb and that of antimony in lead about 0·5% Sb at 0° and about 2% Sb at 250°.

A. R. POWELL.

Preparation and structure of palladium mono- and di-antimonide. L. THOMASSEN (Z. physikal. Chem., 1928, **135**, 383—392).—The alloys were prepared by heating the two metals enclosed in an evacuated quartz tube. The structures of the two alloys were examined by the powder method of Hull and Davey. The monoarsenide has a nickel arsenide structure with a=4·070 Å., c=5·582 Å. The di-arsenide has a pyrites structure with a=6·439 Å.

W. E. DOWNEY.

Eutectic crystals. M. HAMAZUMI (Suiyo-Kwaishi, 1924, **4**, 973—982).—The eutectic is the constituent inlaid within surrounding crystals in polygonal cells; both crystallise simultaneously and independently. The primary crystal affects the orientation of the eutectic.

CHEMICAL ABSTRACTS.

Shrinkage of glass threads during heating. I. SAWAI and O. MORISAWA (Z. anorg. Chem., 1928, **173**, 361—372).—The behaviour of threads of lead borate glass when heated under varying loads has been determined. With small loads of the order of 50—500 g./mm.² the initial expansion is followed by a contraction beginning at 180—190° and ending at 395—360° according to the load. Then follows a small range during which no change in length takes place, and finally rapid expansion ensues, due to the great decrease in the viscosity as the softening point is approached. The shrinkage is shown to be due to release of the longitudinal strains in the thread produced in its formation by rapidly drawing it out from a molten mass of the glass. When the viscosity of the glass decreases sufficiently to make these strains greater than the sum of the load and the viscosity, shrinkage takes place. With loads of about 1 kg./mm.² shrinkage occurs, but the length of the thread remains constant between 200° and 400°. With higher loads the load is greater than the sum of the viscosity and the internal stresses, therefore no shrinkage takes place on heating.

A. R. POWELL.

M. p. of mixtures of picric acid and mononitronaphthalene. JOVINET (Mém. Poudres, 1928, **23**, 36—42).—The m.-p. curve shows the existence of a 1 : 1 compound, m. p. 71°. The cooling curve for the mixture containing 70 parts of picric acid to 30 parts of mononitronaphthalene (the French shell-filling explosive M.M.N.) has been studied. To obtain homogeneous charges from the molten charge it must be agitated continuously until the temperature falls to 71° and then seeded at this point with cold powdered

explosive. If this is not done, picric acid will segregate on the walls of the container and the core will be poor in picric acid. S. BINNING.

Solubility of potassium ferricyanide in water between 0° and 100°. J. A. N. FRIEND and W. N. SMIRLES (J.C.S., 1928, 2242—2245).—The density- and solubility-temperature curves for potassium ferricyanide do not show the break obtained from the less accurate results of earlier workers. J. GRANT.

Solubility of diphenyldiethylcarbamide in water, alcohol, and other organic solvents. L. DESVERGNES (Ann. chim. analyt., 1928, [ii], **10**, 226—228).—Diphenyldiethylcarbamide is practically insoluble in cold water and only very slightly soluble (0·03%) in boiling water. It is readily soluble in cold alcohol and very soluble in hot alcohol; in 77% alcohol the solution separates into two layers at 50°. A similar effect is obtained with a solution in 60% methyl alcohol at 50° and with an aqueous acetone solution at 40°. The solubilities of the compound in twelve organic solvents at 0°, 20°, and 50° are tabulated. A. R. POWELL.

Solubility of alkali soaps in hydrocarbons. J. WEICHHERZ (Naturwiss., 1928, **16**, 654).—Contrary to the usual statements, it has been found that alkali soaps are readily soluble in hydrocarbons. The properties of the solution depend on the kind of soap used and on the structure of the hydrocarbon. The solutions are usually highly viscous or gelatinous, becoming more mobile at higher temperatures. The addition of small amounts of phenol, alcohol, or water often increases the solubility. The influence of this on the formation and properties of emulsions of the hydrocarbon–soap solution in water is discussed. A. J. MEE.

Determination of ionic partition coefficients. E. ALLEMANN (Z. Elektrochem., 1928, **34**, 373—387; cf. Baur and Allemann, A., 1927, 23).—A method is described for the measurement of single-phase boundary potentials by means of a cell of the type *N*-calomel electrode|conc. KCl|salt AB in water|salt AB in non-aqueous phase|connecting electrolyte|KCl in non-aqueous phase|*N*-KCl in water|*N*-calomel electrode. Fifty salts were investigated, the non-aqueous phase being amyl alcohol, butyl alcohol, or furfuraldehyde. The uni-univalent salts were measured in each of the three solvents, the salts with multivalent ions in butyl alcohol only. In the case of uni-univalent electrolytes, the boundary potentials between two liquid phases can be calculated from the specific ionic partition coefficients. A number of specific ionic partition coefficients for the partition between water saturated with butyl alcohol and butyl alcohol saturated with water are evaluated, and the values are found to be in fair agreement with those calculated from the law of mass action. A method is indicated for determining the influence of the concentration on boundary potentials, and the thermodynamic theory of phase boundary forces is discussed from the point of view of ionic activities. L. L. BIRCUMSHAW.

Adsorption of vapours. A. FLEISCHER (Amer. J. Sci., 1928, [v], **16**, 247—257).—Theoretical. A critical review of current theories of adsorption. C. W. GIBBY.

Charcoal and its adsorption. T. OKAZAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 821—831).—No clear difference was found between samples of charcoal prepared from twenty different kinds of wood, when examined with reference to the adsorption of vapours of water, benzene, ethyl alcohol, and ammonia, and the decolorising of petroleum or aqueous methyl-violet. The activity is found to depend on the temperature of baking: charcoal baked at 300° adsorbs a greater amount of ethyl alcohol vapour than when baked at 500°. C. W. GIBBY.

Adsorption of arsenious oxide by ferric hydroxide. A. BOUTARIC and (MLLE.) G. PERREAU (J. Pharm. Chim., 1928, [viii], **8**, 211—221).—Adsorption of arsenious oxide by ferric hydroxide is almost instantaneous and reaches its limiting value in less than 1 hr. For the same volume of solution the quantity of arsenious oxide adsorbed per g. of ferric hydroxide increases with the initial concentration and for the same concentration the adsorption increases with the volume. The weight of arsenious oxide adsorbed increases with the weight of ferric hydroxide, but in a decreasing ratio. Similar studies with other hydroxides indicated the following order of decreasing adsorption activity: manganese, zinc, cadmium, chromium, iron, aluminium. Magnesium hydroxide exerted no appreciable adsorption. E. H. SHARPLES.

Adsorption of hydrogen, ethylene, acetylene, and ethane by stannous oxide. J. N. PEARCE and (MISS) S. M. GOERGEN (J. Physical Chem., 1928, **32**, 1423—1433).—The adsorption of hydrogen, ethylene, acetylene, and ethane by stannous oxide has been determined at 0°, 78·5°, and 100° and at pressures up to 75 cm. in an apparatus similar to that used by Pease (A., 1923, ii, 472). The stannous oxide, prepared by the addition of stannous chloride to sodium carbonate, was dehydrated in an atmosphere of carbon dioxide at the b. p. of aniline. The adsorption of hydrogen is small at all temperatures, but that of the hydrocarbons is relatively large and decreases rapidly with a rise in temperature. Except for the fact that at 0° ethane is the most readily adsorbed, adsorption decreases at all temperatures in the order acetylene, ethane, ethylene, and hydrogen. Acetylene polymerises slowly in contact with stannous oxide at 100°. Hydrogenation of ethylene occurs at 100° only when the proportion of hydrogen in the reacting mixture is large (75%). Stannous oxide is reduced by hydrogen at 183°. L. S. THEOBALD.

Adsorption of mixtures of easily-condensable gases. S. KLOSKY and L. P. L. WOO (J. Physical Chem., 1928, **32**, 1387—1395).—The adsorption isotherms of butane at 0° and 25°, and of methyl chloride at 25°, 35°, and 45° on titania gel have been determined by the dynamic method described by Klosky and Burggraff (this vol., 580). They agree with the formulæ of Freundlich, Patrick, and Polanyi. The adsorption of sulphur dioxide, alone and mixed with methyl chloride or butane, has also been measured. In this case, the ratio of the relative lowerings of adsorption of the two gases is approximately equal to the inverse ratio of the products of their mol. wt. and viscosities. This relation also applies to the data

of Richardson and Woodhouse (A., 1924, ii, 23) for the adsorption of mixtures of carbon dioxide and nitrous oxide by charcoal. L. S. THEOBALD.

Selective adsorption from gaseous mixtures by a mercury surface formed in the mixture. M. L. OLIPHANT (Phil. Mag., 1928, [vii], **6**, 422—433).—Experiments in which mercury droplets are allowed to fall through columns of mixed gases show that an expanding mercury surface selectively adsorbs carbon dioxide from a mixture of this gas with an excess of hydrogen or of argon, and that the adsorbed gas, which is held with considerable force, forms a unimolecular layer on the mercury surface. These results indicate that the " large-drop " method of measuring surface tension is more trustworthy than Harkins' drop-weight " method, since only the former reveals an initial high surface tension in a gas. A rotating pump suitable for pumping mercury is described.

S. K. TWEEDY.

Adsorption of vapours on an amalgamated platinum surface. J. W. SMITH (J.C.S., 1928, 2045—2051).—In view of the criticisms of Frazer, Patrick, and Smith (A., 1927, 722), the experiments of Lenher (A., 1927, 198) on the adsorption of water vapour and benzene have been extended and confirmed at temperatures near saturation. The vapour pressure of the liquid was always too low, a constant difference of 1·3 mm. for water and 1·6 mm. for benzene being obtained at all temperatures.

J. GRANT.

Electrical condition of hot surfaces during the adsorption of gases. II. A nickel surface at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1928, **A**, **120**, 235—246; cf. A., 1927, 1135).—Using an apparatus and experimental procedure essentially the same as that previously described (*loc. cit.*), measurements have been made of the surface charge acquired by a nickel sheet when heated to 850° in a vacuum ($p<10^{-5}$ mm.), or in contact with hydrogen, oxygen, carbon monoxide, nitrogen, argon, electrolytic gas, steam, carbon dioxide, carbon monoxide " knall gas," and mixtures of nitrogen or argon with oxygen or hydrogen. The magnitude of the charge in a vacuum depends on the temperature of the metal and its previous thermal history. A complete oxidation and reduction is necessary to bring the surface into the " fully normalised condition; after this treatment the charge due to a gas is characteristic of the latter and dependent on the temperature, but is independent of the gas pressure (between 1 and 760 mm.). The charge due to the various gases is readily removed by evacuation at 850°, except in the case of carbon monoxide, where the charge must be " burned off " with oxygen. The nickel sheet becomes covered with a dense film of oxide when heated in oxygen, but this oxidised surface acquires the same charge in a vacuum as the reduced oxide-free surface. The charge due to the reaction product of a mixture of combining gases is at all temperatures identical with that due to the original gaseous mixture. Argon or nitrogen diluted with 2·0% of oxygen or hydrogen gives the full charge due to either of the latter gases. These facts are discussed in conjunction with those established previously. It is suggested that the charge on a hot metal surface in contact with a gas is due to activation of the adsorbed gas molecules, that the initial reduction and oxidation of a nickel sheet bring about a permanent rearrangement of the surface atoms of the metal into a more stable configuration, and that a gas can be held adsorbed on a hot metal surface in at least five different ways, ranging from a purely physical, electrically neutral adsorption to definite stable chemical compound formation, also electrically neutral. Observations on the electrical charging of hot surfaces do not afford any evidence of deep-seated occlusion. L. L. BIRCUMSHAW.

Hydrogen content of silver and copper alloys containing oxide. GUICHARD, CLAUSMANN, and BILLON (Bull. Soc. chim., 1928, [iv], **43**, 748—751).—See this vol., 602.

Adsorption in solutions. XIV. Adsorption of homologous monobasic acids. B. NEKRASSOV. **XV. Hydrolytic and molecular adsorption of the alkaline-earth halides on carbon.** M. TSCHEPELEVETZKI (Z. physikal. Chem., 1928, **136**, 18—33, 33—44).—XIV. The adsorption by various kinds of charcoal of the normal fatty acids from formic to stearic from solutions in water, methyl and ethyl alcohols, acetone, ethyl ether, light petroleum, chloroform, carbon tetrachloride, carbon disulphide, benzene, and toluene has been determined. The curves showing the relationship between the number of carbon atoms in the acid and the percentage adsorption exhibit in the case of solvents containing oxygen in the molecule a sharp minimum in the adsorption at about three carbon atoms, and thereafter a steady rise; for all solvents of this group the Traube adsorption law is valid from butyric acid onwards. The curves for the other solvents exhibit at most an ill-defined minimum, and the adsorption shows little agreement with the Traube rule. Water is anomalous, whilst light petroleum, probably since it is a mixture, conforms more to the first group than to the second. There is a qualitative relationship between the power of adsorption and the dielectric constant of solvents of the first group, but this does not hold for solvents of the second group. For the lower members of a homologous series wood charcoal has a greater adsorptive capacity than blood charcoal, but for the higher members the reverse is the case. The differences in behaviour of wood, sugar, and blood charcoals as regards adsorption are discussed with reference to the structure of the adsorbing surface.

XV. The adsorption by sugar and blood charcoal of the anions from $N/60$ solutions of magnesium, calcium, strontium, and barium chlorides, bromides, and iodides has been measured. The quantity adsorbed decreases in all cases in the order I′, Br′, Cl′, the influence of the cation being relatively slight; beryllium salts exhibit comparatively high adsorption of the anions. The adsorption is not a primary effect, but is the result of an initial formation of insoluble carbonates. Molecular adsorption of certain salts is complicated by the secondary deposition on the adsorbent of insoluble basic salts and hydroxides.

H. F. GILLBE.

So-called hygroscopic water of clays. T. Okazawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, **9**, 15—49).—Isotherms showing the relation between vapour pressure and quantity of water absorbed by clays exhibit discontinuities. The results show that water combines with clay to form hydrates, the composition of which is indicated by the intersection points on the isotherms. The hydrates form solid solutions, the composition of which depends on temperature and humidity. Adsorption fails to account for the data. R. A. Morton.

Acidity of acidic earth and alkaline earth. H. Isobe and Y. Yendo (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 805—820).—The acidity of acid earth is due to the adsorption of acids or acid salts produced by weathering. C. W. Gibby.

Crystalline graphite and its capillary properties. R. Cordebas (Chim. et Ind., 1928, **20**, 223—230).—The capillary nature of the surface of crystalline graphite is discussed in relation to the uses of the latter in industry. The system graphite–water is an illustration of the author's explanation of the influence of surface energy on the physical properties of matter. J. Grant.

Variation of the capillary action of solutions with time. H. M. Trimble (J. Physical Chem., 1928, **32**, 1211—1224; cf. Bigelow and Washburn, this vol., 472).—The variation of capillarity with time has been determined for mixtures of organic solvents at 25° by the capillary-rise method. Mixtures of ethyl ether with benzene, toluene, and acetone show an increase in capillary rise with time; with the mixtures ether–carbon disulphide, ether–nitrobenzene, and ether–amyl alcohol, the rise is more pronounced. Mixtures of carbon disulphide with benzene, chloroform, and carbon tetrachloride show a fall in the capillary rise with time, whilst pentane and acetone with carbon tetrachloride, and ether with chloroform, show a rise to a maximum followed by a fall. The systems benzene–toluene, and carbon tetrachloride–chloroform show no change, and the case in which a fall to a minimum is followed by an increase in capillarity has not been observed. The rate and magnitude of any change are greater the shorter and the smaller is the capillary tube used. Under constant conditions, the nature of the change can be predicted from a knowledge of the surface tension, volatility, and density of the components of the mixture. The conclusion of Washburn and Bigelow (*loc. cit.*) that preferential evaporation and diffusion account for the results is supported. In closed systems with no rubber connexions, changes in capillary rise with time are prevented, and the authors agree with Washburn and Bigelow (*loc. cit.*) that to obtain trustworthy data on the surface tensions of mixtures containing a volatile constituent, evaporation must be prevented. L. S. Theobald.

Electrolytic behaviour of thin films. I. Hydrogen. II. Areas of catalytically active surfaces. F. P. Bowden and E. K. Rideal (Proc. Roy. Soc., 1928, **A**, **120**, 59—79, 80—89).—I. A quantitative investigation has been made of the changes of electrode potential at the surfaces of metallic cathodes during the electrolytic deposition and removal of minute quantities of hydrogen. The potential of the test electrode was measured against a saturated calomel electrode, using an Einthoven string galvanometer. The cathodes employed were mercury, silver, amalgamated silver, platinum, and platinised surfaces, the electrolyte in most cases being $N/5$-sulphuric acid, carefully freed from oxygen by prolonged boiling under reduced pressure and cooling in a hydrogen atmosphere. The marked effect which even a small amount of oxygen has on the apparent rate of growth and decay of hydrogen overvoltage is emphasised. It is found that the electrode potential is a linear function of the surface concentration of the hydrogen, and not, as might be expected if the deposited hydrogen behaved as an amalgam electrode of finite bulk concentration, a logarithmic function. Moreover, the overvoltage depends only on the surface concentration of the added hydrogen, and is independent of the nature of the underlying metal. Apparent differences are due to differences in the real areas of the cathodes, and this gives a method of measuring the accessible areas of metallic surfaces. The amount of hydrogen deposited (measured by two methods) is very small, the deposition of sufficient hydrogen to form only 1/3000 of an atomic layer raising the potential of the cathode 100 millivolts. It is shown that the rate of decay, $-d\Gamma/dt$, of the active material is not proportional to Γ^2 as usually assumed, but is an exponential function of the potential, viz., $-d\Gamma/dt=k_1\epsilon^{-k_2E}$, where E is the electrode potential and Γ the true surface concentration of active hydrogen. The behaviour of the electrode potential and the magnitude of the quantities involved are compatible with the assumption that the potential of the electrode is due to the presence of electric doublets on its surface, the electric moment of these doublets being equal to that given by a proton and a negative hydrogen ion separated from each other by a distance equal to the diameter of a hydrogen atom.

II. The accessible areas of silver, platinum, carbon, and nickel cathode surfaces have been determined by measurement of the amount of deposited hydrogen required to raise the potential by a definite increment, and a comparison has been made of the catalytic activities of these surfaces by observation of the rate of hydrogen evolution. The effects of amalgamation and of treatment of the surfaces by alternate oxidation and reduction, annealing, etching with acid, electroplating, sand-papering, and rolling have been studied. The accessible area of bright platinum is about twice, whilst that of platinised platinum is about 2000 times its apparent area. If, however, the platinum is deposited on a mercury surface, the area is sensibly the same as that of mercury. The accessible area of a sand-papered metal is about ten times its apparent area, and in the case of nickel, activation by alternate oxidation and reduction causes an increase of nearly fivefold. Cold rolling reduces the accessible area. The specific catalytic activities of the various metals for the electro-deposition of hydrogen are found to differ very widely, but for any one metal the specific activity of the surfaces shows only small variations with chemical or thermal treatment. The effect of

alternate oxidation and reduction is chiefly to increase the accessible area by altering the grain size. Violent mechanical treatment, however, although it increases the surface to a much smaller extent, increases the proportion of surface atoms which are out of the crystal lattice and are catalytically the most active. The increase of activity gradually diminishes with ageing of the cathode. L. L. BIRCUMSHAW.

Benzyl ether as a cryoscopic solvent. G. M. BENNETT and G. H. WILLIS (J.C.S., 1928, 2305—2307).—Benzyl ether purified by fractional freezing has m. p. 3·60°, b. p. 184°/2 mm., mean cryoscopic constant 62·7, and latent heat of fusion 24·4. For benzoic and acetic acids the apparent mol. wt. is less than when benzene is used as solvent, but the values are the same for benzyl alcohol. This is said to be due to the tendency for ethers to form complexes with hydroxylic substances. J. GRANT.

Cryoscopic determination of the molecular equilibria of resorcinol and pyrocatechol in aqueous solution. F. BOURION and C. TUTTLE (J. Chim. phys., 1928, **25**, 485—496; cf. this vol., 233).—At 0°, equilibria exist between simple and triple molecules in solutions of resorcinol (0·7–3M) and pyrocatechol (0·3–1·25M), but for concentrations less than 0·7M and 0·3M, respectively, no equilibria were detectable between simple and double molecules. At 100°, the ranges of concentration for single–double molecules are 0·375–1·25M and 0·25–1·0625M, and for single–triple molecules 1·375–2M and 1·125–1·875M, for resorcinol and pyrocatechol, respectively. The association of resorcinol decreases and that of pyrocatechol increases with rise in temperature, and the heats of association of 3 molecules to a triple molecule in aqueous solution at constant volume are +600 and −2400 g.-cal., respectively. J. GRANT.

Dielectric constants of solutions of electrolytes. H. HELLMANN and H. ZAHN (Ann. Physik, 1928, [iv], **86**, 687—716).—A reply to Walden, Ulich, and Werner (this vol., 14). The experimental method used by the latter is regarded as subject to errors which are unimportant in the study of non-conducting liquids, but increase in significance as the conductivity increases. Theoretical and experimental evidence is adduced which tends to show that the recorded large decrease in dielectric constant in solutions of electrolytes is not real. R. A. MORTON.

Absorption spectra of solutions of cobalt chloride, cobalt bromide, and cobalt iodide in concentrated hydrochloric, hydrobromic, and hydriodic acids. W. R. BRODE and R. A. MORTON (Proc. Roy. Soc., 1928, **A**, **120**, 21—33).—By means of the apparatus previously described (cf. this vol., 458), a more detailed study has been made of the absorption spectrum of cobalt chloride in concentrated hydrochloric acid in the blue and green portions of the visible spectrum (400—600 $\mu\mu$). An extension of the analysis previously applied to the selective absorption between 600 and 720 $\mu\mu$ to the whole of the absorption spectrum under investigation indicates that the fine structure in the blue and green regions is a continuation of the vibrational system previously observed (*loc. cit.*). The absorption spectrum of cobalt bromide in hydrobromic acid has also been determined throughout the visible portion of the spectrum, and that of cobalt iodide in hydriodic acid between 500 and 900 $\mu\mu$, by a combination of visual and photographic methods. The absorption of the systems investigated is clearly influenced by the nature of the anion; the replacement of a lighter by a heavier halogen atom causes a shift of the absorption bands in the direction of lower frequencies, and increases the intensity of the low-frequency components as compared with the high-frequency components of the principal band. In the case of cobalt chloride, the resolution of the principal band into its components can be made only on the assumption of six constituents, and this probably holds also for the bromide and iodide. By this method of analysis, the principal band is composed in all cases of component bands, the frequencies of which are from 35 to 40 times the constant frequency difference between these components, this frequency difference being 12·28, 11·70, and 10·79 f, respectively, for the chloride, bromide, and iodide systems. L. L. BIRCUMSHAW.

Refraction and dissociation of electrolytes. II. In methyl and ethyl alcohol. E. SCHREINER (Z. physikal. Chem., 1928, **135**, 461—472; cf. this vol., 708).—The molecular refraction of hydrochloric acid and of lithium chloride in methyl and in ethyl alcohol has been measured. The refraction falls with increase of concentration, probably due to a deformation of the medium due to solvation of the cations. The refraction is greatest in water, less in methyl alcohol, and least in ethyl alcohol. The dissociation constants of the first and second kinds of hydrochloric acid in water are discussed.

W. E. DOWNEY.

Chemical change of acids and salts in solution from the point of view of refractometric data. A. HANTZSCH and F. DÜRIGEN (Z. physikal. Chem., 1928, **136**, 1—17).—Measurements have been made of the densities and refractive indices of aqueous and alcoholic solutions of various acids and their alkali and alkaline-earth salts (cf. this vol., 834).

H. F. GILLBE.

Affinity between asymmetric ions. I and II. S. W. BERGMAN (Arkiv Kemi, Min., Geol., 1928, **9**, Nos. 34 and 42, 1—21, 1—11).—I. Conductivity measurements at 18·0±0·2° have been made with solutions of cinchonine *d*- and *l*-mandelates, cinchonine *d*- and *l*-tartrates, and quinine *d*- and *l*-camphorsulphonates. The values for Λ for each pair of diastereoisomeric salts were found to be approximately equal. Measurements of $[\alpha]_{5250}$ for cinchonine *d*-, *l*-, and *r*-mandelates show that the values $[\alpha]_d-[\alpha]_r$ are about the same as $[\alpha]_l-[\alpha]_r$ and $[\alpha]^{18}_{5250}$ the same as for ammonium *l*-mandelate. There is thus no difference in affinity between optically active acids and bases (cf. Marckwald and Chwolles, A., 1898, ii, 371). The difference in solubility of diastereoisomeric salts is explicable in terms of the energy content of the crystal lattice, and the Bjerrum dissociation theory affords a satisfactory explanation of the results.

II. A series of density determinations has been made with 8 pairs of crystalline and anhydrous

diastereoisomeric salts. The results show that in general the heavier salt has the smaller solubility.
H. BURTON.

Affinity. III and IV. H. VON EULER (Arkiv Kemi, Min., Geol., 1928, **9**, Nos. 30 and 44, 1—6, 1—6).—Theoretical. The author cites examples of fission which may be explained in terms of the affinity between reactant groups and atomic groups of the substrate. H. BURTON.

Copper hydrosols of low electrical conductivity. G. T. R. EVANS (Trans. Faraday Soc., 1928, **24**, 409—412).—Very dark brown copper sols, of specific conductance less than 0·6 mho, may be prepared by striking an arc between a heavy rotating copper cathode and a light copper anode in a cooled vessel containing water of low conductivity. About 8—10 amp. at 80 volts are passed for 2 hrs. and the resulting sol is kept for a day so that the larger particles torn from the electrodes may settle.
F. G. TRYHORN.

Protected silver hydrosols. VI. Sol formation by irradiation. J. VOIGT (Kolloid-Z., 1928, **45**, 319—322).—In order to reduce very dilute solutions of silver nitrate (0·106—0·0106%) and silver oxide (0·005%) by irradiation with a quartz-mercury lamp, the presence of reduction centres is necessary. Sols are not obtained, therefore, after the solutions have been passed through an ultra-filter. Pure gum arabic, before and after irradiation, cannot reduce dilute silver nitrate. Irradiation of a mixture of silver solution and gum arabic effects reduction, giving a precipitate with visible light and forming a silver sol with ultra-violet light. The submicrons of the gum arabic appear to act as reduction nuclei. Ultra-violet light has a peptising influence, for the precipitated silver can be dispersed to a yellow sol by shaking during irradiation. E. S. HEDGES.

Orange-coloured or orange-red colloidal gold solutions. P. P. VON WEIMARN (Kolloid-Z., 1928, **45**, 366—370).—Directions are given for the production of orange gold sols. Solutions of auric chloride and sodium citrate are mixed together in boiling distilled water and a small quantity of dilute potassium cyanide solution is subsequently added. The whole is then kept boiling for a period of many hours. Excess of potassium cyanide gives a quite colourless solution. The sols remain stable for some months; they generally become pure red in time. The change from orange-red to orange on addition of potassium cyanide is considered to be caused by the greater velocity of dissolution of the red colouring ultramicro-crystals of gold. Examples are also given of orange gold sols, the colour of which is due to suspension of a red sol in a yellow dispersion medium (often produced by the action of alkali on reducing substances such as sugar etc.), and it is pointed out that the colour of a sol is not a safe guide to its degree of dispersion. E. S. HEDGES.

Colloidal platinum. IV. Existence of hexahydroxyplatinic acid in colloidal platinum solutions. S. W. PENNYCUICK (J.C.S., 1928, 2108—2117; cf. this vol., 476).—When the clear solution obtained after coagulation of a platinum sol by freezing is conductimetrically titrated, curves are obtained which are closely similar to those obtained with hexahydroxyplatinic acid, $H_2Pt(OH)_6$, the only known strong platinic acid. The acid, lower hydrates of which are probably also present, is probably produced by oxidation during the atomisation of the platinum, and forms part of the colloidal micelle. Its ionisation at the surface would account for the stability of the colloid, coagulation by bases being due to neutralisation. Initial preservation of the acid by means of a freezing mixture is essential for the preparation of a strong stable sol. J. GRANT.

Stability of colloidal ferrous phosphate prepared by means of gelatin or blood-serum. M. MESSINI (Kolloid-Z., 1928, **45**, 322—325).—Following the observation that intravenously injected ferrous sulphate is transformed in the animal body to colloidal ferrous phosphate, the stability of colloidal ferrous phosphate in presence of gelatin and of blood-serum has been studied. The material was prepared by mixing solutions of sodium phosphate and ferrous sulphate in presence of the colloid, and the time interval between mixing and the appearance of flocculation was noted. The protective action of gelatin is observable at a concentration of 2·5 g. per litre and reaches a maximum at 12·5 g. per litre, thereafter remaining constant. The smaller the concentration of ferrous phosphate the greater is its stability; the colloid remains stable for an indefinitely long period at a concentration of 0·006 g. per litre and in presence of 12·5 g. per litre of gelatin. Similar results were obtained with ox-blood serum as the protective colloid. The protective effect is observed at a concentration of 100 c.c. per litre and the colloid seems to be permanently stable when the concentration of ferrous phosphate is 0·006 g. per litre and that of serum 700 c.c. per litre. E. S. HEDGES.

Influence of concentration of a sol on its stability. S. G. CHAUDHURY (J. Physical Chem., 1928, **32**, 1231—1235).—Mainly polemical against Ghosh and Dhar (A., 1927, 305, 617). The possibility that a decrease in the charge of a sol with dilution will tend to sensitise it has been overlooked by previous workers. In explanation of the variation of the coagulating concentration for different electrolytes with dilution it is suggested that the diminution of the charge and of the total surface of sol particles with dilution tends to make the sol unstable if the potential at which the sol coagulates and the relative adsorption of all ions on the surface remain unchanged. The greater distances between the particles of a diluted sol favour stability. L. S. THEOBALD.

Particle size in precipitated zinc sulphide. G. R. LEVI and C. G. FONTANA (Atti R. Accad. Lincei, 1928, [vi], **7**, 502—508).—The particle size of zinc sulphide, obtained by passing excess of hydrogen sulphide into solutions of zinc salts, has been examined by an X-ray method. The solutions used were N-zinc sulphate with, respectively, N-sodium hydroxide, N-ammonia solution, N-acetic acid, and N-acetic acid with N-ammonium acetate. The precipitate was kept for 24 hrs. before examination; the following values were obtained for the particle size, respectively: 19·74, 18·60, 20·60, and 22·00 Å.
R. W. LUNT.

Combining power of chromic oxide sol with acids and bases. R. WINTGEN and H. WEISBECKER (Z. physikal. Chem., 1928, **135**, 182—198).—The fact that acids and bases have affinity for chromic oxide sol may be due to adsorption or salt formation. The experimental data agree within the limits of error with equations based on hydrolysis. The conception of chromic oxide sol as a colloidal solution of an amphoteric electrolyte is confirmed by the fact that the isoelectric point observed agrees with that calculated from the dissociation constants of acids and bases. The adsorption isotherm allows results to be obtained which are in tolerably good agreement with experimental values.

R. A. MORTON.

Action of X-rays on colloidal ceric hydroxide. J. A. V. FAIRBROTHER (Phil. Mag., 1928, [vii], 6, 385—401; cf. A., 1927, 935).—Irradiation by *X*-rays of ceric hydroxide sol is accompanied by a rise in viscosity, the rate of increase becoming rapidly larger with increasing doses of *X*-rays, until eventually the sol sets to a gel. The dose necessary to gel the sol decreases linearly with the time, suggesting that the ageing effect and the action of radiation are additive. The dose required to produce the maximum viscosity lowering in a diluted sol decreases as the stock solution ages; a dose sufficiently in excess of this gels the sol immediately. As the minimum viscosity is approached the percentage decrease in the size of the particles is proportional, in fact almost equal, to the fractional change in viscosity. Beyond the minimum point gelation occurs and the particles show a maximum increase to 1·6 times their normal size; this gelation takes several hours for completion in a dilute sol unless irradiation, which accelerates the process, is prolonged sufficiently. Theoretically, the viscosity (referred to that of water) should be a parabolic function of the dose applied; experiment does not bear this out, probably because the theory assumes the particles do not change in size.

S. K. TWEEDY.

Dissolution of colloidal silver in hydrogen peroxide. H. KOLLER-AEBY (Kolloid-Z., 1928, **45**, 371—374).—In the catalytic decomposition of hydrogen peroxide by colloidal silver, the catalyst does not remain unchanged, and the change undergone depends on the concentration of the sol. In general, the sol changes from a dark brown to a yellowish-brown, but at certain concentrations the colour vanishes completely and the solution fails to show a Tyndall cone. In this change there has been observed an intermediate stage in which the sol has a steel-blue colour. Various experiments with these sols are described. It is suggested that, in the reaction between colloidal silver and hydrogen peroxide, silver oxide or other oxidation products are formed.

E. S. HEDGES.

Role of dielectric constants, polarisation, and dipole moment in colloid systems, especially in non-aqueous media. III. The behaviour of organosols containing electrolytes. WO. OSTWALD (Kolloid-Z., 1928, **45**, 331—345).—The orientation polarisation of a platinum alcohol sol prepared by Errera's electrical disintegration method is the same as that prepared by Svedberg's method, although traces of water are not excluded in the former case. For both types of sol, substances which have not a flocculating effect have not only high dielectric constants, but also high dipole moments; conversely, liquids with very weak dipole moments (benzene, hexane, carbon tetrachloride) have the greatest coagulating effect, whilst toluene and ethyl ether (with slightly higher dipole moments) are more feeble coagulating agents. The chemically-prepared metal sulphide alcohol sols of Errera contain electrolytes and differ from the preceding examples. Although substances with small dielectric constant and low dipole moment are the best flocculants, substances with high dipole moments (*e.g.*, *iso*amyl alcohol) also can coagulate. Further, medium and not maximal concentrations of benzene, hexane, etc. produce the most effective coagulation. This result is unintelligible on the assumption that only the dielectric constant is concerned with the flocculating power. There is, however, a close agreement between the coagulation optimum and the maximum of the molecular polarisation calculated by Debye for alcohol in a dipole-free solvent. The stabilising adsorption layer of the sulphide alcohol sols consists not only of ions, but also of alcohol dipoles; it is considered as a diffuse double layer. In the process of flocculation, a desorption of ions to below the stabilising concentration must occur by the addition of another organic liquid and an adsorption minimum has been established, which agrees with the coagulation optimum. The relation between adsorbability and dipole content is discussed and also that between dipole content and solubility.

E. S. HEDGES.

Structure viscosity of some sols of polymeric carbohydrates. S. TSUDA (Kolloid-Z., 1928, **45**, 325—331).—A capillary viscosimeter having a horizontal capillary is described; it is especially suitable for the study of structure viscosity of colloids at different rates of flow. The Hagen–Poiseuille law is not valid for the viscosity of starch paste, but the three equations of Wo. Ostwald hold, and the properties of the constants of these equations have been studied with starch solutions of different concentrations. The relation between the relative viscosity and the concentration of the starch solution is expressed approximately by the Arrhenius formula, the constants of the formula being determined, not only by the substance, but also by the dimensions of the viscosimeter and by the pressure. At 50°, the viscosity of agar sol follows the Hagen–Poiseuille law, but at 30° it is in accordance with the de Waele–Ostwald law; when subsequently reheated at 50°, the sol still obeys the latter law for some time, but eventually reverts to its original condition.

E. S. HEDGES.

Streaming potential and colloid stability. II. H. R. KRUYT and P. C. VAN DER WILLIGEN (Kolloid-Z., 1928, **45**, 307—319).—Measurements of the streaming potential at a glass capillary have given the following results. The discharging effects of alkali metal ions are unequal, lithium having the least and cæsium the greatest effect. Similarly, magnesium chloride has a greater discharging effect than barium chloride, the latter being nearly equal to hydro-

chloric acid. Tervalent cerium, lanthanum, aluminium, and hexamminocobaltic chlorides, and thorium tetrachloride, a quadri- and a sexa-valent cobalt salt, and a quadrivalent platinum salt were investigated. The discharging effect of the aluminium ion is observed when the concentration is one hundredth of that necessary with the other tervalent salts. The discharge is not connected with hydrolysis. Variation of the anion in a series of potassium salts does not influence the discharging effect, with the exception of the hydroxyl ion, which gives a strong increase in charge. Potassium hydroxide was found also to give a strong charge to capillaries of Jena glass and of quartz. The variation in the discharging effect of different ions of the same valency is ascribed to differences in the density of charge of the hydrated ions. The true *P.D.* between glass and pure water is considered to be indeterminable, since it is greatly affected by small changes in a large number of factors.

E. S. HEDGES.

Liquid phase rule in the formation of oil emulsions. R. KOHLER (Kolloid-Z., 1928, **45**, 345—348).—The amount of olive oil or pea-nut oil containing oleic acid which can be emulsified by dilute sodium carbonate or sodium hydroxide is dependent on the amount of oil present, when the alkali concentration and the total volume of aqueous solution remain constant. For small concentrations of alkali and with small amounts of free fatty acids in the oil, the amount emulsified is greatest for a medium amount of oil. The optimum amount of oil increases with increasing alkali concentration. The observations are in agreement with Wo. Ostwald's solid phase rule of adsorption peptisation. Reference is made to the technical bearing of these results. E. S. HEDGES.

Model of the Pickering emulsion. R. E. LIESEGANG (Kolloid-Z., 1928, **45**, 370—371).—The objects are to show by visual demonstration (1) the partition of a substance in an emulsion and (2) that sodium chloride can act as a solid sheath to the particles. When chloroform is shaken with a dilute solution of methylene-blue, the drops afterwards run together and form a red layer at the bottom of the vessel; the aqueous top layer is blue. If sodium chloride has been dissolved in the methylene-blue solution, the whole of the colour goes into the chloroform layer. Chloroform remains unaltered when shaken with powdered sodium chloride, but when the mixture is covered with a layer of methylene-blue solution the drops of chloroform no longer run together after shaking, each blue drop being coated with a white sheath of undissolved sodium chloride. The diameter of the droplets may be 4 mm. and this is reduced to 1 mm. or less by increasing the amount of sodium chloride. With decrease in the size of droplets the volume of the paste-like mass increases, so that finally no separate aqueous phase is discernible. E. S. HEDGES.

Colloidal state of gelatin solutions and the effect of temperature changes. M. FRANKEL (Kolloid-Z., 1928, **45**, 355—366).—The colloid character of gelatin solutions undergoes a complete change with gentle heating, the extent of the change depending on the duration of the treatment. This phenomenon is termed dissociation. A study has been made of the lowering of viscosity, increase in dialysis, decrease in tendency to gelatinise, and the change in optical properties accompanying dissociation. Experiments on the effect of pepsin on gelatin solutions of different degrees of dissociation have shown that in all cases the same reaction products are formed and that the readiness to react is connected with the progress of dissociation. A constant temperature is necessary in order to obtain constant properties in a gelatin solution. The time required for production of a stable state depends on the temperature and is generally considerable (about 75 hrs.). The influence of temperature is most marked between 5° and 40°; outside these limits, constant properties are more quickly attained. The stable solutions are still affected by further changes of temperature; heating causes more dissociation, whilst cooling causes association. The changes are reversible, provided the alterations of temperature take place sufficiently slowly. Solutions of different degrees of association become closely similar when heated. E. S. HEDGES.

Absorption of water by gelatin. II. The nitrate system. D. JORDAN-LLOYD and W. B. PLEASS (Biochem. J., 1928, **22**, 1007—1018).—Sodium nitrate up to a concentration of 0·6*M* in the presence of nitric acid suppresses the swelling of gelatin due to acid. At greater concentrations its effect depends on the p_H. From p_H 4·0 to 3·5 increasing salt concentration causes swelling; at p_H 3·0 it causes coagulation of the gelatin; at 2*M* coagulation occurs at all p_H values less than 2·3, but dissolution at all values greater than 2·3. At p_H 4·1 over a range of 0—0·7*M* nitrates have no effect on swelling; beyond this range they dissolve the gelatin. Up to a concentration of 0·1*M* sodium nitrate in the presence of sodium hydroxide suppresses the swelling of gelatin due to the alkali. At concentrations greater than this increasing concentration of nitrate is accompanied by an increase in swelling directly proportional to the concentration of the salt present. In solutions more concentrated than 0·1*M* the gelatin is dissolved at 18°. The swelling of gelatin due to nitric acid and sodium hydroxide increases as an exponential function of the temperature. At the isoelectric point (p_H 5·0) sodium nitrate promotes water absorption, swelling being proportional to the logarithm of the concentration of the salt up to 0·1*M*. At greater concentrations swelling is directly proportional to the concentration of the nitrate. Over a p_H range from 5 to 10 and at concentrations of salt greater than 0·1*M* swelling in solutions of sodium nitrate is influenced only by the salt concentration and is independent of the p_H. At p_H 5·0 a rise of temperature from 0° to 12° is accompanied by an increase in swelling which is the same in the absence of nitrate and at all concentrations of nitrate up to 1*M*. In the absence of salt, swelling is at a maximum at 12° and in dilute solutions of nitrate at about 15—18°; in more concentrated solutions there is no temperature of maximum swelling, the gelatin passing into solution as the temperature is raised. The temperature of dissolution is lower the greater is the concentration of

nitrate present. At p_H 7·0 in the absence of salt or in dilute solutions of nitrates the effect of temperature on swelling is similar to its effect at p_H 5. The temperature influences the position of minimum swelling at varying concentrations of nitrate, the salt concentration registered at this point diminishing with rising temperature. S. S. ZILVA.

Influence of organic substances on the thixotropy of ferric oxide sol. H. FREUNDLICH and K. SOLLNER (Kolloid-Z., 1928, **45**, 348—355).—The liquefying action of amino-acids on a thixotropic sol cannot be related to the diminution in hydrogen-ion concentration (which rather promotes setting), for addition of amino-acids (glycine, alanine) both to concentrated, thixotropic ferric oxide sols and to dilute, non-thixotropic sols lowers the hydrogen-ion concentration. The action is considered to be due to the tendency of amino-acids to form complex ferric salts, which are notably hydrophilic. The complexes bound to the colloid particle increase in water content and favour sol formation. Other substances (*e.g.*, sugar) which form complexes with ferric salts also influence the thixotropy in the same sense as do amino-acids. Contrary to results formerly obtained with small quantities of glycine, larger amounts have a peptising effect on ferric oxide sols and thus raise the coagulation value. The relation between time of setting, θ, and electrolyte concentration, c, can be expressed for ferric oxide sols by the formula $\theta=e^{-c/k}$, where k is a constant. E. S. HEDGES.

Cataphoresis in copper oxide sols. Application of Debye and Huckel's theory of electrolytic conduction to colloid particles. H. H. PAINE (Trans. Faraday Soc., 1928, **24**, 412—429).—Measurements were made of the mobility of particles in copper oxide sols before and after addition of electrolytes. The highest mobility observed was $52{\cdot}8\times10^{-5}$ cm. per sec. per volt for a colloid solution of specific conductance $0{\cdot}46\times10^{-6}$ mho. Extrapolation indicated a mobility of about 60×10^{-5} unit for sols of zero conductance. The mobilities are reduced by the addition of electrolytes, the proportional decrement diminishing with increase in the amount of the electrolyte. The greater is the valency of the ion carrying a charge opposite in sign to that carried by the particles, the greater is its effect in reducing the mobility of the copper oxide particles. By the application of the theory of Debye and Huckel it follows that the addition of an electrolyte should cause a decrease in mobility from the value at zero electrolyte concentration which is directly proportional to the square root of the concentration of the electrolyte. This relationship is confirmed by results of measurements with copper oxide sols, and by reference to the data of Freundlich and Zeh for ferric oxide and arsenious sulphide sols. F. G. TRYHORN.

Optical measurement of small degrees of dissociation of the vapours of metallic salts. I. WYNEKEN (Z. physikal. Chem., 1928, **136**, 146—158).—By comparison of the intensity of the mercury absorption line at 2536 Å. in mercuric chloride vapour with that of the same line in pure mercury vapour at known pressures, the degree of dissociation of the salt has been determined. At 180°, α is $2{\cdot}2\times10^{-4}$, and at 250°, $6{\cdot}5\times10^{-4}$, in fair agreement with the values obtained theoretically by application of the Nernst heat theorem. H. F. GILLBE.

Hydrolysis in solutions of potassium laurate as measured by extraction with benzene. J. W. McBAIN and M. EATON (J.C.S., 1928, 2166—2179; cf. this vol., 128).—A study has been made of solutions of potassium laurate with and without the addition of alkali or lauric acid. The hydrolysis of the soap solutions depends only on the simple fatty ions and its magnitude is determined by the extent of the conversion of the fatty acid into acid soap. Unaltered soap solutions contain only slight traces of the free fatty acid. The existence of a definite crystalline compound, potassium hydrogen laurate, reported by Oudemann (Jahresber., 1863, 331), has been confirmed. F. J. WILKINS.

Effect of salts on weak electrolytes. I. Dissociation of weak electrolytes in the presence of salts. H. S. SIMMS (J. Physical Chem., 1928, **32**, 1121—1141; cf. A., 1926, 681).—The influence of ionic strength on the activity coefficients of weak electrolytes as shown by the effect on the dissociation indices (the negative logarithm of the dissociation constant) has been investigated by means of titration data obtained from $0{\cdot}01M$-solutions of various organic acids, bases, and ampholytes alone and in the presence of sodium chloride and of magnesium chloride. The value of the dissociation index ($P_{k'}$) is calculated and plotted against the square root of the ionic strength; the slopes of the resulting curves show the extent of the agreement between the activities found and those required by the Debye–Hückel equation. Singly-charged anions from uni- or bivalent acids satisfy the Debye–Hückel equation in the presence of sodium chloride, magnesium chloride, or the salt of a weak acid. Multivalent anions in the presence of sodium chloride obey a form of this equation modified to include a correction for the distance between the charges. With magnesium chloride, the behaviour is anomalous, the effect being greater with oxalic, malonic, and citric acids than with succinic, azelaic, and sebacic acids. Sulphate ions produce an effect on uni- and bi-valent anions which is opposed to that of the magnesium ions. Cations from amines and amino-acids show a deviation from the Debye–Hückel relationship with both magnesium and sodium chlorides. The isoelectric points fall with an increase in ionic strength. L. S. THEOBALD.

Mean activity coefficient of the hydrogen ion, and of the hydrogen carbonate ion in potassium chloride and concentrated sodium chloride solutions. Dissociation constant of some indicators in these solutions. E. GUNTELBERG and E. SCHIODT (Z. physikal. Chem., 1928, **135**, 393—443).—The mean activity coefficient of the hydrogen and hydrogen carbonate ion, $\sqrt{f_H \cdot f_{HCO_3}}$, and the apparent first dissociation constant of carbonic acid, $K_c=c_H \cdot c_{HCO_3}/(c_{CO_2}+c_{H_2CO_3})$, in potassium chloride solutions from $0{\cdot}1N$ to $3N$, and in sodium chloride solutions of $3N$, $4N$, and $5N$, have been measured. The value of K_c behaves as with other weak acids; it rises from $3{\cdot}2\times10^{-7}$ in pure water to more than

three times this value in N-potassium chloride solution, and then begins to fall; in saturated sodium chloride solution it is only 30% higher than in pure water. The difference between these values and those found by Szyszkowski (A., 1907, ii, 238) and Wilke (A., 1922, ii, 52) are discussed. The dissociation constants of methyl-orange, bromophenol-blue, and dimethyl-yellow were measured in the same solutions. It was found that the salts have a characteristic effect on the dissociation of those acids which yield a univalent cation and a mixed ion. The mean activity coefficient and the dissociation constant of benzoic acid in $3N$-potassium chloride and in $3N$-, $4N$-, and $5N$-sodium chloride were also measured. Benzoic acid has an unusually high activity coefficient in these solutions. The errors in colorimetric p_H determination due to the presence of salts are discussed. W. E. Downey.

Polyiodide equilibrium in aqueous and salt solutions. J. S. Carter (J.C.S., 1928, 2227—2230).—The values of K for the equilibrium $I'+I_2 \quad I_3$ which may be derived from the solubility of iodine at 25° in solutions of sodium iodide in (*a*) water and (*b*) 1·7M-sodium sulphate solution are not constant, and indicate that the tendency to form higher polyiodides increases with increasing initial concentration of iodide. Both iodide and polyiodide are assumed to be completely ionised. The relation between active masses and actual concentrations is much closer than would be expected from considerations of the activities. Determinations of K from the distribution ratio, based on the assumption that neither the iodide nor the polyiodide affects its value, show that in dilute solutions the whole of the iodine is present as tri-iodide, but that more complex periodides exist in concentrated solutions. J. Grant.

Transition temperature of carbon tetrachloride as a fixed point in thermometry. J. C. McCullough and H. E. Phipps (J. Amer. Chem. Soc., 1928, **50**, 2213—2216).—A transition from cubic to monoclinic carbon tetrachloride is shown by the thermometric method to occur at $-48·54°\pm0·02°$, and this is suggested as a thermometric fixed point. S. K. Tweedy.

Influence of pressure on the high–low inversion of quartz. High–low inversion of quartz and the heat capacity of low quartz at 573°. R. E. Gibson (J. Physical Chem., 1928, **32**, 1197—1205, 1206—1210).—I. The temperature of the high–low inversion of quartz under uniform hydrostatic pressures from 1 to 3000 megabars has been determined in an apparatus similar to that described by Smyth and Adams (A., 1923, ii, 490). The temperature of the high–low inversion rises according to the equation $\Delta T=-0·3+2·1\times10^{-2}p+8·6\times10^{-7}p^2$, where p is the pressure in megabars. From the initial pressure coefficient and the "instantaneous volume change" at 575°, the latent heat of inversion calculated by means of the Clausius–Clapeyron equation is 3·1 g.-cal./g.

II. Heating and cooling curves for two cylinders of quartz confirm the observation of Bates and Phelps (A., 1927, 1018) that the high–low inversion of quartz is a phase change which is generally accompanied by superheating and supercooling. At $572·3°\pm0·2°$, it appears that low-quartz may be converted reversibly into high-quartz and only experimental difficulties prevent the two phases being obtained in equilibrium at this temperature. An hypothesis of forced inversion is unnecessary. Low-quartz before passing to the high variety superheats to such an extent that during the inversion the temperature never falls to the equilibrium value. The apparent heat capacity of the low form at 573° is calculated to be 4 ± 1 g.-cal./g. per degree. Quartz at 570° is distinct from quartz at the ordinary temperature, and the inversion at 573° is comparable with any rapid enantiotropic change. L. S. Theobald.

Dissociation of liquid crystals. A. Mlodziejowski (Z. physikal. Chem., 1928, **135**, 129—146).—Liquid crystals having upper and lower dissociation temperatures have been obtained in which the only stable state of aggregation over a certain temperature range must be the liquid crystal state. Mixtures of cholesterol and cetyl alcohol form liquid crystals yielding two solid phases at the lower dissociation temperature and a liquid and a solid phase at the upper temperature. Liquid crystals formed from cholesterol–glycerol mixtures yield a solid and a liquid phase, and two liquid phases at the lower and upper dissociation temperatures, respectively. The possible diagrams corresponding with the above phenomena have been constructed on thermodynamic principles, and from the theoretical data the diagram corresponding with the cholesterol–glycerol system has been identified. The advantages of combining microthermal analysis with the thermodynamic deduction of diagrams in orienting work of the above type are discussed. R. A. Morton.

Decomposition pressure of sulphuric acid containing nitrogen compounds. A. Sanfourche and L. Rondier (Bull. Soc. chim., 1928, [iv], **43**, 815—826).—A more detailed account of work already published (this vol., 943).

Equilibrium diagram of the system antimony–arsenic. Q. A. Mansuri (J.C.S., 1928, 2107—2108).—The thermal diagram shows that antimony and arsenic form a complete series of solid solutions but no chemical compound. The curve has a minimum at 605° (13% As). Micrographic analyses of the etched alloys show that all consist of a single constituent with some coring, fairly large six-sided crystals being observed in the alloy containing 80% As. J. Grant.

Equilibrium diagram of the copper–silicon system. K. Matsuyama (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 665—673).—The copper–silicon diagram has been re-determined and in essentials confirms that given by Rudolphi. The liquidus consists of four branches corresponding with the separation of the α, β, and δ solid solutions and pure silicon. The β solid solution decomposes on cooling into α and γ', with a eutectoid at 795°. Two compounds, Cu_5Si and Cu_3Si, exist. The eutectic of silicon and Cu_3Si melts at 805° and contains 17% Si. C. J. Smithells.

Equilibrium diagram of the aluminium–calcium system. K. Matsuyama (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 783—789).—The liquidus of the aluminium–calcium system consists of four branches corresponding with the separation of the α solid solution, $CaAl_3$,$CaAl_2$, and calcium, respectively. Aluminium dissolves 0·3% of calcium at the ordinary temperature and 0·6% at 616°. Alloys containing 0·6—33·03% Ca are eutectiferous, the eutectic containing 7·55% Ca and melting at 616°. Alloys containing 13·9—42·5% Ca undergo a peritectic reaction on cooling below 700°, forming $CaAl_3$. The liquidus has a maximum of 1079° at 42·5% Ca, corresponding with $CaAl_2$. Alloys containing more than 42·5% Ca are eutectiferous, the eutectic containing 73% Ca and melting at 545°.
C. J. Smithells.

Decomposition of alkaline-earth sulphates. IV. J. Zawadzki, I. Kowalczewski, and S. Zeromski (Rocz. Chem., 1928, **8**, 358—368).—Gypsum passes irreversibly and with considerable velocity into anhydrite at temperatures above 1000°. Measurements of the decomposition pressures of gypsum indicate that the influence of the irreversible subsidiary reaction increases with rise in temperature. The decomposition pressures of anhydrite between 1100° and 1220° are considerably lower than for gypsum, and are equal to those given by gypsum after long heating. The thermal decomposition of anhydrite is reversible, anhydrite being obtained by the action of sulphur trioxide on a mixture of 6 parts of calcium oxide with 1 part of sulphate. Anhydrite decomposes to form the basic sulphate, $2CaO,SO_3$, the heat of reaction being −109·36 g.-cal. The pressures of gas in equilibrium with basic sulphate at temperatures up to 1200° are lower than those found for anhydrite, and the same pressures have been attained by the partial saturation of calcium oxide with sulphur trioxide. R. Truszkowski.

Irreversible dehydration of some crystalline hydrated salts. M. A. Rakuzin (Bull. Soc. chim., 1928, [iv], **43**, 744—747).—Studies of the dehydration and hydration of borax, Glauber's salt, and sodium carbonate have led to the conclusion that the phase rule may be applied only to those crystalline hydrated salts which undergo true thermal dissociation, although it cannot at present be said whether the dehydration reaction is one of dissociation or of decomposition. The spontaneous dehydration of sodium carbonate gives rise to a stable dihydrate and the anhydride forms a monohydrate on re-hydration. J. Grant.

Transition points of compounds of organic solvents and salts. H. Osaka (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 873—887).—The transition temperatures of compounds of inorganic salts with acetone have been determined cryoscopically, by observing the highest temperature reached when a crystal of the compound is added to a supercooled solution of the salt in acetone. C. W. Gibby.

System calcium oxide, silica, and water. J. R. Baylis (J. Physical Chem., 1928, **32**, 1236—1262; cf. Lerch and Bogue, this vol., 21).—The equilibria which are established between different amounts of calcium hydroxide in solution and the hydrous oxides of silica have been investigated. A compound CaO,SiO_2 appears to be formed by the addition of calcium oxide to the washed silica gel obtained from sodium silicate and hydrochloric acid. This is followed by adsorption of further quantities of calcium oxide. The reversibility of the process is established, and it is shown that 30—45% of the calcium hydroxide united with the silica appears to be adsorbed by the compound initially formed. Surface equilibria due to adsorption may retard the rate of hydrolysis of some of the compounds in submerged concrete. Certain conclusions of Lerch and Bogue (*loc. cit.*) are criticised.
L. S. Theobald.

System $2CaO,SiO_2$–MgO–$5CaO,3Al_2O_3$. W. C. Hansen (J. Amer. Chem. Soc., 1928, **50**, 2155—2160).—The equilibrium diagram for the above system is given. There is no evidence that magnesium oxide forms a solid solution with, or replaces the lime in, $5CaO,3Al_2O_3$ or γ-$2CaO,SiO_2$.
S. K. Tweedy.

Ternary system strontium oxide–sucrose–water. W. Reinders and A. Klinkenberg (Z. Elektrochem., 1928, **34**, 406—407).—Polemical against Grube and Nussbaum (cf. this vol., 480).
L. L. Bircumshaw.

Mixed crystals, solutions, and fusions of the system $(K,NH_4)(Cl,NO_3)$. E. Jänecke (Z. angew. Chem., 1928, **41**, 916—924).—The fusion and solubility curves for the various possible binary and ternary systems are recorded. As all the salts except potassium chloride occur in several modifications, the diagrams are complicated. In the quaternary system, the stable solid pair at all temperatures is represented by the combination $NH_4Cl+KNO_3$. C. Irwin.

Composition of crystals obtained from solutions containing sodium sulphate and iodides. III. (Signa.) E. Fabris (Annali Chem. Appl., 1928, **18**, 326—332; cf. A., 1927, 939).—The composition of crystals obtained from various solutions containing sodium sulphate and lithium iodide is investigated.
E. W. Wignall.

Action of carbon monoxide on metallic chlorides. L. Belladen and A. Sommariva (Gazzetta, 1928, **58**, 443—449).—If the action of carbon monoxide on metallic chlorides is determined by the equilibria MCl_2+CO $M+COCl_2$, $COCl_2$ $CO+Cl_2$, and MCl_2 $M+Cl_2$, the percentage of carbonyl chloride at equilibrium at 700° should be of the order of 10^{-12}. Measurements were made of the quantity of carbonyl chloride produced when carbon monoxide was passed at various speeds over heated metallic chlorides, and the equilibrium quantity was obtained by extrapolating to zero velocity. With lead, silver, cupric, and nickel chlorides the percentages of carbonyl chloride formed at temperatures between 450° and 750° varied from 0·17 to 1·12. Since these values are much greater than those predicted for this reaction, it is suggested that a secondary reaction occurs, $2CO$ $C+CO_2$, followed by $2CO_2 \rightleftharpoons 2CO+O_2$, and $2MCl_2+O_2$ $2MO+2Cl_2$. Support is lent to this by the facts that barium hydroxide placed in the reaction tube is partly converted into carbonate, and that carbonyl chloride

(about 1·0%) is formed when pure carbon dioxide is passed over heated metallic chlorides.

F. G. TRYHORN.

Thermodynamics based on statistics. I and II. G. N. LEWIS and J. E. MAYER (Proc. Nat. Acad. Sci., 1928, **14**, 569—575, 575—580).—I. An attempt is made to derive the second law of thermodynamics in exact form from simple statistical principles, and also to obtain unambiguous definitions of correlated quantities such as temperature, pressure, and entropy. In defining the instantaneous state of a system it is unnecessary to consider in detail every mechanically significant property of each particle. The field of specification can be divided into a number of regions, and it is sufficient to describe the detailed state by specifying the number of molecules of each independent constituent comprised in each region. The possibility of finding a mode of partition into finite regions so that the individual detailed states are of the same order of probability is discussed, and the assumption made that not only is such a division possible for every system, but also that there is, for every system, a natural mode of partition into finite regions of this kind. It is not necessary to assume that the natural mode of division completely determines the sizes and shapes of the individual regions, but that it does determine completely the quantity log Ω, where Ω represents the total number of recognisably different ways in which the particles can be distributed among the regions.

II. It is shown that the basic assumption laid down regarding the natural division of the field of specifications describing the states of individual particles into regions so as to give unique significance to log Ω includes within itself the second law of thermodynamics. The mode of partition for an ideal monatomic gas is considered.

A. J. MEE.

Thermodynamic equilibrium in the universe. F. ZWICKY (Proc. Nat. Acad. Sci., 1928, **14**, 592—597).—The postulate of a thermodynamic equilibrium in the universe as ordinarily applied leads to conflicting results as regards the distribution of radiation in the universe and the equilibrium between matter and radiation. The basis of the problem must be extended if it is to agree with actual conditions, the postulate being applied to the whole chain of reactions : radiation ⇌ protons and electrons ⇌ higher nuclei ⇌ dust particles ⇌ gaseous nebulæ ⇌ stars ⇌ swarms of stars (galactic systems). A consistent statistical treatment of the equilibrium of these different forms of matter in the universe on the basis of the postulate seems likely to give results in agreement with the facts.

A. J. MEE.

Thermodynamic integration factor for the derivation of the general form corresponding with the van der Waals–Clausius equation. A. PRESS (Z. Physik, 1928, **49**, 306—310).—Mathematical.

R. W. LUNT.

Thermodynamic calculations [for hydrocarbons]. D. F. SMITH (Ind. Eng. Chem., 1928, **20**, 859—860).—Calculated free energy values for hydrocarbons are often based on unsatisfactory thermal data and are untrustworthy. Even when they are accurate, predictions relative to the products of reactions which are based on free energy alone are fallacious, as the reaction velocity is an important additional factor.

C. IRWIN.

Free energy of formation of fused alkali hydroxides. G. DEVOTO (Gazzetta, 1928, **58**, 450—457 ; cf. this vol., 135, 955).—The polarisation curves for the fused hydroxides of lithium, sodium, and potassium have been derived by the method previously described. Owing to decomposition the values for lithium hydroxide are untrustworthy, but from the measurements with fused sodium hydroxide and potassium hydroxide the free energies of formation of these compounds have been determined for temperatures between 400° and 700°.

F. G. TRYHORN.

Calculation of the fugacities of a solution. G. VAN LERBERGHE (Bull. Acad. roy. Belg., 1928, [v], **14**, 349—371).—Mathematical. The formula for the fugacities of a solution previously deduced (Compt. rend., 1925, **181**, 851) may be derived by a simpler method. Analogous formulæ applicable to special cases of dissolution are derived by the asymptotic method of Donder (A., 1925, ii, 790) and the application of these to the systems carbon disulphide–methylal, ethyl iodide–ethyl acetate, water–sulphuric acid are considered.

F. G. TRYHORN.

Heat capacity and entropy of cæsium alum from 18° to 300° Abs. Entropy of aluminium ion. Potential of the aluminium electrode from thermal data. W. M. LATIMER and B. S. GREENSFELDER (J. Amer. Chem. Soc., 1928, **50**, 2202—2213).—The heat capacity of cæsium alum measured between 18° and 300° Abs. gives the entropy at 298·1° Abs. as 163·85 g.-cal./1°. The f. p. of cæsium and rubidium alum solutions were determined between 0·0017 and 0·0124*M*. The f.-p. depressions of the two salts are identical linear functions of the concentration. From these results the activity coefficients of the alums are computed. The heat of dissolution of cæsium alum is $+13{,}560\pm25$ g.-cal./mol. at 298·1° Abs., and from these results the entropy of the aluminium ion in hypothetical one-molal solution is $-70·9$ g.-cal./1° per mol. at 298·1° Abs., giving $+1·69\pm0·01$ volts as the potential of the aluminium electrode.

S. K. TWEEDY.

Heat of combustion of benzoic acid in international joules. W. JAEGER and H. VON STEINWEHR (Z. physikal. Chem., 1928, **135**, 305—346).—The heat of combustion of benzoic acid has been redetermined using the same calorimeter as was used by Fischer and Wrede (*ibid.*, 1909, **69**, 218). The apparatus has been improved by the introduction of a stirring device underneath the bomb and an improved recorder for marking the commencement and end of the period of electrical heating used in standardising the calorimeter. The calculations involved in using a platinum thermometer to measure temperatures have been revised and an allowance has been made for the heat evolved by the iron wire used to start combustion. The applicability of Newton's law of cooling to the temperature rise of the calorimeter was tested and found valid. Benzoic acid of special purity from two sources was used. The mean result of seventeen experiments gave

26·437 kilojoules per g. at 19·3° as the heat of combustion of benzoic acid (cf. Fischer and Wrede, 26·449; Dickinson, 26·436). The mean of these three values, 26·441 kilojoules per g., together with the heat equivalent (1 g.-cal.=$4{\cdot}184_2$ joules at 15°), gives 6319·3 g.-cal. per g. as the heat of combustion of benzoic acid. W. E. DOWNEY.

Heat of dilution of solutions of low concentration. S. M. NAUDÉ (Z. physikal. Chem., 1928, **135**, 209).—Heats of dilution have been determined for the following: sucrose, chloral hydrate, glycine, carbamide, and mercuric cyanide; hydrochloric, nitric, sulphuric, salicylic, and benzoic acids; lithium and sodium chlorides and sodium nitrate. The results are in agreement with Nernst's theory (cf. this vol., 127, 368). R. A. MORTON.

Heat of dilution of salts at low concentrations. W. NERNST and W. ORTHMANN (Z. physikal. Chem., 1928, **135**, 199—208).—See A., 1927, 733. R. A. MORTON.

Strong electrolytes and the dependence of conductivity on *P.D.* G. JOOS (Physikal. Z., 1928, **29**, 570).—Polemical against Gyemant (this vol., 953). W. E. DOWNEY.

Transport number of the cation in aqueous solutions of nickel salicylate. F. E. JONES and C. R. BURY (J. Physical Chem., 1928, **32**, 1272—1275; cf. A., 1927, 315).—Transport numbers determined at 25° throughout the range 0·02—0·2 mol./1000 g. water (maximum solubility at 25°) in aqueous solutions of nickel salicylate decrease from 0·612 to 0·573, and indicate that the salt ionises for the most part in a normal manner. The anomalous decrease in transport number with increasing concentration indicates the presence of small amounts of a complex acid ion. L. S. THEOBALD.

Theoretical potential of alkaline-earth metals. G. DEVOTO (Z. Elektrochem., 1928, **34**, 326—327).—Polemical against Drossbach (this vol., 481). The results of Roth and Chall (*ibid.*, 593) are in close agreement with those of the author. L. F. GILBERT.

Normal potential of the iodine–iodide electrode. G. JONES and B. B. KAPLAN (J. Amer. Chem. Soc., 1928, **50**, 2066—2076).—The change in activity of the iodide ion with dilution is computed from the *E.M.F.* of the concentration cells Ag,AgI|$0{\cdot}1N$-KI|xN-KI|AgI,Ag. Reproducible results were obtained only when x exceeds 0·02. The activity coefficients, f, at 25° are given by the formula (cf. Scatchard, A., 1925, ii, 397): $\log f = 0{\cdot}125c - 0{\cdot}373\sqrt{c}$. The *E.M.F.* of the cell Pt,$I_2(s)$|$0{\cdot}01N$-KI|$0{\cdot}1N$-calomel electrode is −0·3374 volt at 25° and −0·3275 volt at 0°. The *E.M.F.* of the cells Pt|xN-KI+I_2(unsat.)|xN-KI+$I_2(s)$|Pt are recorded, where x=0·01, 0·02, 0·05, and 0·1, the low concentration of the unsaturated solution being determined by means of the equilibrator (this vol., 863). From the results the normal potential of the saturated iodine–iodide electrode, with the iodide ion at unit activity, against the normal calomel electrode is calculated to be −0·2544 volt at 25° and −0·2522 volt at 0°. The value against the normal hydrogen electrode is −0·5362 volt at 25°. S. K. TWEEDY.

Influence of movement of electrolyte on the steadiness of the potential of the oxygen electrode. H. V. TARTAR and V. E. WELLMAN (J. Physical Chem., 1928, **32**, 1171—1177).—A study of the influence of movement of the electrolyte on the potential of the oxygen electrode in acid, neutral, and alkaline solutions shows the potential to remain steady for a constant rate of flow of the electrolyte. Bright platinum electrodes gave values reproducible to within a few (3) millivolts with a carefully-controlled rate of flow, but heavily platinised electrodes show "drift" of potential and are affected to a greater extent by the rate of flow of the electrolyte. The apparatus used is described. The behaviour of the oxygen electrode is most easily interpreted by assuming the formation of a soluble substance, possibly hydrogen peroxide. L. S. THEOBALD.

Electrokinetic potential between the solid and liquid states of a single substance. F. FAIRBROTHER and F. WORMWELL (J.C.S., 1928, 1991—1997).—Observations on the contact potential between the solid and liquid forms of a substance have been made by a cataphoretic method in which the movement of the suspended solid in an electric field of 50—100 volts/cm. was measured. The solid is positively charged and the *P.D.* is in all cases less than that for glass in distilled water. The largest value is shown by ice in water, and no *P.D.* could be detected with benzene and other substances of low dielectric capacity. This apparent contradiction of Coehn's rule is discussed with reference to Errera's suggestion (this vol., 705) that the transition from liquid to solid involves an intermediate state in which the associated molecules have an electric moment greater than that of the ordinary molecules. J. GRANT.

Reduction potential and oxidation. L. RAPKINE (Compt. rend. Soc. Biol., 1927, **96**, 1280—1282; Chem. Zentr., 1928, i, 706).—In certain cellular oxidations the mobilisation of hydrogen and simultaneous activation of molecular oxygen must be postulated. A. A. ELDRIDGE.

Diffusion of a hydrogen potential or reduction potential through platinum and palladium. R. KÖHLER (Z. physikal. Chem., 1928, **135**, 369—382).—If a hydrogen potential is set up on the outer side of a platinum crucible of 0·05—0·10 mm. wall thickness, the effect slowly appears on the inner side of the crucible. The hydrogen potential may be set up by cathodic polarisation or by chromous chloride. For changes in the inner potential not exceeding 80 millivolts the time taken is such that the hydrogen must diffuse proportionately to the square of the thickness of the platinum. The diffusion through palladium obeys the law of diffusion. The diffusion effect of the reduction potential of twelve various reducing agents through thin palladium (0·02 mm.) has also been examined. It is found that the diffusion effect is greater the greater is the reduction potential of the substance used. The reduction potential depends, also, on the hydrogen absorption of the palladium. Continual use of a palladium plate enlarges the pores and thus gives different values for the rate of diffusion. Absorption and outgassing open up the metal structure. W. E. DOWNEY.

Extrapolation of *E.M.F.* measurements to unit ionic activity. D. I. HITCHCOCK (J. Amer. Chem. Soc., 1928, **50**, 2076—2079).—The *E.M.F.* of a cell such as $Ag,AgCl|HCl|H_2$, the mean activity of the ions being γ, is given by (1) $E-E_0-2k \log M-2k \log \gamma$, where M is the molality of the acid and $k=2{\cdot}3RT/nF$. According to the Debye–Hückel theory, (2) $-\log \gamma=0{\cdot}5\sqrt{M}-BM$. Combination of (1) and (2) gives $E+2k \log M-k\sqrt{M}=E'-E_0-2kBM$, which is a linear relation between E' and M and may be used for extrapolation. The method, which, if a spline is used, is in agreement with the complete theoretical equation of Hückel up to $0{\cdot}1M$, is applied to the above cell at 20°, 25°, and 30°, the respective values of E_0 being 0·2253, 0·2223, and 0·2193 volt. S. K. TWEEDY.

Antimony–antimony trioxide electrode and its use as a measure of acidity. E. J. ROBERTS and F. FENWICK (J. Amer. Chem. Soc., 1928, **50**, 2125—2147).—Cubic antimony trioxide undergoes transition to the orthorhombic variety at 570°±10°, the free energy change of the transformation being +1800±200 g.-cal./mol., and the free energy of formation of the cubic oxide −149,690 g.-cal./mol. at 25°. Antimony trioxide formed by the hydrolysis of the trichloride consists chiefly of orthorhombic crystals. The potential of the antimony–antimony trioxide electrode attains its maximum accuracy when unstable solid phases (*e.g.*, orthorhombic oxide) and dissolved oxygen are eliminated and when the equilibrium is approached from the alkaline side. Under these conditions, using cubic oxide, the potential is a linear function of the logarithm of the hydrogen-ion activity of the solution and has the value 0·1445±0·002 volt with respect to a hydrogen electrode in a solution of the same activity at 25°. Air need not be excluded if the electroaffinity, E_0, is fixed by means of two or more buffers in the desired range. The following concentrations must not be exceeded in the electrode: hydrochloric acid, $0{\cdot}16M$; phosphoric acid, $0{\cdot}15M$; sulphuric or nitric acid, $1M$; sodium hydroxide, $2M$. The electrode, because it is permanent, constant, and requires only little attention, is considered to be superior to the hydrogen electrode. The p_H values at 25° of certain buffer solutions were measured against the hydrogen electrode. Data from two sources lead to a calculated value of −0·3341 volt for the potential of the decinormal calomel electrode. S. K. TWEEDY.

***P.D.* measurements with a ferromagnetic compound of manganese and arsenic.** L. F. BATES (Phil. Mag., 1928, [vii], **6**, 593—597; cf. this vol., 468).—The *P.D.* between a hot electrode of the above alloy in contact with manganous ions against a similar, cold electrode is investigated as a function of the temperature difference. Pronounced changes occur as the substance passes through its magnetic critical temperature. S. K. TWEEDY.

Current density–potential measurements. A. DADIEU (Z. Elektrochem., 1928, **34**, 301—305).—Examples are given of the satisfactory determination of decomposition potentials in the electrolysis of solutions by commencing with high voltages and gradually diminishing them, where abnormal current–voltage curves would result on raising the voltage from zero (cf. Monatsh., 1926, **47**, 471). L. F. GILBERT.

Valency. X. Electrometric titration of Vernon's α- and β-dimethyltelluronium bases. F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 1997—2010; cf. this vol., 349).—The molecular conductivity of the α-base at 25° increases from 3 to 6 and that of the β-base from 31 to 36 for an increase in v from 32 to 512. In both cases saturation with carbon dioxide increases μ to about 40 (v=32), but the normal value is restored when a current of pure air is passed through the solutions. Conductivity-titration curves show breaks corresponding with the compound $[TeMe_2OH]Cl$, but afford no indication of a more basic compound or of the normal salt. In addition, titrations of the β-base with a glass electrode show a second inflexion at about 50% neutrality corresponding with the basic salt, $2TeMe_2O,HCl$, which has not been obtained in the free state, although the formation of Vernon's oxy- and dioxy-iodides is not indicated. The f.-p. data taken during progressive neutralisation confirm the conclusion that the free bases are only slightly dissociated in the solution, the i-factor in both cases being about 1·1, whilst the hydroxy-halides are dissociated almost completely. Details are given of the products deposited from solution during neutralisation by hydriodic acid. J. GRANT.

Cells [with unattackable electrodes] contradicting the second principle of thermodynamics. V. KARPEN (Compt. rend., 1928, **187**, 418—420; cf. this vol., 246).—The *E.M.F.* of a cell formed by a well-platinised platinum anode and an Acheson graphite cathode in air-free distilled water, or in a saturated solution of sodium hydroxide, depends on the temperature and varies in sense and magnitude according to the proportion of dissolved air. Since the electrodes are not likely to be attacked under these conditions, and since the heat of reaction calculated by the second law of thermodynamics from the *E.M.F.* of the cell is of an abnormal magnitude and varies abnormally with the temperature, such cells appear to contradict this law. J. GRANT.

Periodic passivity of chromium and chromium alloys, and the influence of temperature on passivity potentials. B. STRAUSS and J. HINNÜBER (Z. Elektrochem., 1928, **34**, 407—415).—An apparatus is described for the continuous registration of the potential at an electrode, and by means of it the potentials in dilute sulphuric acid, dilute hydrochloric acid, and mixtures of both, of chromium–iron alloys and chromium–nickel–iron alloys of varying composition which could be rendered passive, have been measured over several days. It is found that periodic phenomena occur, not only with chromium, but also with the alloys (cf. Adler, A., 1912, ii, 891). A necessary condition for the active–passive change is the presence of two phases which act as local elements. In one case the second element is iron carbide, separated out from the austenite present, and in the other case it is iron oxide. Theories of passivity are discussed, and it is pointed out that the assumption of an oxygen film as the cause of passivity explains

the fact that the change from active to passive metal and *vice versa* takes place continuously and without transition potential; if, on the other hand, the oxide skin theory is accepted, a definite transition potential should occur. A mechanism is suggested for the periodic phenomenon, based on the action of local elements and on the occurrence of a concentration polarisation. Investigation of the influence of change of temperature on passivity potentials shows that, under certain conditions, the normal effect of fall of potential with rising temperature may be masked, and the potential may even rise. This phenomenon is explained from the point of view of the oxygen-film theory. L. L. BIRCUMSHAW.

Detonation-wave in gaseous mixtures and the pre-detonation period. W. PAYMAN (Proc. Roy. Soc., 1928, A, **120**, 90—109).—Intense compression- or "shock-"waves may be sent through a gaseous mixture by detonating or rapidly burning a solid or gaseous explosive in contact with the mixture. By means of an adaptation of Töpler's "Schlieren" method, photographic records have now been obtained of the shape and appearance of the hitherto invisible shock-wave and of its speed of propagation, and these have been used to supplement and extend the information obtained by other workers using direct methods of photography only. The method (for full details see Payman and Robinson, B., 1926, 421; Payman and Shepherd, B., 1927, 30) has been applied to a study of the pre-detonation period, and in particular of the mode of inception of detonation in a gaseous mixture. The effect of the position of the point of ignition (an electric spark) on the initial movement of the flame in a closed tube has been examined, and an explanation advanced for the observed retardation of the flame, which suggests that it occurs simultaneously with the break-up of the flame front into two separate portions moving in opposite directions. The character of the compression-waves has previously been postulated from their effects on the flame. It is now shown that they are not due to the spark, as has been hitherto supposed. They are much more marked than the spark-wave, and travel at a speed much greater than that of sound in the gaseous medium through which they are passing. They appear to have their origin in the gases behind the flame front, *i.e.*, in gases in which the process of combustion has begun some time previously, and are probably due to renewed chemical activity behind the flame front. Direct evidence in favour of the theory of renewed chemical activity has been obtained by Ellis and Wheeler (A., 1927, 317). Under the experimental conditions and with the mixtures used, the detonation-wave also always appears to have its origin behind the flame front. Experiments to ascertain under what conditions the detonation-wave might be set up in advance of the flame gave negative results. Investigations have also been made of the influence of the compression-waves on the movements of the flame when restrictions are present before detonation is set up, on their mode of propagation during the suppression of detonation when the flame passes from a narrow into a wider tube, and on the effect of ignition by a fuse or detonator on the initial movement of the flame in electrolytic gas. L. L. BIRCUMSHAW.

Striated photographic records of explosion waves. II. Explanation of the striæ. C. CAMPBELL and A. C. FINCH (J.C.S., 1928, 2094—2106; cf. A., 1927, 833).—Since striæ of gradually increasing periods are obtained when conical explosion tubes are used, they cannot be accounted for by vibrations in the photographic apparatus. Longitudinal or transverse vibrations in the walls of the explosion tube are also eliminated as a cause of the phenomenon, because the periods of the striæ are the same for rubber and glass tubes and also for glass tubes embedded in concrete. Photographs of the flame taken (*a*) through two windows at right angles and (*b*) with the explosion tube pointing towards the camera show that the flame traverses a helical path. Further, photographs of the flame taken through a horizontal slit in a vertical tube indicate that a luminous tail of flame persists for an appreciable time and that this tail is also rotating. It is suggested that the striæ may be most satisfactorily explained by assuming that the gaseous mixture is itself in a state of rotation. F. J. WILKINS.

Combination of hydrogen and oxygen by electric discharges. R. D. RUSK (Physical Rev., 1928, [ii], **32**, 287—292).—When a mixture of hydrogen and oxygen (2 : 1 vols.) is ignited by an electric spark or hot wire at about 3 cm. pressure, the usual explosion becomes a more quiet combustion with visible flame; below this pressure combination occurs only by collision. Logarithmic decrease in pressure was obtained in equivalent volumes in the Geissler discharge for constant current, whilst excess of oxygen increased and excess of hydrogen decreased the rate of combination. The number of water molecules formed per pair of ions at the lower pressures is much less than unity, but increases with increasing pressure, and approximates to unity at a pressure such that the time between molecular collisions is of the order of magnitude of the life of an excited hydrogen atom. A. A. ELDRIDGE.

Decomposition of nitrogen pentoxide. I. Unimolecular reaction and its arrest at low pressures. G. SPRENGER (Z. physikal. Chem., 1928, **136**, 49—76).—Nitrogen pentoxide reacts almost instantaneously with nitric oxide and with nitrogen trioxide. The complete decomposition equation $2N_2O_5=O_2+4NO_2\rightleftharpoons 2N_2O_4$ is the result of a primary decomposition $N_2O_5=N_2O_3+O_2$ accompanied by the secondary reactions $N_2O_3+N_2O_5=4NO_2\rightleftharpoons 2N_2O_4$ and $NO+N_2O_5=3NO_2\rightleftharpoons 1{\cdot}5N_2O_4$. At pressures between 0·01 mm. and 0·05 mm. the reaction no longer follows its normal course: on allowing the pentoxide to pass from a small vessel at about 15 mm. pressure to a larger one at about 0·01 mm. pressure, the ordinary reaction commences with about the normal velocity, but is then arrested. The results obtained are discussed relatively to those of Hirst and Rideal. H. F. GILLBE.

Kinetics of nitrous acid. IV. Kinetics of nitrous acid formation from nitric acid and nitric oxide. E. ABEL, H. SCHMID, and S. BABAD (Z. physikal. Chem., 1928, **136**, 135—145).—The

velocity of the total reaction $HNO_3+2NO+H_2O \rightleftharpoons 3HNO_2$ is, if the back reaction be eliminated, independent of the partial pressure of nitric oxide, but proportional to the concentration of hydrogen and nitrate ions and of nitrous acid; the reaction is thus autocatalytic. The velocity diminishes as the ionic concentration increases. The retardation produced by sulphate ions is ascribed to the removal of hydrogen ions by the formation of HSO_4 ions. The rate of formation of nitrous acid is given by $k[HNO_2][H^{\cdot}][NO_3']$, where k has a value varying from 1·6 to 0·8 as the ionic concentration rises from zero to 1·1M, time being expressed in minutes. The mechanism of the reaction is given by $H^{\cdot}+NO_3'+HNO_2 \rightarrow N_2O_4+H_2O$, followed by $N_2O_4+2NO+2H_2O \rightarrow 4HNO_2$. H. F. GILLBE.

Transition of butyl bromide. G. DIENGER (Z. physikal. Chem., 1928, **136**, 93—134).—The velocity of the reaction *iso*butyl bromide $\rightleftharpoons$ *tert.*-butyl bromide has been determined at a number of temperatures between 178·5° and 240°. Michael's observation, viz., that having regard to the position of equilibrium the velocity of the reaction from right to left is much too small, is confirmed. In the temperature interval investigated there exists a range over which the reaction velocity is negligible, but is, however, attainable only from the *tert.*-butyl bromide side.
H. F. GILLBE.

Hydrolysis of sucrose by acids: hydrogen-ion concentration and hydrolysing power. H. COLIN and (MLLE.) A. CHAUDUN (Bull. Soc. chim., 1928, [iv], **43**, 721—725; cf. A., 1927, 115, 835).—Variations in the rates of inversion of sucrose by acid do not correspond with variations in the sugar, acid, or hydrogen-ion concentrations, or with the addition of neutral salts. If, therefore, the *E.M.F.* of a concentration cell is strictly proportional to the hydrogen-ion concentration of the solution, the reaction cannot be considered as unimolecular and due to hydrogen ions alone. J. GRANT.

Hydrolysis of *o*-benzoicsulphinide (saccharin) and of *o*-sulphonamidobenzoic acid. K. TAUFEL, C. WAGNER, and W. PREISS (Z. Elektrochem., 1928, **34**, 281—291; cf. A., 1926, 518).—The hydrolysis of *o*-benzoicsulphinide and of the intermediate product *o*-sulphonamidobenzoic acid in the subsequent conversion into ammonium hydrogen *o*-sulphobenzoate has now been studied quantitatively in detail. Ionisation constants for the above substances and velocity coefficients for the reactions concerned have been obtained. The results confirm the previous view that the sweetness of food products containing "saccharin" or its sodium salt is only slightly affected by heating at 100°. L. F. GILBERT.

Kinetics of the decomposition of calcium carbonate hexahydrate. B. TOPLEY and J. HUME (Proc. Roy. Soc., 1928, **A**, **120**, 211—221).—A quantitative study has been made of the endothermic reaction $CaCO_3,6H_2O=CaCO_3+6H_2O$ by means of dilatometric measurements. It has been previously found (A., 1927, 526) that the reaction is autocatalytic (the velocity passing through a maximum at about 50% decomposition) and that the autocatalysis is not eliminated by fine grinding of the crystals. The reaction rate is influenced by the inclusion in the hydrate of small quantities of foreign substances, and is also extremely sensitive to temperature. The mechanism of the change is discussed from the point of view of an "interface reaction," in which the only molecules (ions or ionic groups) which react are those in a layer immediately adjacent to molecules in the space lattice of the resultant solid phase. This assumption is considered to be fundamental for the explanation of the apparent autocatalysis observed. *A priori*, several possibilities are considered, but the following hypothesis is the only one in accordance with the sigmoid form of the decomposition curve obtained experimentally: when the frequency of nucleus (calcite) formation on the surface of a particle, and the rate of propagation of the change from a point where a nucleus has formed, are relatively such that the majority of the particles have at least one nucleus before more than a very small fraction of the total reaction has taken place, then the total area of the interface for all the particles will increase as the reaction proceeds, and pass through a maximum. The observed reaction rate is proportional to the area of this interface. It is shown that the increase in the velocity of the reaction is due to a true temperature effect, and not to an increase in the effective surface due to break-up of the crystals at the higher temperature. On the basis of the above views, an expression is obtained which gives a curve for the decomposition velocity which falls off less rapidly than the experimental curve. Reasons are suggested for this. A consequence of the view that the reaction spreads from a limited number of nuclei is that the rate da/dt should increase as the particle radius diminishes. This is shown to be the case. The temperature coefficient has been measured from 0° to 15°, and the empirical Arrhenius constant A calculated from $d \log_e k/dT=A/RT^2$. For crystals of hexahydrate prepared from solutions containing $Cu(NH_3)_4^{++}$, A was found to be 41,350, and from lime–sucrose solutions, it was 35,780. A kinetic mechanism is suggested which involves the vibration frequency of ions in the interface between the two solid phases, and the distribution of energy among the vibrating ions. L. L. BIRCUMSHAW.

Reaction between nitrogen pentoxide and ozone. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1928, **136**, 77—92).—The reaction between nitrogen pentoxide and ozone is bimolecular, and is probably a result of a series of chain reactions. In agreement with the work of Warburg and Leithauser, a new oxide of nitrogen, probably NO_3, is formed during the reaction. H. F. GILLBE.

Corrosion by acids and rusting of iron containing copper. S. S. STEINBERG.—See B., 1928, 674.

Principles of polymerisation. J. SCHEIBER (Chem. Umschau, 1928, **35**, 181—190).—Various examples of polymerisation (simple and complex) are considered in an endeavour to derive general principles of the mechanism. The presence of an unsaturated grouping is recognised as the activating factor in polymerisation, the degree of which depends on external conditions (temperature, catalysts, etc.) as well as on the state of aggregation. The effect on

polymerising power of substituent groups in the molecule is discussed and general rules for their action are derived. E. LEWKOWITSCH.

Acid and salt effects in catalysed reactions. XV. Catalytic activity of hydrochloric acid in the hydrolysis of ethyl acetate. H. M. DAWSON and W. LOWSON (J.C.S., 1928, 2146—2154; cf. Harned and Pfanstiel, A., 1922, ii, 255).—The catalytic effects produced by hydrochloric acid in the hydrolysis of ethyl acetate have been examined over a range of acid concentration of 0·0002—0·2*M*. The initial velocity was in all cases proportional to the concentration of the acid. The catalytic activity of the hydrogen ion would thus appear to be determined by its concentration and not by its thermodynamic activity. This result indicates that the primary reaction is one which is not affected by the ionic environment. It is suggested, therefore, that hydrolysis is preceded by the interaction of hydrogen ions with electrically neutral ethyl acetate molecules. F. J. WILKINS.

Acid and salt effects in catalysed reactions. XVI. Catalytic effects in the iodination of mesityl oxide. H. M. DAWSON and A. KEY (J.C.S., 1928, 2154—2165).—The reaction between mesityl oxide and iodine in dilute aqueous solution is similar to, but more rapid than, the reaction between acetone and iodine. It is catalysed by acids, and for a given concentration of hydrogen ions its velocity is proportional to the concentration of mesityl oxide and independent of the concentration of iodine. The rate of disappearance of iodine is therefore determined by the velocity of some preliminary transformation, probably keto-enol in character, of the mesityl oxide. The catalytic coefficients for H^+, OH^-, H_2O, $CH_3{\cdot}CO_2H$, $CH_3{\cdot}CO_2^-$, $H_2PO_4^-$, and $HPO_4^=$ have been determined. The relative values of these coefficients for the mesityl oxide reaction differ very considerably from their relative values for the acetone reaction. The course of the autocatalysed reaction can be explained in terms of the joint catalytic action of the hydrogen ion and the water molecule.

Pure mesityl oxide has m. p. —41·5°. F. J. WILKINS.

Acidic and basic catalysis of acetylation reactions. J. B. CONANT and G. M. BRAMMANN (J. Amer. Chem. Soc., 1928, 50, 2305—2311).—Measurements were made of the rate of acetylation of β-naphthol by acetic anhydride in glacial acetic acid solutions buffered to definite hydrogen-ion activities. The rate varied nearly a million-fold, and was dependent on the acidity or basicity of the medium. The maximum rate was at $p_H^{(HOAc)}$ —4·5, the minimum at about $p_H^{(HOAc)}$ +2·0; over this range the rate was apparently proportional to hydrogen-ion activity. Between +2·0 and +5·0 the rate increased again, showing that the process was subject to both acid and basic catalysis. R. K. CALLOW.

Definition of "area" in the case of contact catalysts. F. H. CONSTABLE (Nature, 1928, 122, 399—400).—The maximum area of a contact catalyst for physical chemical purposes is the area of the envelope of the unimolecular film of hydrogen atoms closely packed, all in contact with each other and with the catalyst surface, which completely covers it. If the adsorbed molecules were large, the area of a very irregular surface measured by the number of adsorbed molecules would appear to decrease. Bowden and Rideal's method (this vol. 1088) would probably give smaller results than correspond with this definition. A. A. ELDRIDGE.

Decomposition of hydrogen peroxide on glass powder in the presence of salts. (MISS) W. M. WRIGHT (Z. Elektrochem., 1928, 34, 298—300).—The rate of decomposition of aqueous hydrogen peroxide in the presence of glass powder is increased when various salts are added, by amounts greater than those due to the salts alone, thus confirming Elissafov's work with glass-wool (A., 1915, ii, 681). Mercurous chloride acts exceptionally, its addition retarding the rate of decomposition. The rate of decomposition in presence of glass powder and silver nitrate has been particularly carefully studied and is proportional to the amount of adsorbed silver. The adsorption, on glass powder, of silver ions follows the isotherm $a=c^{1/n}$. L. F. GILBERT.

Autocatalysis in the formation and decomposition of cupric oxide. J. OKAYAMA (Z. Elektrochem., 1928, 34, 294—298).—The reduction of cupric oxide to copper by hydrogen, and the oxidation, by oxygen, of copper to cupric oxide are autocatalytic reactions, the first result confirming that of Pease and Taylor (A., 1922, ii, 148). L. F. GILBERT.

Thermal decomposition of ammonia on tungsten, molybdenum, and nickel. I. C. H. KUNSMAN (J. Amer. Chem. Soc., 1928, 50, 2100—2113).—The thermal decomposition of ammonia on tungsten, molybdenum, and nickel filaments was investigated by observing the accompanying pressure increase. The reaction appears to be of zero order on the former two filaments (cf. Hinshelwood and Burk, A., 1925, ii, 691), but at sufficiently reduced pressure the reaction tends to become unimolecular. The reaction rate is lowered by the presence of nitrogen or hydrogen (contrary, in the case of molybdenum, to Burk's results; A., 1927, 426), but this retardation decreases and disappears at higher temperatures. Thoriated tungsten filaments showed no increase in activity over filaments of pure tungsten. At the lower temperatures (600—900°) the heat of activation E is approximately constant at 45,000 g.-cal. for the three metals; at the higher temperatures the decrease in E is greatest for nickel and least for tungsten. The relative catalytic activity of the metals seems to depend primarily on the catalyst surface, and therefore on the constant A in the formula $k=Ae^{-E/RT}$. S. K. TWEEDY.

Catalytic oxidation of ammonia. VII. L. ANDRUSSOV.—See B., 1928, 669.

Catalytic oxidation of ammonia. F. RASCHIG.—See B., 1928, 669.

Electrolytic preparation of cuprous oxide. E. ABEL and O. REDLICH (Z. Elektrochem., 1928, 34, 323—326).—Details are given for the preparation of cuprous oxide, free from metallic copper and cupric

oxide, by the electrolysis, with copper electrodes, of slightly alkaline solutions of sodium chloride.

L. F. GILBERT.

[Controlled] electrolytic oxidation of organic substances. C. MARIE and G. LEJEUNE (Compt. rend., 1928, **187**, 343—344).—The addition of anodic depolarising agents (oxidisable organic substances, *e.g.*, alcohols) lowers the potential necessary for the electrolysis of pure solutions of acids and bases, the fall being characteristic for the substance added for a particular anode. In order to limit the oxidation of the alcohol and so obtain the aldehyde, a low anodic potential and a high alcohol concentration are used with intermittent current to enable reaction to take place between the alcohol and the unstable oxide formed on the platinum anode. If these conditions are not maintained the aldehyde is further oxidised to the acid.

J. GRANT.

Photochemical reactions promoted by intermittent monochromatic light. M. PADOA and N. VITA (Gazzetta, 1928, **58**, 461—472; cf. A., 1927, 528).—Comparison has been made of the yields of the reaction $2FeI_2+I_2=2FeI_3$ when illuminated by continuous and intermittent light, respectively. In general the yield was increased by the use of intermittent light, but the augmentation depended both on the wave-length of the light and on the frequency of interruption of the illumination. The wave-lengths used were 670·8, 589·6, 587, 535, and 460·7 μμ, and the illumination could be interrupted up to a maximum of 560 times per second. With light of wave-length 460·7 μμ a maximum ratio of the yields in continuous and intermittent light of about 2·0 was obtained. This maximum occurred periodically as the frequency of interruption was increased, the maxima appearing irregularly at interruption frequencies of 32, 98, 138, 157, 202, 253, 270, 318, 357, 390, 450, and 513 per second. Similar results were obtained with green light, except that the yield ratio was lower (about 1·70) and the maxima (at frequencies 22, 259, and 532) were fewer in number. The yield with this light was unaltered except in the neighbourhood of these maxima. With yellow light the maximum yield ratio was 1·62 at an interruption frequency of 311. Except within the limits 20—40, 260—370 interruptions per second the yield was unaltered by intermittent illumination with this light. Intermittent red light gave a maximum yield ratio 1·37 with an interruption frequency 472. These results are discussed from a quantum point of view and it is suggested that the periodic maxima are due to the formation of active molecules which are the seats of adiabatic transformations, and that the life of these molecules is greater the greater is their energy level.

F. G. TRYHORN.

Influence of light on the colour of ferric chloride solutions. K. S. RITCHIE (J. Physical Chem., 1928, **32**, 1269—1271).—Exposure to sunlight or other sources of intense light of hydrochloric acid solutions of ferric chloride results in an increase in intensity of the colour of the solution; on removal of the light the solutions slowly return to their initial condition. The fraction of incident light transmitted during a given exposure reaches a maximum near the commencement of the yellow region of the spectrum and falls rapidly to the green. Increased light absorption also results from heating a solution of ferric chloride.

L. S. THEOBALD.

Photo-oxidation of organic compounds by dichromates. J. PLOTNIKOV [with G. DEUTSCH, B. KUNST, M. PAVLIČEK, D. VRANJICAN, D. BARBETTI, and N. MUIC] (Chem.-Ztg., 1928, **52**, 669—671).—The action of sunlight on solutions of potassium dichromate containing various organic substances has been studied. No marked reaction is observed with ordinary charcoal, even after 3 months' irradiation, nor do salts of manganese, cobalt, copper, uranyl, or iron exert any catalytic influence. Colloidal carbon reacts vigorously, with the formation of a voluminous precipitate. Solutions containing hydrogen, methane, and coal gas become somewhat cloudy after irradiation, whilst ethylene and acetylene react rapidly. Methyl alcohol yields formaldehyde and a copious precipitate of chromic hydroxide; no formic acid is formed, although the reaction velocity increases after a certain time. Amyl alcohol yields an aldehyde and a brown precipitate of a chromium chromate, *n*-propyl alcohol yields propaldehyde and traces of propionic acid, whilst from *iso*propyl alcohol acetone, acetic acid, and formic acid are obtained. Acetone is oxidised to acetic and formic acids, with traces of the corresponding aldehydes. A solution of potassium dichromate in ethylene glycol rapidly becomes strongly alkaline and deep green in colour, glycollaldehyde and glyoxal being produced; under the same conditions glyceric acid and aldehyde and dihydroxyacetone are produced from glycerol solutions. Triphenylmethane is unaltered and benzene remains almost unchanged even in presence of ferric chloride, but toluene yields a variety of products. Phenol forms benzoquinone and a mixture of polyhydric phenols. *o*- and *m*-Xylenes yield tolualdehydes and acids, whilst from *p*-xylene some formic acid is produced. Quinol forms primarily benzoquinone, but phthalic acid also has been isolated from the reaction products. Resorcinol and pyrocatechol yield trihydric phenols, benzoquinone, and other similar compounds. A solution containing *o*-cresol decomposes with evolution of carbon dioxide and separates into two layers, of which the lower contains unchanged cresol, chromic hydroxide, and a tarry substance, and the upper benzoic and oxalic acids. Naphthalene and α-naphthol are unchanged after 10 months' illumination. The behaviour of a number of aniline dyes is described: in several cases fluorescent solutions are obtained. Aniline is rapidly converted into aniline-black, and *p*-aminophenol into benzoquinone and ammonia. Results with ψ-cumene indicate that the possibility of terpene formation is dependent on a symmetrical molecular structure. Dihydroxyanthraquinone breaks down into benzoquinone and carbon dioxide. Mixtures of *iso*pulegol and ammonium dichromate in various proportions yield on irradiation in aqueous or alcoholic solution only about 1% of *iso*pulegone, whereas *iso*eugenol undergoes extensive oxidation. The oxidation of *n*-octyl alcohol, which is catalysed by uranyl nitrate, yields

only about 5% of aldehyde as a result of the absorption of the active radiation by a precipitate which forms on the walls of the vessel very soon after the commencement of the reaction. Similar conditions hold for the oxidation of *iso*safrole, but in presence of uranyl nitrate a yield of about 50% is obtained.

H. F. GILLBE.

Oxidation of carbohydrates, fats, and nitrogenous products by air in presence of sunlight. C. C. PALIT and N. R. DHAR (J. Physical Chem., 1928, **32**, 1263—1268; cf. A., 1925, ii, 884).—The passage of air in presence of tropical sunlight through solutions of the following substances is accompanied by oxidation which increases with an increase in intensity of the light: galactose, arabinose, sucrose, dextrose, lævulose, lactose, maltose, starch, glycogen, carbamide, glycine, α-alanine, hippuric acid, sodium urate, potassium stearate, palmitate, oleate, and oxalate. Zinc oxide is an effective photo-sensitiser in all these cases. Solutions of sodium nitrite and arsenite, and of arsenious acid, were not oxidised by this treatment. The efficacy of sunlight and other artificial lights in the treatment of disease is considered to be due to the increased metabolism which results from the activation of the cells of the body by absorption of the light.

L. S. THEOBALD.

Action of light on diazo-derivatives. A. SEYEWETZ and D. MOUNIER (Bull. Soc. chim., 1928, [iv], **43**, 827—838).—See this vol., 493.

New photographic phenomenon. F. WEIGERT (Naturwiss., 1928, **16**, 613—614).—When a silver chloride-gelatin plate is exposed to plane polarised light and is physically developed after fixing, the silver which separates is doubly refracting. The optic axis of the new anisotropic system is parallel to the electric vector of the polarised light. An experiment is described which shows that the anisotropic latent image is also latent to a sensitive polarimeter.

A. J. MEE.

Optical sensitisation of silver iodide. K. BAUKLOH.—See B., 1928, 655.

Herschel effect by exposure to short wavelengths. LÜPPO-CRAMER.—See B., 1928, 692.

Sterry effect with silver chloride. LÜPPO-CRAMER.—See B., 1928, 692.

Condensible gas modifications formed under the influence of electrodeless discharges. J. TAYLOR (Nature, 1928, **122**, 347).—The condensible product obtained in a liquid air trap when hydrogen is subjected to an electrodeless discharge is shown to give a spectrogram identical with that of water at low pressure; carbon dioxide bands were also in evidence. With oxygen a condensible product yielding a spectrogram similar to that obtained from a discharge in carbon dioxide is formed. The quantity of gas disappearing is proportional to the quantity of electricity that has traversed the walls of the containing vessel; the disappearance must be due to chemical interaction of the gaseous ions with the electrolytic products and ions of the glass. Thus, from the simplest point of view, for every two electronic charges transferred across the glass two atoms of sodium are liberated and the SiO_3 radical breaks down into SiO_2+O, the latter atom then uniting with a hydrogen molecule. The glass is, however, a complex electrolytic solution containing carbon compounds and probably peroxides.

A. A. ELDRIDGE.

Lithium sulphite and some derivatives. J. A. N. FRIEND and D. W. POUNDER (J.C.S., 1928, 2245—2248; cf. Rohrig, A., 1888, 649).—Anhydrous *lithium sulphite*, $LiSO_3$, has been isolated and the existence of the monohydrate has been confirmed. No evidence of the dihydrate described by Rohrig has been obtained. Although all attempts to isolate lithium hydrogen sulphite were unsuccessful, its derivatives with acetone, acetaldehyde, and benzaldehyde were prepared.

F. J. WILKINS.

Interaction of cuprous chloride and chromates of potassium in sodium chloride solution. H. J. P. VENN and V. EDGE (J.C.S., 1928, 2142—2146; cf. Rosenfeld, A., 1879, 693).—When cuprous chloride, dissolved in a concentrated solution of sodium chloride, is mixed in the cold with a solution of potassium chromate or dichromate, precipitates are formed which vary in colour and composition according to the manner of mixing. The precipitates have been analysed, and equations involving basic copper salts have been proposed, according to which the formation of these basic salts is ascribed to secondary reactions. A new *basic copper chromate*, $3CuO,2CuCrO_4,4H_2O$, has been identified.

F. J. WILKINS.

Effect of alkalinity on basic cupric sulphates. O. A. NELSON (J. Physical Chem., 1928, **32**, 1185—1190).—The products obtained by adding sodium hydroxide solution to copper sulphate at various values of p_H have been investigated. The ratio Cu/SO_3 in the products varies from 3·40 to 20·73 over the range of p_H 5·3—9·4 and a smooth curve results from plotting the values obtained. The existence of the many basic cupric sulphates previously reported is thus not supported; only one compound of the formula $7CuO,2SO_3$ is indicated. The composition of the products obtained by laboratory methods depends on the method of preparation and on the ratio of the reacting substances. The case of copper sulphate is analogous to that of aluminium sulphate (Miller, A., 1924, ii, 48).

L. S. THEOBALD.

Basic magnesium carbonate. T. NISHIMURA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 838—872).—Normal magnesium carbonate, $MgCO_3,3H_2O$, loses carbon dioxide rapidly on exposure to air, but begins to absorb it again after some time. It is hydrolysed by water to $Mg(OH)_2,0{\cdot}82CO_2,nH_2O$. If magnesium hydroxide is suspended in water and air passed through, $Mg(OH)_2,0{\cdot}74CO_2,mH_2O$ is produced. These two substances are stable when dry.

C. W. GIBBY.

Calcium nitride. P. DUTOIT and A. SCHNORF (Compt. rend., 1928, **187**, 300—302).—The nitridation of calcium is autocatalytic and is most rapid when the calcium is finely divided, *e.g.*, is prepared by the complete decomposition of calcium hexammine (formed in a solution of calcium in liquid ammonia)

at a low temperature and pressure. Oxidising agents render the calcium passive, but reducing agents act in such cases as catalysts which suppress the passivity, whilst the alkali metals and moisture do not affect the reaction, the speed of which rises to a maximum at 450°, falls to zero at 600°, and increases again beyond the m. p. of calcium. Except at low temperatures, when there is a deficit of 2—3%, the amount of nitrogen fixed corresponds with the formula Ca_3N_2, and the pressure of nitrogen evolved on re-heating is highest if the original nitride is prepared at a low temperature, if the re-heating is rapid, and if the time between the two operations is short. The nitride may be black, bluish-black, reddish-brown, green, or yellow, according as it is prepared at 350°, 350—600°, 600—850°, 850—1100°, or above 1100°, respectively, and each type has a particular dissociation vapour pressure, the dissociation of the yellow variety alone being reversible. The black nitride is pyrophoric. These phenomena may be explained by the assumption that the unstable combination CaN is formed at low temperatures and then decomposes irreversibly. J. GRANT.

Hydrated tricalcium aluminate. A. TRAVERS and SEHNOUTKA (Compt. rend., 1928, **187**, 381—382).—The salt, $Al_2O_3,3CaO,21H_2O$, is prepared in well-formed needles by the addition of 1000 c.c. of $M/30$-potassium aluminate hydrate ($KAlO_2,3H_2O$) solution to 1100 c.c. of a mixture of 1000 c.c. of $M/47$-calcium nitrate solution and 100 c.c. of saturated lime water. The p_H value must fall between 11·55 and 11·62 in order to avoid the formation of a microcrystalline variety of alumina, which, however, is distinguished from the aluminate by its insolubility in 0·1N-hydrochloric acid. J. GRANT.

Electrolytic removal of iron from aluminium salts. L. WASILEWSKI and S. MANTEL.—See B., 1928, 669.

Aluminium arsenide. G. NATTA and L. PASSERINI (Gazzetta, 1928, **58**, 458—460).—Pure aluminium arsenide (d 3·60, m. p. 1200°) may be prepared by heating together the elements to about 800°. X-Ray analysis, by the powder method, of the microcrystalline product indicates crystals of the monometric type characteristic of blendes, with a unit cell of edge 5·62 Å., containing four molecules of AlAs. The structure is non-ionic, and the density calculated from the crystallographic data is 3·81. F. G. TRYHORN.

Reactions in the evolution flask. S. KITASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 832—837).—An investigation of the extent to which sulphur contained in iron is converted into hydrogen sulphide by hydrochloric acid. Free sulphur is attacked by hydrochloric acid only in presence of a large quantity of iron, when hydrogen sulphide is produced. Copper sulphide is attacked in the cold by 4—4·5N-acid, and by 0·3—0·35N-boiling acid, with evolution of hydrogen sulphide. Sulphates (copper, iron, manganese) are not attacked by concentrated hydrochloric acid. C. W. GIBBY.

Molybdenum-blue, its properties and composition. L. A. MUNRO.—See B., 1928, 640.

Deniges' phospho-cœruleomolybdenum compound. A. VERDA (Pharm. Acta Helv., 1928, **3**, 4—9; Chem. Zentr., 1928, i, 1641).—Deniges' phospho-cœruleomolybdenum compound is not always obtained on reduction of molybdic acid in presence of phosphoric acid, but only when aluminium or tin is employed. The compound is soluble in ether. A. A. ELDRIDGE.

Uranyl sulphate. A. COLANI (Bull. Soc. chim., 1928, [iv], **43**, 754—762; cf. A., 1927, 830).—The solubility of uranyl sulphate in mixtures of water and sulphuric acid, and the equilibria produced between it and the alkali sulphates, have been studied at 25°, using the method of residues. This avoids errors due to supersaturation of the solutions with uranyl sulphate, and to the difficulty in removing the crystals of the solid phases in the pure state. The *double sulphates*, $(NH_4)_2(UO_2)_2(SO_4)_3,5H_2O$, $K_2(UO_2)_2(SO_4)_3,5H_2O$, and $Na_4(UO_2)(SO_4)_3,3H_2O$ are recognised for the first time, the solubility curve obtained for sodium sulphate differing in shape and in the nature of the solid phases from those for ammonium and potassium sulphates, although all the compounds obtained behaved like true double salts. A correspondence exists between the combination of uranyl sulphate with sulphuric acid and with the alkali sulphates indicating the existence of the compound $UO_2SO_4,2H_2SO_4,xH_2O$, stable at 100° (cf. Meyer and Kasper, A., 1926, 925). J. GRANT.

Hydrofluorides of organic bases and a study of hydrofluoric acid. J. F. T. BERLINER and R. M. HANN (J. Physical Chem., 1928, **32**, 1142—1162).—The products obtained by the addition of an excess of hydrofluoric acid (48%) to each of 25 organic amines have been investigated. In most cases, they crystallise well and, excepting the cases of metanilic and sulphanilic acids and o-toluidine in which decomposition occurs, they sublime unchanged when heated. Characteristic m. p. were obtained for the hydrofluorides of m-nitroaniline 207—209°, p-nitroaniline 173—174°, anthranilic acid 217—218°, and ethylaniline 170—171°. Analysis indicated the derivatives to be of the type Base,4HF. They are soluble in and are hydrolysed by water to a certain extent. Titration with sodium hydroxide and indicators accounted for only 0·75 of the hydrofluoric acid, and electrometric titrations demonstrated that one of the four molecules of acid is distinct in the nature of its reactions and union to the base, whilst the remaining molecules are identical in this respect. An explanation is advanced and discussed in relation to the properties of hydrofluoric acid and its inorganic compounds. An electronic structure which explains the formation of compounds of the type Base,HF,3HF is suggested, and previous work in this field is discussed. L. S. THEOBALD.

Action of nitrogen on manganese. G. VALENSI (Compt. rend., 1928, **187**, 376—378).—The numerous formulæ proposed for manganese nitride are explained by the fact that pyrophoric manganese, obtained from the amalgam by distillation, adsorbs pure nitrogen at 760 mm. pressure in quantities which are almost a linear function of the temperature. The dissociation isotherms of the product richest in nitrogen

are analogous to those for chromium (this vol., 956) and probably represent solutions of a nitride which always contains more nitrogen than that required by the formula Mn_3N_2. J. GRANT.

Composition and properties of ferric sulphide. F. FEIGL and E. BACKER (Z. anal. Chem., 1928, 74, 393—398; cf. A., 1927, 1042).—When the washed precipitate of empirical composition Fe_2S_3, formed by precipitation of a tartrate-containing solution of ferric salt with ammonium sulphide, reacts in neutral solution with mercuric and cadmium salts, it behaves as ferrous and ferric sulphide, respectively. This suggests that the substance is a mixture of the valency isomerides S:Fe·S·Fe:S and FeS,FeS_2. The dependence of the composition of the precipitated sulphide on the conditions of precipitation has been worked out by Krepelka and Podrouzek (A., 1925, ii, 703). These factors are also valid for the mercaptides of iron. Solutions of ferric salts give ferrous mercaptide with ethyl mercaptan. When, however, the concentration of ferric ion is depressed by addition of tartrate and such a solution is run slowly into an alcoholic solution of ethyl mercaptan, *ferric ethyl mercaptide* results. When a solution of ferric chloride is added to a solution of barium sulphide, or when freshly-precipitated ferric sulphide is treated with a solution of barium sulphide, a substance approximating to the composition $BaFe_2S_4$ is obtained (cf. Malfatti, A., 1909, ii, 581). The compound reacts with mercuric salts as the original ferric sulphide. It is very unstable and is decomposed by mere washing with water. The compounds described by Malfatti are probably mixed sulphides rather than thioferrites. When moist ferric hydroxide is treated with ammonium sulphide the sulphide formed has the composition Fe_2S_3, whilst that obtained by precipitation from a solution of ferric salt containing tartrate has the initial composition $Fe_2S_3,(NH_4)_2S$.

J. S. CARTER.

Iron carbonyl and carbonyl iron. A. MITTASCH. —See B., 1928, 675.

Nature of Prussian-blue. D. DAVIDSON and L. A. WELO (J. Physical Chem., 1928, 32, 1191—1196).—The magnetic susceptibilities of soluble and insoluble Prussian-blue have been measured at −70°, 2·1°, and the ordinary temperature. The formulæ $KFe[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$ for soluble and insoluble Prussian-blue, respectively, lead to values of the Curie constants 4·05 and 3·92, and of the magneton numbers 28·3 and 27·8, respectively, all of which are within the limits obtained for ferric ions by previous workers. Formulations as polynuclear compounds (cf. Reihlen and Zimmermann, A., 1927, 233) do not satisfy the magnetic data. Conductivity measurements on the closely-related ferric ferricyanide support this evidence against the existence of a complex polynuclear ion in the two forms of Prussian-blue. Magnetic data on hydroferrocyanic acid and the ferrocyanides of sodium, potassium, and calcium are also given.

L. S. THEOBALD.

Sampling granular material. B. BAULE and A. BENEDETTI-PICHLER (Z. anal. Chem., 1928, 74, 442—456).—Theoretical and mathematical. From the theory of probability formulæ are derived from which the errors in sampling, the necessary degree of fineness, and the minimum weight of sample at any definite degree of fineness can be calculated at any stage of the process. A. R. POWELL.

Method of evaluation of analyses. I. O. LIESCHE.—See B., 1928, 657.

Radiometric microanalysis. V. R. EHRENBERG (Biochem. Z., 1928, 197, 467—475; cf. A., 1926, 328, 929; this vol., 383).—Since in most cases the precipitates obtained are neither further treated nor weighed, the reaction product may be added before precipitation in the solid form. Immediate and complete precipitation of the smallest amounts of the substance to be determined is thus obtained. The method involving the precipitation of lead as chromate, as described for nitrogen determination, can be used for the determination of many other elements. The delicacy of the method has been greatly increased and the time for analysis much shortened by the use of an electrometer fifty times as sensitive as that previously employed. Iron is determined by the procedure given for calcium, chromate precipitation being used. Potassium may be determined by the cobaltinitrite method, or the potassium permanganate, which is used for the radiometric analysis, may be decomposed with excess of oxalate and the excess of oxalate precipitated by lead or calcium. Sørensen's method for the titration of formaldehyde (cf. A., 1910, ii, 556) may be adapted for radiometric analysis. Carbon may be determined in the wet way and the process is also applicable to the determination of this element in elementary analysis. W. MCCARTNEY.

Destruction of organic matter in toxicological examinations. P. E. HEEDERIK (Pharm. Weekblad, 1928, 65, 861—879).—The methods proposed and in general use are described and discussed. Destruction is incomplete in the methods of Magnin and Stettbacher and of Fresenius and von Babo, but is complete in those of Kerbosch and of Wagenaar. A modified apparatus is suggested for the Kerbosch method; addition of potassium permanganate and use of increased quantities of sulphuric acid have no appreciable effect. In removing excess of nitric acid, an air-bath is recommended. S. I. LEVY.

Volumetric micro-analysis and centrifugovolumetry. R. F. LE GUYON (Ann. Chim., 1928, [x], 10, 50—112).—A more detailed account of work already published (A., 1925, ii, 1202; 1926, 927; 1927, 223, 372, 537; this vol., 36, 860).

H. BURTON.

Analysis by sedimentation. O. ARRHENIUS and H. RIEHM (Medd. K. Vetenskapsakad. Nobel-Inst., 1927, 6, No. 14).—Methods are described for the rapid analysis of small quantities of sulphate, calcium, magnesium, phosphate, and potassium ions by precipitation, centrifuging, and measurement of the volume of the precipitate. The smallest amount which can be determined in the case of phosphate is 0·1 mg., and in the case of sulphate 4 mg. For the determination of sulphate the solution must be between $N/13$ and $N/20$ and for calcium between

$N/200$ and $N/450$. For the other three ions, all concentrations can be used. W. E. DOWNEY.

Indicating equipment for industrial p_H measurements. H. C. PARKER.—See B., 1928, 627.

Use of the quinhydrone electrode in electrometric titrations. II. A. J. RABINOVITSCH and V. A. KARGIN (Z. Elektrochem., 1928, **34**, 311—316; cf. A., 1927, 221).—Discrepancies between p_H values as obtained from quinhydrone and hydrogen electrode measurements, respectively, are due to the effect of atmospheric carbon dioxide, as are the two maxima observed by MacInnes (this vol., 36) in the electrometric titration of acids, using the quinhydrone electrode. The agreement of p_H values obtained by Kolthoff and Bosch (A., 1927, 533) with the different electrodes in buffered solutions, in apparent contradiction to the authors' results, is ascribed to the fact that the solutions of Kolthoff and Bosch were more strongly buffered. L. F. GILBERT.

Determination of water in combustible materials by means of magnesium methyl iodide. A. TAUBMANN.—See B., 1928, 629.

Determination of water in bleaching powder, jelly, etc. T. SOMIYA.—See B., 1928, 640.

Micro-analysis. L. BERMEJO Y VIDA (Chim. et Ind., 1928, **20**, 221—222).—Determinations of the effects of time and temperature on Pregl's micro-Carius method show that the ease of the removal of halogen elements from an organic molecule is inversely proportional to their chemical activities, higher temperatures and longer times being required for aromatic halides and particularly for nuclear derivatives. Dihalogen derivatives are more readily resolved when the halogens are different than when they are the same, unless the halogens are attached to the same carbon atom, and poly-derivatives higher than tetrahalogen derivatives are removed with progressive facility. Removal is assisted by the presence of a nitro-group. Seasonal variations (in Madrid) in the weights of absorption tubes used for micro-combustions are avoided by the use of U-tubes with capillary ends. Sulphur compounds react more easily in the presence of a high proportion of lead chromate, and for cyanides, ferrocyanides, etc. traces of nickel or iron oxides should be added in addition. The volumetric method is preferable for the micro-determination of sulphur. J. GRANT.

Apparatus for micro-determination of dissolved oxygen [in water]. T. G. THOMPSON and A. C. MILLER.—See B., 1928, 656.

Determination of oxygen in water. F. LIEBERT and W. M. DEERNS.—See B., 1928, 656.

Micro-analytical determination of sulphur in organic compounds by titration. B. KUBOTA and S. HANAI (Bull. Chem. Soc. Japan, 1928, **3**, 168—172).—The sulphur compound is volatilised from a platinum boat in a stream of hydrogen and the vapours are passed over heated, freshly-reduced nickel. The whole of the sulphur is retained as nickel sulphide. If the compound is not volatile, *e.g.*, sulphonates, the material in the boat is covered with reduced nickel. The nickel is dissolved in acid and the evolved hydrogen sulphide absorbed in an ammoniacal solution of cadmium chloride. Cadmium sulphide is determined iodometrically. J. S. CARTER.

Detection of sulphide and thiosulphate. F. FEIGL (Z. anal. Chem., 1928, **74**, 369—376).—No reaction occurs when solutions of iodine and sodium azide are mixed, but in presence of sulphide or thiosulphate vigorous evolution of nitrogen occurs. Although the reaction is represented stoicheiometrically by the equation $2NaN_3+I_2=2NaI+3N_2$, it appears that a co-ordinative linking between iodine and sulphur is necessary before the reaction can proceed. Neither elementary sulphur nor, with the exception of thiocyanate, other sulphur compounds give this effect. The induced reaction is given by insoluble and naturally-occurring sulphides. Since arsenides, selenides, antimonides, or tellurides do not give the effect, the presence of sulphide in minerals etc. may be detected by adding the finely-powdered substance to a solution containing azide and iodine. When the substance becomes wetted, vigorous evolution of nitrogen occurs if sulphide is present. Reaction in presence of copper sulphide is rather slow. Minute quantities of thiosulphate or sulphide may be detected by this method, either by microscopical or direct observation. The presence of 1 part of sulphide in 1000 parts of sulphate may readily be detected using only 0·05 g. of material. The azide–iodine reaction is more sensitive than the lead acetate, nitroprusside, or methylene-blue method for the detection of hydrogen sulphide in natural waters. Thiosulphate may be detected at a dilution 1 in 6×10^6.

Using the above reaction it has been shown that the product obtained by fusing selenium with sulphur is a true sulphide and not a mechanical mixture. J. S. CARTER.

Application of the catalytic effect of carbon disulphide to the iodometric determination of azides and to the detection of carbon disulphide. F. FEIGL and E. CHARGAFF (Z. anal. Chem., 1928, **74**, 376—380).—The azide–iodine reaction (preceding abstract) occurs quantitatively and with great rapidity in presence of carbon disulphide, especially when alcohol or acetone is also present. The reaction scheme is apparently: $2NaN_3+2CS_2=2CS(NaS)N_3$; $2CS(NaS)N_3+I_2=2NaI+N_3{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}N_3$; $N_3{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}N_3=2CS_2+3N_2$.

The presence of carbon disulphide may be detected by adding 1—2 c.c. of a solution $0·5N$ and $0·1N$ with respect to sodium azide and iodine, respectively, to 5 c.c. of the suspected solution. Immediate evolution of nitrogen occurs when the concentration of carbon disulphide is greater than 1 in 5×10^4. With smaller quantities the evolution is delayed. If the solution also contains sulphides a slight excess of $0·1N$-iodine solution is first added. Minute quantities of carbon disulphide may be detected by adding starch and 1 drop of $0·01N$-iodine solution followed by 2 c.c. of $0·5N$-sodium azide solution, previously treated with $0·01N$-iodine solution and starch until a blue colour just appeared. When carbon disulphide is present the blue colour disappears. A blank test should be carried out at the same time.

To determine azides a known excess of $0{\cdot}1N$-iodine solution is added to a solution of 0·5 c.c. of carbon disulphide in 6—8 c.c. of acetone. On adding the solution of azide, evolution of nitrogen occurs. After 5—10 min. 250 c.c. of water are added and the excess of iodine is titrated with $0{\cdot}1N$-arsenite solution. The back titration should be of the order 2—3 c.c. The method is applicable to the determination of insoluble azides which yield the corresponding iodide and soluble potassium azide with potassium iodide.

Addition of insufficient potassium iodide to silver azide gives a bright yellow additive compound, AgI,AgN_3. J. S. Carter.

Colorimetric [micro-]determination of sulphuric acid. J. Yamazaki (Bull. Chem. Soc. Japan, 1928, **3**, 173—180).—Sulphate is precipitated from slightly acid solutions and in presence of acetone as benzidine sulphate. After filtration and washing with 90% acetone the benzidine sulphate is dissolved in a mixture of equal volumes of absolute alcohol and $0{\cdot}1N$-sodium hydroxide solution. A few drops of a solution of barium chloride are added and the whole is made acid. Excess of a 1% solution of furfuraldehyde is added to an aliquot and the yellow colour compared with that given by a standard solution. The method is suitable for the determination of inorganic and total sulphate in urine. Phosphates interfere and the presence of large amounts of chloride is not desirable. When the solutions concerned are colourless, sulphates can be determined rapidly by adding excess of benzidine hydrochloride and determining the concentration of benzidine in the supernatant liquid. The rapid method can be applied to urine after the latter has been decolorised by animal charcoal. J. S. Carter.

Iodometric determination of persulphate. A. Schwicker (Z. anal. Chem., 1928, **74**, 433—441).—In the direct iodometric determination of persulphate a large excess of potassium iodide is necessary to obtain complete reaction in a short time. This excess may be dispensed with and accurate results obtained in 10—15 min. if the persulphate solution is treated with 20% of its weight of ammonium chloride. The persulphate content of solutions free from ammonium salts may also be determined by boiling with sodium hydroxide and potassium iodide to convert part of the latter into iodate, acidifying with sulphuric acid, and titrating the liberated iodine. Alternatively, the neutral solution may be boiled with excess of sodium thiosulphate, with which persulphate reacts to form dithionate, and the excess of thiosulphate titrated with iodine. Persulphate oxidises ferrocyanide to ferricyanide in neutral solution and the latter may be determined iodometrically in acid solution; it also oxidises stannous chloride to stannic chloride in cold dilute hydrochloric acid and the excess of stannous chloride may be titrated with iodine.

A. R. Powell.

Determination of nitrites in cellulose nitrate. Koehler and Marqueyrol.—See B., 1928, 656.

Detection of phosphate [in presence of arsenate] and molybdate. F. Feigl [with P. Krumholz] (Z. anal. Chem., 1928, **74**, 386—392).—Phosphoric acid may be detected in presence of considerable amounts of arsenic acid by placing a drop of the suspected solution on a quantitative filter-paper (qualitative papers usually contain a small amount of phosphate) and adding one drop of a nitric acid–ammonium molybdate solution. A drop of a saturated solution of benzidine in acetic acid is now added and the moist paper held in ammonia vapour. A blue colour indicates the presence of phosphoric acid. The presence of phosphate in insoluble phosphates, minerals, or slags may be detected by treating about 10 mg. of substance on a filter-paper in the manner described. For the corresponding test-tube reaction 2 c.c. of solution are treated with three drops of the nitric acid–molybdate solution and three drops of the benzidine solution and 1% ammonia added until the turbidity persists. The limiting concentration of phosphoric acid detectable by this method is 1 in 3×10^6.

Owing to complex formation many of the reactions of molybdic and oxalic acids are masked in presence of each other. The reaction between permanganate and oxalic acid, although not repressed, is considerably retarded in presence of molybdic acid. A solution of ammonium molybdate containing 5 mols. of tartaric acid per mol. of molybdic acid gives a precipitate with phosphoric acid, but not with arsenic acid. J. S. Carter.

Indophenol reaction in inorganic chemistry. J. Stiepovich and A. Sà (Rev. Cent. Estud. Farm. Bioquim., 1927, **16**, 384—385; Chem. Zentr., 1928, i, 1556).—In the indophenol test for chlorine the production of hypochlorite is necessary, sodium or potassium hydroxide or carbonate, but not hydrogen carbonate, being added. Carbonate can be detected in a dilution of 1 in 5000. Tertiary phosphates yield indophenol-blue immediately in the cold; secondary phosphates react slowly in the cold but rapidly on warming, whilst primary phosphates do not react.

A. A. Eldridge.

Centigram elementary analysis. I. Determination of carbon and hydrogen, with automatic regulation of combustion. II. Nitrogen determination. B. Bobrański and E. Sucharda (Rocz. Chem., 1928, **8**, 290—324).—A method is described for the micro-determination of carbon, hydrogen, and nitrogen, involving the use of only 2—3 centigrams of substance. The method for the determination of carbon and hydrogen is similar to that of Pregl, the combustion tube being filled with successive layers of silver gauze, copper oxide, and lead chromate precipitated on pumice, platinised asbestos, silver gauze, lead peroxide, and silver gauze. The temperature of the lead peroxide layer is maintained at 200°. The method for the determination of nitrogen is also based on that of Pregl, the volume of nitrogen evolved being read in a nitrometer graduated in 0·02 c.c., and 1·2% of the volume read being deducted as a correction for alkali solution adhering to the glass. R. Truszkowski.

Analysis of silicates by decomposition with alkali hydroxides in a nickel crucible. C. J. van Nieuwenburg and H. H. Dingemans.—See B., 1928, 671.

Determination of sodium-ion concentration by means of a sodium amalgam electrode. G. ETTISCH and K. JOACHIMSOHN (Z. Elektrochem., 1928, **34**, 404—406).—Details are given of an improved method for measuring sodium-ion concentrations by means of a sodium amalgam electrode. Special precautions are taken to prevent hydrogen evolution at the surface of the amalgam, and the formation of alkaline solution on account of the hydrolysis of the amalgam. Reproducible measurements are obtainable, using quite small quantities of solution and amalgam. L. L. BIRCUMSHAW.

Specific reagents for silver and a new sensitive test for silver. F. FEIGL (Z. anal. Chem., 1928, **74**, 380—386).—The silver salt of *p*-dimethylaminobenzylidenerhodanine, $AgC_{12}H_{11}N_2OS_2$, is precipitated from acid, neutral, or ammoniacal solutions of silver salts on addition of an acetone solution of the reagent as a flocculent, reddish-violet precipitate. When the concentration of silver is very small the precipitate is brown and contains the free base. Since the rhodanine base is readily soluble, and the silver salt absolutely insoluble, in carbon disulphide, carbon tetrachloride, etc., it is desirable when very small quantities of silver are concerned to shake the solution with one of these solvents after precipitation. A solution of 0·03 g. of base in 100 c.c. of acetone is recommended for the detection of small amounts of silver. The limiting concentrations of silver detectable by hydrochloric acid and the rhodanine base are 1 in 10^5 and 1 in 5×10^6, respectively, the latter reagent being sufficiently sensitive to detect the solubility of silver chloride in water. The above reaction may be used to detect the presence of traces of silver in minerals, metals, and salts. The presence of silver in coinage, platinum, etc. may be detected by making a scratch with the material on unglazed porcelain. The streak is treated with a drop of nitric acid and the porcelain warmed over a flame to remove excess of acid. The porcelain is now placed in an acetone solution of the rhodanine base to which a drop of dilute nitric acid has been added. If silver was present in the metal a reddish-violet zone occupies the position of the original streak. Mercury interferes, but may be removed by strongly heating the porcelain prior to treatment with nitric acid.

The reagent is prepared by boiling an equimolecular mixture of rhodanine (Nencki, J.C.S., 1877, ii, 872; Holmberg, A., 1906, i, 811) and *p*-dimethylaminobenzaldehyde in glacial acetic acid under reflux for 1 hr. The condensation product is precipitated with water and crystallised from boiling alcohol. J. S. CARTER.

Determination of salts in dilute solution by the opacity of fine suspensions produced in the solutions. A. BOUTARIC and G. PERREAU (Rev. gen. Colloid., 1928, **6**, 113—117).—The opacity (measured by a Fery spectrophotometer) which is produced when a fine precipitate is formed in a solution of a salt by adding a suitable reagent may be prevented from changing appreciably with time by the addition of a solution of dextrin or of gum arabic. The concentration of the gum may vary between 0·4 and 20% without affecting the results. If the temperature is maintained constant within 0·1° an accuracy of 0·5% may be attained in the determination of suitable salts. Silver and chlorine as silver chloride, phosphates as silver phosphate, and magnesium as magnesium hydroxide may be determined in this way. In determining barium or sulphates as barium sulphate, 15 min. should elapse before comparative readings of opacity are made. The method is not applicable to the determination of calcium as calcium oxalate, since the addition of gum arabic accelerates the formation of precipitates of this substance. F. G. TRYHORN.

Micro-determination of calcium. F. ROGOZINSKI (Rocz. Chem., 1928, **8**, 275—279).—Calcium is precipitated quantitatively as sulphate in presence of 4 vols. of alcohol, and is weighed as the hydrated sulphate, 0·27 mg. of calcium being determinable by this method. Chlorides and magnesium have a slight influence on the accuracy of this method only when present in very great excess. R. TRUSZKOWSKI.

Detection of magnesium in rocks by means of the diphenylcarbazide reaction. F. FEIGL (Z. anal. Chem., 1928, **74**, 398—399).—*X*-Ray analysis supports the author's formulation of dolomite as the complex compound $Ca[Mg(CO_3)_2]$ (A., 1927, 1161). J. S. CARTER.

Sensitive colour reactions for magnesium. H. D. BARNES (J. S. Afr. Chem. Inst., 1928, **11**, 67—68).—A neutral magnesium salt solution containing 0·5 mg. of metal/litre yields a definite orange colour when 10 c.c. of the solution are treated with 0·2 c.c. of a 0·1% solution of Clayton-yellow and 0·5 c.c. of 4*N*-sodium hydroxide solution. With more concentrated solutions of magnesium salts (5 mg./litre) a brick-red colour is obtained. Calcium in concentrations not exceeding 300 mg./litre does not interfere, but larger amounts produce opalescent solutions with the alkali. A. R. POWELL.

Applications of the " zinc " test for cassiterite. G. H. STANLEY.—See B., 1928, 614.

Determination of copper in iron and steel. E. ZINDEL.—See B., 1928, 643.

Apparatus for the investigation of air, and its content of foreign vapours, especially of mercury vapour. A. BUSS (Chem. Fabr., 1928, 503—504).—A compact form of apparatus containing a small electrically-driven rotary air-pump which sucks the air to be tested through two condensation tubes, immersed in liquid air, and then into a measuring vessel, is described. Mercury vapour is totally condensed in the first U-tube when the velocity of flow does not exceed 1·5—2 litres/min. Using about 2 litres of liquid air the apparatus may be left to work without attention for about 2 hrs. H. F. GILLBE.

Potassium hydrogen sulphate fusions [in analysis of aluminous refractories]. W. R. KERR.—See B., 1928, 642.

Colorimetric determination of iron by means of potassium thiocyanate. L. S. VAN DER VLUGT (Chem. Weekblad, 1928, **25**, 495—496).—0·1 mg. of iron present in 100 c.c. of solution may be detected,

even in presence of other salts, if the solution contains 2% of sulphuric acid and 10 c.c. of 20% thiocyanate solution be added. Oxidation to the ferric state is best effected by use of potassium persulphate in boiling acid solution. S. I. LEVY.

Application of photo-electric spectrophotometry to micro-analysis. H. VON HALBAN and E. ZIMPELMANN (Z. Elektrochem., 1928, **34**, 387—393; cf. von Halban and Siedentopf, A., 1922, ii, 332).—The photo-electric spectrophotometric method developed by von Halban and his collaborators has been applied to the determination of small quantities of ferric iron by means of thiocyanate and of titanium as titanium peroxide. Quantities of iron ranging from 1 to 0·001 mg. in 50 c.c. of solution can be determined by this means with an accuracy of 1%, whilst the smallest detectable quantity is 0·00002 mg. of iron in 50 c.c. of solution. The method could be applied to the determination of the iron in a drop of blood. The smallest detectable quantity of titanium in 50 c.c. of solution is 0·0001 mg., and 0·01 mg. can be determined with an accuracy of 1%. The possible sources of error in the practical application of the method are discussed. L. L. BIRCUMSHAW.

Simultaneous potentiometric determination of iron, copper, and arsenic. E. ZINTL and F. SCHLOFFER (Z. angew. Chem., 1928, **41**, 956—960).—The difficulties of the methods of Kolthoff and Tomicek (A., 1925, ii, 72) and of Buehrer and Schupp (B., 1926, 282) in the simultaneous potentiometric determination of iron and copper are due to the presence of chloride ions. In sulphuric acid, using chromous sulphate as reducing agent, sharp end-points are obtained for copper, iron, copper with iron, copper with iron and chromate, and copper with iron and arsenic. The results are unaffected by the presence of lead, nickel, cobalt, aluminium, chromic salts, or manganese. C. HOLLINS.

Persulphate method for determining chromium plus vanadium in chrome vanadium tungsten steels. H. H. WILLARD and P. YOUNG.—See B., 1928, 643.

Volumetric determination of vanadium in chrome vanadium tungsten steels. H. H. WILLARD and P. YOUNG.—See B., 1928, 643.

Separation and determination of bismuth by means of cupferron. A. PINKUS and J. DERNIES (Bull. Soc. chim. Belg., 1928, **37**, 267—283).—Bismuth is precipitated completely from solutions of its salts containing free hydrochloric or nitric acid not exceeding a N-solution by the addition of a 5% solution of cupferron added drop by drop from a burette until at least 0·3 g. of cupferron has been added for every 0·1 g. of bismuth present. The yellowish-white, flocculent precipitate is collected, washed with a 0·1% solution of the precipitant, dried, and gently ignited to bismuth oxide for weighing. The method affords a rapid means of separating bismuth from cadmium, lead, zinc, arsenic, silver, and quinquevalent antimony. Cadmium and lead are precipitated quantitatively by cupferron from neutral solutions. A. R. POWELL.

Spot of light-reading device for galvanometers. T. T. SMITH (J. Opt. Soc. Amer., 1928, **17**, 155—161).

Spectrographs for the analysis of metals. EWALD (Chem. Fabr., 1928, 501—503).—A description of a number of commercial types. H. F. GILLBE.

Radon pump. L. F. CURTISS (J. Opt. Soc. Amer., 1928, **17**, 77—80).—The arrangement consists of two Topler pumps in series and a number of accessories to provide for the purification of the radon and the manipulation of the mercury. The advantages of the design are that it eliminates all rubber tubing and all stopcocks through which the mercury may pass, and that it makes the use of liquid air very convenient and allows a more rapid manipulation than is possible with a pump depending solely on purification by chemical means. L. L. BIRCUMSHAW.

"Acid-alkalimeter"; a direct-reading p_H meter. K. H. GOODE (J. Opt. Soc. Amer., 1928, **17**, 59—71).—The objection to the use of a single thermionic valve in conjunction with a p_H meter is the necessity of employing a microammeter or millivoltmeter as an indicating device. An instrument of this type using three valves has been previously described (cf. A., 1925, ii, 1196). Difficulties have been encountered in the use of this, however, and a new form is described. Two valves of the oxide-coated filament type are used and the indicating instrument is a special Weston three-terminal voltmeter-ammeter. Full details are given for the adjustment of the resistances and controls. L. L. BIRCUMSHAW.

McBain–Bakr balance for sorption of vapours by fibrous and film materials. P. T. NEWSOME (Ind. Eng. Chem., 1928, **20**, 827).—The material, such as cellulose or cellulose esters, is suspended in the apparatus maintained at constant temperature from the calibrated quartz spring and evacuated to constant weight at a pressure of $<0·01$ mm. By introducing successive small quantities of water from a capillary and observing the pressure and elongation of the spring, absorption curves at various temperatures may be obtained. Similar observations during the gradual removal of water vapour with a vacuum pump yield the corresponding desorption curves. A device is described for determining the absorption of vapours of liquids which attack stopcock grease. F. R. ENNOS.

Micro-apparatus for the determination of mol. wt. by the cryoscopic method. K. IWAMOTO (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 719—722).—A Beckmann apparatus of reduced size is described with which the mol. wt. of small quantities of material (7—30 mg.) can be determined, using 1·5 c.c. of solvent. C. J. SMITHELLS.

Simple method for measuring rotatory dispersion. I. BENCOWITZ (J. Physical Chem., 1928, **32**, 1163—1170).—The method described eliminates the use of a cadmium–quartz lamp, is accurate to within 0·02%, and permits a complete determination of rotatory dispersion for 10 wave-lengths to be made in 5 hrs. Monochromatic light is replaced by portions

of light from a continuous spectrum, and any wave-length of which the rotation in quartz is known can be employed. L. S. THEOBALD.

Apparatus for the determination of gas densities by the Bunsen effusion method. H. KAHLE (Z. angew. Chem., 1928, **41**, 876—880).—Errors due to irregularities in the aperture of the diffusion disc are eliminated by passing the gas, in an enclosed apparatus capable of rotation about its axis, alternately in opposite directions through the aperture. F. G. TRYHORN.

Laboratory aspirator. E. N. BATES and G. P. BODNAR (U.S. Dep. Agric. Circ., 1927, **9**, 1—12).—The device (U.S.P. 1,524,012) separates granular substances by means of a current of air passing through a thin stream of the substances.

CHEMICAL ABSTRACTS.

Temperature measurement between 20° and 90° Abs. F. HENNING (Naturwiss., 1928, **16**, 617).—Onnes and Tuyn (Leiden Communications Suppl., 1926, **58**) have prepared a table giving the resistance ratio $w'-R_t'/R_0'$, from degree to degree for a standardised platinum resistance thermometer. This table can be used for any platinum resistance thermometer within the range of 20—90° Abs. by the aid of an empirical formula. A. J. MEE.

Automatic pipette. O. ORTH (Chem. Fabr., 1928, 492).—The pipette has a glass tap at the bottom and is expanded to a bulb at the top. The graduation mark is on the constriction below the bulb and a capillary filling tube ends on a level therewith. The pipette is filled from a wash-bottle at a lower level and any surplus runs back. The filling and air release connexions are either fused in or taken through a rubber stopper. C. IRWIN.

Reproduction of scales by electric discharge to a photographic plate. J. H. CHESTERS (Nature, 1928, **122**, 349).

Space model of the periodic system of the elements. A. S. RAMONDT (Chem. Weekblad, 1928, **25**, 496—498).—A method of constructing a model of a spiral representation is described, and the horizontal projection of a thread joining the positions of the elements is set out. S. I. LEVY.

Geochemistry.

Medicinal muds of Crimean salt lakes. A. F. SAGAIDACHNUI (Trans. State Inst. Appl. Chem. Moscow, 1927, No. 5, 25—52).—The composition of the waters of Moinak lakes is tabulated, and the formation of the mud is discussed. For the formation and regeneration of the mud a low salt concentration, favouring bacterial life and gelation of colloids, is necessary; for its preservation it is necessary that the salt concentration of the water should increase, so as to suppress biochemical processes tending to form non-colloidal calcium carbonate.

CHEMICAL ABSTRACTS.

Red soils of Cochin China. V. AGAFONOV (Compt. rend., 1928, **187**, 428—431).—These soils, which occur in layers 5—6 m. deep and consist of aggregates of amorphous grains (diameter 0·1 micron) principally of bauxite, stilpnosiderite, and hydrated aluminosilicates, are produced by the decomposition of basalts. This corresponds with the progressive disappearance of magnesia and the alkalis, the oxidation of ferrous oxide, and an increase in the water, alumina, and titania contents, transparent red bowlingite being formed as an intermediate product. Although they may contain 0·1% K and 0·43% N, their structure and low p_H value render them unsuitable for agriculture in rainy districts. J. GRANT.

Changes of certain clays into acidic ones through weathering. T. OKAZAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 776—784).—It is suggested that the acidity of clays is due to the weakness of the combination of silica and alumina, and to the consequently easy decomposition of alkaline or neutral clays by weathering.

C. W. GIBBY.

Lavas of the Sous-le-Vent islands of the Society Archipelago. A. LACROIX (Compt. rend., 1928, **187**, 397—401).—The so-called granite of this region is in reality an olivine gabbro having the same composition as the porphyric basaltic olivine with which it is associated. Pegmatoids which are also found, are the result of a differentiation under special conditions of the same magma (cf. *ibid.*, 397), but are richer in alumina, alkalis, titania, and phosphorus, and poorer in magnesia than the related basalt. Other basalts are also found, with traces of free silica, the proportions of sodium and potassium being often the same; slatite is an exception.

J. GRANT.

Zeolites as fossilising substances. H. UDLUFT (Arkiv Kemi, Min., Geol., 1928, **9**, No. 33, 15 pp.).—Fossilised wood from the basaltic tufa on the lower slopes of Mt. Elgon in British East Africa was found to contain crystals of natrolite, mesolite, and apophyllite, whilst calcite had apparently played a part in building up the structure and a certain amount of the original organic wood substance was still present. It is suggested that the wood was dehydrated above 150° in the tufa beds and then subjected to the action of hydrothermal epimagmatic solutions which deposited in succession natrolite, apophyllite, and calcite. The mineralisation appeared to have been affected by the original structure of the wood in that the mineral crystals were elongated in the direction of the circulation along the wood fibres and the wood cells seemed to be filled first.

A. R. POWELL.

Some metamorphosed dolerites from Broken Hill. W. R. BROWNE (J. Proc. Roy. Soc. New South Wales, 1927, **61**, 383—400).—The petrographical characters of a series of basic rocks at Broken Hill are described and the probable chemical changes involved in their metamorphism are discussed.

C. W. GIBBY.

Petrological notes on some New South Wales alkaline basic rocks. W. R. Browne (J. Proc. Roy. Soc. New South Wales, 1927, **61**, 371—382).—A description of six rocks found in New South Wales. C. W. Gibby.

The Great Bahama Bank. Marine carbonate sediments. R. M. Field (Amer. J. Sci., 1928, [v], **16**, 239—246).—Specimens of calcareous muds from the lagoons of the Great Bahama Bank have been collected and are being examined. C. W. Gibby.

Occurrence of tridymite and cristobalite in a granite xenolith. A. A. Weymouth (Amer. J. Sci., 1928, [v], **16**, 237—238).—The following minerals have been identified in a disintegrated granite rock in Idaho: quartz, orthoclase, oligoclase, muscovite, biotite, chlorite, garnet, iron oxide, zircon, tridymite, and cristobalite. Its composition is compared with that of an artificially prepared silica brick. C. W. Gibby.

New platinum mineral in Rustenburg norites. R. A. Cooper (J. Chem. Met. Min. Soc. S. Africa, 1928, **28**, 281—283).—A new platinum sulpharsenide, discovered in Rustenburg norites, has the composition Pt 64·2, Pd 9·4, S 17·7, As 7·7%, corresponding with the formula $Pt(S,As)_2$. The greater part of the palladium is entirely independent of the platinum. C. W. Gibby.

Crystallophyllian rocks of Mayombe (French equatorial Africa). V. Babet (Compt. rend., 1928, **187**, 348—350).—These rocks, which are considered to belong to the superior zone characterised by albite and the hydroxyl minerals (chlorite, sericite, epidotite), fall into two classes: (1) Feldspathic (albite) gneiss type containing layers of sericite, and alkaline or calco-alkaline in character. Quartz when present is granoblastic and the free alumina content rises to about 5%, showing that in spite of the analogy to the granites in composition the rocks are derived from altered granites or arkoses. (2) Non-feldspathic mica schists and epidotites containing chlorite and albite crystals in quartz inclusions, with beds of primary calcite. With the exception of the epidotite they may contain up to 11% of free alumina. Analyses are given. J. Grant.

Minerals. III. H. Collins (Chem. News, 1928, **137**, 168—170).

Organic Chemistry.

Catalytic hydrogenation of different types of unsaturated compounds. III. Hydrogenation of conjugated systems. S. V. Lebedev and A. O. Yakubchik (J.C.S., 1928, 2190—2204).—The catalytic hydrogenation of di*iso*propenyl, b. p. 69°, d_4^{20} 0·7262, divinyl, and piperylene, b. p. 41·5°, d_4^{20} 0·6852, has been studied by the methods previously employed (this vol., 613). Hydrogenation in each case is of type II (*loc. cit.*), the curves consisting of three sections. Hydrogenation of di*iso*propenyl proceeds at a similar rate to that of isoprene. The first section of the curve is horizontal up to the critical point (69% hydrogenation); the rate of absorption then increases in the second portion corresponding with the hydrogenation of methyl*iso*propylethylene, and finally decreases rapidly, this third stage corresponding with the hydrogenation of tetramethylethylene. In order to study the process of hydrogenation up to the critical point it was interrupted at 25% and 50% hydrogenation and the composition of the product determined by the methods previously employed. The proportion of the various products present at 25%, 50%, and 69% (critical point) hydrogenation are, respectively, di*iso*propenyl, 64, 28, 0%; di*iso*propyl, 14, 28, 38%; *as*-methyl*iso*propylethylene, 16, 32, 45%; tetramethylethylene, 6, 16, 17%. The experimentally determined quantities of di*iso*propenyl, di*iso*propyl, and total hexylenes lie on almost straight lines, but the curve for the individual hexylenes shows breaks which are probably due to isomeric change produced by the action of sulphur dioxide, which is shown to isomerise *as*-methyl*iso*propylethylene to tetramethylethylene. The hydrogenation of di*iso*propenyl in the presence of ethylene derivatives of different degrees of substitution has been studied and it is found that the ethylene derivative is generally hydrogenated after the critical point (which retains its original position) in places determined by the degree of substitution. When camphene is added the beginning of the hydrogenation of this substance is distinctly separated from the end of the first section of the curve; the whole of the *as*-disubstituted ethylene is hydrogenated after the critical point and hence does not alter the amount of fully saturated molecules then present. The latter are therefore formed before the critical point and must arise from the simultaneous (or almost simultaneous) addition of 2 mols. of hydrogen to the conjugated system. The curve for divinyl is of similar type; the first section, relating to the conjugated system, ends at the critical point (76% hydrogenation, unchanged by admixture with substituted ethylene derivatives) when the composition of the product is divinyl, 0; butane, 52; n-Δ^{α}-butylene, 34; n-Δ^{β}-butylene, 14%. The second portion of the curve pertains to Δ^{α}- and the third to Δ^{β}-butylene. Similarly with piperylene, the first section ends at the critical point (74% hydrogenation) where the composition is piperylene, 0; propylethylene, 15; *s*-methylethylethylene, 39; pentane, 46%. The second portion, where more rapid absorption of a further 6·5% of hydrogen occurs, corresponds with propylethylene, and the third (19·5% hydrogen) with *s*-methylethylethylene. Hydrogenation of piperylene mixed with various ethylene derivatives was also studied, and of these camphene, methylheptenone, and tetramethylethylene form independent sections of the hydrogenation curve. J. W. Baker.

Allyl transposition and additive derivatives of erythrene hydrocarbons. C. Prévost (Ann. Chim., 1928, [x], **10**, 113—146).—A more detailed

account of work already reviewed (A., 1926, 496; 1927, 131, 337, 748, 749, 851; this vol., 152, 613).

H. Burton.

Preparation of tetramethylethylene. J. C. Earl (J. Proc. Roy. Soc. New South Wales, 1927, 61, 68—72).—A good yield of tetramethylethylene can be obtained by dehydrating dimethylethylcarbinol with oxalic acid to trimethylethylene, from the chlorohydrin of which dimethyl*iso*propylcarbinol is obtained by the action of magnesium methyl iodide. This gives the hydrocarbon on dehydration with dilute sulphuric acid or concentrated oxalic acid.

C. W. Gibby.

Allene hydrocarbons. M. Bouis (Ann. Chim., 1928, [x], 9, 402—465).—Allenes, R·CH:C:CH$_2$, where *R* is an alkyl group, are prepared from the appropriate substituted allyl alcohol, R·CH(OH)·CH:CH$_2$, formed by the action of the appropriate Grignard reagent on acraldehyde. The following compounds are described: Δ-δ-*methylpenten-γ-ol*, b. p. 125°/760 mm., d^{23} 0·8368, n_D^{23} 1·4263; Δ^{α}-ε-methylhexen-γ-ol has b. p. 58°/15 mm., 146° (corr.)/760 mm., d^{21} 0·8288, n_D^{21} 1·4285. These by the action of phosphorus tribromide with cooling in the presence of pyridine yield pure allyl bromides, R·CH:CH·CH$_2$Br, the isomeric change going to completion in each case (cf. Burton and Ingold, this vol., 634), and thus are obtained Δ^{β}-*α-bromopentene*, b. p. 123—124°, 35°/25 mm., d^{20} 1·2545, n_D^{20} 1·4731; Δ^{β}-*α-bromohexene*, b. p. 42—44°/10 mm., d^{16} 1·2119, n_D^{16} 1·4778; Δ^{β}-*α-bromo-δ-methylpentene*, b. p. 46°/18 mm., d^{24} 1·2208, n_D^{24} 1·4723; Δ^{β}-*α-bromoheptene*, b. p. 62—64°/10 mm., d^{17} 1·1682, n_D^{17} 1·4760; Δ^{β}-*α-bromo-ε-methylhexene*, b. p. 60°/15 mm., d^{21} 1·1782, n_D^{21} 1·4750. These by boiling with anhydrous sodium acetate in acetic acid yield the corresponding acetates and thus are obtained Δ^{β}-*hexenyl*, b. p. 171—173°, d^{18} 0·8976, n_D^{18} 1·4282, Δ^{β}-*δ-methylpentenyl*, b. p. 163°, d^{22} 0·8990, n_D^{22} 1·4260, Δ^{β}-*heptenyl*, b. p. 192—194° (corr.), d^{18} 0·8915, n_D^{18} 1·4314, Δ^{β}-*ε-methylhexenyl*, b. p. 182—184° (corr.), d^{20} 0·8836, n_D^{20} 1·4280, *acetates*; Δ^{β}-pentenyl acetate has d^{22} 0·9019, n_D^{22} 1·4219. Hydrolysis of these with aqueous methyl-alcoholic sodium hydroxide yields the corresponding carbinols, R·CH:CH·CH$_2$·OH, and thus are obtained Δ^{β}-*hexen-α-ol*, b. p. 158—160°, d^{16} 0·8490, n_D^{16} 1·4403 (*naphthylurethane*, m. p. 76°); Δ^{β}-*δ-methylpenten-α-ol*, b. p. 150°, d^{21} 0·8348, n_D^{21} 1·4357; Δ^{β}-*hepten-α-ol*, b. p. 177—179° (corr.), d^{20} 0·8421, n_D^{20} 1·4410; Δ^{β}-*ε-methylhexen-α-ol*, b. p. 169° (corr.), d^{20} 0·8355, n_D^{20} 1·4390. Addition of bromine at 0° to the allyl bromides (above) yields the tribromides, R·CHBr·CHBr·CH$_2$Br, and thus are obtained *αβγ-tribromo-δ-methylpentane*, b. p. 131—132°/18 mm., m. p. 35°, d^{25} 1·9139, n_D^{25} 1·5470; *αβγ-tribromo-ε-methylhexane*, b. p. 134—135°/12 mm., d^{21} 1·8116, n_D^{21} 1·5380; *αβγ-tribromopentane*, b. p. 122—124°/18 mm., d^{19} 2·0741, n_D^{19} 1·5589; *αβγ-tribromohexane*, b. p. 127—129°/11 mm., d^{16} 1·9429, n_D^{16} 1·5506; *αβγ-tribromoheptane*, b. p. 142—143°/12 mm., d^{17} 1·8112, n_D^{17} 1·5393. Fusion with 75—80% potassium hydroxide converts these into the allene dibromides, R·CHBr·CBr:CH$_2$, and thus are obtained Δ^{α}-*βγ-dibromopentene*, b. p. 75—76°/12 mm., d^{19} 1·7442, n_D^{19} 1·5316; Δ^{α}-*βγ-dibromohexene*, b. p. 83—85°/9 mm., d^{14} 1·6381, n_D^{14} 1·5248; Δ^{α}-*βγ-dibromo-δ-methylpentene*, b. p. 81°/124 mm., d^{24} 1·6035, n_D^{24} 1·5180; Δ^{α}-*βγ-dibromoheptene*, b. p. 108—110°/12 mm., d^{18} 1·5595, n_D^{18} 1·5200; Δ^{α}-*βγ-dibromo-ε-methylhexene*, b. p. 100—101°/12 mm., d^{20} 1·5493, n_D^{20} 1·5155. The allenes, R·CH:C:CH$_2$, are obtained (yield 50—60% calculated on the original allyl alcohol) by dropwise addition of these dibromides to zinc dust in boiling alcohol and thus are prepared *ethylallene* ($\Delta^{\alpha\beta}$-*pentadiene*), b. p. 45°, d^{20} 0·6890, n_{α}^{20} 1·4100, n_D^{20} 1·4149, n_{β} 1·4209; *propylallene*, b. p. 78°, d^{17} 0·7198, n_{α}^{17} 1·4246, n_D^{17} 1·4298, n_{β}^{17} 1·4353; iso*propylallene*, b. p. 70°, d^{22} 0·7061, n_{α}^{22} 1·4201, n_D^{22} 1·4232, n^{22} 1·4308; *butylallene*, b. p. 106° (corr.), d^{21} 0·7374, n^{21} 1·4321, n_D^{21} 1·4360, n_{β}^{21} 1·4427, n_{γ}^{21} 1·4493; iso*butylallene*, b. p. 96° (corr.), d^{19} 0·17225, n_{α}^{19} 1·4251, n_D^{19} 1·4282, n_{β}^{19} 1·4353. These all show slight optical exaltation (about 0·5) which increases with the mol. wt. of the derivative and is greater with branched chains than with straight chains. Addition of 1 mol. of bromine in carbon tetrachloride solution to propylallene occurs mainly at the βγ double linking, a little of the αβ product being formed as a by-product. Further addition of bromine yields, with the appropriate allene, *αββγ-tetrabromopentane*, b. p. 120°/3 mm., d^{22} 2·2939, n_D^{22} 1·5916; *αββγ-tetrabromohexane*, b. p. 130°/3 mm., d^{15} 2·1873, n_D^{15} 1·5850; *αββγ-tetrabromoheptane*, b. p. 140°/3 mm., d^{20} 2·0675, n_D^{20} 1·5718. The action of a 35% acetic acid solution of hydrogen bromide on ethylallene at 0° yields a mixture of products from which were isolated a mixture which probably contains Δ^{α}-β-bromopentene (since by treatment with alkali it yields an acetylene, forming a copper derivative) and Δ^{β}-β-bromopentene (yields propionic acid on oxidation) together with *ββ-dibromopentane*, b. p. 62—63°/18 mm., d_4^{16} 1·6452, n_D^{16} 1·5031. Hydration of the allenes with concentrated sulphuric acid at −10° and subsequent treatment with water yields the corresponding methyl ketones, CH$_2$R·CO·CH$_3$, whilst by the action of sodamide the sodium derivative of the isomeric acetylene, CH$_2$R·C:CNa, is obtained.

J. W. Baker.

Reaction between acetylene and sulphur at temperatures up to 650°. J. B. Peel and P. L. Robinson (J.C.S., 1928, 2068—2070).—In confirmation of the results of Meyer and Sandmeyer (A., 1884, 45) and contrary to those of Capelle (A., 1908, i, 201) and de Coninck (*ibid.*, 750) it is found that the liquid products obtained by the interaction of sulphur and acetylene consist of (*a*) carbon disulphide, (*b*) thiophen, and (*c*) thiophten. At most only 77% of the sulphur is found in the distillate, the remainder probably being converted into hydrogen sulphide. Ignition occurs at 275°, but the reaction is inconveniently slow below 300°. At 325°, 500°, and 650° the proportions of the three products formed are, respectively, (*a*) 77, 77, and 83%, (*b*) 9, 12, and 5%, (*c*) 6, 6, and 3%, the optimum temperature for the formation of thiophen, d_4^{20} 1·0615, γ^{20} 32·58, being 500°.

J. W. Baker.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. I. Decomposition of methyl alcohol by catalysts composed of copper and zinc. P. K. Frolich, M. R. Fenske,

and D. QUIGGLE (Ind. Eng. Chem., 1928, **20**, 694—698; cf. Lewis and Frolich, B., 1928, 359).—The catalytic decomposition of methyl alcohol at 360° and a total pressure of 1 atm. with mixtures of zinc and copper oxides in varying proportions has been studied. Maximum decomposition and formation of carbon monoxide occurred when zinc oxide was present in excess, although the addition of only 3 mol.-% of zinc oxide to copper oxide increases decomposition. The effect of adding a small amount of copper oxide to zinc oxide is not so marked. The decomposition of methyl alcohol is thought to proceed in two stages: $MeOH \longrightarrow H_2+H \cdot CHO \longrightarrow 0 \cdot 5H \cdot CO_2Me+CO+H_2$. The extent to which the reaction proceeds depends largely on the zinc : copper ratio of the catalyst. The addition of a small amount of copper to zinc oxide favours the formation of carbon monoxide, whereas the addition of a small amount of zinc oxide to copper favours the formation of methyl formate. R. A. PRATT.

Tests for methyl alcohol. E. W. TODD (Proc. Nova Scotian Inst. Sci., 1927, **16**, 147—151).—The tests for methyl alcohol in the presence of ethyl alcohol using morphine, or milk and resorcinol, as also the older U.S. Pharmacopœia test (oxidation by copper spiral and detection of formaldehyde by Schiff's reagent), are inferior to the 1926 U.S. Pharmacopœia test, viz., the oxidation by acid permanganate to formaldehyde, giving a violet colour with Schiff's reagent. S. J. GREGG.

Constitution of citronellol and rhodinol. V. GRIGNARD and J. DŒUVRE (Compt. rend., 1928, **187**, 270—273).—Ozonisation of citronellol in aqueous acetic acid solution shows that it consists of βζ-dimethyl-Δ^{α}-octen-θ-ol and about 24% of βζ-dimethyl-Δ^{β}-octen-θ-ol; the latter occurs in smaller amounts (18%) in samples previously submitted to acid treatment. By the action of acetic acid containing small amounts of water on citronellal, a *glycol*, b. p. 115—118°/3 mm., m. p. 65—66°, is obtained which is probably the intermediate compound concerned in the cyclisation of citronellal into *iso*pulegol. It is pointed out that in this cyclisation it is immaterial whether the double linking is in the α- or the β-position in citronellal, since *iso*pulegol may arise by the dehydration of either of the isomeric intermediate compounds. G. A. C. GOUGH.

Citronellol and rhodinol. V. GRIGNARD and J. DŒUVRE (Compt. rend., 1928, **187**, 330—334).—Bourbon geraniol which, by Glichitch's method (A., 1923, ii, 661), contains 51·9% of free and 15·9% of combined alcohols gives on distillation a "geraniol-rhodinol" fraction, b. p. 116—122°/18 mm., containing 50% of "rhodinol" as determined by the warm formylation method, and giving on ozonisation 80% of acetone and 32% of formaldehyde and formic acid. Geraniol obtained by rectification of citronellol on ozonisation gives 51% of formaldehyde and formic acid and 92% of acetone, a result which supports the structure $CMe_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot OH$. Glycollaldehyde is also formed, and formic acid and formaldehyde probably result from hydrolysis of its peroxide, $CH_2 \cdot OH \cdot CH{:}O_2$. Isomerides differing in the position of the double linking about the ξ-carbon atom may also be present (cf. A., 1925, i, 772). *l*-Rhodinol, isolated by Barbier and Bouveault's benzoyl chloride method, and having b. p. 118—119·5°/18 mm., d_4^{15} 0·860, n_D^{15} 1·4574, $[\alpha]_D^{17}$ +1·87°, bromine value 103 (allophanate, m. p. 105—106°), gives on ozonisation yields of formaldehyde, formic acid, and acetone which indicate the presence of 45—45·7% of the α-form and 52—53% of the β-isomeride. These figures are unchanged by a fresh treatment with benzoyl chloride. *l*-Rhodinol, prepared by Tiemann and Schmidt's method, had b. p. 117—118·5°/17 mm., d^{15} 1·0864, $n_D^{15 \cdot 8}$ 1·4601, bromine value 102, and gave on ozonisation figures indicating the presence of 25% of the α- and 71% of the β-form. *d*-Citronellol, b. p. 119—121°/20 mm., d_D^{17} 0·856, n_D^{17} 1·4617, α_D^{16} +2·33°, bromine value 109, obtained from Java citronella oil, gives results on ozonisation indicating the presence of 24% of α- and 80% of β-form. When treated with benzoyl chloride at 150° for 8 hrs. and hydrolysed, this *d*-citronellol affords a product, b. p. 118—119°/18 mm., d^{15} 0·860, n^{15} 1·4572, α^{15} +2·30°, bromine value 96 (allophanate, m. p. 104·5—105·5°), containing 39% of α- and 59% of β-isomeride. Treatment with dry hydrogen chloride for 2 hrs. at 150° yields a similar product, d^{15} 0·863, n_D^{17} 1·4577, containing 42% of α- and 54% of β-isomeride. Both benzoyl chloride and hydrogen chloride thus produce isomerisation of the β- to the α-form, and it is concluded that Barbier and Bouveault's "rhodinol" is not present as such in the natural essences. The latter contain "citronellol," a mixture of about 80% of the Δ^{β}-octene (the "citronellic" form), and 20% of the Δ^{α}-octene (α-form). Certain acid influences produce isomerisation until the mixture contains about 50% of the α-form, and since this mixture forms the "rhodinol" of Barbier and Bouveault, it is proposed to term the α-isomeride the "rhodinic" form.

R. BRIGHTMAN.

Configuration of βγ-butylene glycol. J. BÖESEKEN and (MLLE.) R. COHEN (Rec. trav. chim., 1928, **47**, 839—848).—A sample of βγ-butylene glycol of biological origin (cf. Kluyver and others, A., 1926, 203), b. p. 177—180°, α_D^{20} +2·42° (l=2), gave on fractionation mainly the solid *meso*-glycol, m. p. 25°; the presence of a little racemic glycol was shown by resolution of the hydrogen sulphate or hydrogen 3-nitrophthalate with strychnine and brucine. Synthetic βγ-butylene glycol, prepared from Δ^{β}-butylene by way of the dibromide and diacetate, or, better, by oxidation with peracetic acid to monoacetate followed by hydrolysis, was mainly the *dl*-compound and was resolved ($[\alpha]_D$ −3·2° and +5°) in the form of its hydrogen sulphate by means of brucine. The *meso*-glycol has little effect on the conductivity of boric acid, whilst the *dl*-glycol definitely lowers it, indicating a greater distance between the hydroxyl groups in the latter case. The formation of a *trans*-glycol by the action of peracetic acid shows that the stable butylene is a *cis*-compound. C. HOLLINS.

Ditertiary glycols and certain of their heterocyclic derivatives. E. PACE (Atti R. Accad. Lincei, 1928, [vi], **7**, 757—764).—Treatment of acetonylacetone with a magnesium alkyl bromide

and decomposition of the resulting compound with water yield ditertiary glycols, $OH·CMeR·CH_2·CH_2·CMeR·OH$, converted into tetrahydrofuran derivatives if left in a desiccator containing sulphuric acid or if heated in acetic acid solution at 120—150° in presence of sulphuric acid or zinc chloride, and into substituted tetrahydropyrroles if heated with a slight excess of concentrated alcoholic ammonia at 150° for about 2 hrs. The following compounds were obtained in this way: βε-*Dimethylhexane*-βε-*diol*, m. p. 92—93°; γζ-*dimethylheptane*-γζ-*diol*, b. p. 172—173°; δη-*dimethyloctane*-δη-*diol*, b. p. 198—200°, which reacts readily with gaseous hydrogen bromide to give the corresponding dibromo-compound; 2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*, b. p. 119·5°, apparently identical with Pogorzelsky's di*iso*crotyl oxide (A., 1899, 785); 2 : 5-*dimethyl*-2 : 5-*diethyltetrahydrofuran*, b. p. 165°; 2 : 5-*dimethyl*-2 : 5-*dipropyltetrahydrofuran*, b. p. 186°; 2 : 2 : 5 : 5-*tetramethyltetrahydropyrrole*, b. p. 108° (cf. Pauly and Hültenschmidt, A., 1904, i, 88); 2 : 5-*dimethyl*-2 : 5-*diethyltetrahydropyrrole*, b. p. 125°, unstable in the air; 2 : 5-*dimethyl*-2 : 5-*dipropyltetrahydropyrrole*, b. p. 147—149°, unstable in the air.

T. H. POPE.

Reactions relating to carbohydrates and polysaccharides. XVI. Separation and identification of the isomeric ethylideneglycerols. H. S. HILL, A. C. HILL, and H. HIBBERT (J. Amer. Chem. Soc., 1928, **50**, 2242—2249).—The separation of the two isomeric ethylideneglycerols from a mixture by fractional distillation was incomplete. The action of benzoyl chloride in dry pyridine on the mixture yielded a product which could be separated by crystallisation from light petroleum into αγ-*ethylideneglyceryl* β-*benzoate*, m. p. 86°, and αβ-*ethylideneglyceryl* γ-*benzoate*, b. p. 144—145°/2 mm., d_4^{17} 1·1618, n_D^{17} 1·5145. These were separated in the proportions of 1 : 1·8 and 1 : 4 from the products prepared by the action of acetylene and paracetaldehyde, respectively, on glycerol. αγ-*Ethylideneglycerol*, b. p. 52°/2 mm., d_4^{17} 1·1477, n_D^{17} 1·4532, and αβ-*ethylideneglycerol*, b. p. 68—70°/1 mm., were obtained by hydrolysis of the benzoates. The action of methyl iodide and silver oxide yielded β-*methyl* αγ-*ethylideneglyceryl ether*, b. p. 80°/23 mm., d_4^{17} 1·0705, n_D^{17} 1·4375. and γ-*methyl* αβ-*ethylideneglyceryl ether*, b. p. 58—61°/23 mm., d_4^{17} 1·0224, n_D^{17} 1·4177, from which glyceryl β-methyl ether and α-methyl ether, respectively, were obtained by hydrolysis.

R. K. CALLOW.

Colour reactions of mannitol. L. EKKERT (Pharm. Zentr., 1928, **28**, 433).—Oxidation of mannitol with bromine water followed by the addition of a small quantity of phenacetin, resorcinol, α-naphthol, β-naphthol, codeine, or morphine and then concentrated sulphuric acid or phosphoric acid or fuming hydrochloric acid led to characteristic colour reactions in each case.

I. VOGEL.

Nitric oxide and carbon monoxide compounds of so-called univalent iron and nickel. H. REIHLEN, A. VON FRIEDOLSHEIM, and W. OSWALD (Annalen, 1928, **465**, 72—96).—A reply to Manchot (this vol., 35) and Hieber and Sonnekalb (*ibid.*, 511). The following appears to be new. When ethyl mercaptan is treated with nitric oxide in presence of potassium hydroxide a 95% yield of ethyl sulphide is produced: $2EtSH+2NO=Et_2S+N_2O+H_2O$. The reaction between nickel sulphate, nitric oxide, ethyl mercaptan, and potassium hydroxide gives 84% of almost pure ethyl hyponitritonickel sulphide, NO·Ni·SEt. When the reactants are modified, products of varying composition are obtained, but all of them contain a relatively large proportion of the hyponitrito-compound. A mixture of ferrous hydroxide and potassium ethyl sulphide is converted by carbon monoxide into the *compound*, $Fe_2(SEt)_2(CO)_6$, m. p. (high vacuum) 67° after softening.

H. BURTON.

Bromoformic esters. K. W. ROSENMUND and H. DÖRING (Arch. Pharm., 1928, **266**, 277—280).—Carbonyl bromide, prepared by Bartal's method (A., 1906, i, 731), interacts with ethyl alcohol in cold light petroleum to give a meagre yield of *ethyl bromoformate*, b. p. 116°. In a similar way, n-*propyl bromoformate*, b. p. 79—80°/108 mm., iso*amyl bromoformate*, b. p. 58°/14 mm., and *benzyl bromoformate*, b. p. 96°/15 mm., are obtained. These compounds are all violently lachrymatory, and are unstable, even when preserved in a sealed tube. Because of its instability, the ethyl ester cannot be used in the scission of alkaloids, like ethyl chloroformate. Carbonyl bromide interacts with 8-hydroxyquinoline as a brominating agent, the products being the 5-bromo- and 5 : 7-dibromo-derivatives.

W. A. SILVESTER.

Acidic and basic catalysts of acetylation reactions. J. B. CONANT and G. M. BRAMMANN.—See this vol., 1101.

Decomposition of acetyl peroxide and the mechanism of Kolbe's electro-synthesis. O. J. WALKER (J.C.S., 1928, 2040—2045; cf. Fairweather and Walker, A., 1927, 119; Fichter, A., 1926, 500).—The thermal decomposition of acetyl peroxide in the pure state or in solution gives rise to only small quantities of ethane, although comparatively large amounts of methane are formed. Methane is never found in the anode gases during the electrolysis of acetates. This evidence, together with the fact that peroxides have not been isolated by electrochemical means even at low temperatures, constitutes important evidence against the peroxide theory of the mechanism of Kolbe's reaction.

Acetyl peroxide in aqueous acetic acid solution is decomposed by ultra-violet light into carbon dioxide, ethane, and methane. The relative proportion of ethane is much higher than in the corresponding thermal decomposition.

F. J. WILKINS.

Resolution of racemic chlorobromoacetic acid. H. J. BACKER and H. W. MOOK (J.C.S., 1928, 2125—2130).—Chlorobromoacetic acid (Crompton and others, *ibid.*, 1920, **117**, 691; 1921, **119**, 1874), b. p. 103—104°/11 mm., m. p. 31·5° (lit. 25° and 38°), k_{25} $5·7\times10^{-2}$ (*potassium hydrogen* and normal *potassium* salts), is resolved by means of its *brucine* salt, *brucine* l-*chlorobromoacetate*, $+2—3H_2O$, separating first. From this by treatment with excess of sodium hydroxide, extraction of the brucine with chloroform, and neutralisation the value $[M]_D$ $+6·3°$ is found for

the sodium salt, the value for the undissociated acid being $[M]_D$ −28°. The rotations of the acid and its salts are determined for various wave-lengths. The active acid and its salts are stable in aqueous solution at the ordinary temperature, but not in the presence of strong bases and, contrary to the finding of Read and McMath (A., 1926, 1024), racemisation of the brucine salt in chloroform is more rapid than that of the neutral salts in aqueous solution. Hydroxyl ions rapidly catalyse the racemisation of the salts, the velocity coefficient of racemisation being determined with various concentrations of alkali. The catalytic action of the hydroxyl ion is increased by addition of neutral salts, especially with cations of higher valency. J. W. BAKER.

Conductometric titration of sodium salts of fatty acids of high mol. wt. P. EKWALL (Kolloid-Z., 1928, **45**, 291—306).—The conductometric titration of high-molecular, saturated fatty acids differs from that of sodium acetate in that the titration curve shows three breaks. This is due to the formation of acid soaps containing the sodium salt and free acid in the proportions 1 : 1 and 1 : 2. The breaks are less marked in the titration curve of sodium oleate, probably in consequence of the high colloid content of the original solution and also the greater solubility of the acid oleate. A rectilinear titration curve is obtained when the soap solution is at very great dilution. The conclusions reached from these experiments concerning the existence of acid soaps are in agreement with those deduced by other means.
E. S. HEDGES.

***iso*Oleic acids.** K. H. BAUER and J. MITSOTAKIS (Chem. Umschau, 1928, **35**, 137—139).—The *iso*oleic acids (C_{18}, with double linking elsewhere than $\iota : \kappa$) are solid at the ordinary temperature and give lead salts insoluble in alcohol; they may therefore be present in hardened fatty acids isolated by Twitchell's lead salt method. The acids from a hardened groundnut oil were ozonised in the form of their methyl esters and the fission products oxidised with hydrogen peroxide. From the products there were isolated: *n*-decane-$\alpha\kappa$-dicarboxylic acid, m. p. 123—124°, azelaic acid, m. p. 106°, *n*-hexoic acid, b. p. 235—250°. These indicate the presence in the original hardened acid of Δ^{μ}-heptadecene-α-carboxylic acid, formed most probably by reduction of one double linking in linoleic acid. C. HOLLINS.

Esters of α-linolenic acid hexabromide from Philippine lumbang oil. M. L. A. VICENTE and A. P. WEST (Philippine J. Sci., 1928, **36**, 73—77).—The following esters of α-linolenic acid hexabromide (cf. A., 1927, 540) have been prepared: n-*propyl*, m. p. 144—146°; iso*propyl*, m. p. 141—143°; iso-*butyl*, m. p. 136—138°, and *amyl*, m. p. 133—135°. The solubilities of these esters in numerous organic solvents are quoted. H. BURTON.

[Ethyl] hydrogen dicarboxylates. E. FOURNEAU and S. SABETAY (Bull. Soc. chim., 1928, [iv], **43**, 859—861).—When mixtures of dicarboxylic acids and their ethyl esters are heated below the decomposition temperature of the acid, ethyl hydrogen dicarboxylates are obtained. The reaction must be carried out in absence of moisture. Ethyl hydrogen oxalate; succinate, b. p. 146—149°/17 mm., d^{21} 1·148, n_D^{21} 1·4323; adipate, b. p. 169—170°/17 mm., m. p. 28—29°, d^{20} 1·081, n_D^{20} 1·4384; suberate, b. p. 186—188·5°/16 mm., m. p. 21—22°, 1·037, n_D^{23} 1·4412, and sebacate, b. p. 202—203°/15 mm., m. p. 35°, have been prepared. H. BURTON.

Use of toluenesulphonic esters in place of halogen esters in malonic ester syntheses. D. H. PEACOCK and P. THA (J.C.S., 1928, 2303—2305).—Esters of *p*-toluenesulphonic acid may be used in place of halogen esters in the preparation of substituted malonic esters from ethyl sodiomalonate, and ethyl methyl-, ethyl-, and phenoxyethyl-malonates have thus been prepared. β-Phenoxyethyl alcohol is converted by the action of *p*-toluenesulphonyl chloride and 20% sodium hydroxide solution into β-*phenoxyethyl* p-*toluenesulphonate*, m. p. 80°.
J. W. BAKER.

Inversion of geometrical isomerides by an exothermic reaction. Conversion of maleic into fumaric acid. P. NEOGI, S. NEOGI, and M. P. CHATTERJI (J. Indian Chem. Soc., 1928, **5**, 279—283; cf. Skraup, A., 1891, 1320, 1338).—When an aqueous solution of maleic acid containing manganese dioxide in suspension is treated with sulphur dioxide for 5 min. a 50% conversion into fumaric acid takes place, and the temperature of the solution rises from 27° to 60°. At 15° there is only 10% conversion, but at 90° the transformation is again 50%. The interchange does not take place with either manganese or sulphur dioxide alone, or with both reagents in presence of alcohol or ether. Lead and barium peroxides with sulphur dioxide, or phosphoric oxide alone, do not cause any conversion, neither do the products of interaction of manganese and sulphur dioxides. The results support Skraup's vibration theory (*loc. cit.*). H. BURTON.

Rupture of the six-carbon chain of adipic acid. II. J. VON BRAUN, F. JOSTES, and H. WAGNER (Ber., 1928, **61**, [*B*], 1423—1431).—Revision of previous work (A., 1926, 1128) in the light of the criticisms of Fuson (this vol., 738) confirms the suggestion of the latter that ethyl β-diethylaminopropionate and not the α-isomeride is produced by cleavage of ethyl αα′-dibromoadipate under the influence of diethylamine. The postulated intermediate formation of a *cyclo*butane derivative is accepted, but the structure of the amine molecule is regarded as the factor controlling fission or production of a diaminoadipic ester.

Ethyl α-diethylaminopropionate, b. p. 69—71°/13 mm., is prepared from ethyl α-bromopropionate and a moderate excess of diethylamine (cf. Fuson, *loc. cit.*) and is converted by methyl iodide into the very hygroscopic *methiodide*, m. p. 69—70°. Reduction of the ester with sodium and alcohol gives β-*diethylamino*-n-*propyl alcohol*, b. p. 56—58°/13 mm. [*methiodide*, m. p. 263° (decomp.)]. γ-Diethylamino-*n*-propyl alcohol methiodide has m. p. 188°. Methylethylamine, prepared from benzenesulphonmethylethylamide, b. p. 173°/13 mm., and ethyl αα′-dibromoadipate yield a mixture of *ethyl* β-*methylethylaminopropionate*, b. p. 75—80°/13 mm. (non-crystalline *picrate* and *hydrochloride*), and *ethyl* αα -*di-*

methylethylaminoadipate, b. p. 160—165°/13 mm., which contains a little of the unsaturated ester, $CO_2Et·CH(NMeEt)·CH_2·CH:CH·CO_2Et$. *Benzenesulphonmethyl*-n-*propylamide*, b. p. 182—183°/13 mm., is hydrolysed by concentrated hydrochloric acid at 160° to methyl-*n*-propylamine, b. p. 61—62° (non-crystalline *picrate*; very hygroscopic *hydrochloride*, m. p. 150°; *phenylmethyl*-n-*propylcarbamide*, m. p. 95°). With ethyl αα′-dibromoadipate the base affords *ethyl* β-*methyl*-n-*propylaminopropionate*, b. p. 83—85°/13 mm. (very hygroscopic *hydrochloride*, m. p. 111—112°; *picrate*, m. p. 75—77°), and non-homogeneous ethyl dimethyl-*n*-propylaminoadipate, b. p. 170—180°/13 mm. *Benzenesulphon*iso*propylamide*, b. p. 190°/13 mm., from *iso*propylamine and benzenesulphonyl chloride, is converted by methyl iodide and alkali hydroxide into *benzenesulphonmethyl*iso*propylamide*, b. p. 175°/13 mm., from which *methyl*iso*propylamine*, b. p. 50°, d_4^{19} 0·7026, is derived; the *hydrochloride*, m. p. 77°, *acetyl* derivative, b. p. 69—70°/13 mm., and *benzoyl* compound, b. p. 144°/13 mm., of the base are described. *Phenylmethyl*iso*propylcarbamide*, m. p. 131°, non-crystalline *methyl*iso*propylcarbamide*, and *phenylmethyl*iso*propylthiocarbamide*, m. p. 120°, have been prepared. With ethyl αα′-dibromoadipate, the base yields almost equal proportions of *ethyl* β-*methyl*iso*propylaminopropionate*, b. p. 84—86°/13 mm. (*picrate*, m. p. 85—86°), and impure ethyl di-αα′-methyl*iso*propylaminoadipate. 3-Methylhexahydropyridine, b. p. 125°, prepared by reduction of 3-methylpyridine with sodium and alcohol and purified through the *benzoyl* derivative, b. p. 185—186°/13 mm., m. p. 44—45°, converts ethyl αα′-dibromoadipate into a mixture of almost equal parts of *ethyl* β-3-*methylpiperidylpropionate*, b. p. 111—112°/13 mm. (*hydrochloride*, m. p. 167—169°; *picrate*, m. p. 98—99°), and *ethyl di*-αα′-3-*methylpiperidyladipate*, m. p. 61—63° (*hydrochloride*, m. p. 191°; *picrate*, m. p. 196°). 2-Methylpiperidine yields similarly *ethyl* β-2-*methylpiperidylpropionate*, b. p. 117—119°/14 mm. (*picrate*, m. p. 123°), and non-homogeneous ethyl di-αα′-2-methylpiperidyladipate. *trans*-Decahydroquinoline and ethyl αα′-dibromoadipate afford *ethyl* β-*decahydroquinolylpropionate*, b. p. 155—156°/13 mm. (*hydrochloride*, m. p. 165—167°; *picrate*, m. p. 102°), and *ethyl di*-αα′-*decahydroquinolyladipate*, m. p. 107—108°.

H. Wren.

Synthesis of cyclic compounds. III. Reduction of some unsaturated cyano-esters by moist aluminium amalgam. New synthesis of ββ′β′-tetramethyladipic acid. Further evidence for the multiplanar configuration of the *cyclo*heptane ring. I. Vogel (J.C.S., 1928, 2010—2032).—A number of unsaturated cyano-esters of the type $CR_1R_2:C(CN)·CO_2Et$, where R_1R_2 is *gem*-dimethyl, or CR_1R_2 is *cyclo*pentylidene, *cyclo*hexylidene, *cyclo*heptylidene, or *trans*-decahydronaphthylidene, have been prepared. By reduction with moist aluminium amalgam in ether they yield a mixture of the saturated cyano-esters, $CHR_1R_2·CH(CN)·CO_2Et$ (I) (main product), and the bimolecular compounds, $(·CR_1R_2·CH(CN)·CO_2Et)_2$ (II), the relative yields of (I) and (II) in the cases enumerated above being 63 and 21, 79 and 13, 84 and 6, and 72 and 12%, respectively. These results are in harmony with the alteration of the carbon tetrahedral angle postulated by the Thorpe–Ingold valency deflexion theory and confirm the earlier conclusions (Baker and Ingold, J.C.S., 1923, **123**, 122; Dickens, Horton, and Thorpe, A., 1924, i, 1313; Baker, A., 1925, i, 1277) concerning the multiplanar configuration of the *cyclo*heptane ring. The following new compounds are described and revised physical data given in the paper. Ethyl α-cyano-ββ-dimethylacrylate, m. p. 33° (lit. 28°), which condenses with alcoholic potassium cyanide to give a 60% yield of *as*-dimethylsuccinic acid (ethyl ester, b. p. 100°/15 mm., 1·4209, $d_4^{22·7}$ 0·9945); ethyl *r*-*iso*propylcyanoacetate, b. p. 99°/16 mm., n_D 1·4243, d_4^{20} 0·9855, γ^{20} 31·82; *ethyl* αδ-*dicyano*-ββγγ-*tetramethylbutane*-αδ-*dicarboxylate* (*monoamide*, m. p. 95°), which by hydrolysis with concentrated hydrochloric acid for 12 hrs. yields βββ′β′-tetramethyladipic acid. *Ethyl* r-cyclo*pentylcyanoacetate*, b. p. 129°/13 mm., n_D 1·4536, d_4^{20} 1·0246, γ^{20} 34·77, by hydrolysis yields cyclo*pentylmalonic acid*, m. p. 165°. Condensation of ethyl *cyclo*pentylidenecyanoacetate with alcoholic potassium cyanide gives an 81% yield of 1-carboxy*cyclo*pentane-1-acetic acid, m. p. 160° (lit. 154·5—155·5°) [*anhydride*, b. p. 135—137°/13 mm., m. p. 32°; *anilic acid*, m. p. 169° (decomp.); *ethyl* ester, b. p. 129°/13 mm., $n_D^{20·2}$ 1·4477, $d_4^{20·2}$ 1·0412]. Ethyl *cyclo*hexylidenecyanoacetate has b. p. 151°/12 mm., n_D 1·4974, d_4^{20} 1·0558, γ^{20} 37·89; *ethyl* r-cyclo*hexylcyanoacetate*, b. p. 145°/14 mm., n_D 1·4612, d_4^{20} 1·0210, γ^{20} 35·58; the *ester*, $[·C(>C_5H_{10})·CH(CN)·CO_2Et]_2$, m. p. 87°; *ethyl* cyclo*heptylidenecyanoacetate*, b. p. 160°/12 mm., $n_D^{18·6}$ 1·5003, $d_4^{18·6}$ 1·0534, γ^{20} 37·57, is obtained in 31% yield by the condensation of *cyclo*heptanone with ethyl cyanoacetate in the presence of piperidine at 100°, and condenses with alcoholic potassium cyanide to yield 1-carboxy*cyclo*heptane-1-acetic acid, m. p. 159° [Dickens, Horton, and Thorpe, *loc. cit.*, give 153°; *anhydride*, m. p. 16°, b. p. 166°/13 mm.; *anilic acid*, m. p. 159° (decomp.)]: *ethyl* r-cyclo*heptylcyanoacetate*, b. p. 149°/11 mm., n_D 1·4664, d_4^{20} 1·0206, γ^{20} 36·09, which hydrolyses to cyclo*heptylmalonic acid*, m. p. 164·5° (decomp.): the *ester* $[·C(>C_6H_{12})·CH(CN)·CO_2Et]_2$, m. p. 74°. *Ethyl* trans-*decahydro*-β-*naphthylidenecyanoacetate*, b. p. 196°/14 mm., n_D 1·5108, d_4^{20} 1·0519, γ^{20} 37·51, is obtained in 61% yield by condensation of *trans*-β-decalone, b. p. 106°/12 mm., n_D 1·4809, d_4^{20} 0·9787, γ^{20} 36·57, with ethyl cyanoacetate in the presence of piperidine; *ethyl* r-trans-*decahydro*-β-*naphthylcyanoacetate*, b. p. 186°/12 mm., n_D 1·4802, d_4^{20} 1·0301, γ^{20} 36·33, hydrolyses to *decahydro*-β-*naphthylmalonic acid*, m. p. 122° (decomp.); ethyl benzylidenemalonate has b. p. 163°/14 mm., n_D 1·4872, d_4^{20} 1·0759, γ^{20} 35·59; *cyclo*pentanone, b. p. 129·5°/761·5 mm., n_D 1·4383, d_4^{20} 0·9486, γ^{20} 33·85; *cyclo*hexanone, b. p. 47°/15 mm., n_D 1·4521, d_4^{20} 0·9457, γ^{20} 34·51; *cyclo*heptanone, b. p. 71°/19 mm., 1·4635, d_4^{20} 0·9496, 35·37. The parachors of all the above compounds have been determined, the observed values for the ring constants in the five-, six-, and seven-membered rings being 10·2, 8·4, and 6·0, respectively, whilst that for the *trans*-decahydro-β-naphthalene ring is 17·6, almost exactly twice the value obtained for the *cyclo*hexane ring.

The volume of the methylene group ($[P_1]/n$) in the *cyclo*heptane ring is 39·7, a value which approximates closely to that of the methylene group in an open-chain hydrocarbon, and this gives further support to the view that the *cyclo*heptane ring is multiplanar.
J. W. BAKER.

Differentiation of tartaric, citric, and oxalic acids amongst themselves. D. I. PERIETZEANU (Bul. Soc. chim. Romania, 1928, **10**, 49).—A solution of copper acetate in presence of concentrated acetic acid gives with tartaric acid a precipitate of copper tartrate soluble in dilute hydrochloric acid and in 30% sodium hydroxide. Citric acid produces no precipitate, whilst the precipitate of copper oxide obtained with oxalic acid is insoluble in 30% sodium hydroxide solution, but soluble in excess of concentrated hydrochloric acid. C. HOLLINS.

Electrolytic reduction of dithiodiacetic acid. E. LARSSON (Ber., 1928, **61**, [*B*], 1439—1443).—Polarisation experiments indicate little hope of the successful reduction of dithiodiacetic acid to thiolacetic acid at a platinum cathode. On the other hand, thiolacetic acid is almost quantitatively produced when the dithio-acid dissolved in 2*N*-sulphuric acid is reduced at a lead cathode in a divided cell, the anode being a carbon rod immersed in dilute sulphuric acid. Reduction can be effected either with constant cathode potential or constant current density, but the current yields are usually higher if the former method is used unless a sufficiently small current density is employed. H. WREN.

Optically active α-arsenocarboxylic acids. H. J. BACKER and C. H. K. MULDER (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 301—303).—α-Arsenocarboxylic acids are obtained in good yield by the action of potassium arsenite on the potassium salt of the appropriate α-bromocarboxylic acid, $CHRBr\cdot CO_2K + K_3AsO_3 = CHR(AsO_3K_2)\cdot CO_2K + KBr$, and thus are prepared *α-arsenobutyric acid*, m. p. 127° (*diquinine* salt, $+5H_2O$), and *α-arsenovaleric acid*, m. p. 114° (*diquinine* salt, $+4H_2O$). These acids titrate as dibasic acids, and by fractional crystallisation of the diquinine salts from dilute alcohol the optically active acids are obtained. The rotatory dispersion of these acids and their barium salts has been investigated. Neutralisation of both acidic functions causes a reversal in the sign of the rotation. The following values are obtained: d-*α-arsenopropionic acid*, $[M]_D$ +41·0° (*barium* salt, −8·5°); d-*α-arsenobutyric acid*, +25·7° (*barium* salt, −10·5°); d-*α-arsenovaleric acid*, $[M]_D$ +19·3° (*barium* salt, −15·6°). The active barium salts are not racemised in aqueous solution at 100°, but the free acids readily racemise, especially in the presence of mineral acids, the racemisation being a unimolecular reaction.
J. W. BAKER.

Photo-oxidation of organic compounds by dichromates. J. PLOTNIKOV and others.—See this vol., 1102.

Identification of hexamethylenetetramine and formaldehyde; rapid analytical differentiation of the compounds in a mixture. M. V. IONESCU (Bull. Soc. chim., 1928, [iv], **43**, 677—680).—Formaldehyde and dimethyldihydroresorcinol react in cold solution with quantitative precipitation of methylenebisdimethyldihydroresorcinol, m. p. 187°. The same product is formed from hexamethylenetetramine in boiling solution. Determination of the two substances in presence of one another is based on the observation that formaldehyde is quantitatively precipitated as the methylene derivative after 15 min. at the ordinary temperature, whereas hexamethylenetetramine does not react to an appreciable extent until the solution is boiled. H. WREN.

Stearaldehyde. R. FEULGEN and M. BEHRENS (Z. physiol. Chem., 1928, **177**, 221—230).—Reduction of acid chlorides to aldehydes by Rosenmund's method (A., 1918, i, 300) proceeds more rapidly if freshly-precipitated barium sulphate is used for the preparation of the palladium catalyst. Stearyl chloride furnishes a mixture of stearaldehyde (*thiosemicarbazone*, m. p. 111°) and a *dimeride*, $(C_{18}H_{36}O)_2$, m. p. 55°, which is sparingly soluble in alcohol, does not react with Schiff's reagent, and does not reduce ammoniacal silver nitrate. When distilled from an oil-bath at 140—200°/1 mm., it gives stearaldehyde.

Palmitaldehydethiosemicarbazone has m. p. 109°.
H. BURTON.

Heintz's aldol and its preparation. F. ADAMANIS (Rocz. Chem., 1928, **8**, 349—357).—Heintz's aldol is prepared by shaking acetone with sodium hydroxide for 30 hrs., and is converted by the action of magnesium methyl bromide into βδ-dimethylpentane-βδ-diol, which on dehydration yields βδ-dimethyl-Δ^{β}-penten-δ-ol. R. TRUSZKOWSKI.

Alkali fission of pentoses. F. FISCHLER and R. BOETTNER (Z. physiol. Chem., 1928, **177**, 264—269).—When a 1% solution of xylose or arabinose is mixed with a solution containing 0·04*M*-sodium carbonate and 4—6% of sodium sulphite and then distilled carefully a neutral distillate is obtained which reduces ammoniacal silver nitrate and Fehling's solution in the cold, restores the colour to Schiff's reagent, and gives the iodoform reaction. The distillate contains methylglyoxal and glycollaldehyde (cf. A., 1926, 1170). Acetone, acetaldehyde, and formaldehyde are not formed. It is suggested that fission of the pentose molecule occurs, yielding glycollaldehyde and glyceraldehyde, which under the influence of alkali is transformed first into dihydroxyacetone and then into methylglyoxal. H. BURTON.

Oxidation of carbohydrates, fats, and nitrogenous products by air in presence of sunlight. C. C. PALIT and N. R. DHAR.—See this vol., 1103.

Mechanism of carbohydrate oxidation. IX. Action of copper acetate solutions on dextrose, lævulose, and galactose. W. L. EVANS, W. D. NICHOLL, G. C. STROUSE, and C. E. WARING (J. Amer. Chem. Soc., 1928, **50**, 2267—2285).—The oxidation of dextrose, lævulose, and galactose at 50° in aqueous solutions saturated with copper acetate was studied. The amounts of glucosone, formic, carbonic, glyoxylic, and oxalic acids formed were determined, and their relation to time and oxygen consumption (measured by the formation of cuprous oxide) was investigated. The presence of glycollic acid was shown by qualitative tests. The hydrogen-ion concentration was also

measured during the course of the reaction. Glucosone was formed from dextrose and lævulose, and was apparently formed by oxidation of the enediol derived from the hexose by enolisation. No galactosone was found, probably owing to its being used up as rapidly as it formed. Formic acid is regarded as arising from the oxidation of hydroxymethylene resulting from decomposition of the enediol. In support of this hypothesis, it was found that hydroxypyruvic acid was oxidised by copper acetate to formic acid (2 mols.) and carbon dioxide (1 mol.). Moreover, glycollaldehyde was similarly oxidised to formic acid. Carbon dioxide began to appear in the sugar oxidation at about the same time that glucosone production reached a maximum. It was considered to be a decomposition product of an α-ketogluconic acid formed by oxidation of the glucosone, and this was supported by the above experiments with hydroxypyruvic acid. Carbon dioxide was not produced from galactonic or gluconic acid, glyoxal, or glycollic acid, which were unaffected by copper acetate. The glyoxylic, oxalic, and glycollic acids were considered to be derived from the Δ^{β}-diol formed from glucosone by enolisation and the fission of this into an active form of erythrose and a half-active form of glyoxal, $>$C(OH)·CHO. The latter then yields the products found. The hydrogen-ion concentration increased in the course of the reaction. This would diminish the concentration of enediol and result in the decreased production of formic acid, which is actually found. The hexosone Δ^{β}-diol does not appear to oxidise to a $\beta\gamma$-diketohexose. The view is expressed that aldehydes exist in two forms, those active towards oxidising agents and those not active. The former are derivatives of hydroxymethylene, *i.e.*, the hydrogen is bound to oxygen and the carbon is bivalent. In the inactive molecules the carbon is quadrivalent. An equilibrium exists between these two forms which may be shifted by a change in the hydrogen-ion concentration. The conversion of aldehydes into carbonates in alkaline solution is explained on this basis. R. K. CALLOW.

System of the simple sugars and α-substituted fatty acids. K. FREUDENBERG (Naturwiss., 1928, **16**, 581—587).—A discussion, in the light of modern work, of the systematic derivation of configuration and nomenclature. R. K. CALLOW.

Reactions between sugars and amino-compounds. IV. H. VON EULER, E. ERIKSSON, and E. BRUNIUS (Svensk Kem. Tidskr., 1928, **40**, 163—171).—Dextrose and protein derivatives interact slowly with reduction of the amino-nitrogen, and the mixture will decolorise methylene-blue in approximately neutral solution. A similar reaction takes place when sodium zymophosphate or sodium hexosemonophosphate is substituted for the dextrose; in these cases a small amount of salt formation ensues as a secondary reaction. Dextrose and alkali hydroxide interact, forming sodium glucosoxide, slight decomposition also taking place. On account of the small extent of this decomposition, the resulting products cannot be certainly identified, but probably consist mainly of dihydroxyacetone and methylglyoxal. Experiments with N- and $2N$-solutions of dextrose and glycine to which a dilute methylene-blue solution was added showed that decolorisation took place when the p_{H} value of the solution was above 8, no action resulting below this. Incubation of the mixed solutions for varying periods before addition of the methylene-blue was found to shorten the time required for subsequent decolorisation; this could not be ascribed to action between the dextrose and the alkali used. If ammonia is used in place of sodium hydroxide no reduction takes place even after an incubation period of 24 hrs. Solutions of purified candioline-sodium (sodium zymophosphate) or sodium hexosemonophosphate and glycine reacted in a similar manner, decolorising methylene-blue. Dihydroxyacetone alone reduces methylene-blue, but as the time required for decolorisation increases greatly with diminishing concentrations of dihydroxyacetone, the action is possibly due to small amounts of impurities. Experiments with solutions of dihydroxyacetone to which a suspension of yeast had been added gave inconclusive results. Illumination of the above solutions by exposure to a quartz–mercury-vapour lamp showed that the system glycine–dextrose–methylene-blue was only slightly affected by light, the acceleration of the reaction being somewhat greater when the dextrose was replaced by sodium hexosemonophosphate. H. F. HARWOOD.

Mechanism of the formation of osazones. B. GLASSMANN and (MRS.) ROCHWARGER-WALBE (Ber., 1928, **61**, [*B*], 1444—1451).—Small quantities of ammonia in the presence of aniline and phenylhydrazine can be determined accurately by destruction of the latter with boiling Fehling's solution, collection of the distillate in 0·1N-hydrochloric acid, and titration of the excess of the latter in the presence of methyl-orange. After titration, the aniline in the distillate is weighed as tribromoaniline and the ammonia is calculated from the difference. More rapid results are obtained by taking advantage of the quantitative adsorption of ammonia from a very dilute solution of ammonia, aniline, and phenylhydrazine by permutit, from which the two bases last named are readily washed away. The ammonia liberated from the permutit by treatment with alkali hydroxide is colorimetrically determined by Nessler's solution. It is thus shown that phenylhydrazine in acetic acid solution at 100° undergoes partial autoreduction to benzene, aniline, ammonia, and nitrogen. Determinations of total ammonia in the filtrates obtained in a series of osazone preparations give results agreeing with the calculated values and thus afford analytical confirmation of Fischer's formulation. When the decomposition of phenylhydrazine in acetic acid solution is taken into account, there is no reason to assume that the base has a direct oxidising action in the production of osazones in the sense of the equation $NHPh{\cdot}NH_2+H_2O=NH_2Ph+NH_3+O$.
H. WREN.

Action of titanium tetrachloride on derivatives of sugars. I. Preparation of α-acetochlorosugars and transformation of β-methylglucoside into its α-form. E. PACSU (Ber., 1928, **61**, [*B*], 1508—1513).—The action of tin tetrachloride on β-glucosides and β-acetylsugars is slow and accompanied by slight decomposition in its final stage (cf.

this vol., 275). Silicon tetrachloride has no appreciable action. Tetra-acetyl-β-methylglucoside is rapidly isomerised by titanium tetrachloride in chloroform to the α-variety without decomposition. The change appears to differ fundamentally from that effected by tin tetrachloride, since a coloured, additive compound immediately separates from the solution. This compound is immediately decomposed by water with production of colourless solutions. Completely acetylated mono- and di-saccharides are more drastically affected by titanium tetrachloride than by tin tetrachloride, since the 1-acetyl group suffers quantitative replacement by chlorine with the production of acetochlorosugars in excellent yield and in a high state of purity. The following transformations are recorded: β-penta-acetylglucose into α-acetochloroglucose, m. p. 73°, $[\alpha]^{20}$ +167·85° in chloroform; β-penta-acetylmannose into α-acetochloromannose, m. p. 83°, $[\alpha]_D^{20}$ +90·58° in chloroform; β-octa-acetyllactose into hepta-acetyl-α-chlorolactose, m. p. 122°, $[\alpha]_D^{20}$ +83·97° in chloroform; β-octa-acetylgentiobiose into *hepta-acetyl-α-chlorogentiobiose*, m. p. 142—143°, $[\alpha]_D$ +89·22° in chloroform; β-penta-acetylsalicin into β-tetra-acetylchlorosalicin, m. p. 160°, $[\alpha]_D^{20}$ +12·02° in chloroform. H. WREN.

[Octa-acetyl]tetrathiodiglucose. F. WREDE and O. HETTCHE (Z. physiol. Chem., 1928, **177**, 298—300).—When tetra-acetylthioglucose (A., 1922, i, 525) is treated with excess of sulphur chloride in dry ether *octa-acetyltetrathiodiglucose*, m. p. 208°, $[\alpha]_D^{20}$ −307·6° in chloroform, is obtained. On hydrolysis with cold methyl-alcoholic ammonia it gives sulphur and octa-acetyldithioglucose (A., 1920, i, 13). Similar products could not be obtained using sulphur dichloride and selenium monochloride. H. BURTON.

Carbohydrates of the readily hydrolysable hemicellulose of the pine. E. HAGGLUND, F. W. KLINGSTEDT, T. ROSENQVIST, and H. URBAN (Z. physiol. Chem., 1928, **177**, 248—263).—Pine wood is digested with a solution of sodium hydrogen sulphite in sulphurous acid and the hydrolysed extract (18% of the wood) obtained after neutralisation with calcium carbonate is acidified, treated with α-naphthylamine sulphate to precipitate α-ligninsuphonic acid (cf. Klason, this vol., 622), then with activated charcoal, and finally hydrolysed with dilute sulphuric acid. After evaporation and separation into fractions soluble and insoluble in 80% alcohol it is found that a small amount of lignin (0·3% of wood) remains in solution. Sugar determinations on both fractions gave the following results (figures express percentage of hydrolysed hemicellulose): xylose and possibly arabinose (17), mannose (42·7), galactose (4·2), galacturonic acid (3·2), lævulose (4), and dextrose (28·9). H. BURTON.

Pectin and hemicelluloses of the flax plant. S. T. HENDERSON (J.C.S., 1928, 2117—2125).—Extraction of unretted flax fibre with 0·5% ammonium oxalate solution at 80—90° for 7 hrs. and subsequent removal of the methoxyl groups from the product by alkaline hydrolysis yields a gelatinous pectin which has the composition of a galactosetetragalacturonic acid, $(C_6H_{10}O_5, 4C_6H_8O_6-H_2O)_n$ (containing 20·7% of -uronic carbon dioxide; cf. Nanji, Paton, and Ling, J. Soc. Chem. Ind., 1925, **44**, 253T, who found 17·6%). From this is obtained a *copper* salt, $3(C_6H_7O_6)_2Cu,C_6H_8O_6,4H_2O$, derived from polygalacturonic acid without a combined hexose group. Hydrolysis of the pectin with 2% sulphuric acid (or, better, with 1% hydrochloric acid) gave yields up to 40% of an insoluble polygalacturonic acid $(C_6H_8O_6)_n$ (probably a purer form of the α-acid described by Ehrlich and Schubert, A., 1926, 547) together with a soluble *acid* (soluble *barium* salt) and a syrup containing galactose and arabinose, the latter arising either from adsorbed pentose or from partial decarboxylation of the galacturonic residues. Extraction of flax straw or fibre with water at 100—145° in a manner similar to that employed by Ehrlich leaves no pectin soluble in ammonium oxalate, the main product being calcium-magnesium salts (2% of the weight of the straw; 9·7% -uronic carbon dioxide), which yield free acids corresponding with the general hemicellulose formula $C_6H_{10}O_5$, but containing varying amounts of -uronic acid residues, and a solid hexopentosan (5%) which on hydrolysis yields arabinose, xylose, galactose, and a small amount of a fermentable hexose, and by oxidation with nitric acid (*d* 1·15) yields mucic acid. Hence flax fibre probably contains carboxylated hemicellulose of a non-pectic nature. Thus it is not trustworthy to determine pectin in flax by determining -uronic anhydride, *i.e.*, by the carbon dioxide evolved on boiling with hydrochloric acid (*d* 1·06). J. W. BAKER.

Lignin. IV. Soluble pinewood lignin obtained by different methods. A. FRIEDRICH (Z. physiol. Chem., 1928, **176**, 127—143; cf. A., 1927, 861).—In a series of soluble lignin preparations from pinewood by means of methyl alcohol and hydrochloric acid, the degree of methylation (14·5% OMe originally) depends, not only on the absence of water, but especially on the length of time the solvent is allowed to react; the maximum figure reached (20 hrs.) is 23·2% OMe (=2 methoxyl groups per mol.). This falls after treatment of the products with alkali hydroxide, one methoxyl group being lost, presumably from an ester group. Time of reaction being important, an ester or acetal linking between lignin and cellulose is excluded, since these would be alkylated very rapidly; the increase in methoxyl content therefore results from alkylation of already dissolved lignin.

A soluble lignin having the same methoxyl content as the original lignin is best obtained by treating woodmeal with a mixture of 1 vol. of glacial acetic acid and 3 vols. of concentrated hydrochloric acid at 100°, and precipitating the product by dilution of the filtered liquid, acetic acid being removed by dissolving in alcohol and reprecipitation with water; the product (10·5% OMe) is hydrolysed with alkali hydroxide to remove combined acetic acid (4 mols.), and then contains 14·4% OMe. This lignin reacts with 0·5 mol. of phenylhydrazine (thus confirming the double mol. wt. of lignin in its ketonic form), and takes up 2 methyl groups on methylation, one of which is removed by alkali hydroxide. It gives a tribenzoyl derivative, and with thionyl chloride a trichloro-compound. A soluble lignin with 14·5—15·5% OMe is also obtained by using acetone or chloroform and hydrogen chloride; chloroform does not react with

the lignin. Lignin precipitated from alcohol or chloroform by ether and benzene has the formula $C_{33}H_{36}O_{12}$; the mother-liquors contain an ether-soluble substance of lignin-like composition, and a benzene-soluble substance richer in carbon and hydrogen; the residual wood contains a third lignin which is not solubilised by the acetic acid method. C. HOLLINS.

Synthesis of glucosides and glucose esters of hydroxycarboxylic acids. K. JOSEPHSON (Arkiv Kemi, Min., Geol., 1928, **9**, No. 36, 1—11).—Acetobromoglucose and silver 2-hydroxy-*m*-toluate react in boiling xylene, yielding the *tetra-acetyl*-d-*glucose* ester of *2-hydroxy*-m-*toluic acid*, m. p. 148°, $[\alpha]_D$ $-37·4°$ in chloroform. Similar treatment of silver 4-hydroxy-*m*-toluate affords a mixture of the *tetra-acetyl*-d-*glucose* ester of *4-hydroxy*-m-*toluic acid*, m. p. 147°, $[\alpha]_D$ $-33·7°$ in chloroform, and 4-β-*tetra-acetyl*-d-*glucosidoxy*-m-*toluic acid*, m. p. 161°. This last compound is hydrolysed by barium hydroxide solution to 4-β-d-*glucosidoxy*-m-*toluic acid*, m. p. 148—149°, $[\alpha]_D$ $-48·4°$ in water, which undergoes fission with emulsin. Acetobromoglucose and silver hydroxydimethoxybenzoate (Herzig and Wenzel, A., 1902, i, 463) give the *tetra-acetyl*-d-*glucose* ester, m. p. 161°, $[\alpha]_D$ $-15·4°$ in chloroform. Sugar derivatives could not be obtained from quinic acid or *iso*propylidenequinide. H. BURTON.

Digitalis glucosides. I. Digitoxigenin and *iso*digitoxigenin. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, **78**, 573—581).—When kept for 1 hr. in solution in methyl-alcoholic potassium hydroxide digitoxigenin is converted into iso*digitoxigenin*, a neutral substance, m. p. 271°; this could not be hydrogenated. On warming with dilute sodium hydroxide and acidification with acetic acid there was obtained iso*digitoxigeninic acid*, $C_{23}H_{36}O_5$, m. p. 250° (identical with the dixigenic acid of Kiliani and Cloetta, A., 1899, i, 932; 1921, i, 39) [*methyl* ester, m. p. 128°; methyl ester *semicarbazone*, m. p. 156° efferv.)]. The above ester, with chromic acid, gave iso*digitoxigonic methyl* ester, $C_{24}H_{34}O_5$, m. p. 190° (*semicarbazone*, m. p. 243°), which, on hydrolysis, neutralised two equivalents of alkali and, on re-acidification with mineral acid, gave iso*digitoxigonic acid*, m. p. 212—213°.

*iso*Digitoxigeninic acid gave, with hypobromite, a lactone acid, iso*digitoxigenic acid*, $C_{23}H_{34}O_5$, m. p. 229°. The results are therefore entirely similar to those previously obtained with *iso*strophanthidin, and indicate that in digitoxigenin also the lactone ring contains a βγ-unsaturated linking.

C. R. HARINGTON.

Production of bases from carbonyl compounds. A. SKITA and F. KEIL [with A. VON GRAETZEL and E. BAESLER] (Ber., 1928, **61**, [*B*], 1452—1459).—Catalytic reduction of Schiff's bases in acid solution can be effected satisfactorily only with the more stable members of the group, since with less stable compounds the rate of hydrolysis exceeds that of hydrogenation. In neutral solution or suspension the absorption of hydrogen is inadequate, but formation of secondary bases occurs readily after addition of ammonia or a primary amine. It is frequently more advantageous to start with a mixture of aldehyde and amine instead of pre-formed Schiff's base. Aldehydes of high mol. wt. in presence of ammonia are reduced exclusively to secondary amines, whereas the simpler aldehydes afford tertiary amines. Ketones in presence of ammonia or primary amines give secondary bases.

cyclo*Hexyl-γη-dimethyloctylideneamine*, b. p. 170—172°/18 mm., from citral and *cyclo*hexylamine is converted by hydrogen in the presence of alcohol, acetic acid, and colloidal platinum into cyclo*hexyl-γη-dimethyloctylamine*, b. p. 151—153°/14 mm. (*hydrochloride*, m. p. 154—155°; *picrolonate*, m. p. 174—175°). In neutral solution, iso*amyl-γη-dimethyloctylideneamine*, b. p. 150—154°/20 mm., affords iso*amyl-γη-dimethyloctylamine*, b. p. 142—145°/17 mm. (*hydrochloride*, m. p. 168—169°; *picrolonate*, m. p. 142—145°/17 mm.). In aqueous suspension in the presence of ammonia, *ethyl-γη-dimethyloctylideneamine*, b. p. 113—115°/12 mm., yields *ethyl-γη-dimethyloctylamine*, b. p. 135—137°/13 mm. (*hydrochloride*, m. p. 102—103°; non-crystalline *nitroso*-compound; *picrolonate*, m. p. 196—197°). *Methyl-γη-dimethyloctylideneamine*, b. p. 107—109°/13 mm., affords *methyl-γη-dimethyloctylamine* in very modest yield.

Hydrogenation of citral in aqueous suspension in presence of colloidal platinum and ammonia gives *di-γη-dimethyloctylamine*, b. p. 191—193°/15 mm. (*hydrochloride*, m. p. 141—142°), obtained also by reduction of citral oxime. Heptaldehyde, under similar conditions, yields diheptylamine, m. p. 30°, b. p. 270—272° (hydrochloride, m. p. 250°). Acetaldehyde and propaldehyde or the oximes afford triethylamine and tripropylamine, respectively.

Di*iso*propylamine, b. p. 84° (hydrochloride, m. p. 212—214°; *picrate*, m. p. 140°), is prepared from acetone, whilst methyl ethyl ketone affords methylethylcarbinol and di-*sec*.-butylamine, b. p. 230—233° (hydrochloride, m. p. 215—216°). Di-α-ethylpropylamine is prepared in about 20% yield from diethyl ketone. *cyclo*Hexanone yields a mixture of *cyclo*hexanol and *di*cyclo*hexylamine*, b. p. 128—130°/20 mm. (*hydrochloride*, m. p. about 340°). Ethyl*sec*.-butylamine, b. p. 96—98°, and cyclo*hexylethylamine*, b. p. 161° (*hydrochloride*, m. p. 182—183°), are derived from ethylamine and methyl ethyl ketone or *cyclo*hexanone, respectively. H. WREN.

Reaction between α-oxides and α-monochlorohydrins and hydrazine. A. K. PLISOV (Ukraine Chem. J., 1928, **3**, [Sci.], 125—131).—Ethylene oxide on addition of excess of hydrazine hydrate yields a mixture of *as*-di-β-hydroxyethylhydrazine and β-*hydroxyethylhydrazine*, b. p. 146—153°/25 mm. Trimethylethylene oxide similarly yields as-*di*-β-*hydroxy*-αβ-*dimethylpropylhydrazine*, b. p. 185—190°/44 mm. The use of the corresponding α-monochlorohydrins leads to the production of the same products, indicating that the chloro-derivatives pass through the stage of oxide before combining with hydrazine.

R. TRUSZKOWSKI.

General reaction of amino-acids. II. H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, **78**, 745—756).—The azlactones obtained by the action of acetic anhydride on leucine, phenylalanine, and aspartic acid yield, with acetic anhydride and pyridine, the same

acetamidoketones as do the amino-acids; it is possible, therefore, that such azlactones represent an intermediate stage in the reaction recently observed (this vol., 874). Methylaspartic acid gives no ketone, in accordance with the view previously expressed (*loc. cit.*) that the reaction cannot take place in the absence of replaceable hydrogen in the α-position; β-amino-acids, on treatment with acetic anhydride and pyridine, undergo simple acetylation. Aspartic acid, when warmed with acetic anhydride and pyridine, gave a substance which, on hydrolysis with hydrochloric acid, yielded ammonium chloride and β-hydroxylævulic acid and when heated with phenylhydrazine acetate gave carbon dioxide and diacetylbisphenylhydrazone, and is therefore regarded as *β-acetamidolævulic acid*. Glutamic acid gave only 15—20% of the theoretical amount of carbon dioxide owing to formation of pyrrolidonecarboxylic acid; the remaining reaction product was *γ-acetamido-δ-ketohexoic acid*, since, on hydrolysis and treatment with ammonia, it gave 2 : 5-*dimethylpyrazine*-3 : 6-*dipropionic acid*, m. p. 211—213°. Serine gave a substance with the qualitative reactions of a ketone. Phenylserine gave no ketone, but was converted into the azlactone of β-acetamidocinnamic acid. Histidine gave *methyl α-acetamido-β-iminazoylethyl ketone*, which on hydrolysis with hydrochloric acid yielded *methyl α-amino-β-iminazoylethyl ketone dihydrochloride*, m. p. 205—206°. Tryptophan yielded *methyl α-acetamido-β-indolylethyl ketone*. C. R. HARINGTON.

Colour reaction of creatine and of carbamide. E. PITTARELLI (Arch. Farm. sperim., 1928, **45**, 173—176).—An alkaline solution of creatine when treated with sodium nitroprusside and a small quantity of a persulphate gives slowly a permanent red coloration, which can also be produced immediately if a trace of potassium ferricyanide is added to the mixture. This reaction detects creatine at a dilution of 1 in 50,000; it is also given by carbamide, but in this case the limiting dilution is 1 in 500 only.

E. W. WIGNALL.

Action of Grignard reagent on α-aminodicarboxylic acids. S. KANAO and S. INAGAWA (J. Pharm. Soc. Japan, 1928, No. 553, 238—252).—Ethyl aspartate gives with magnesium phenyl bromide tetraphenylaminobutanediol (Paal and Weidenkaff, A., 1907, i, 131). Tetra-alkylbutanediols undergo ring formation when heated with 33% sulphuric acid, yielding 2 : 2 : 5 : 5-tetra-alkyl-4-aminotetrahydrofurans. Thus, *γ-amino-βε-dimethylhexane-βε-diol*, m. p. 87—88°, b. p. 151—153°/19 mm., $[\alpha]_{D}^{20}$ −17·7° in absolute alcohol (*hydrochloride*, m. p. 89—89·5°; N-*benzoyl* derivative, m. p. 146—147°), obtained from ethyl *l*-aspartate and magnesium methyl iodide, is converted into 4-*amino*-2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*, b. p. 66—67°/23 mm., d_4^{20} 0·9021, n_D^{20} 1·4412, $[\alpha]_D^{20}$ −8·03° in alcohol (*hydrochloride*, m. p. 262°; N-*benzoyl* derivative, m. p. 136°). *δ-Amino-γζ-diethyloctane-γζ-diol*, b. p. 182—183°/19 mm., obtained from the same ester and magnesium ethyl bromide, is converted into 4-*amino*-2 : 2 : 5 : 5-*tetraethyltetrahydrofuran*, b. p. 113—113·5°/13 mm. (corr.), d_4^{20} 0·9168, n_D^{20} 1·4678, $[\alpha]_D^{20}$ −9·59° (*hydrochloride*, m. p. 270—275°). *ζ-Amino-δη-dipropyldecane-δη-diol*, b. p. 173—174°/19 mm., and *ι-amino-εθ-dibutyldecane-εθ-diol*, b. p. 180—184°/19 mm., are described. Glutamic and α-aminoadipic esters, on the contrary, give no tetra-alkyl or aryl derivatives with organo-magnesium halides; they take only two alkyl or aryl groups and close the ring, yielding α-pyrrolidonyl or α-piperidonyl derivatives. Thus, ethyl *d*-glutamate gives with magnesium methyl iodide *β-2-pyrrolidonylpropan-β-ol*, b. p. 201—202°/15 mm., with magnesium ethyl bromide, *γ-2-pyrrolidonylpentan-γ-ol*, m. p. 91—92°, b. p. 209—210°/11 mm., $[\alpha]_D^{20}$ −7·1° in water, which is reduced with sodium and methyl alcohol to *γ-2-pyrrolidylpentan-γ-ol*, b. p. 214—218°/757 mm., d_4^{20} 0·9577, n_D^{20} 1·4718 (*hydrochloride*, m. p. 160—161°, $[\alpha]_D^{20}$ −9·22° in water; *picrate*, m. p. 147—148°), with magnesium butyl iodide *ε-2-pyrrolindonylnonan-ε-ol*, m. p. 102—103°, with magnesium and bromobenzene α-(2-pyrrolidonyl)diphenylcarbinol, m. p. 190—191°, $[\alpha]_D^{20}$ −86·38° in chloroform (racemic *compound*, m. p. 182—183·2°), with magnesium benzyl chloride α-(2-pyrrolidonyl)-α-benzyl-β-phenylethan-α-ol, m. p. 202°. Ethyl α-aminoadipate gives with magnesium phenyl bromide α-(2-piperidonyl)diphenylcarbinol, m. p. 225—226°. K. ISHIMURA.

Separation of histidine and arginine. IV. Preparation of histidine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **78**, 627—635).—Crude dried hæmoglobin is hydrolysed with 8*N*-sulphuric acid; excess of the latter is removed as barium sulphate, the filtrate is concentrated and treated with silver oxide in excess and barium hydroxide to p_H 7·4; the precipitate is decomposed with hydrogen sulphide and the filtrate treated with sulphuric acid to 5% and then with mercuric sulphate; the precipitate is collected and decomposed with hydrogen sulphide in presence of sulphuric acid, and the filtrate from the mercuric sulphide adjusted to p_H 7·2 with barium hydroxide; the filtered solution is concentrated and treated with alcohol; a 4—5% yield of histidine, contaminated with traces of tyrosine, is obtained. The histidine is finally purified, with little loss, through the dihydrochloride, separated by treatment of the aqueous hydrochloric acid solution of the crude substance with saturated alcoholic hydrogen chloride. C. R. HARINGTON.

Dibenzoylarginine. K. FELIX and K. DIRR (Z. physiol. Chem., 1928, **176**, 29—42).—Nitration of dibenzoylarginine affords *di*-m-*nitrobenzoylarginine*, decomp indef. at about 225°, acid hydrolysis giving *m*-nitrobenzoic acid and arginine. Dibenzoylarginine heated with acetic anhydride yields dibenzoylacetylanhydroarginine (not crystallised), converted by hot water into benzoylacetylcarbamide and 3-*benzamido*-2-*piperidone*, m. p. 186—187°. It is concluded, therefore, that dibenzoylarginine is
NHBz·C(:NH)·NH·$[CH_2]_3$·CH(NHBz)·CO_2H. *d*-Dibenzoylarginine has m. p. 235° (decomp.), the *hydrochloride* having the decomposition point, 218°, attributed by Gulewitsch (A., 1899, i, 834) to the parent substance. The *ethyl ester hydrochloride* has m. p. 148°, sintering at 140°, and $[\alpha]_D^{20}$ −8°. *dl*-Dibenzoylarginine has m. p. 230° or (+1H_2O) 176°. The *ethyl ester hydrochloride* has m. p. 143°, sintering at 135°. The significance of the acid-binding power of

dibenzoylarginine is discussed (cf. Felix and Müller, this vol., 535). Modifications are given for the preparation of arginine from gelatin by acid hydrolysis and separation as the flavianate. A. WORMALL.

Synthesis of γ-dimethylaminocrotonic methylbetaine (crotonbetaine). W. LINNEWEH (Z. physiol. Chem., 1928, **176**, 217—221; cf. this vol., 665).—γ-Chlorocrotonic acid, prepared from epichlorohydrin, is heated with alcoholic trimethylamine and a trace of sodium iodide at 100° to give crotonbetaine identical with that isolated from ox-muscle. C. HOLLINS.

Decomposition of polypeptides containing amino-acids not known to occur in nature. VIII. Polypeptides containing $\alpha\alpha'$-diaminosuberic acid. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1928, **9**, 336—361).—Suberic acid may be brominated at atmospheric pressure if care be taken to exclude moisture. By treating $\alpha\alpha'$-dibromosuberic acid with concentrated aqueous ammonia and ammonium carbonate in closed vessels at 85—95°, good yields are obtained of $\alpha\alpha'$-diaminosuberic acid. The *brucine* salt of the derived *$\alpha\alpha'$-diformamidosuberic acid*, m. p. 209—210°, does not resolve optically. The following derivatives are described: *$\alpha\alpha'$-Bischloroacetamidosuberic acid*, m. p. 215—217°. NN'-*Bisglycyl-$\alpha\alpha'$-diaminosuberic acid* ($+2H_2O$), m. p. above 290°. *Bis-$\alpha\alpha'$-bromopropionamidosuberic acid*, m. p. 207°. NN'-*Bis*-(dl-*alanyl*)-*$\alpha\alpha'$-diaminosuberic acid* ($+1H_2O$), m. p. above 290°. NN'-*Bis*-(dl-*α-bromo-γ-methylvaleroyl*)-*$\alpha\alpha'$-diaminosuberic acid*, m. p. 208—209°. NN'-*Bis*-(dl-*leucyl*)-*$\alpha\alpha'$-diaminosuberic acid* ($+3H_2O$), m. p. above 290°. NN'-*Bis*-(dl-*α-bromo-γ-methylvaleroylglycyl*)-*$\alpha\alpha'$-diaminosuberic acid*, m. p. 194—195°. *Bis*-(dl-*leucylglycyl*)-*$\alpha\alpha'$-diaminosuberic acid*, m. p. 168—171°. *Bis*-(*chloroacetyl*-dl-*leucyl*)-*$\alpha\alpha'$-diaminosuberic acid*, m. p. 170—175°, decomp. 188—190°. *Bis*-(*glycyl*-dl-*leucyl*)-*$\alpha\alpha'$-diaminosuberic acid*, sinters at 165°, m. p. (strong frothing) 190—195°. *Bis*-(*chloroacetyl*-dl-*alanyl*)-*$\alpha\alpha'$-diaminosuberic acid*, sinters 195—196°, m. p. 202—203°, decomp. 216—218°. *Bis*-(*glycyl*-dl-*alanyl*)-*$\alpha\alpha'$-diaminosuberic acid*, m. p. 136—138°, decomp. 210°. Unless otherwise stated, these all decompose at the m. p. The pentapeptides are hygroscopic, give filterable precipitates with phosphotungstic acid, and give a good biuret reaction. They are not hydrolysed by yeast juice. When hydrolysed by heating in aqueous solution at 160—165°, bis-*dl*-leucylglycyl-$\alpha\alpha'$-diaminosuberic acid gives glycyl-leucine anhydride, and in smaller quantities glycine and leucine. Bisglycyl-*dl*-leucyl-$\alpha\alpha'$-diaminosuberic acid yields leucylglycine anhydride and leucine. Bisglycyl-*dl*-alanyl-$\alpha\alpha'$-diaminosuberic acid gives alanylglycine anhydride (?) and glycine (?) or alanine (?). In no case were unaltered polypeptide, $\alpha\alpha'$-diaminosuberic acid, or its decomposition products detected. F. E. DAY.

Reducing power of cysteine. E. C. KENDALL and D. F. LOEWEN (Biochem. J., 1928, **22**, 649—668; cf. Dixon and Tunnicliffe, A., 1927, 961).—Further experiments are recorded to show that cysteine cannot reduce indigo-carmine and that cystine cannot oxidise reduced indigo-carmine or reduced indigo in the absence of a third component which functions as an activating agent and is produced through the action of oxygen or sodium disulphide on indigo-carmine. Iron cannot activate the ·SH or ·S·S· grouping, but it influences the velocity of reaction between oxygen and indigo-carmine. This results in an increased concentration of the activating agent. Agitation of the solution and other physical factors influence the formation of the activating agent. It is destroyed by heat. Iron neither accelerates nor prevents the action of sodium disulphide on indigo-carmine. The activating agent appears to be an unstable oxygen or sulphur additive product of indigo-carmine and its essential action involves the activation of the sulphur atom which permits the sulphydryl and disulphide groupings to manifest their latent reducing or oxidising power. In the presence of a constant concentration of the activating agent the velocity of oxidation and reduction is determined by the ratio C·SH/C·S·S·C grouping. S. S. ZILVA.

Hydrolysis of guanidine carbonate. J. BELL (J.C.S., 1928, 2074—2077; cf. A., 1926, 825).—Guanidine carbonate is hydrolysed to carbamide in boiling aqueous solution. The carbamide undergoes further partial transformation to ammonium carbonate. The hydrolysis is dependent on the primary dissociation of the salt to guanidine and carbonic acid, the subsequent decomposition being due to the instability of guanidine in boiling aqueous solution. F. J. WILKINS.

Guanidine. II. Synthesis of creatinol [*N*-methyl-*N*-(β-hydroxyethyl)guanidine]. H. SCHOTTE, H. PRIEWE, and H. ROESCHEISEN (Z. physiol. Chem., 1928, **174**, 119—176; cf. Schotte and Priewe, A., 1926, 717).—The best method of preparing amino-alcohols is that in which ethylene chlorohydrin is treated with liquid carbonyl chloride and the isolated β-chloroethyl chloroformate allowed to react with amines in benzene solution to give β-chloroethyl alkylcarbamates of the constitution $CH_2Cl\cdot CH_2\cdot CO_2NHR$; on decomposition with excess of sodium hydroxide (3—4 mols.) the last named yield amino-alcohols, $HO\cdot CH_2\cdot CH_2\cdot NHR$. The aminoethanols can be converted into the corresponding guanido-alcohol (*a*) by the Erlenmeyer synthesis, whereby the amine salt reacts with cyanamide, or (*b*) by the use of Rathke's method, in which the aminoethanol is treated with a salt of *S*-alkyl*iso*thiocarbamide. The mechanism of the latter reaction is discussed and the "addition" theories of Schenck (A., 1912, i, 424) and of Lecher and Graf (A., 1923, i, 761) are rejected in favour of a "decomposition" theory, which postulates the formation of cyanamide by decomposition of the alkyl*iso*thiocarbamide and a subsequent Erlenmeyer synthesis. *S*-Ethyl*iso*thiocarbamide hydrobromide and methyl-β-hydroxyethylamine with small amounts of water yield creatinol hydrobromide. A large number of salts and derivatives of creatinol have been prepared and examined, but the free base has been isolated only as a colourless syrup. Creatinol is very stable towards acids and is not affected when kept for 15 hrs. at the ordinary temperature (or heated for 4 hrs.) with concentrated hydrochloric acid, but it is sensitive to the action of alkalis. 2*N*-

Sodium hydroxide at the ordinary temperature decomposes creatinol hydrobromide with the formation of ammonia; after several weeks the decomposition is complete and 2 mols. of creatinol yield 1 mol. of ammonia and 1 mol. of methylaminoethanol, together with some carbamide and a fourth substance (? hydantoin alcohol). *N*-Ethyl-*N*-β-hydroxyethylguanidine and *N*-*iso*amyl-*N*-β-hydroxyethylguanidine have also been synthesised by the Erlenmeyer method.

β-Chloroethyl chloroformate treated with methylamine in benzene solution yields *β-chloroethyl methylcarbamate*, b. p. 110—112°/15 mm., which on treatment with sodium hydroxide yields methyl-β-hydroxyethylamine; condensation of the last named with *S*-ethyl*iso*thiocarbamide hydrobromide yields *creatinol hydrobromide*, m. p. 101—103°. The following salts of creatinol are described: *picrate*, m. p. 166°; *hydrochloride*, m. p. 78° (after sintering); *picrolonate*, m. p. 236—237° corr. (sinters at 234°); double *salts* of the hydrochloride with mercuric chloride ($C_4H_{12}ON_3Cl,6HgCl_2$), m. p. 220—221° (sinters at 216°), and cadmium chloride ($C_4H_{12}ON_3Cl,CdCl_2$), m. p. 190—191°; *chloroaurate*, m. p. 125—126° (sinters at 90°); *chloroplatinate*, decomp. at 185—186°. *Creatinol*, obtained as a colourless, strongly alkaline syrup by treatment of the hydrobromide with sodium ethoxide, gives a *carbonate*, decomp. at 171°. Creatinol hydrobromide treated with benzoyl chloride yields *tribenzoylcreatinol*, m. p. 98—99·5°, and with *p*-toluenesulphonyl chloride yields *di-p-toluenesulphonylanhydrocreatinol*, m. p. 174·5—175°. Creatinol is very stable towards acids, but when heated in a sealed tube at 160° for 16 hrs. with concentrated hydrochloric acid it yields ammonia, methylethylenediamine, *anhydrocreatinol* (iminotetrahydroglyoxaline) (isolated as the *picrate*, m. p. 194—195°), and a *substance*, $C_3H_9O_2N$, isolated as the *picrolonate*, m. p. 226°, and *picrate*, m. p. 101—102°. Treatment of creatinol with 48% hydrogen bromide solution for 6 hrs. at 200° yields ethylenediamine and methylethylenediamine. *β-Hydroxyethylethylamine*, b. p. 169—170° (*picrate*, m. p. 125—126°), on heating with cyanamide and ethyl alcohol in a sealed tube at 100° for 8 hrs., yields NN-*ethylguanidoethanol*, isolated as the *picrate*, m. p. 158°. *Hydroxyethyl*-iso*amylamine*, b. p. 203—204°/750 mm., 93—94°/10 mm., prepared from β-chloroethyl *iso*amylcarbamate, treated in the same way, yields NN-iso*amylguanidoethanol*, isolated as the *picrate*, m. p. 117—118°. The preparation of *β-chloroethyl benzylcarbamate*, b. p. 158°/0·8 mm. and 218—220°/15 mm., and of *benzyl-β-hydroxyethylamine*, b. p. 105°/about 1 mm. and 148—149°/13 mm. (*picrate*, m. p. 134—135°), is also described. The reaction between aniline and *S*-ethyl*iso*thiocarbamide hydrobromide has been studied with varying amounts of the reactants and different conditions (temperature, time, and the solvent) and the yields of mono- and di-phenylguanidine are tabulated. Monophenylguanidine heated at 100° for 25 hrs. with aniline yields no diphenylguanidine, whilst only a small yield is obtained at 150°. Diethylcyanamide and aniline hydrochloride heated with ethyl alcohol for 20 hrs. in a sealed tube at 100° yield N'-*phenyl*-NN-*diethylguanidine* (*picrate*, m. p. 120° corr.). Dimethylcyanamide and ammonium chloride in the presence of alcoholic ammonia yield dimethylguanidine, and diethylcyanamide yields diethylguanidine. The preparation of *NN*-dimethyl-*N'*-ethylguanidine, *s*-tetraethylguanidine, ωω-diethyldiguanide, and s-*tetraethyldiguanide* (*picrate*, m. p. 147—148° corr.) is described. A. WORMALL.

Rathke's guanidine synthesis and hydrolysis of guanidines. H. LECHER (Z. physiol. Chem., 1928, **176**, 43—45).—A discussion of Rathke's method for synthesising guanidines from ammonia or amines and *ψ*-thiocarbamides or their salts (cf. preceding abstract), and on the rival views of Lecher and Schotte concerning the mechanism of hydrolysis of guanidines (cf. Lecher and Demmler, A., 1927, 755; Schotte, Z. angew. Chem., 1926, **39**, 677).

A. WORMALL.

Malononitrile and malononitrile condensations. I. R. SCHENCK and H. FINKEN [with P. MICHAELIS and H. PLEUGER] (Annalen, 1928, **462**, 158—173).—Malononitrile condenses with ethyl oxalate in presence of (absolute) alcoholic potassium ethoxide to give the *potassium* derivative, m. p. 205°, of *ethyl ββ-dicyano-α-hydroxyacrylate*, and with methyl oxalate etc. to give the *potassium* derivative of the corresponding methyl ester. The *sodium*, *silver* (m. p. 176°), and *diethylamine* salts of the ethyl ester and the *silver* salt of the methyl ester are described. When malononitrile is treated with a defect of ester etc., the *dipotassium* derivative of *ααδδ-tetracyano-βγ-dihydroxybutadiene* (*βγ-dihydroxybutadiene-ααδδ-tetracarboxylonitrile*) results.

Similarly, malononitrile condenses with ethyl formate to give the *potassium* derivative, m. p. 268°, of *hydroxymethylenemalononitrile* (corresponding *silver* salt described), and with ethyl cyanoacetate to give the *potassium* derivative of *cyanohydroxymethylenemalononitrile*, $(CN)_2C{:}C(CN){\cdot}OK$, whereas it does not condense with ethyl benzoate, and with ethyl carbonate gives a mixture of products. The last-named potassium derivative appears to contain an impurity of the constitution $(CN)_2C{:}C(OEt){\cdot}OK$, or (less probably) $CN{:}C(OEt){:}C(CN){\cdot}OK$.

The above silver derivative of methyl ββ-dicyano-α-hydroxyacrylate is converted by methyl and ethyl iodides into *methyl ββ-dicyano-α-methoxyacrylate* and *methyl ββ-dicyano-α-ethoxyacrylate*, respectively. Similarly are obtained *ethyl ββ-dicyano-α-methoxy-* and *ethyl ββ-dicyano-α-ethoxy-acrylate*. All four esters decompose when distillation is attempted, and undergo hydrolysis in moist air to give either *ββ-dicyano-α-methoxy-* or *ββ-dicyano-α-ethoxy-acrylic acid*, decomposing when heated.

Careful addition of dilute alcoholic ammonia to an ethereal solution of ethyl ββ-dicyano-α-ethoxyacrylate produces *ββ-dicyano-α-ethoxyacrylamide*, m. p. 141° (corresponding *methoxy-amide*, m. p. 140°). Both amides are converted by concentrated aqueous ammonia into the *ammonium* salt, $(CN)_2C{:}C(ONH_4){\cdot}CO{\cdot}NH_2$.

When silver ββ-dicyano-α-methoxyacrylate is decomposed with hydrogen sulphide in an anhydrous solvent, *methyl ββ-dicyano-α-hydroxyacrylate* results

(*ammonium* salt, m. p. 209°; *phenylhydrazine* salt, m. p. 104°). The similarly formed *ethyl* ester gives an *ammonium* salt, m. p. 176°, and a *phenylhydrazine* salt, m. p. 100°. E. E. TURNER.

Malononitrile and malononitrile condensations. II. R. SCHENK and H. FINKEN [with P. MICHAELIS, K. PAPE, and F. PLEUGER] (Annalen, 1928, **462**, 267—283).—Malononitrile condenses with acetone in absolute alcoholic potassium methoxide solution to give *dicyanodimethylethylene*, m. p. 171·5° (decomp.), passing slowly into a *dimeride* (two possible formulæ proposed). Malononitrile and benzophenone similarly afford *dicyanodiphenylethylene*, m. p. 136°, fluorenone and the nitrile giving *dicyanomethylenefluorene*, m. p 213°. Of the above new compounds only the first-named combines with bromine.

Prolonged heating of oxalic esters with malononitrile in presence of sodium ethoxide or diethylamine (see preceding abstract) gives rise to *trismalononitrile* I, $(C_3H_2N_2)_3$, m. p. about 290°, whilst when ammonia is passed into a suspension of malononitrile in benzene, *trismalononitrile* II, m. p. 218°, is formed. At 222°, the latter passes with vigour into *trismalononitrile* III, m. p. about 300° (charring). Trismalononitriles I and III are possibly identical. Trismalononitrile II is converted by boiling aniline into a *substance*, $C_{12}H_9N_5$, for which various formulæ are suggested. The possible constitutions of I and III are discussed.

The use of malononitrile as a cryoscopic solvent is suggested and some determinations are made. The depression constant is determined as 48·90 (Klostermann, Diss., Münster, 1918, found 50·03). The nitrile is a strongly dissociating solvent, giving a normal mol. wt. for *p*-nitrophenol. Some mol. wt. determinations in succinonitrile are also described. E. E. TURNER.

Alkylation of hexacyanochromic acid [hydrochromicyanic acid]. F. HÖLZL and F. VIDITZ (Monatsh., 1928, **49**, 241—264; cf. Hartley, J.C.S., 1914, **105**, 521; Hölzl, A., 1927, 864; this vol., 279).—The alkylation of hydrochromicyanic acid must be expected to yield products analogous to those from decomposition of the acid, on which they thus throw light; no derivatives of the undecomposed acid are obtained.

Potassium chromicyanide is treated with methyl sulphate in (or without) methyl alcohol for 3 hrs. at 40—50°, and the product is cooled and filtered. From the filtrate, potassium methyl sulphate is precipitated by ether; further addition of ether precipitates a red, tarry *substance* (I). The brown residue, the main product, is washed with water and dried at 105°, yielding a greyish-green product (II), $Cr_2(CN)_4(OH)_2,6H_2O,MeNC$; this on keeping over calcium chloride yields a product (III), $Cr_2(CN)_3(OH)_3,3H_2O,2MeNC$, which slowly absorbs water from the air to give (IIIA), $Cr_2(CN)_3(OH)_3,4H_2O,MeNC$.

The action of methyl iodide on silver chromicyanide yields unsatisfactory products; that of dry hydrogen chloride on potassium chromicyanide in absolute ethyl alcohol yields $[CrCl_3(EtOH)_3]$ (cf. Koppel, A., 1902, ii, 83), and in acetonitrile a brown *substance* (V), containing acetonitrile: $Cr_2(CN)_3(OH)_3,7H_2O,MeCN$. The action of methyl sulphate on an aqueous solution of potassium chromicyanide at 40—50° yields a red liquid, from which a silver *derivative* (Cr : Ag = 1 : 2) is obtained.

Schemes are given for the gradual evolution of these products: thus the hypothetical $[(MeNC)_3Cr(CN)_3]$ (A) by loss of methylcarbylamine from 2 mols. would yield the substance $[(MeNC)_3Cr(CN)_3Cr(CN)_3]$ (B); a *product* which probably has this constitution (containing a triple bridge of co-ordinated cyanide ion) is obtained by the action of methyl sulphate on potassium chromicyanide in absolute alcohol. The substance (B) is then considered to be hydrolysed by water, yielding ultimately the *substance* $[(H_2O)_3Cr(CN)_3Cr(OH)_3]$, (VI), which can be prepared ($+2H_2O$) by the action of methyl sulphate in absence of solvent, and treating the product with water, without removing adhering methyl sulphate; by adding silver nitrate the substance $Ag_2[(H_2O)_3Cr(CN)_3Cr(OH)_3]$ is obtained. (This suggests that these substances may have amphoteric properties; and by the action of aqueous pyridine on (V) a *substance* is obtained, regarded as having the constitution $(C_5H_5N)_2H_2\{(MeCN)(HO)_2[Cr(CN)_3Cr(OH)_3]_2\},11H_2O$.

The above, and many other, bicentric compounds can be expressed by the general formula $[n_3Zx_3Zx_3]$, where Z is a central tervalent atom of sextuple co-ordination, x a univalent negative ion, and n a unitary co-ordinand, *e.g.*, H_2O, RNC. The limit of intramolecular decomposition of a bicentric compound from $H_2[Zx_6]$ is $H_3[x_3Zx_3Zx_3]$.

From the decomposition schemes, the substances (II), (III), and (IIIA) are formulated:
$[(MeNC)(H_2O)_2Cr(CN)_3Cr(CN)(OH)_2],4H_2O$,
$[(MeNC)_2(H_2O)Cr(CN)_3Cr(OH)_3],2H_2O$, and
$[(MeNC)(H_2O)_2Cr(CN)_3Cr(OH)_3],2H_2O$; each of these has a triple bridge of co-ordinated cyanide ion.

As a side reaction, substances containing methosulphate ion are obtained; of these the substance (I) (see above) has the ratio Cr : $MeSO_4' = 1 : 2$, and since it does not give a precipitate with silver nitrate except after long boiling, it is represented $[(MeNC)_4Cr(CN)_2Cr(MeNC)_4](MeSO_4')$, in which there is a double co-ordinated CN bridge. E. W. WIGNALL.

Cyanogen compounds of the platinum metals. III. Cyanogen compounds of osmium. F. KRAUSS and G. SCHRADER (J. pr. Chem., 1928, [ii], **119**, 279—286).—The preparation of potassium osmocyanide, $K_4[Os(CN)_6],3H_2O$ (Claus, *ibid.*, 1862, [i], **85**, 160; Martius, Annalen, 1861, **117**, 361), is repeated: the substance is obtained colourless. The corresponding *copper* and *nickel* salts, and their ammonia *compounds*, $Cu_2[Os(CN)_6],4NH_3$ and $Ni_2[Os(CN)_6],6NH_3$, and *strychnine hydro-osmocyanide* are prepared. A simple osmium cyanide could not be obtained (cf. Moraht and Wischin, A., 1893, ii, 380) and the above compounds could not be oxidised to derivatives of tervalent osmium. E. W. WIGNALL.

Reaction between organo-magnesium halides and alkyl sulphonates. H. GILMAN and L. L.

HECK (J. Amer. Chem. Soc., 1928, **50**, 2223—2230).—The reaction between organo-magnesium halides and alkyl sulphonates, usually formulated as $2RSO_3Alk+2R'MgX \longrightarrow 2R'Alk+(RSO_3)_2Mg+MgX_2$ (I), yields the product R'Alk in not more than 50% yield if the reagents are used in equimolecular proportions. Actually, an alkyl halide is formed as well, and each of these two products is formed in equivalent amount and in increased yield if the reagents are used in the proportions required by the equations now suggested, viz., $RSO_3Alk+R'MgX \longrightarrow R'Alk+RSO_3MgX$ (II), and $RSO_3Alk+RSO_3MgX \longrightarrow AlkX+(RSO_3)_2Mg$ (III). Confirmation of this scheme is given by the separation of magnesium naphthalene-2-sulphonate and *n*-butyl iodide from the product of reaction of iodomagnesium naphthalene-2-sulphonate and *n*-butyl *p*-toluenesulphonate. The occasional formation of hydrocarbons is attributed to hydrolysis of unused RMgX in working up the reaction product. The alternative scheme of Rossander and Marvel (this vol., 732) is not favoured.

Reactions analogous to (III), with the formation of *n*-butyl halides, occurred between *n*-butyl *p*-toluenesulphonate and magnesium ethoxyiodide, magnesium phenoxyiodide, magnesium *p*-tolylsulphinyl bromide, magnesium iodide, and magnesium bromide. Ethyl sulphate and magnesium iodide or magnesium ethyl bromide yielded ethyl iodide and ethyl bromide, respectively. Ethyl *p*-toluenesulphonate and magnesium phenyl iodide yielded ethylbenzene and ethyl iodide. *n*-Butyl *p*-toluenesulphonate yielded *n*-butyl iodide with magnesium *n*-propyl iodide, *n*-amylbenzene and *n*-butyl chloride with magnesium benzyl chloride, phenyl *n*-butyl sulphide with magnesium *p*-thiophenyl iodide, and methyl-*n*-butylaniline, b. p. 225—230° (picrate, m. p. 93°) (cf. Frohlich and Wedekind, A., 1907, i, 512; Komatsu, A., 1913, i, 39), with methylanilinomagnesium bromide. The *p*-toluenesulphonic ester of ethyl lactate and magnesium phenyl bromide (cf. Kenyon, Phillips, and Turley, A., 1925, i, 507) yielded only ethyl α-bromopropionate, and none of the expected ethyl α-phenylpropionate. Ethyl *cyclo*hexylsulphonate and magnesium phenyl bromide yielded ethylbenzene, ethyl bromide, *magnesium* cyclo*hexylsulphonate* ($+6H_2O$), and a *compound*, m. p. 107°. The expected cyclo*hexylsulphone* had m. p. 73°, and was prepared by oxidation of the *sulphide*, b. p. 145°/11 mm., d_{20}^{20} 1·0031, n^{25} 1·5663. No reaction took place between phenyl *p*-toluenesulphonate and magnesium bromide.

R. K. CALLOW.

Synthesis of tertiary aliphatic arsines using Grignard's reagent. E. GRYSZKIEWICZ-TROCHIMOWSKI (Rocz. Chem., 1928, **8**, 250—253).—The following tertiary arsines were prepared by the action of Grignard's reagents on arsenious oxide: *tri*-n-*butylarsine*, b. p. 102—104°/8 mm., d_4^{21} 0·9931; *tri*-n-*amylarsine*, b. p. 146—149°/10 mm., d_4^{20} 0·9799; *tri*-n-*hexylarsine*, b. p. 165—169°/6—7 mm., $d_4^{22.5}$ 0·9660; *tri*-n-*heptylarsine*, b. p. 197—199°/9 mm., d_4^{17} 0·9568; *tri*-n-*octylarsine*, b. p. 238—240°/9—10 mm., d_4^{19} 0·9357.

R. TRUSZKOWSKI.

Relation between atomic grouping and specific affinity. VIII. Additive compounds of thallium dienol salts and carbon disulphide. F. FEIGL and E. BACKER (Monatsh., 1928, **49**, 401—412).—The ability of the thallium salts of dienols to form coloured additive compounds with carbon disulphide appears to depend on the presence of the ·CO·CH₂·CO· group. Substitution in the methylene group or replacement of carbonyl oxygen by the anil residue inhibits reaction. The compounds are resistant towards dilute acids and bases. When decomposed by sulphuric acid in the presence of potassium iodide and ether they yield thallous iodide, carbon disulphide, and the ketone, and hence are formulated $C{<}\begin{smallmatrix}CR^1\cdot O\cdot Tl\\ CR^2\cdot O\cdot Tl\end{smallmatrix}{>}CS_2$. They are usually prepared by mixing a solution of the requisite thallium derivative with carbon disulphide. The following new compounds are described: *thallium acetylacetone*, $C_5H_7O_2Tl$, and the corresponding additive *compound*, $C_6H_6O_2S_2Tl_2$, decomp. about 80°; *thallium γ-methylacetylacetone*; *thallium* salt of benzoylacetone and its additive *compound*; *thallium γ-methylbenzoylacetone*; *thallium dibenzoylmethane* and its additive *product*, decomp. about 150°; additive *compound*, $C_{17}H_8O_3S_2Tl_2$, from ethyl acetoacetate, thallium carbonate, and carbon disulphide and the analogous *product*, $C_{12}H_{10}O_3S_2Tl_2$, from ethyl benzoylacetate; thallium *salts* and non-crystalline, additive compounds from ethyl acetylpyruvate, ethyl benzoylpyruvate, and ethyl oxalacetate. Thallium derivatives or additive compounds could not be obtained from δ-ketopentan-β-ol, benzoylacetoneanil, ethyl malonate, ethyl diacetylsuccinate, diacetyl, or acetonylacetone.

R. A. PRATT.

***pp'*-Di-iododiphenylmethane.** A. M. NASTUKOFF and V. W. SCHELJAGIN (J. pr. Chem., 1928, [ii], **119**, 303—305).—Iodobenzene condenses with formaldehyde in concentrated sulphuric acid, heated under reflux, to yield pp'-*di-iododiphenylmethane*, m. p. 92—93°, b. p. 238—241°/40 mm., identified by oxidation to *pp'*-di-iodobenzophenone (Hoffmann, A., 1891, 1236).

E. W. WIGNALL.

Benzene model based on the electron theory and the substitution laws. M. ULMANN (Z. angew. Chem., 1928, **41**, 674—680).—A formula for benzene is proposed in which alternate carbon atoms assume complete electron octets, these CH groups thus having each a resultant charge of +3, at the expense of the remaining CH groups, which have a resultant charge of −3. The relation of this formula to the substitution laws is discussed.

A. DAVIDSON.

Physical properties of *o*-dichlorobenzene. T. S. CARSWELL (Ind. Eng. Chem., 1928, **20**, 728).—By modifying Holleman's method of preparation from *o*-chloronitrobenzene (cf. A., 1905, i, 41) a product is obtained having b. p. 180·3° (corr.)/760 mm., crystallising point −16·7°, d_{15}^{15} 1·3112, d_{20}^{20} 1·3088, n_D^{22} 1·5518.

R. A. PRATT.

Hydrogenation of nitrobenzene by platinum-black. G. VAVON and CRAJCINOVIC (Compt. rend., 1928, **187**, 420—422).—Catalytic hydrogenation of nitrobenzene with platinum-black in presence of benzaldehyde yields phenyl-*N*-phenylnitrone and

phenylbenzylhydroxylamine (cf. Cusmano, A., 1922, i, 143), and in presence of piperonal, *piperonyl-N-phenylnitrone*, $CH_2O_2{:}C_6H_3{\cdot}NPh{\cdot}OH$, m. p. about 135°. This confirms the view that the reduction of nitrobenzene alone proceeds through the stage of phenylhydroxylamine (cf. Cusmano, A., 1917, i, 641; Nord, A., 1920, i, 21). E. W. WIGNALL.

Laws of aromatic substitution. IX. B. FLURSCHEIM and E. L. HOLMES (J.C.S., 1928, 2230—2242).—In continuation of previous work (this vol., 876) the nitration of a further series of toluene derivatives of the type $PhCR_3$ in which R_3 is H_2CN, $H(CO_2Et){\cdot}CN$, $H(CN)_2$, $(CO_2Et)_2{\cdot}CN$, $(CO_2Et)(CN)_2$, $HCl(CN)$, $H(OH)(CN)$ and $H(:N{\cdot}C_6H_4{\cdot}NO_2m)$, has been studied, the proportion of *m*-nitro-compound produced being, respectively, 12·70 (cf. Baker and others, this vol., 403, found 14%), 37·20, 67·90, 69·55, 87·5, 50·05, 43·55, 87·05%. Benzonitrile gave 88·25% (cf. Baker, *loc. cit.*, 80·53%) and benzaldehyde gave 78·65%. It is supposed that benzylidene-*m*-nitroaniline (*hydrochloride*) nitrates as the free anhydro-base, since its solution in concentrated sulphuric acid is intensely yellow, and from the fact that addition of ammonium sulphate during nitration causes an inappreciable change in the proportion of *m*-isomeride formed. The results are discussed on the basis of the authors' theory of alternating affinity demand. *Ethyl phenylcyanomalonate*, b. p. 140—141°/1 mm., is obtained by the action of sodium on a mixture of ethyl phenylacetate (? phenylcyanoacetate) and ethyl chloroformate. The action of ethyl chloroformate on the sodium derivative of phenylmalononitrile yields *ethyl phenyldicyanoacetate*, m. p. 60°, from which by nitration is obtained *ethyl* m-*nitrophenyldicyanoacetate*, m. p. 133—134·5° (crystallised from chloroform). J. W. BAKER.

Nature of the alternating effect in carbon chains. XXVIII. Preparation and properties of benzyl fluoride. C. K. INGOLD and E. H. INGOLD (J.C.S., 1928, 2249—2262).—Distillation, in Jena glass vessels, of benzyltrimethylammonium, dibenzyldimethylammonium, and tribenzylmethylammonium fluorides (prepared by neutralisation of the quaternary hydroxides with hydrofluoric acid) in a water-pump vacuum gives a 60% yield of *benzyl fluoride*, m. p. —35° (corr.), b. p. 40—40·5°/14 mm., 139·9°/760 mm. (corr.), $d_4^{25 \cdot 3}$ 1·02278, $n_D^{25 \cdot 3}$ 1·48919. When benzyl fluoride is stored in certain glass vessels an autocatalytic decomposition may set in with almost explosive violence, hydrogen fluoride being evolved and an opaque white vitreous mass of composition $(C_7H_6)_x$ formed. The same product is obtained by the action of concentrated sulphuric acid or hydrofluoric acid in platinum vessels. The physical and chemical properties of benzyl fluoride are discussed from the point of view of the greater rigidity of the valency electrons and greater intensity of the external field in the case of combined fluorine than for the other halogens. Thus, in agreement with this, fluorine has the lowest refraction values and differs sharply from the other halogens in contributing practically nothing to dispersion. The ultra-violet absorption spectrum of benzyl fluoride, plotted from experiments conducted in $N/100$- to $N/1600$-alcoholic solutions, shows that its maximum absorption (ε 508, λ 2508) falls in place in the series *p*-xylene, benzene, benzyl fluoride, benzaldehyde, benzoic acid, as a somewhat feebly *m*-orienting member. In agreement with this, nitration with a mixture of nitrous acid-free absolute nitric acid, and acetic anhydride at 5° yields *o*- 28·1, *m*- 17·5, and p-*nitrobenzyl fluoride*, m. p. 38·5°, 52·5%, respectively. The ratios para/½ ortho for benzyl fluoride and chloride are 3·89 and 3·28, respectively, showing that the direct effect (Ingold and Vass, this vol., 402) of fluorine in orientation is stronger than that of chlorine, the sequence for the halogens being F > Cl > Br > I, the tautomeric effect (Ingold and Shaw, this vol., 164) being in the reverse order. In agreement with the former sequence, it is found that, under conditions in which benzyl chloride reacts completely, a large percentage of benzyl fluoride is recovered unchanged after treatment with boiling aqueous potassium carbonate solution, zinc dust and boiling alcohol, 33% alcoholic trimethylamine at 44° for 20 hrs., and boiling sodium ethoxide solution for 1 hr. Distillation of *o*-, *m*-, and *p*-nitrobenzyltrimethylammonium fluorides causes energetic decomposition with much charring, the only identifiable products being *o*-, *m*-, and *p*-nitrobenzaldehydes. J. W. BAKER.

Nature of the alternating effect in carbon chains. XXIX. Further experiments bearing on the problem of the *ortho-para* ratio in aromatic substitution. C. K. INGOLD and C. C. N. VASS (J.C.S., 1928, 2262—2267).—The nitration of *p*-fluorochlorobenzene (prepared by the Gattermann reaction from *p*-fluoroaniline) in the presence of increasing quantities of sulphuric and fuming sulphuric acids has been studied and the proportion of 2-nitro-(*o*-fluoronitro-) and 3-nitro-(*o*-chloronitro-)isomerides produced determined by thermal analysis. The ratio *o*-fluoronitro-/*o*-chloronitro- increases from 0·262 with 4·5 mols. of nitric acid in the absence of sulphuric acid to 0·429 with 1 mol. of nitric acid in the presence of 1·5 mols. of sulphuric acid and 2·8 mols. of free sulphur trioxide. This effect is explained by the greater affinity of the unshared chlorine electrons for a positive field (the sequence for the halogens being I > Br > Cl > F), the presence of the strong acid polarising the chlorine atom (incipient salt formation; cf. Baker, this vol., 870) to a greater extent than in the case of fluorine, and thus diminishing its *op*-orienting power. These considerations explain the result of Hove (A., 1927, 757), who obtained 40% of the *o*-fluoronitro-isomeride by nitration of *p*-fluorobromobenzene in the presence of a large excess of sulphuric acid. Swarts (A., 1916, i, 133) found 27·75% of the *o*-fluoronitro-isomeride by nitration of *p*-fluorochlorobenzene in the absence of sulphuric acid (cf. this paper, 20·8%), but it is shown that his thermal analysis data need revision, and, moreover, contrary to his observations, it is not possible to obtain quantitative decomposition of the *o*-fluoronitro-compound with sodium methoxide, and a simultaneous complete absence of any decomposition of the other isomeride. J. W. BAKER.

Rubrene. Constitution of rubrene. C. MOUREU, C. DUFRAISSE, and L. ENDERLIN (Compt. rend., 1928, **187**, 406—407).—Oxidation of rubrene by chromic acid yields *o*-dibenzoylbenzene; it is therefore suggested that the constitution of rubrene is $C_6H_4{\ll}{}^{h}_{CPh}{>}C{:}C{<}{}^{h}_{CPh}{\gg}C_6H_4$ (cf. Moureu, Dufraisse, and others, this vol., 53, 594, 628; Willemart, *ibid.*, 996). E. W. WIGNALL.

Catalytic preparation of alkylanilines. I. B. C. ROY (J. Indian Chem. Soc., 1928, **5**, 383—386). —When a mixture of aniline and ethyl alcohol is passed over an asbestos–thoria catalyst at 350—390°, the conversion into ethylanilines is 63·4—66·7%. With aniline and methyl alcohol at 410—430° the yield of dimethylaniline is 40—30%, with simultaneous production of 32·8—45% of methylaniline. H. BURTON.

Odour and constitution among mustard oils [thiocarbimides]. IV. Effect of fluorine substitution. G. M. DYSON (Perf. Ess. Oil Rec., 1928, **19**, 341—342; cf. this vol., 283, 514, 748).—The odours of 4-fluoro- and 4-fluoro-3-methyl-phenylthiocarbimides are intermediate between those of phenylthiocarbimide and its 4-chloro-derivative. The effect of the methyl group is to accentuate the true thiocarbimide odour. 3-Fluoro-, 3-fluoro-4- and -6-methyl-phenylthiocarbimides have been prepared and they possess a thiocarbimide odour. 3-Fluoro-4-nitrophenylthiocarbimide has no characteristic odour. H. BURTON.

2 : 5 : 6-Trichloro-*m*-4-xylidine and its derivatives. E. BUREŠ and J. BORGMANN (Casopis Ceskosloven. Lek., 1927, **7**, 270—280; Chem. Zentr., 1928, i, 1171).—The action of chlorine in acetic acid on 4-acetamido-*m*-xylene, m. p. 123°, at the ordinary pressure and temperature, without a catalyst, yields 2 : 5 : 6-trichloro-4-acetamido-*m*-xylene, m. p. 208·5° (lit. 190—192°). 2 : 5 : 6-Trichloro-*m*-4-xylidine has m. p. 204° (sulphate; hydrochloride, m. p. 217°; benzoyl derivative, m. p. 174—175°); 2 : 5 : 6-trichloro-*m*-4-xylenol, m. p. 174° (lit. 169°), forms mercury and bismuth salts; the methoxy-compound has m. p. 53·5°. 2 : 5 : 6-Trichloro-*m*-xylene has m. p. 179·5°; 3 : 5 : 6-trichloro-2 : 4-dimethylbenzonitrile, m. p. 218°; 3 : 5 : 6-trichloro-2 : 4-dimethylbenzoic acid, m. p. 191·5°; 2 : 4 : 5 : 6-tetrachloro-*m*-xylene, m. p. 219° (lit. 210°). A. A. ELDRIDGE.

5-Bromo-*m*-4-xylidine. E. BUREŠ and A. MANDEL-BORGMANNOVA (Časopis Československ. Lek., 1927, **7**, 257—269; Chem. Zentr., 1928, i, 1170—1171).—Bromination of *m*-4-xylidine under pressure, at the ordinary temperature without a catalyst and in absence of sunlight, yields 5-bromo-*m*-4-xylidine, m. p. 49—50° (hydrochloride; sulphate, m. p. 183°; picrate, m. p. 122°; benzoyl derivative, m. p. 183°). 5-Bromo-3-methylbenzoic acid has m. p. 178°; 5-bromo-*m*-4-xylenol has b. p. 231°, m. p. 4°; it forms basic *mercuric*, $C_6HBrMe_2(OH){\cdot}HgOH$, and *bismuth*, $[C_6H_2BrMe_2O]_2{\cdot}Bi(OH)_4,Bi_2O_3$, compounds. 5-*Bromo*-4-*methoxy*-m-*xylene* has b. p. 140°; the *ethoxy*-compound has b. p. 142°, and the *acetoxy*-compound, b. p. 257—258°; 4 : 5-dibromo-*m*-xylene has b. p. 257°; 6-bromo-2 : 4-dimethylbenzonitrile, m. p. 218°; 6-bromo-2 : 4-dimethylbenzoic acid, m. p. 186° (*sodium* and *mercury* salts; *methyl*, m. p. 174°, *ethyl*, m. p. 176°, *propyl*, m. p. 178°, iso*butyl*, m. p. 182°, and *amyl*, m. p. 181°, esters). A. A. ELDRIDGE.

5-Bromo-*m*-4-xylidine. A. S. WHEELER and R. E. THOMAS (J. Amer. Chem. Soc., 1928, **50**, 2286—2287).—5-Bromo-*m*-4-xylidine was prepared by a variation of the method of Noelting, Braun, and Thesmar (A., 1902, i, 588). The hydrochloride and benzoyl derivative, m. p. 186°, were prepared. Diazotisation in sulphuric acid and boiling yielded 5-bromo-*m*-4-xylenol (*methyl ether*, b. p. 232°, d_{4}^{23} 1·362; *ethyl ether*, b. p. 246°, d_{23}^{23} 1·290). By diazotisation of the amine and Gattermann and Sandmeyer reactions, 4-*chloro*-5-*bromo*-m-*xylene*, b. p. about 250°, and 5-*bromo*-4-*cyano*-m-*xylene*, m. p. 86—87°, were prepared. With β-naphthol and phenol the diazotised amine gave 5-*bromo*-m-*xylene*-4-*azo*-β-*naphthol*, m. p. 136°, and -*azophenol*, m. p. 166°, respectively. R. K. CALLOW.

***p*-Cymene. X. 2 : 5-Diamino-*p*-cymene and certain new [azo] dyes.** A. S. WHEELER and R. W. BOST.—See B., 1928, 666.

Molecular rearrangements accompanying deamination of aralkylamines. (MLLE.) J. LÉVY and P. GALLAIS (Bull. Soc. chim., 1928, [iv], **43**, 862—868).—When amines of the type $CRAr_2{\cdot}CH_2{\cdot}NH_2$ (R=H, Me, or Et), prepared by reducing the corresponding aldoximes, are treated with nitrous acid, hydrocarbons of the form CRAr:CHAr are obtained. Thus, ββ-diphenylethylamine (*hydrochloride*, m. p. 237—238°; *acetyl* derivative, m. p. 88°; *benzoyl* derivative, m. p. 143—144°) affords stilbene. ββ-*Diphenyl*-n-*propylamine*, b. p. 179—182°/22 mm., d^{18} 1·027 (*hydrochloride*, m. p. 261—263°; *acetyl* derivative, m. p. 106—107°; *benzoyl* derivative, m. p. 82—83°), gives α-methylstilbene, and ββ-*diphenyl*-n-*butylamine*, b. p. 125°/24 mm., d^{20} 1·20 (*hydrochloride*, m. p. 252°; *acetyl* derivative, m. p. 114°; *benzoyl* derivative, m. p. 144—145°), yields α-ethylstilbene. H. BURTON.

Comparison of mechanisms of deamination of aralkylamines and of dehydration of the corresponding alcohols. (MLLE.) J. LÉVY, P. GALLAIS, and D. ABRAGAM (Bull. Soc. chim., 1928, [iv], **43**, 868—881; cf. preceding abstract).—A study of the deamination by nitrous acid of amines of the type $CHArAr'{\cdot}CHMe{\cdot}NH_2$ shows that unsaturated hydrocarbon formation is general but the type of product varies with Ar and Ar'. Thus when Ar=Ph and Ar'=p-MeO·C_6H_4· migration of the phenyl group occurs, but when Ar=Ar'=Ph no migration takes place, hydrogen being lost by the methyl group. Dehydration of the corresponding alcohols by distillation with pumice moistened with concentrated sulphuric acid is not analogous. In the examples analogous to the above, migration of the anisyl group is effected, whilst in the diphenyl-substituted alcohol both migration of the phenyl group and loss of hydrogen from the methyl group occur. It is concluded that the alcohols are not necessarily intermediates in the deamination process, and also that

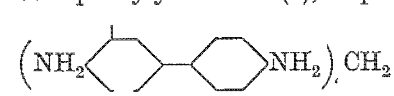
this change can take place either with or without molecular rearrangement.

β-Amino-γγ-diphenylpropane (*hydrochloride*, m. p. 280—282°; *acetyl* derivative, m. p. 107—108°; *benzoyl* derivative, m. p. 203—204°) is converted by nitrous acid into *γγ-diphenyl-Δ$^{\alpha}$-propylene*, b. p. 293°, n^{20} 1·596, which is oxidised by chromic and acetic acids to benzophenone and by perbenzoic acid in chloroform solution to an *oxide*, b. p. 300°, 182—185°/16 mm., n^{20} 1·5745, differing from the oxide prepared from αα-diphenyl-Δ$^{\alpha}$-propylene (Lagrave, this vol., 270). When this oxide is heated with anhydrous zinc chloride, a *compound*, $C_{15}H_{14}O$ (*semicarbazone*, m. p. 158°; *oxime*, m. p. 156°), is obtained. Dehydration of αα-diphenyl*iso*propyl alcohol, b. p. 305—307°, m. p. 62° (acetyl derivative, m. p. 77—78°), gives a mixture of γγ-diphenyl-Δ$^{\alpha}$-propylene and α-methylstilbene. Distillation of α-phenyl-α-anisyl-*n*-propyl alcohol affords *α-phenyl-α-anisyl-Δ$^{\alpha}$-propylene*, b. p. 183°/16 mm., m. p. 53°, oxidised by perbenzoic acid to *α-phenyl-α-anisyl-β-methylethylene oxide*. This is isomerised by treatment with hot 50% sulphuric acid or by distillation to *α-phenyl-α-anisylacetone*, b. p. 225°/25 mm., d^{20} 1·159 [*oxime* (I), m. p. 189—190°; *semicarbazone*, m. p. 178—179°], which is unaffected by concentrated sulphuric acid at 0°, and after treatment with alcoholic potassium hydroxide and subsequent oxidation yields phenyl anisyl ketone. Reduction of (I) with sodium and alcohol gives *β-amino-α-phenyl-α-anisylpropane*, b. p. 207—208°/19 mm., m. p. 63—64° (*hydrochloride*, m. p. 215—216°; *benzoyl* derivative, m. p. 181—182°), deaminated to *β-phenyl-α-anisyl-Δ$^{\alpha}$-propylene*, m. p. 86—87°, prepared also by dehydration of β-phenyl-α-anisyl*iso*propyl alcohol. Dehydration of α-phenyl-α-anisyl*iso*propyl alcohol gives *α-phenyl-β-anisyl-Δ$^{\alpha}$-propylene*, m. p. 103—104°, obtained also by dehydration of *α-phenyl-β-anisyl-*n*-propyl alcohol*, b. p. 210—215°/18 mm., in turn prepared from magnesium phenyl bromide and α-anisylpropaldehyde. *α-Phenyl-α-anisylethane*, prepared by reducing the corresponding ethylene with sodium and alcohol, has b. p. 180—182°/19 mm., *d* 1·06, n^{20} 1·5735. H. BURTON.

***NN′*-Diphenyl-*o*-phenylenediamine.** C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 1988—1989).—The product of the action of *o*-aminodiphenylamine and iodobenzene (Wieland and Müller, A., 1913, i, 1386) is not *NN′*-diphenyl-*o*-phenylenediamine but *o*-aminotriphenylamine, identical with the compound prepared by Piccard and Brewster (A., 1922, i, 370). The former compound is most conveniently prepared by the method of Clemo, Perkin, and Robinson (A., 1924, i, 1337). J. W. BAKER.

***N*-Methyl derivatives of 2-phenylnaphthylene-1 : 3-diamine.** C. S. GIBSON, W. S. KENTISH, and J. L. SIMONSEN (J.C.S., 1928, 2131—2142).—Re-examination of the isomeric *NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamines described by Lees and Thorpe (J.C.S., 1907, **91**, 1296) has shown that these compounds are *cis–trans*-isomerides. The *cis*-configuration is ascribed to the α-compound (I), which yields only monoacetyl and mono-*p*-toluenesulphonyl derivatives. In the *trans*- or β-compound (II), the hydrogen atoms of both secondary amino-groups are highly reactive. Attempts to resolve the two bases into optically active forms were unsuccessful. Improved methods for the preparation of the bases, as well as indirect conversion of the α- into the β-form, are described. *p*-Toluenesulphonyl chloride reacts with 2-phenylnaphthylene-1 : 3-diamine [acetylacetate, m. p. 175° (lit. 185°)] in pyridine solution, giving, as the main product, *α-di-*p*-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine* (III), dimorphic, m. p. 188—189° and 203—205° (stable). A second *disulphonamide* (*β-di-*p*-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine*?), m. p. 173—175°, *tri-*p*-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine*, m. p. 153—154°, and a *compound* (tetrasulphonyl derivative?), m. p. about 213°, are also obtained. Methylation of (III) yields *di-*p*-toluenesulphonyl-NN′-dimethyl-2-phenylnaphthylene-1 : 3-diamine*, m. p. 305°, giving, on hydrolysis, a quantitative yield of the β-base (II) (*diacetyl* derivative, m. p. 207—208°; *di-*d*-methylenecamphor* derivative, m. p. 277—279°). The α-base (I) yields a *monoacetyl* derivative, m. p. 203°, *mono-*p*-toluenesulphonyl* derivative, m. p. 219—220°, and a *mono-*d*-methylenecamphor* derivative, m. p. 167—168°. The dinitrosoamine, m. p. 180—181°, prepared from either base (cf. Thorpe and Lees, *loc. cit.*), gives, on reduction with tin and hydrochloric acid, a quantitative yield of the β-compound (II), of which, accordingly, it is a derivative. Trimethyl-2-phenylnaphthylene-1 : 3-diamine, m. p. 104—105° (lit. 98—99°), gives an *acetyl* derivative, m. p. 178°. M. CLARK.

Didiphenylylmethane derivatives. J. TURSKI and J. DALINSKI (Rocz. Chem., 1928, **8**, 281—289).—Benzidine condenses with formaldehyde to yield tetra-aminodidiphenylylmethane (I), m. p. 159°, which



(I.)

can be hexazotised but not octazotised. Azo dyes cannot be prepared from this base, but a number of reddish-brown triarylmethane dyes can be obtained from it by further condensation with various bases. R. TRUSZKOWSKI.

Halogen derivatives of *o*- and *p*-azophenol. L. HUNTER and R. S. BARNES (J.C.S., 1928, 2051—2058).—The "dichloramine-*T*" method of halogenation (Orton and King, *ibid.*, 1911, **99**, 1185), previously employed for chlorination and iodination (this vol., 629), is now extended to bromination. When the method is applied to the progressive halogenation of *o*- and *p*-azophenol (2 : 2′- and 4 : 4′-dihydroxyazobenzeze), chlorine, bromine, and iodine can be introduced atom by atom up to the tetrasubstituted stage. The orientation of the halogen atoms in the azophenol molecule is determined by reduction to the corresponding aminophenol. *p*-Azophenol yields only the 3 : 3′- and not the 3 : 5-dihalogeno-derivative on dihalogenation. In the monosubstituted *o*-azophenols, the halogen atom occupies the 5-position to the exclusion of the 3-position; iodine oxidises and does not substitute *p*-azophenol, yielding the quinhydroneazine $O:C_6H_4:N\cdot N:C_6H_4:O,HO\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot OH$, which

on further oxidation is converted into *p*-benzoquinone-azine, $O:C_6H_4:N\cdot N:C_6H_4:O$. The following are described (A=4 : 4′-dihydroxyazobenzene ; B=2 : 2′-dihydroxyazobenzene) : 3-*Chloro*-A, m. p. 184° (*diacetate*, m. p. 160—161° ; *dibenzoate*, m. p. 158—159°) ; 3 : 3′-*dichloro*-A, m. p. 195° (*diacetate*, m. p. 199° ; *dibenzoate*, m. p. 226°) ; 3 : 5 : 3′-*trichloro*-A, m. p. 172° (*diacetate*, m. p. 207—208° ; *dibenzoate*, m. p. 189°) ; 3 : 5 : 3′ : 5′-*tetrachloro*-A (+$6H_2O$), m. p. 225°, anhyd. m. p. 240° (*diacetate*, m. p. 240° ; *dibenzoate*, m. p. 244°) ; 3-*bromo*-A, m. p. 153° (*diacetate*, m. p. 142° ; *dibenzoate*, m. p. 165—166°) ; 3 : 3′-*dibromo*-A, m. p. 175° (*diacetate*, m. p. 161° ; *dibenzoate*, m. p. 227°) ; 3 : 5 : 3′-*tribromo*-A, m. p. 184° (*diacetate*, m. p. 172° ; *dibenzoate*, m. p. 216°) ; 3 : 5 : 3′ : 5′-tetrabromo-A (*diacetate*, m. p. 240° ; *dibenzoate*, m. p. 265°) ; 3 : 3′-*dichloro*-5 : 5′-*dibromo*-A, m. p. 262° ; 5-*chloro*-B, m. p. 164° (*diacetate*, m. p. 117° ; *dibenzoate*, m. p. 119°) ; 5 : 5′-*dichloro*-B, m. p. 267° (*diacetate*, m. p. 199° ; *dibenzoate*, m. p. 243°) ; 3 : 5 : 5′-trichloro-B (*diacetate*, m. p. 189° ; *dibenzoate*, m. p. 247°) ; 3 : 5 : 3′ : 5′-*tetrachloro*-B, m. p. 246—247° (*diacetate*, m. p. 195° ; *dibenzoate*, m. p. 186°) ; 5-*bromo*-B, m. p. 154° (*diacetate*, m. p. 142° ; *dibenzoate*, m. p. 215°) ; 5 : 5′-*dibromo*-B, m. p. 249° (*diacetate*, m. p. 211° ; *dibenzoate*, m. p. 202°) ; 3 : 5 : 3′ : 5′-tetrabromo-B (*diacetate*, m. p. 210—211° ; *dibenzoate*, m. p. 214°) ; 5-*iodo*-B, m. p. 149—150° (*diacetate*, m. p. 138° ; *dibenzoate*, m. p. 159°) ; 5 : 5′-*di-iodo*-B, m. p. 153° (*diacetate*, m. p. 145° ; *dibenzoate*, m. p. 147°) ; 3 : 5 : 3′ : 5′-*tetraiodo*-B, m. p. 98—99° (*dibenzoate*, m. p. 241°) ; 4-*chloro-2-acetamidophenyl acetate*, m. p. 170° ; 2 : 4-*dichloro-6-aminophenol*, m. p. 109° (decomp.) (*hydrochloride*) ; 4-*iodo-6-aminophenol*, m. p. 139° (*hydrochloride*) ; 2 : 4-*di-iodo-6-aminophenol*, m. p. 120° (*hydrochloride*). M. CLARK.

Preparation of some halogenoaminophenols. I. Mixed tetrahalogen derivatives of *o*-azophenol. II. Halogen derivatives of *p*-hydroxyazobenzene. L. HUNTER and R. S. BARNES (J.C.S., 1928, 2058—2067).—I. The chloroamine method of halogenation has been applied to the progressive mixed halogenation of *o*-azophenol. Five of the six theoretically possible symmetrical 3 : 5 : 3′ : 5′-tetrahalogeno-*o*-azophenols have been prepared and reduced to the corresponding 2 : 4-dihalogeno-*o*-aminophenols. The following are described (2 : 2′-dihydroxyazobenzene = A) : 5 : 5′-*Dichloro*-3 : 3′-*dibromo*-A, m. p. 259° (decomp.) (*diacetate*, m. p. 203° ; *dibenzoate*, m. p. 212°) ; 4-*chloro-6-bromo-2-aminophenol*, m. p. 89—90° (*hydrochloride* ; *diacetyl* derivative, m. p. 130° ; *dibenzoyl* derivative, m. p. 180·5°) ; 3 : 3′-*dichloro*-5 : 5′-*dibromo*-A, m. p. 263° (*diacetate*, m. p. 199° ; *dibenzoate*, m. p. 201°) ; 6-*chloro-4-bromo-2-aminophenol*, m. p. 93° (*hydrochloride* ; *diacetyl* derivative, m. p. 137° ; *dibenzoyl* derivative, m. p. 182°) ; 5 : 5′-*dichloro*-3 : 3′-*di-iodo*-A, m. p. 272° (decomp.) (*diacetate*, m. p. 205° ; *dibenzoate*, m. p. 254°) ; 4-*chloro-6-iodo-2-aminophenol*, charring at about 90° (*hydrochloride* ; *diacetyl* derivative, m. p. 169°) ; 5 : 5′-*dibromo*-3 : 3′-*di-iodo*-A, m. p. 255° (decomp.) (*diacetate*, m. p. 186° ; *dibenzoate*, m. p. 252°) ; 4-*bromo-6-iodo-2-aminophenol*, decomp. [*hydrochloride* ; *diacetyl* derivative, m. p. 190° (decomp.) ; *dibenzoyl* derivative, m. p. 185°] ; 3 : 3′-*dibromo*-5 : 5′-*di-iodo*-A, m. p. 256° (*diacetate*, m. p. 217° ; *dibenzoate*, m. p. 215°) ; 6-*bromo-4-iodo-2-aminophenol*, m. p. 90° (*hydrochloride* ; *diacetyl* derivative, m. p. 196° ; *dibenzoyl* derivative, m. p. 194—195°).

II. Since iodo-*p*-azophenols could not be prepared (preceding abstract), iodine-substituted *p*-aminophenols were obtained by reducing the iodo-derivatives of *p*-hydroxyazobenzene, which are readily accessible by the chloroamine method of halogenation. The iodo-aminophenols were separated from the aniline simultaneously formed by means of their differently soluble hydrochlorides. Direct halogenation of *p*-hydroxyazobenzene gave the 3 : 5-dihalogeno-compounds. The monohalogen derivatives were therefore synthesised by coupling diazotised aniline with the *o*-halogenophenols. The following are described (B=4-hydroxyazobenzene) : 3-Bromo-B, m. p. 80° (*hydrochloride*, m. p. 159° ; *acetate*, m. p. 98° ; *benzoate*, m. p. 113°) ; 3-*iodo*-A, m. p. 77—78° [*hydrochloride*, m. p. 172° (decomp.) ; *acetate*, m. p. 103—104° ; *benzoate*, m. p. 105°] ; 3-*chloro-5-bromo*-A, m. p. 125·5° (*acetate*, m. p. 133·5° ; *benzoate*, m. p. 118·5°) ; 2-chloro-6-bromo-4-aminophenol (*diacetyl* derivative, m. p. 168·5° ; *dibenzoyl* derivative, m. p. 111—112°) ; 3-*chloro-5-iodo*-A, m. p. 110·5° (*acetate*, m. p. 124° ; *benzoate*, m. p. 115°) ; 2-*chloro-6-iodo-4-aminophenol*, m. p. 169° (decomp.) (*hydrochloride* ; *diacetyl* derivative, m. p. 155° ; *dibenzoyl* derivative, m. p. 157°) ; 3-*bromo-5-iodo*-A, m. p. 128·5° (*acetate*, m. p. 127—128° ; *benzoate*, m. p. 85°) ; 2-*bromo-6-iodo-4-aminophenol*, m. p. 185° (decomp.) (*hydrochloride* ; *diacetyl* derivative, m. p. 186° ; *dibenzoyl* derivative, m. p. 148°) ; 3 : 5-*di-iodo*-A, m. p. 128—129° (*acetate*, m. p. 162° ; *benzoate*, m. p. 137—139°) ; 2 : 6-di-iodo-4-aminophenol, m. p. 173° (lit. 169—171°) (*diacetyl* derivative, m. p. 209°). M. CLARK.

Azo-derivatives of tyrosine. A. MOREL and P. SISLEY (Bull. Soc. chim., 1928, [iv], **43**, 881—883 ; cf. A., 1927, 1212).—When tyrosine is treated with nitrous acid in the cold and in absence of light only part of the amino-nitrogen is lost (maximum 40%). When tyrosine is diazotised under the same conditions as fibroin (*loc. cit.*) and after 36 hrs. the mixture is treated with β-naphthol two colouring matters are obtained. These are 3-β-*naphtholazotyrosine*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(OH)\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, slightly soluble in alcohol, and α-*hydroxy*-β-3-(β-*naphtholazo*)-4-*hydroxyphenylpropionic acid*, more readily soluble in alcohol. H. BURTON.

Diazo-compounds. A. ANGELI (Atti R. Accad. Lincei, 1928, [vi], 7, 699—705).—Largely polemical against Hantzsch. Consideration of the behaviour of diazo-compounds shows that their reactions may be explained satisfactorily without the help of stereoisomerism. T. H. POPE.

***cyclo*Hexyloxy-derivatives.** L. PALFRAY and S. SABETAY (Bull. Soc. chim., 1928, [iv], **43**, 900—903).—*cyclo*Hexyl chloromethyl ether (I) is converted by sodium methoxide in boiling toluene into cyclo*hexyl methoxymethyl ether*, b. p. 61·5—62·5°/15 mm., d^{16} 0·9375, n_D^{16} 1·4391, and by acetic anhydride and sodium acetate into cyclo*hexyl acetoxymethyl ether*, b. p.

96·5—97°/13 mm., d^{15} 1·022, n_D^{15} 1·4465. When (I) is heated with cuprous cyanide, cyclo*hexyloxyacetonitrile* (II), b. p. 102—103°/15 mm., d^{18} 0·9825, n_D^{18} 1·4561, is formed: this is converted by methyl-alcoholic hydrogen chloride into *methyl* cyclo*hexyloxyacetate*, b. p. 110°/16 mm., d^{20} 1·034, n_D^{20} 1·4508. Treatment of (II) with magnesum methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride gives cyclo*hexyloxyacetone*, b. p. 98—98·5°/17 mm., d^{17} 0·9686, n_D^{17} 1·4522, *phenyl* cyclo*hexyloxymethyl ketone*, b. p. 178°/14 mm., d^{20} 1·071, n_D^{20} 1·5365 (*hydrazone*, m. p. 113°; *semicarbazone*, m. p. 123°), and *benzyl* cyclo*hexyloxymethyl ketone*, b. p. 185—186°/14 mm., d^{21} 1·044, n_D^{21} 1·520, respectively.

cyclo*Hexane*-1 : 4-*diol di*(*methoxymethyl*) *ether* has b. p. 121—122°/13 mm., d^{17} 1·038, n_D^{17} 1·449.

H BURTON.

Δ³-*cyclo*Hexenol. S. SABETAY and L. PALFRAY (Bull. Soc. chim., 1928, [iv], 43, 906—909).—4-Chloro*cyclo*hexanol (*ethyl ether*, b. p. 84—85°/16 mm., d^{20} 1·028, n^{20} 1·4622, from magnesium methyl iodide and the *chloromethyl ether*, b. p. 117·5°/15 mm., n_D^{20} 1·4942) is oxidised by chromic acid to 4-*chloro*cyclo*hexanone*, which, when regenerated from its *semicarbazone*, m. p. 191°, has b. p. 95°/17 mm., $n_D^{20.5}$ 1·4867. When 4-chloro*cyclo*hexanol is heated with sodium in dry ether for 2 days, Δ³-*cyclo*hexenol, b. p. 67—68°/14 mm., d^{20} 0·9425, n_D^{20} 1·4627 (phenylcarbimide derivative, m. p. 82°), is obtained (cf. von Baeyer, A., 1894, i, 174).

H. BURTON.

Extraction of phenols from alkaline solution with ether. G. VAVON and N. ZAHARIA (Compt. rend., 1928, **187**, 346—348).—All phenols are extracted by ether from their solutions in sodium hydroxide, to an extent depending on the hydrolysis of the phenoxide and the solubility of the free phenol in the phenoxide solution and in ether. The percentage extracted increases with the mol. wt. of the phenol and is considerably greater with *o*-substituted phenols than with the *m*- or *p*-isomerides. Ether extraction thus affords a means of distinguishing between *o*-phenols and the *m*- and *p*-isomerides and of partly separating a mixture of phenols. Excess of alkali decreases the extraction, but for substituted phenols it is advisable to replace ether by light petroleum or other solvent. Thus thymol dissolved in 1 mol. of sodium hydroxide is extracted to the extent indicated by the following solvents: ether 88%, benzene 38%, carbon tetrachloride 25%, light petroleum 22%. The following percentages of phenols are extracted by ether from a solution in 1 mol. of sodium hydroxide at 15°, using 0·01 mol. in 10 c.c. of solution, and extracting with 20 c.c. of ether: phenol 7·5, *o*-cresol 20·8, *m*-cresol 15·0, *p*-cresol, 13·3, *o*-ethylphenol 44·7, *p*-ethylphenol 25·3, *m*-4-xylenol 43, *p*-xylenol 37·7, *o*-propylphenol 68·5, *p*-propylphenol 28·7, *o*-allylphenol 48, *p*-allylphenol 24·3, *o*-*iso*propylphenol 72·7, *p*-*iso*propylphenol 32·6, *o*-butylphenol 80·7, *p*-butylphenol 28·7, "*o*-ψ-butylphenol" 97, "*p*-ψ-butylphenol" 30·6, *o*-allyl-*o*-cresol 70·6, di-*o*-propylphenol 97·7, di-*o*-allylphenol 91·7, thymol 88, carvacrol 82·5, *o*-phenylphenol 52·5, α-naphthol, 16·7, β-naphthol 23.

R. BRIGHTMAN.

Constitution of dinitro-*m*-cresols. S. M. SANE and S. S. JOSHI (J. Indian Chem. Soc., 1928, **5**, 299—301).—When 3-chloro-4 : 6-dinitrotoluene is fused with sodium acetate and acetamide (Borsche, A., 1918, i, 11), 4 : 6-dinitro-*m*-cresol, m. p. 74°, is obtained, the p-*toluenesulphonate*, m. p. 110—111°, of which, when treated with ammonia in boiling xylene, affords 4 : 6-dinitro-*m*-toluidine. Bromination of the dinitrocresol gives 2-*bromo*-4 : 6-*dinitro*-m-*cresol*, m. p. 115—116°, which when treated with *p*-toluenesulphonyl chloride and diethylaniline yields 3-chloro-2-bromo-4 : 6-dinitrotoluene, m p. 81—82° (Cohen and Smithells, J.C.S., 1914, **105**, 1909). The compound described by Gibbs and Robertson (*ibid.*, 1889) as the bromo-derivative of 2 : 6-dinitro-*m*-cresol, m. p. 74°, is the 2-bromo-derivative of 4 : 6-dinitro-*m*-cresol.

H. BURTON.

Ethers of *cyclo*hexanediols. L. PALFRAY and S. SABETAY (Bull. Soc. chim., 1928, [iv], **43**, 895—900).—Methylation of *cyclo*hexane-1 : 2-diol with methyl iodide and dry silver oxide gives a mixture of the monomethyl, b. p. 74—76°/15 mm., d^{18} 1·001, n_D^{18} 1·4572, and *dimethyl ethers*, b. p. 65—66°/15 mm., d^{18} 0·9652, n^{18} 1·446. The action of hydrogen chloride on a mixture of the diol and 40% formaldehyde is to furnish cyclo*hexane*-1 : 2-*diol di*(*chloromethyl*) *ether*, b.p. 136—137°/16 mm., n_D^{21} 1·488, which reacts with sodium in benzene solution, yielding a chlorine-free product, b. p. 62—65°/15 mm., n_D^{18} 1·4555 (cf. Sabetay and Sandulesco, this vol., 1140), together with solid derivatives. Methylation of *cyclo*hexane-1 : 3-diol affords its *monomethyl ether*, b. p. 97—98°/15 mm., together with an iodine-containing product, b. p. 65—66°/15 mm. cyclo*Hexane*-1 : 3-*diol diethyl ether*, b. p. 85—86°/15 mm., d^{18} 0·9127, n_D^{18} 1·440, is obtained by the action of magnesium methyl iodide on the corresponding *di*(*chloromethyl*) *ether*, b. p. 144—145°/14 mm., n_D^{17} 1·4922. Methylation of *cis*-*cyclo*hexane-1 : 4-diol gives a mixture of the cis-*monomethyl*, b. p. 102—103°/15 mm., d^{19} 1·023, n_D^{19} 1·4671, and cis-*dimethyl ethers*, b. p. 67·5—68°/14 mm., d^{18} 0·9526, n_D^{18} 1·444. The corresponding trans-*mono*- and -*di*-*methyl ethers* have b. p. 102·5—103°/15 mm., d^{19} 1·021, n_D^{20} 1·4649, and b. p. 68—69°/15 mm., n_D^{18} 1·443, respectively. The question of possible isomerisation during etherification (cf. Palfray and Rothstein, this vol., 632) is reserved. cyclo*Hexane*-1 : 4-*diol di*iso*butyl ether*, b. p. 122—124°/13 mm., d^{19} 0·8833, n_D^{19} 1·441, is prepared from magnesium *iso*propyl bromide and the corresponding *di*(*chloromethyl*) *ether*, b. p. 148—149°/14 mm., m. p. about 44°, n_D^{21} 1·4936.

If the total amount of silver oxide is added at the beginning of the methylation experiment, a violent reaction results and by-products are formed. Methylene iodide was isolated from *cyclo*hexane-1 : 4-diol, and a ketone, b. p. 84—87°/15 mm., n_D^{19} 1·471, probably *cyclo*hexanolone, from the 1 : 2-diol. H. BURTON.

Mixed ethers from alcohols used in perfumery. P. SCHVING and S. SABETAY (Bull. Soc. chim., 1928, [iv], **43**, 857—859).—Primary and secondary alcohols react with alkyl chloroformates in presence of chloroform and pyridine, yielding the corresponding *O*-carbethoxy-derivatives. Tertiary alcohols must be converted into the sodium derivative and then treated with the alkyl chloroformate in ether. O-*Carbethoxy*-derivatives of the following

alcohols are described: β-phenylethyl, b. p. 140—141°/17 mm., d^{22} 1·063, n_D^{22} 1·4889; benzyl, b. p. 122—124°/20 mm., d^{24} 1·084, n_D^{24} 1·4899; cinnamyl, b. p. 164—166°/16 mm., 1·5214; anisyl, b. p. 166—167°/16 mm., 1·501; geraniol, b. p. 145—148°/17 mm., n_D^{21} 1·453; citronellol, b. p. 141—142°/18 mm., n_D^{22} 1·442; linalool, b. p. 127—128°/16 mm., n_D^{21} 1·4508. Using allyl chloroformate, b. p. 110—111·5°/765 mm., from allyl alcohol and carbonyl chloride, O-*carballyloxy*-derivatives of the following alcohols have been prepared: β-phenylethyl, b. p. 152—152·5°/17 mm., d^{20} 1·06, n_D^{20} 1·4936; cinnamyl, b. p. 176—178°/16 mm.; linalool, b. p. 139°/18 mm., d^{23} 0·9473, n^{22} 1·459; geraniol, b. p. 157·5—158°/18 mm. The O-*carbomethoxy*-derivatives of rhodinol, b. p. 137—138°/19 mm., n_D^{18} 1·451; cinnamyl alcohol, b. p. 158—161°/19 mm., n^{18} 1·5356, and β-phenylethyl alcohol, b. p. 133—134°/19 mm., n_D^{19} 1·494, are also described. β-*Phenylethyl chloroformate*, b. p. 120°/18 mm., n_D^{21} 1·511, reacts with rhodinol and *cyclo*hexanol, yielding the corresponding mixed *carbonates*, b. p. 191°/2 mm., n_D^{21} 1·501, and b. p. 194°/19 mm., n_D^{19} 1·507, respectively. β-*Phenylethyl carbonate* has b. p. 190°/2 mm., m. p. 56°.

H. BURTON.

Photo-oxidation of adrenaline. T. VACEK (Compt. rend. Soc. Biol., 1927, **97**, 1739—1741; Chem. Zentr., 1928, i, 1504).—Radiation of short wave-length increases the oxidisability of adrenaline. Pure adrenaline dissolved in hydrochloric acid is most stable; alkaline solutions decompose more rapidly.

A. A. ELDRIDGE.

Reactivity of iodine in organic solvents. I. F. FEIGL and E. CHARGAFF (Monatsh., 1928, **49**, 417—428).—The action of iodine on the silver derivative of saccharin has been studied. Brown solutions of iodine in ether, alcohol, dioxan, *cyclo*hexanol, and *cyclo*hexene react with the silver derivative of saccharin to give silver iodide quantitatively. Of the violet solutions of iodine in chloroform, benzene, carbon disulphide, carbon tetrachloride, and light petroleum, the first two behave as if they belonged to the ether dioxan class, whilst the remainder react with the silver derivative of saccharin to form only small amounts of silver iodide. The velocity of silver iodide formation depends on the solvent used for the iodine. The authors consider that this is due to the state of combination of the iodine, and depends on the physical properties of the solvent, such as dielectric constant, only in so far as these are related to solvate formation. Hydrolysis of the product with acidified potassium iodide solution gives saccharin and iodine, the latter indicating formation of hypoiodous acid.

R. A. PRATT.

Synthesis of certain iodo-alkoxy-acids and mechanism of reactions by which they are formed. E. L. JACKSON and L. PASIUT (J. Amer. Chem. Soc., 1928, **50**, 2249—2260).—The reaction of β-chloro-α-iodo-β-phenylpropionic acid with water or alcohols to give β-hydroxy- or β-alkoxy-derivatives (cf. Erlenmeyer, A., 1896, i, 302) takes place in the absence of potassium hydroxide. The α-iodo-β-alkoxy-acids are also conveniently prepared by the reaction of iodine monochloride with cinnamic acid dissolved in the appropriate alcohol. Of the possible mechanisms of the first reaction, the one involving the intermediate formation of the lactone is eliminated by the reaction of methyl β-chloro-α-iodo-β-phenylpropionate with absolute methyl alcohol to give the β-methoxy-ester, whilst the reaction of the α-iodo-α-methyl acid with methyl alcohol eliminates the possibility of intermediate formation of the α-iodocinnamic acid. The remaining alternatives are direct replacement of chlorine by the alkoxyl group and intermediate formation of cinnamic acid by elimination of iodine monochloride, the latter reacting with the alcohol to give the alkyl hypoiodite, which then adds on to the double linking of the cinnamic acid. This last hypothesis is favoured by several facts. Cinnamic acid is formed in the reaction, in small quantity with methyl alcohol, but in increasing quantity, concurrently with decreasing yield of the β-alkoxy-acid, with increase of mol. wt. of the reacting alcohol. The occurrence of the reaction in presence of excess of calcium carbonate makes unlikely the formation of the cinnamic acid by the action of hydrochloric or hydriodic acid. The decreased yield with higher alcohols is attributed to consumption of the iodine monochloride in side-reactions with the alcohol. This explanation of the mechanism is also consistent with the results of the preparations from iodine monochloride, cinnamic acid, and alcohol, in which the yield also falls with higher alcohols, but is improved by using excess of iodine monochloride, and brought down to the yield in the first method by gradual addition of the iodino monochloride. Further, the reaction of the alcohol and the β-chloro-α-iodo-acid is very slow in comparison with the reaction of iodine monochloride, cinnamic acid, and the alcohol.

α-Iodo-β-hydroxy-β-phenylpropionic acid was also prepared by passing chlorine into a suspension of iodine and cinnamic acid in water, and the methoxy- and ethoxy-acids by passing chlorine into solutions in the appropriate alcohol. The β-chloro-α-iodo-acid was conveniently prepared in large quantity by addition of iodine monochloride to cinnamic acid in carbon tetrachloride solution. The following α-iodo-alkoxy-acids are described: -β-methoxy-, m. p. 168—169° (*methyl* ester, m. p. 68—69°); -β-ethoxy-, m. p. 137—138°; -β-n-*propoxy*-, m. p. 110—111°; -β-iso-*propoxy*-, m. p. 113—114°; -β-n-*butoxy*-, m. p. 93—94°; -β-*iso*butoxy-, m. p. 89—90°, and -β-tert.-*butoxy*-β-*phenylpropionic acid*, m. p. 113—114°. β-*Chloro-α-iodo-β-phenyl-α-methylpropionic acid*, m. p. 104—105° (decomp.), was prepared by addition of iodine monochloride to α-methylcinnamic acid, and yielded, with methyl alcohol, *α-iodo-β-methoxy-β-phenyl-α-methylpropionic acid*, m. p. 169—170°. The reaction of iodine monochloride and methyl alcohol with crotonic acid yielded *iodomethoxybutyric acid*, m. p. 83—84°. The structure assigned to the α-iodo-β-alkoxy-acids was confirmed by the formation of β-methoxy-β-phenylpropionic acid by the action of zinc in methyl alcohol, and by the formation of acetophenone from α-iodo-β-*iso*propoxyphenylpropionic acid and of propiophenone from α-iodo-α-methyl-β-methoxyphenylpropionic acid by reaction with alcoholic potassium hydroxide followed by hydrolysis of the product by dilute sulphuric acid.

R. K. CALLOW.

Betaines. III. P. PFEIFFER [with H. BEHR, B. BREYER, O. CLARENZ, and H. KUBLER] (Annalen, 1928, **465**, 20—52).—Reduction of *cis-α-m*-nitrophenylcinnamic acid with ferrous hydroxide gives cis-α-m-*aminophenylcinnamic acid*, m. p. 189—191° [*hydrochloride*, m. p. 229—232° (decomp.); *silver* salt; *benzoyl* derivative $+H_2O$, m. p. 184—185°], which when methylated with a large excess of methyl iodide and potassium hydroxide affords the *methiodide*, m. p. 158° (decomp.), of cis-α-m-*dimethylaminophenylcinnamic acid*. Treatment of this with moist silver oxide yields the corresponding cis-*betaine*,

$NMe_3\cdot C_6H_4\cdot CH{:}CPh\cdot COO+H_2O$, m. p. 186—188° [(decomp.); *hydrochloride*, m. p. 178° (decomp.); *hydrobromide*, decomp. 170°; *nitrate*, m. p. 144—146° (decomp.); *perchlorate*, m. p. 170° (decomp.); *chloroplatinate* $+H_2O$, m. p. 168° (decomp.)]. The analogous trans-*betaine* $+H_2O$, m. p. 112—114° [*hydrochloride*, m. p. 163° (decomp.); *hydrobromide* $+H_2O$, m. p. 148—152° (decomp.); *nitrate*, m. p. 166—169° (decomp.); *perchlorate*, m. p. 173° (decomp.); *chloroplatinate* $+0{\cdot}5H_2O$, m. p. 196°], is obtained similarly from the *methiodide*, m. p. 163—167° (decomp.), of trans-α-m-*dimethylaminophenylcinnamic acid*, prepared by methylation of trans-α-m-*aminophenylcinnamic acid*, m. p. 192° (*benzoyl* derivative, m. p. 255—256°; *methyl* ester, m. p. 117°; *ethyl* ester, m. p. 65°). The *hydriodides* of these betaines are identical with the above methiodides.

p-Dimethylaminobenzaldehyde when condensed with *p*-nitrophenylacetonitrile in presence of sodium ethoxide gives 4-*nitro*-4′-*dimethylamino*-α-*cyanostilbene*, m. p. 240—241° (*methiodide* $+2H_2O$), which is hydrolysed by warm concentrated sulphuric acid, forming two isomeric p-*dimethylamino*-α-p-*nitrophenylcinnamamides*, *A* and *B*, having m. p. 221—222° and 256°, respectively. Hydrolysis of *A* with methyl- and ethyl-alcoholic hydrogen chloride gives the *methyl* and trans-*ethyl* p-*dimethylamino*-α-p-*nitrophenylcinnamate* (I), m. p. 169—170° and 134—135°, respectively. Hydrolysis of *B* affords in addition to (I) a second (cis-)*isomeride*, m. p. 138—139°, oriented by the action of hot concentrated sulphuric acid, when indone ring-formation occurs. p-*Dimethylamino*-α-p-*nitrophenylcinnamic acid* has m. p. 249°. The *methiodide*, m. p. 160—161° (decomp.), of (I) is decomposed by silver oxide in hot aqueous solution, yielding

the *betaine*, $NMe_3\cdot C_6H_4\cdot CH{:}C(C_6H_4\cdot NO_2)\cdot COO$, m. p. 210—211° (*perchlorate*). Similar treatment of the *methiodide*, m. p. 201°, of m-*dimethylaminocinnamic acid* gives the corresponding *betaine* $+H_2O$, m. p. 128°, m. p. (anhydrous) 206—207° (*hydrobromide*, m. p. 193—196°; *perchlorate*, m. p. 230—231°).

Reduction of 2-nitro-4′-dimethylamino-4-cyanostilbene [*methiodide* (II), m. p. 203°] with stannous chloride gives the corresponding 2-*amino*-derivative, m. p. 226° (*dihydrochloride*). The *methiodides* (III and IV) of *methyl* and *ethyl* 2-*nitro*-4′-*dimethylaminostilbene*-4-*carboxylate* (*methonitrate*) have m. p. 192° and 147°, respectively. When (II) and (III) are decomposed with silver oxide in hot aqueous solution the

betaine, $NMe_3\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_3(NO_2)\cdot COO$, $+3H_2O$, m. p. (anhydrous) 220—222° (*hydrochloride* $+2H_2O$), is obtained, but the product from (II) has a low m. p.

Condensation of *p*-dimethylaminobenzaldehyde with *p*-cyanophenylacetonitrile in presence of a small amount of piperidine at 100—130° affords 4′-*dimethylamino*-α : 4-*dicyanostilbene*, m. p. 205°, hydrolysed by methyl-alcoholic hydrogen chloride to *methyl* 4′-*dimethylamino*-α-*cyanostilbene*-4-*carboxylate*, m. p. 178° [*ethyl* ester (V), m. p. 145°]. The *methiodide* of (V) is transformed in the usual way into the *betaine*,

$NMe_3\cdot C_6H_4\cdot CH{:}C(CN)\cdot C_6H_4\cdot \overline{CO}O+1{\cdot}5H_2O$, m. p. 205° (*hydrochloride* $+2H_2O$).

The successful isolation of *cis*- and *trans*-forms of betaines in the α-phenylcinnamic acid series supports the authors' idea that the betaines are to be regarded as dipolar compounds, not as internal ring compounds (cf. A., 1922, i, 738). H. BURTON.

Di(*cyclo*hexylalkyl)acetic acids. XIV. L. A. DAVIES and R. ADAMS (J. Amer. Chem. Soc., 1918, **50**, 2297—2298; cf. Arvin and Adams, this vol., 1003).—Whilst the introduction of a *cyclo*hexyl group at the end of certain straight-chained aliphatic acids produces compounds bactericidal toward *B. leprae*, the introduction of two such groups, producing compounds of the type

$C_6H_{11}\cdot[CH_2]_x\cdot CH(CO_2H)\cdot[CH_2]_y\cdot C_6H_{11}$, did not enhance the activity. The following compounds were prepared by methods previously described (Hiers and Adams, A., 1926, 1136; Adams, Stanley, Ford, and Peterson, this vol., 62): diethyl esters of substituted malonic acids: cyclo*hexyl*-β-cyclo*hexylethyl*-, b. p. 192°/4·5 mm., d_4^{20} 1·016, n_D^{20} 1·4747; cyclo*hexylmethyl*-β-cyclo*hexylethyl*-, b. p. 186—188°/3 mm., d_4^{20} 1·003, n_D^{20} 1·4725; *di*-(β-cyclo*hexylethyl*)-, b. p. 200—202°/1·5 mm., d_4^{20} 0·9931, n_D^{20} 1·4722; β-cyclo*hexylethyl*-γ-cyclo*hexylpropyl*-, b. p. 210—211°/3·5 mm., d_4^{20} 0·9928, n_D^{20} 1·4713; *di*-(γ-cyclo*hexylpropyl*)-, b. p. 216—218°/3 mm., d_4^{20} 0·9811, n_D^{20} 1·4710; β-cyclo*hexylethyl*-δ-cyclo*hexylbutyl*-, b. p. 208—210°/2·5 mm., d_4^{20} 0·9817, n_D^{20} 1·4710; and the following substituted acetic acids: cyclo*hexyl*-β-cyclo*hexylethyl*-, b. p. 182—186°/4 mm., d_4^{20} 0·9915, n_D^{20} 1·4852; cyclo*hexylmethyl*-β-cyclo*hexylethyl*-, m. p. 50—51°, b. p. 207—208°/5 mm.; *di*-(β-cyclo*hexylethyl*)-, m. p. 73—76°, b. p. 210—213°/1·5 mm.; β-cyclo*hexylethyl*-γ-cyclo*hexylpropyl*-, m. p. 46·5—47°, b. p. 213—214°/3 mm.; *di*-(γ-cyclo*hexylpropyl*)-, m. p. 42·5—45°, b. p. 216—218°/3 mm.; β-cyclo*hexylethyl*-δ-cyclo*hexylbutyl*-, b. p. 221—223°/4 mm., d^{20} 0·9647, n_D^{20} 1·4831.

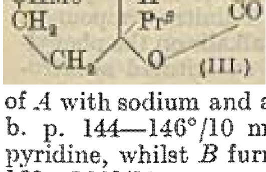
R. K. CALLOW.

Dicyclic hydroaromatic and *cyclo*pentane lactones. J. VON BRAUN and W. MÜNCH (Annalen, 1928, **465**, 52—72).—Δ^1-*cyclo*Hexenylacetic acid (I), b. p. 140°/12 mm., can be distilled under reduced pressure without lactone formation, but lactonisation can be effected by treatment with sulphuric acid (cf. Wallach, A., 1907, i, 616). When *cyclo*hexylideneacetic acid (II) is treated with sodium hydroxide solution an equilibrium mixture of 40% of (I) and 60% of (II) is obtained. Prolonged interaction of ethyl 1-hydroxy*cyclo*hexylacetate with an acetic acid solution of hydrogen bromide and subsequent treatment with zinc dust gives a halogen-containing oil (cf. Wallach, *loc. cit.*). When this is hydrolysed by

aqueous-alcoholic potassium hydroxide and then acidified with sulphuric acid, immediate extraction with ether affords a product completely soluble in sodium carbonate solution. If the acidified mixture is kept for some time there is obtained about 10% of the *lactone*, $C_6H_{10}<\overset{CH_2}{\underset{O}{}}>CO$, b. p. 129—130°/13 mm., d_4^{15} 1·0913, n_D^{15} 1·4784. An explanation of the formation of this lactone is advanced involving the elimination of hydrogen bromide from the intermediate bromo-ester, subsequent re-addition in a reverse direction, replacement of the bromine by hydroxyl, and final lactonisation. Oxidation of the lactone with 30% nitric acid gives a mixture of adipic and butane-αβδ-tricarboxylic acids (*ethyl* ester, b. p. 183—185°/20 mm.). *Ethyl* cyclo*hexylacetate* has b. p. 100—101°/14 mm. Similar treatment of ethyl 1-hydroxy*cyclo*hexyl*iso*butyrate gives, in addition to cyclo*hexyl*iso*butyric acid*, m. p. 62—63°, about 70% of the dicyclic *lactone*, $C_6H_{10}<\overset{CMe_2}{\underset{O}{}}>CO$, m. p. 56°.

[With E. DEUSSER.]—Condensation of *cyclo*pentenyl chloride with ethyl malonate in presence of sodium and toluene affords, in addition to ethyl *cyclo*pentenylmalonate (cf. Noller and Adams, A., 1926, 1137), some *ethyl di*cyclo*pentenylmalonate*, b. p. 192—193°/14 mm. Decarboxylation of the free *acid* yields *di*cyclo*pentenylacetic acid*, b. p. 168—170°/11 mm. Lactonisation of Δ^2-*cyclo*pentenylacetic acid with sulphuric acid gives the *compound* $C_5H_8<\overset{CH_2}{\underset{O}{}}>CO$, b. p. 126—127°/14 mm., d_4^{22} 1·113, n_D^{22} 1·4778, oxidised by nitric acid to glutaric acid. Hydrogen bromide–zinc dust treatment of ethyl 1-hydroxy-2-methyl*cyclo*hexylacetate gives mainly the *lactone*, b. p. 136—137°/13 mm., d_4^{19} 1·068, n_D^{19} 1·4764, of 2-*hydroxy-2-methyl*cyclo*hexylacetic acid*, m. p. 107°. Reduction of this lactone with sodium and alcohol gives a 70% yield of β-2-*hydroxy-2-methyl*cyclo*hexylethyl alcohol*, b. p. 153—155°/13 mm., m. p. 75—76°, which is converted by 60% sulphuric acid at 100° into an internal *oxide*, b. p. 175—176°, d_4^{27} 0·9372, n_D^{27} 1·4602, together with material of high b. p. *Ethyl* 2-*methyl*cyclo*hexylacetate* has b. p. 145—147°/13 mm.

Hydrolysis of ethyl mentheneacetate, b. p. 135—137°/10 mm., d_4^{17} 0·9518, n_D^{17} 1·4642, $[\alpha]_D^{17}$ +32·79° (cf. Wallach, A., 1902, i, 799; *loc. cit.*), with aqueous-alcoholic potassium hydroxide and subsequent distillation of the acid obtained gives some lactone in addition to the corresponding acid. The hydrogen bromide–zinc dust treatment of ethyl mentholacetate affords 4% of menthylacetic acid, b. p. 164—166°/10 mm., d_4^{21} 0·9761, n_D^{21} 1·4698, $[\alpha]_D^{21}$ +18°, together with a mixture of isomeric *lactones* (III), separable



by prolonged cooling into *A*, b. p. 156—159°/10 mm., m. p. 114—115°, $[\alpha]_D^{15}$ −24·68° in pyridine, and *B*, b. p. 156—159°/10 mm., d_4^{17} 1·0153, $[\alpha]_D^{15}$ −30·6° in pyridine. Reduction of *A* with sodium and alcohol gives a *glycol*, $C_{12}H_{24}O_2$, b. p. 144—146°/10 mm., m. p. 94°, $[\alpha]_D^{20}$ +9·7° in pyridine, whilst *B* furnishes an isomeric *glycol*, b. p. 163—166°/10 mm., m. p. 108°, $[\alpha]_D^{18}$ +20° in pyridine, together with a small amount of lower-melting substance. The glycol of m. p. 108° is converted by 60% sulphuric acid at 100° into a γ-*oxide*, $C_{12}H_{22}O$, b. p. 94—96°/9 mm., d_4^{19} 0·9292, n_D^{19} 1·470, $[\alpha]^D$ +23·4°.

H. BURTON.

Chlorobenzoylacetic esters and their derivatives. A. WAHL and J. ROLLAND (Ann. Chim., 1928, [x], 10, 5—49).—Partly an account of work already abstracted (this vol., 289). The following is new. As by-products in the preparation of methyl *o*-, *m*-, and *p*-chlorobenzoylacetates (*copper* derivatives) there are formed o-, m-, and p-*chlorobenzoyldehydracetic acids*, m. p. 216°, 172°, and 242°, respectively. When the esters are treated with phenylhydrazine, 1-*phenyl*-3-o-, -m-, and -p-*chlorophenyl*-5-*pyrazolones*, m. p. 113—114°, 144°, and 140°, respectively, are produced. The corresponding 1-p-*nitrophenyl* derivatives have m. p. 203—204°, 189°, and 200—200·5°, respectively. The action of nitrous acid on the esters gives *methyl oximino*-o-, -m-, and -p-*chlorobenzoylacetates*, m. p. 90—91°, 113—114°, and 124—125°, respectively, whilst with hydroxylamine there are formed 3-o-*chlorophenyl*iso*oxazolone*, m. p. 138° [*benzylidene*, m. p. 152°; p-*dimethylaminobenzylidene*, m. p. 199°, and 3 : 4-*dihydroxybenzylidene*, m. p. 233—235° (decomp.), derivatives]; 3-m-*chlorophenyl*iso*oxazolone*, m. p. 98° (*benzylidene*, m. p. 116°; p-*dimethylaminobenzylidene*, m. p. 192°, and 3 : 4-*dihydroxybenzylidene*, m. p. 190—192°, derivatives), and 3-p-*chlorophenyl*iso*oxazolone*, m. p. 152° (*benzylidene*, m. p. 154°; p-*dimethylaminobenzylidene*, m. p. 200°, and 3 : 4-*dihydroxybenzylidene*, m. p. 201—203°, derivatives). When these *iso*oxazolones are treated with isatin chloride in presence of benzene and phosphorus pentachloride there are formed the *o*-, *m*-, and *p*-chloro-substituted *compounds*,

$$\begin{array}{l} C_6H_4Cl{\cdot}C\text{——}C{:}C<\overset{NH}{\underset{CO}{}}>C_6H_4 \\ \quad\ N\diagdown_{O}\diagup CO \end{array}$$

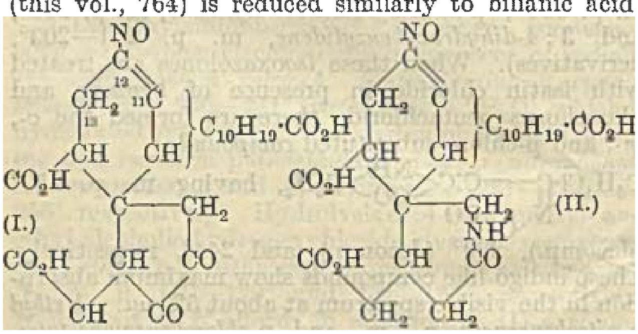
having m. p. 250° (decomp.), 239° (decomp.), and 244°, respectively. These indigo-like compounds show maximum absorption in the visible spectrum at about 520 μμ. *Methyl* p-*nitrobenzeneazo*-o-, -m-, and -p-*chlorobenzoylacetates*, obtained from the original esters and *p*-nitrobenzenediazonium chloride, have m. p. 104—105°, 174—175°, and 206—207°, respectively.

Determination of the amounts of enol form in the methyl chlorobenzoylacetates by the bromine titration method gives a value of approximately 25% for each isomeride, but it is shown that the percentage of enol in freshly-distilled *o*-ester (20·5) increases on keeping (25·5 after 1·5 hrs.). Hydrolysis of the esters with 20% sulphuric acid affords *o*-chloroacetophenone (p-*nitrophenylhydrazone*, m. p. 215°; *semicarbazone*, m. p. 159—160°), m-*chloroacetophenone*, b. p. 227—229°, d_4^0 1·213 (p-*nitrophenylhydrazone*, m. p. 175—176°; *oxime*, m. p. 88°), and *p*-chloroacetophenone (p-*nitrophenylhydrazone*, m. p. 239°; *semicarbazone*, m. p. 200—201°), respectively. When these ketones are heated with aqueous sodium sulphite at 170° for 20 hrs. in an autoclave, the *m*-compound does not react, but with the *o*- and *p*-derivatives there are formed the *sodium* salts (+2H_2O) of *acetophenone*-o- and -p-*sulphonic acids* [*phenylhydrazones*, m. p. 212° (decomp.) and 215° (decomp.), respectively].

H. BURTON.

Optical resolution of a spirocyclic compound of the allene type. H. J. Backer and H. B. J. Schurink (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 370—371).—*cyclo*Butane*spirocyclo*butane-1 : 1′-dicarboxylic acid, prepared in 80% yield by a modification of Fecht's method (A., 1907, i, 906), is resolved by crystallisation of its *dibrucine* salt, decomp. 135°, from water. The active *ammonium* salt has $[\alpha]_D$ +0·13°, from which the free acid, $[M]_D$ +1·9° (ether), is obtained. Röntgen analysis of dibenzylidenepentaerythritol (Read, J.C.S., 1912, **101**, 2090) shows that the distribution of the carbon valencies of the spiran carbon atom is tetrahedral. It is obtained in both dextro- and lævo-rotatory crystals, α_D ±2°/mm., the optical activity of which is due to the asymmetric distribution of the molecules, since no trace of optical activity can be detected in solution. J. W. Baker.

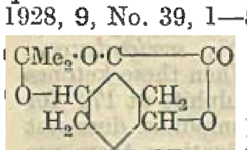
Bile acids. XXI. M. Schenck and H. Kirchhof (Z. physiol. Chem., 1928, **177**, 280—294).—When the nitroso-compound (I) (this vol., 1007) is reduced with zinc dust and acetic acid, two *substances*, $C_{24}H_{35}O_8N$, possibly stereoisomerides, having m. p. 240—242° with frothing and 230—232°, respectively, are obtained. Hydrolysis of the former with hydrochloric acid gives hydroxylamine and bilianic acid, thus showing it to be bilianic acid oxime. Nitric acid converts it into (I). The nitroso-compound (II) (this vol., 764) is reduced similarly to bilianic acid



di*iso*oxime, m. p. 258—260° (decomp.), the rearrangement product of bilianic acid dioxime. When this is hydrolysed with hydrochloric acid, hydroxylamine and the two stereoisomeric compounds, $C_{24}H_{35}O_8N$, m. p. 200—205° and 260°, respectively, previously described (*loc. cit.*) are obtained.

Attention is directed to a recent paper by Wieland and Vocke (this vol., 1007) showing that C_{11} is quaternary. In this case the double linking between C_{11} and C_{12} should be placed between C_{12} and C_{13}. H. Burton.

Benzoyl*iso*propylidenequinide and benzoylquinide. K. Josephson (Arkiv Kemi, Min., Geol., 1928, **9**, No. 39, 1—5).—The *iso*propylidene ether of quinic acid lactone (cf. Fischer, A., 1921, i, 419) is converted by benzoyl chloride in presence of pyridine into *benzoyl*iso*propylidenequinide* (I), m. p. 140°, [α] +13·2° in chloroform, which



is hydrolysed by warm aqueous-alcoholic sulphuric acid to *benzoylquinide*, m. p. 148°, [α] −6·9° in alcohol. H. Burton.

Naphthalene derivatives. [Sulphonic acids of 6-hydroxy-2-naphthoic acid.] I. G. Farbenind. A.-G.—See B., 1928, 597.

Manufacture of hydroaromatic dicarboxylic acids. J. D. Riedel A.-G.—See B., 1928, 665.

Benzylideneaniline and benzylidene-*p*-toluidine as ammonoaldehyde-acetals. H. H. Strain (J. Amer. Chem. Soc., 1928, **50**, 2218—2223; cf. A., 1927, 767).—Franklin's view of Schiff's bases as aldehyde-acetals of an ammonia system of compounds is supported by the fact that they undergo an analogous series of reactions—ammonolysis, Cannizzaro reaction, benzoin condensation, nitridation, and polymerisation. Ammonolysis of benzylideneaniline and benzylidene-*p*-toluidine by keeping in liquid ammonia solution yielded aniline and *p*-toluidine, respectively, and amarine, the last being produced by condensation of the benzylideneimine first formed. The Cannizzaro reaction, carried out by treatment with potassium amide (2 mols.) in liquid ammonia, yielded, respectively, phenylbenzylbenzamidine (*benzenesulphonyl* derivative, m. p. 148°) and p-*tolylbenzylbenzamidine*, m. p. 127—127·5° (also obtained from benz-*p*-toluidide and benzamide by heating with phosphorus pentachloride), which are ammonoesters, together with aniline or *p*-toluidine. The mechanism of this reaction is discussed. The benzoin condensation, with potassium cyanide in liquid ammonia, yielded, respectively, *benzoinanilanilide*, CHPh(NHPh)·CPh:NPh, m. p. 185—200°, and *benzoin*-p-*tolil*-p-*toluidide*, m. p. 122°. Nitridation, with iodine in liquid ammonia, gave a tarry product from benzylideneaniline, containing traces of phenylcarbylamine and benzonitrile. The action of potassium amide (less than 1 mol.) on benzylideneaniline and benzylidene-*p*-toluidine yielded, respectively, *polymerides*, $C_{33}H_{29}N_3$, m. p. 132—134° (*hydrochloride*), and $C_{35}H_{33}N_3$, m. p. 136—137°. An excess of potassium amide converted these into the corresponding benzamidines. R. K. Callow.

Nitration of 4-halogeno-2-hydroxy- and 2-halogeno-4-hydroxy-benzaldehydes. H. H. Hodgson and T. A. Jenkinson (J.C.S., 1928, 2272—2280).—Direct mononitration of the 4-halogenosalicylaldehydes gives exclusively the 5-nitro-derivatives, since bromination of these substances yields the identical compounds obtained by nitration of the 3-bromo-4-halogenosalicylaldehydes. The sodium salts of both nitro- and nitrobromo-derivatives are yellow, in accordance with their *p*-nitrophenolic structure. The sodium salts of the 5-bromo-4-halogeno-3-nitrosalicylaldehydes, prepared for comparison, are bright red, indicating an *o*-nitrophenolic structure. Dinitration of the 4-halogenosalicylaldehydes gives the 3 : 5-dinitro-derivatives. The 2-halogeno-4-hydroxybenzaldehydes are similarly converted into the 5-nitro- and 3 : 5-dinitro-compounds. The brown colours produced by alkalis on the phenylhydrazones of certain of these substituted *m*-nitrobenzaldehydes are in accord with the observations of Chattaway and Clemo (J.C.S., 1923, **123**, 3043). The following are described (A=2-hydroxybenzaldehyde; B=4-hydroxybenzaldehyde): *4-chloro-5-nitro*-A, m. p. 116° [*phenylhydrazone*, m. p. 188° (decomp.);

p-*nitrophenylhydrazone*, m.p. 294° (decomp.); *semicarbazone*, decomp. above 300°]; 4-*chloro*-3 : 5-*dinitro*-A, m. p. 153° [*phenylhydrazone*, m. p. 219°; p-*nitrophenylhydrazone*, m. p. 286° (decomp.); *semicarbazone*, m. p. 225° (decomp.)]; 2-*chloro*-5-*nitro*-B, m. p. 125° [*phenylhydrazone*, m. p. 166° (decomp.); p-*nitrophenylhydrazone*, m. p. 266° (decomp.); *semicarbazone*, m. p. 266° (decomp.)]; 2-*chloro*-3 : 5-*dinitro*-B, m. p. 93° [*phenylhydrazone*, m. p. 210° (decomp.); p-*nitrophenylhydrazone*, m. p. 267° (decomp.); *semicarbazone*, m. p. 192° (decomp.)]; 4-*chloro*-3-*bromo*-A, m. p. 124° [*phenylhydrazone*, m. p. 204°; p-*nitrophenylhydrazone*, m. p. 298° (decomp.)]; 3-*chloro*-2-*bromo*-B, m. p. 177° [p-*nitrophenylhydrazone*, m. p. 253° (decomp.)]; 3 : 4-*dibromo*-A, m. p. 129° [p-*nitrophenylhydrazone*, decomp. above 220°]; 2 : 3-*dibromo*-B, m. p. 192° [p-*nitrophenylhydrazone*, m. p. 254° (decomp.)]; 4-*chloro*-3-*bromo*-5-*nitro*-A, m. p. 137° [*phenylhydrazone*, m. p. 229° (decomp.); *sodium* salt]; 4-*chloro*-5-*bromo*-A, m. p. 125° [*phenylhydrazone*, m. p. 200°; p-*nitrophenylhydrazone*, m. p. 280° (decomp.)]; 4-*chloro*-5-*bromo*-3-*nitro*-A, m. p. 116° [*sodium* salt; *phenylhydrazone*, m. p. 241° (decomp.)]; 2-*chloro*-3-*bromo*-5-*nitro*-B, m. p. 140° [*phenylhydrazone*, m. p. 205° (decomp.)]; 4-*bromo*-5-*nitro*-A, m. p. 128° [*phenylhydrazone*, m. p. 189°; p-*nitrophenylhydrazone*, m. p. 301° (decomp.); *semicarbazone*, decomp. above 210°]; 4-*bromo*-3 : 5-*dinitro*-A, m. p. 143° [*phenylhydrazone*, m. p. 209° (decomp.); p-*nitrophenylhydrazone*, m. p. 250° (decomp.); *semicarbazone*, m. p. 224° (decomp.)]; 2-*bromo*-5-*nitro*-B, m. p. 131° [*silver* and *copper* salts; *phenylhydrazone*, m. p. 181° (decomp.); p-*nitrophenylhydrazone*, m. p. 265° (decomp.); *semicarbazone*, m. p. 267° (decomp.)]; 2-*bromo*-3 : 5-*dinitro*-B, m. p. 110° [*silver* salt; *phenylhydrazone*, m. p. 186° (decomp.); p-*nitrophenylhydrazone*, m. p. 248° (decomp.); *semicarbazone*, m. p. 188° (decomp.)]; 2 : 3-*dibromo*-5-*nitro*-B, m. p. 155° [*phenylhydrazone*, m. p. 204° (decomp.)]; 3 : 4-*dibromo*-5-*nitro*-A, m. p. 114°; 4 : 5-*dibromo*-A, m. p. 132° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 266° (decomp.)]; 4 : 5-*dibromo*-3-*nitro*-A, m. p. 118° [*silver* salt; *phenylhydrazone*, m. p. 236° (decomp.)]; 4-*iodo*-5-*nitro*-A, m. p. 118° [*silver* salt; *phenylhydrazone*, m. p. 177° (decomp.); p-*nitrophenylhydrazone*, m. p. 297° (decomp.); *semicarbazone*, decomp. at 230—240°]; 3-*bromo*-4-*iodo*-5-*nitro*-A, m. p. 145°; 4-*iodo*-3 : 5-*dinitro*-A, m. p. 160° [*silver* salt; *phenylhydrazone*, m. p. 229° (decomp.); p-*nitrophenylhydrazone*, m. p. 257° (decomp.); *semicarbazone*, decomp.]; 5-*bromo*-4-*iodo*-A, m. p. 117° [*sodium* and *silver* salts; *phenylhydrazone*, m. p. 151°; p-*nitrophenylhydrazone*, m. p. 266° (decomp.)]; 5-*bromo*-4-*iodo*-3-*nitro*-A, m. p. 153° [*silver* salt; *phenylhydrazone*, m. p. 245° (decomp.)]; 2-*iodo*-5-*nitro*-B, m. p. 162° [*silver* salt; *phenylhydrazone*, m. p. 204° (decomp.); p-*nitrophenylhydrazone*, m. p. 273°; *semicarbazone*, m. p. 211° (decomp.)]; 2-*iodo*-3 : 5-*dinitro*-B, m. p. 162° [*silver* and *copper* salts; *phenylhydrazone*, m. p. 197° (decomp.); p-*nitrophenylhydrazone*, m. p. 240° (decomp.); *semicarbazone*, m. p. 205° (decomp.)]; 3-*bromo*-2-*iodo*-B, m. p. 204°. M. CLARK.

Manufacture of unsaturated aldehydes. I. G. FARBENIND. A.-G.—See B., 1928, 634.

Synthesis of cyclic compounds. IV. Catalytic decomposition of suberic acid and preparation of suberone directly from mixtures of suberic and azelaic acids. I. VOGEL (J.C.S., 1928, 2032—2035).—A 40% yield of *cyclo*heptanone is obtained by the dry distillation at 280—290° of an intimate mixture of suberic acid, an equal weight of iron filings, and 5% by weight of crystallised barium hydroxide, the product being colourless and free from the black, tarry impurities which are formed by the distillation of the calcium or thorium salts. The mixture of suberic and azelaic acids obtained by the oxidation of ricinoleic acid with nitric acid (Baker and Ingold, J.C.S., 1923, **123**, 122) after crystallisation from benzene may similarly be converted directly into *cyclo*heptanone (suberone) which is separated from a small quantity of a liquid of the same b. p. by means of its hydrogen sulphite compound. J. W. BAKER.

Possibility of ring-chain valency tautomerism, and of a type of mobile-hydrogen tautomerism analogous to the Wagner-Meerwein rearrangement. V. Pinacolic electron displacement as an explanation of various intramolecular transformations. C. W. SHOPPEE (Proc. Leeds Phil. Soc., 1928, **1**, 301—311).—The mechanism of various intramolecular changes is discussed, including the pinacol-pinacolin change, pinacolic deamination, the Wagner-Meerwein change, the benzil-benzilic acid transformation, and the conversion of α-hydroxy- and α-chloro-ketones into carboxylic acids, and an attempt is made to correlate them on the basis of tautomeric change (cf. this vol., 414). The mechanism advanced is termed "pinacolic electron displacement," and occurs when both an electron source and an electron sink are present in the molecule. A cationic or anionic reagent is necessary to achieve these conditions or to complete the reaction. Examples not accounted for or explained unsatisfactorily by previous theories are considered and shown to be explicable on this theory, which also predicts new types of intramolecular change. C. W. SHOPPEE.

Nierenstein reaction. M. NIERENSTEIN (Nature, 1928, **122**, 313).—Polemical and explanatory (cf. Bradley and Robinson, this vol., 759). A. A. ELDRIDGE.

Action of bromine on azomethine derivatives of fluorene. A. NOVELLI (Anal. Asoc. Quím. Argentina, 1927, **15**, 423—429).—The addition of bromine to azomethine derivatives of fluorene (cf. this vol., 180) yielded products similar to those obtained from Schiff's bases (cf. Berg, A., 1925, i, 817), in which the bromine appeared to have added on at the >C:N– double linking. The bromine was sufficiently reactive to attack silver and gold in dry solvents, and the compounds were decomposed by water with the formation of the corresponding ketone and the hydrobromide of the brominated amine. 2 : 7-*Dibromofluorenone*-p-*dimethylaminoanil dibromide* and the corresponding p-*diethyl* compound, m. p. 210° (darkening at 180°), were prepared. Decomposition by water yielded 2 : 7-dibromofluorenone and a brominated amine (not isolated). R. K. CALLOW.

Configuration of *o*-substituted benzophenone oximes. J. Meisenheimer, R. Hanssen, and A. Wachterowitz (J. pr. Chem., 1928, [ii], **119**, 315—367).—Further exceptions to the general rule that benzophenone oximes carrying one *o*-substituent exist only in the *syn*-form are recorded. By the Friedel–Crafts reaction with benzoyl chloride *m*-4-xylyl methyl ether yields 50—70% of 3-*methoxy*-4 : 6-*dimethylbenzophenone*, b. p. 199—200°/12—13 mm., 10% of the 3-hydroxy-compound, m. p. 140—141°, b. p. 202°/20 mm., and 10—30% of 2-*hydroxy*-3 : 5-*dimethylbenzophenone*, b. p. 202°/20 mm. The 3-methoxy-ketone gives two oximes; the α-(syn-)*oxime*, m. p. 138—139°, b. p. 218°/10 mm. (*benzoate*, m. p. 135—136°), is converted by phosphorus pentachloride into 3-*methoxy*-4 : 6-*dimethylbenzanilide*, m. p. 141—142°, and thence by hydrolysis into the corresponding *acid*, m. p. 185—186°; Gunter's acid, m. p. 170·5° (A., 1884, 1347), is probably an isomeride. The β-(anti-)*oxime*, m. p. 119—120°, not obtainable from the α-oxime, yields with phosphorus pentachloride *benzoic* 6-*methoxy*-m-4-*xylidide*, m. p. 154—155°, isomeric with the 4-*methoxy*-m-5-*xylidide*, m. p. 48—49° (*hydrochloride*, decomp. 70°), obtained synthetically from 5-nitro-*m*-4-xylyl methyl ether, b. p. 268—269°, and 5-methoxy-*m*-4-xylidine. 3-*Ethoxy*-4 : 6-*dimethylbenzophenone*, b. p. 190—200°/10 mm. (crude), also gives two oximes; the α-(syn-)*oxime*, m. p. 148—149°, is converted by phosphorus pentachloride into 3-*ethoxy*-4 : 6-*dimethylbenzanilide*, m. p. 156—157°; the β-(anti-)*oxime* melts at 133—134°. 3-Hydroxy-4 : 6-dimethylbenzophenone (cf. Linari, A., 1904, i, 64) yields a single (anti-)*oxime*, m. p. 182—183°, from which by the action of phosphorus pentachloride even at −20° only a phosphoric *derivative*, decomp. 90—100°, is obtainable, but is converted by Beckmann's reagent into *benzoic* 3-*acetoxy*-m-4-*xylidide*, m. p. 127—128° (hydrolysed by alkali to the 3-*hydroxy*-m-4-*xylidide*, m. p. 173—174°), and a little 3-*hydroxy*-4 : 6-*dimethylbenzanilide*, m. p. 211—212°, more easily obtainable by heating the oxime hydrochloride above its m. p. 2-Hydroxy-4 : 6-dimethylbenzophenone also gives only one *oxime*, m. p. 153—154°, the *syn*-configuration of which is shown by its conversion by phosphorus pentachloride into 2-*phenyl*-5 : 7-*dimethylbenzoxazole*, m. p. 99—100°, which yields benzoic 3-hydroxy-*m*-4-xylidide, m. p. 187—188° (Auwers, Bundesmann, and Wieners, A., 1926, 608), on distillation.

4-*m*-Xylyl benzoate, m. p. 38—39°, b. p. 186—188°, when submitted to the Fries reaction (cf. Auwers and Jordan, A., 1925, i, 264), is recovered for the most part unchanged, small yields of 2 : 3 : 5- and 3 : 4 : 6-hydroxydimethylbenzophenones being obtained together with the 4 : 2 : 5-isomeride, m. p. 160—161° (cf. Bartolotti and Linari, A., 1903, i, 177), which is synthesised from *p*-xylyl methyl ether by way of 4-methoxy-2 : 5-dimethylbenzophenone, m. p. 60—61°, b. p. 202—204°/12—13 mm. By the use of fresh aluminium chloride, however, the normal 2 : 3 : 5-product is obtained almost exclusively.

The effect of *o*-halogen in determining *syn*-configuration in benzophenone oximes is not disturbed by the presence of an *o*′-methoxyl group, the orienting effect of various *o*′-methoxyl groups being in the order: halogen or carboxyl, hydroxyl or methoxyl, amino, methyl. 2 : 4-*Dichloro*-2′-*bromobenzophenone*, m. p. 33—34°, b. p. 227—228°/20 mm., prepared from *m*-dichlorobenzene and *o*-bromobenzoyl chloride (b. p. 131°/19 mm.), gives no oxime, but under alkaline conditions yields 2-*chloro*-2′-*bromo*-4-*hydroxybenzophenone*, m. p. 158—160°, and 3-op-*dichlorophenylindoxazen*, m. p. 78°, b. p. 212—214°/12 mm., and probably traces of 6-*chloro*-3-o-*bromophenylindoxazen*. 2-*Bromo*-5-*nitro*-2′-*hydroxy*-5′-*methylbenzophenone*, m. p. 151—152°, prepared from *p*-tolyl methyl ether and 2-bromo-5-nitrobenzoyl chloride, is readily converted by alkali into 2-*nitro*-7-*methylxanthone*, m. p. 224°, from which by the action of methyl-alcoholic potassium hydroxide 5-*nitro*-2 : 2′-*dihydroxy*-5′-*methylbenzophenone*, m. p. 146—148°, is obtained; the xanthone yields no oxime. 2-*Bromo*-5-*nitro*-2′-*hydroxy*-5′-*methylbenzophenone oxime*, m. p. 218°, is converted by alkali into a *compound*, $C_{14}H_{10}O_4N_2$, m. p. 148°, which may be either 5-nitro-3-(4-hydroxy-*m*-tolyl)indoxazen or the nitromethylxanthoxime, and by phosphorus pentachloride into a phosphoric derivative. 2-*Bromo*-2′-*hydroxy*-5′-*methylbenzophenone*, m. p. 78·5°, from *p*-tolyl methyl ether and *o*-bromobenzoyl chloride, is converted by hot alkali into 2-methylxanthone, m. p. 125·5° (lit. 105°); it also gives a single *oxime*, m. p. 144·5°, from which no Beckmann transformation products are obtainable. 2-*Bromo*-2′-*methoxy*-5′-*methylbenzophenone*, m. p. 50—51°, obtained by methylation of the hydroxy-ketone, yields a single *oxime*, m. p. 193°, the configuration of which (*syn* with reference to the bromophenyl group) is shown by its conversion by methyl-alcoholic potassium hydroxide into 3-(4-*methoxy*-m-*tolyl*)*indoxazen*, b. p. 170°/0·5 mm., and by phosphorus pentachloride into o-*bromobenzoic* 4-*methoxy*-m-*toluidide*, m. p. 130—131°.

C. Hollins.

Application of the Hoesch reaction to nitrobenzonitriles. M. Yamashita (Bull. Chem. Soc. Japan, 1928, 3, 180—182).—Resorcinol condenses with *p*-nitrobenzonitrile in presence of ethereal hydrogen chloride and zinc chloride (Hoesch, A., 1915, i, 820) to give 4-nitro-2′ : 4′-dihydroxybenzophenone, m. p. 203° (cf. Korczyński and Novakovski, this vol., 523; *dimethyl ether*, m. p. 123—124°). Similarly, *m*-nitrobenzonitrile affords 3-*nitro*-2′ : 4′-*dihydroxybenzophenone*, m. p. 228° (*dimethyl ether*, m. p. 116—117°). Phloroglucinol with *m*- and *p*-nitrobenzonitriles yields 3-*nitro*-, m. p. 194°, and 4-nitro-2′ : 4′ : 6′-trihydroxybenzophenone, m. p. 246—247°, respectively. *o*-Nitrobenzonitrile does not condense with resorcinol or phloroglucinol.

H. Burton.

Active component of paracoto bark. Synthesis of protocotoin and methylprotocotoin. E. Spath and H. Bretschneider (Monatsh., 1928, **49**, 429—437).—The nitrile of piperonylic acid is condensed with phloroglucinol in dry ether in presence of zinc chloride and gaseous hydrogen chloride and the resulting ketimine hydrolysed. The crude piperonoylphloroglucinol is partly methylated with diazomethane and the products are separated by fractional distillation in a high vacuum. The protocoin obtained had, after purification, m. p.

140—141°, showing no depression when mixed with the natural product. Methylprotocotoin was recovered from the product insoluble in alkali. The transformation of natural protocotoin into 3 : 5-*dimethoxy*-3′ : 4′-*methylenedioxy*-2-*phenylcumarone*, m. p. 117°, by the action of ethyl bromoacetate and sodium ethoxide, proves that the hydroxyl group of protocotoin is *ortho* to the carbonyl group. R. A. PRATT.

Monoacetals of α-bromodibenzoylmethane. C. DUFRAISSE and A. GILLET (Bull. Soc. chim., 1928, [iv], **43**, 883—888).—Phenyl α-bromo-ββ-dialkoxy-β-phenylethyl ketones, $CHBrBz\cdot CPh(OR)_2$, are prepared by treating the dibromides of phenyl β-alkoxystyryl ketones with alcohols in presence of potassium acetate, and also by the addition of alcohols to phenyl α-bromo-β-alkoxystyryl ketones in presence of sodium alkoxides. Moisture must be excluded in the first method. *Phenyl α-bromo-ββ-dimethoxy-β-phenylethyl ketone* has m. p. 91—92°; the corresponding *diethoxy*- and *dipropoxy*-derivatives have m. p. 70° and 83—84°, respectively. These acetals are very readily hydrolysed by small amounts of acid, and the bromine is eliminated quantitatively by boiling alcoholic potassium hydroxide. When heated they lose the appropriate alcohol. *Phenyl α-bromo-β-methoxy-β-ethoxy-β-phenylethyl ketone*, m. p. 89—90°, is obtained as the main product in each of the four methods used for its preparation, but a small amount of the second possible racemic modification appears to be formed at the same time. When this ketone is heated, methyl alcohol and phenyl α-bromo-β-ethoxystyryl ketone are produced. H. BURTON.

New condensation of ketones with phenols. "Phorone di-*m*-cresyl ether." J. B. NIEDERL (J. Amer. Chem. Soc., 1928, **50**, 2230—2235).—Treatment of *m*-cresol and acetone or phorone with concentrated sulphuric acid yielded a condensation product, termed by the author "*phorone di*-m-*cresyl ether*" (I), m. p. 127°; b. p. 270°; [a better name would be *anhydrodi*-β-(4-*hydroxy*-2-*methylphenyl*)-β-*methyl*-*n*-*propyl ketone*]. The mechanism of formation appears to be the addition of sulphuric acid to phorone, elimination of sulphuric acid between the product and *m*-cresol, and, finally, ether formation.

$$\begin{array}{l} Me\cdot C_6H_3\cdot CMe_2\cdot CH_2 \\ O\!<\qquad\qquad\quad >\!CO \\ Me\cdot C_6H_3\cdot CMe_2\cdot CH_2 \end{array}$$

(I.)

The *dibromo*-derivative, m. p. 215°, was obtained by bromination in carbon tetrachloride, and the *tetranitro*-derivative, m. p. 243°, accompanied by β-(*nitro*-4-*hydroxy*-2-*methylphenyl*)*iso**valeric acid*, m. p. 108° (*disodium* salt), by boiling with concentrated nitric acid. Chromic acid in glacial acetic acid oxidised the compound with the formation of dimethylmalonic acid and β-4-*hydroxy*-2-*methylphenyliso**valeric acid*, m. p. 107° (*dibromo*-derivative, m. p. 140°). R. K. CALLOW.

Condensation products [ketones and naphthindanones] from aromatic hydrocarbons or derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1928, 665.

Action of magnesium ethyl bromide on acenaphthenequinone. N. MAXIM (Bull. Soc. chim., 1928, [iv], **43**, 769—778).—Magnesium ethyl bromide reacts readily with acenaphthenequinone, affording 9 : 10-*diethylacenaphthene*-9 : 10-*glycol*, m. p. 197°, which on dehydration with glacial acetic acid is converted into the orange-yellow 9 : 10-*diethylideneacenaphthene*, m. p. 140°, and not a β-pinacolin as in the dehydration of 9 : 10-diphenylacenaphtheneglycol (Beschke, A., 1909, i, 917). Oxidation of 9 : 10-diethylideneacenaphthene with chromic and acetic acids gives acenaphthenequinone and acetic acid. R. BRIGHTMAN.

Benzanthrone derivatives. I. G. FARBENIND. A.-G.—See B., 1928, 598.

Manufacture of benzanthrones. I. G. FARBENIND. A.-G.—See B., 1928, 666.

Anthraquinone derivatives. I. G. FARBENIND. A.-G.—See B., 1928, 598.

Manufacture of 1-anthraquinonyl ketones. I. G. FARBENIND. A.-G.—See B., 1928, 665.

Nitro-compounds of arylaminoanthraquinones, their derivatives and substitution products. I. G. FARBENIND. A.-G.—See B., 1928, 665.

Manufacture of chloroperylenequinones. F. BENSA.—See B., 1928, 666.

Cornin: a glucoside from *Cornus florida*, L. E. R. MILLER (J. Amer. Pharm. Soc., 1928, **17**, 744—750).—Cornin was extracted from the root bark of *C. florida*, L., by cold percolation with water. The pure material, $C_{19}H_{21}O_9\cdot OMe$, has $[\alpha]^{25}$ −180·6° to −181·4°, and m. p. 182—183° if heated rapidly. It is readily soluble in water, but sparingly soluble in the usual organic solvents. It hydrolysed by emulsin and is thus probably a β-glucoside of dextrose. B. W. ANDERSON.

[Constitution of] sesamin. S. H. BERTRAM, J. P. K. VAN DER STEUR, and H. I. WATERMAN (Biochem. Z., 1928, **197**, 1—7). Sesamin, $C_{18}H_{16}O_5$, m. p. 122·7°, $[\alpha]_l^{16}$ +72·77°, was obtained in 0·11—0·27% yield from sesame oil and evidence is given that it is 2 : 2′-dipiperonyltetrahydrofuran. On distilling with zinc dust, sesamin gives a phenolic substance. Oxidation with chromic anhydride in acetic anhydride at 40° yielded a little piperonylic acid. Clowes and Tollens' method for the determination of methylenedioxy-groups was found untrustworthy for piperonyl derivatives, but indicated that two such groups were present. When boiled with 10% alcoholic hydrochloric acid, sesamin gave a *compound*, m. p. 122°, $[\alpha]_D$ +121·5°; it is suggested that the ether of *sec*.-methylpiperonyl alcohol might be closely related to sesamin. The fact that the refraction of sesamin was considerably higher than that of this ether made it probable that sesamin contained a tetrahydrofuran ring. When boiled with acetyl chloride, sesamin gave an oily additive *compound*, which lost acetyl chloride on heating. L. C. BAKER.

Kakishibu. IV. Constitution of shibuol. III. S. KOMATSU and N. MATSUNAMI (Mem. Coll. Sci. Kyoto, 1928, **11**, 205—210).—The tinctorial properties of shibuol, its azo-derivative, and its metallic salts have been compared with those of myricetin, quercetin, and catechin and their corresponding derivatives.

Shibuol closely resembles myricetin, but differs from catechin and quercetin, from which it is concluded that the number of free hydroxyl groups present in the phenolic portion of the shibuol molecule is probably the same as in myricetin. *Benzeneazoshibuol*, $C_{26}H_{20}O_7N_4$, is obtained in 85% yield as a reddish-brown powder by coupling shibuol with benzenediazonium chloride; reduction with sodium hyposulphite yields a *substance*, $C_{15}H_{14}O_7N$. Shibuol, when treated with zinc dust in alkaline solution at 50°, yields phloroglucinol and gallic acid (cf. A., 1923, i, 1197), but is unaffected by zinc and acetic acid at 50°; with magnesium powder and acetic acid reduction occurs, giving a soluble, red substance similar to that obtained with flavones. Reduction of *tetramethylshibuol* (cf. following abstract) with hydriodic acid (*d* 1·18) at 130° gave a violet-brown substance insoluble in ether, but readily soluble in other organic solvents; an analysis is given but no formula is assigned. C. W. Shoppee.

Kakishibu. V. Methylation of shibuol. S. Komatsu, N. Matsunami, and M. Kurata (Mem. Coll. Sci. Kyoto, 1928, **11**, 211—216).—Shibuol has been methylated using methyl sulphate under various conditions. The results (below) suggest that shibuol possesses four free hydroxyl groups: this agrees with the formation of tetra-acetyl-shibuol (A., 1925, i, 950). *Shibuol dimethyl ether* is obtained as a violet-brown powder when methylation occurs in sodium carbonate solution. *Shibuol trimethyl ether*, sinters at 220°, m. p. 260° (decomp.), is obtained as a yellowish-brown powder by methylation at 5° in alkali hydroxide solution; if the reaction temperature is raised, *shibuol tetramethyl ether* is also obtained as a brown powder sintering at 200°, m. p. 230—240°, which is insoluble in alkali. A specimen of shibuol tetramethyl ether prepared from the trimethyl ether (methyl iodide and silver oxide) had m. p. 208—210°. An *acetylshibuol trimethyl ether* was also obtained. C. W. Shoppee.

Toad poisons. I. Composition of Chinese drug "Senso." II. Poisonous constituents of secretion of Japanese toad (*Bufo bufo japonicus*). M. Kotake (Annalen, 1928, **465**, 1—11, 11—20, and Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7,785—789, 790—804).—I. Extraction of powdered "Senso" with alcohol affords bufagin, $C_{29}H_{38}O_7$, m. p. 220—221° (cf. Shimizu, A., 1916, i, 698; Kodama, Act. Schol. Med. Univ. Imp. Kyoto, 1920, **3**, III, 299; 1921, **4**, II, 213; 1922, **4**, III, 355). Reduction of bufagin with hydrogen in presence of palladium-black and alcohol gives a mixture of *α-tetrahydrobufagin* $+2H_2O$, m. p. 130—140°, m. p. (anhydrous) 225—230° (*acetyl* derivative, m. p. 238°), and *β-tetrahydrobufagin*, m. p. 208—210°. Acetylation of this last compound gives a mixture of the α-acetyl derivative together with the *β-acetyl* derivative, m. p. 254—257°; the same mixture is produced when *diacetylbufagin*, m. p. 196—197°, is reduced catalytically. Oxidation of bufagin with chromic anhydride in acetic acid yields *bufagone*, $C_{29}H_{36}O_7$, m. p. 232—235° (*oxime*, m. p. 170—173°), which is not capable of being acetylated. Bufagin contains an acetyl group (hydrolysis with potassium hydroxide).

Bufalin chloride, m. p. 218—220° (cf. Kodama, *loc. cit.*), is obtained by the action of hydrogen chloride on the bufagin-free extract of "Senso." It is converted by acetic anhydride and sodium acetate into *acetylanhydrobufalin*, $C_{29}H_{36}O_6$, m. p. 221—225°, and oxidised by chromic and acetic acids to *bufalinone chloride*, m. p. 251—252°. When this is heated with acetic anhydride and sodium acetate *anhydrobufalinone*, $C_{27}H_{32}O_5$, m. p. 181—183°, is obtained.

II. Extraction of the skins of *Bufo bufo japonicus* with alcohol and subsequent removal of fat and cholesterol gives 0·7% of *gamabufotalin* (I), $C_{27}H_{38}O_6$, m. p. 261—263° with frothing (*diacetyl* derivative, m. p. 225°), which is hydrolysed by alcoholic potassium hydroxide to *gamabufotalinic acid*, $C_{24}H_{36}O_6$, m. p. 207—209° (decomp.), and formic acid. Reduction of (I) with hydrogen in presence of palladium-black gives *hydrogamabufotalin*, $C_{24}H_{38}O_5$,EtOH, m. p. 131—133°, together with an amorphous, acidic substance. The action of concentrated hydrochloric acid on (I) is to furnish *anhydrogamabufotalin*, m. p. 263° with frothing. Treatment of (I) with 95% formic acid gives after 20 hrs. at 12—15° a *diformyl* derivative, m. p. 156—157°, after 2 days at 27—30° a *substance*, $C_{57}H_{72}O_{13}$, m. p. 212—214°, and after 3 days an uncrystallisable product. These reaction products are converted by concentrated hydrochloric acid into anhydrogamabufotalin.

When the residue from the alcoholic extract of the toad skins after removal of fat, cholesterol, and gamabufotalin is treated with ethereal hydrogen chloride, *gamabufalin chloride*, $C_{27}H_{39}O_5Cl$, m. p. 217—219°, is obtained. This is converted by treatment with acetic anhydride and sodium acetate into *acetylanhydrogamabufalin*, $C_{29}H_{40}O_6$, m. p. 227—229°. *Acetylgamabufalin*, m. p. 256—258°, is obtained by acetylation of the above residue. H. Burton.

Hydrogenation of acyclic terpenes. S. Sabetay and J. Bleger (Bull. Soc. chim., 1928, [iv], **43**, 839—845).—Catalytic reduction of rhodinol, b. p. 113—115°/16 mm., d^{18} 0·8654, n_D^{11} 1·463, $[\alpha]^{14}_D$ −3·78° in 75% alcohol, by the Fokin–Willstatter method gives dihydrorhodinol (γη-dimethyloctanol), b. p. 109—109·5°/15 mm., d^{18} 0·830, n_D^{15} 1·437, $[\alpha]^{11}_D$ −3·67° (acetate, b. p. 115·5—116°/18 mm., n_D^{11} 1·4283), which has an odour resembling rose. When geraniol is completely hydrogenated the product appears to be identical with the alcohol obtained from γη-dimethyloctylamine and nitrous acid (Wallach, A., 1912, i, 569). Reduction of citronellal affords a dihydrocitronellal, b. p. 81·5—82°/13 mm., d_4^{17} 0·822, n_D^{17} 1·4273, $[\alpha]_D^{13}$ +10·8° (cf. von Braun, A., 1924, i, 3). The aldehyde grouping was not reduced in any experiment. H. Burton.

Citronellal and rhodinal. A. Verley (Bull. Soc. chim., 1928, [iv], **43**, 845—854).—Pure citronellal, b. p. 82°/2 mm., d_{20}^{20} 0·8682, n_D^{20} 1·4534, $[\alpha]_D$ +9·19°, gives a homogeneous semicarbazone, m. p. 83·5°. From this and a study of the dispersion curve it is concluded that citronellal exists in one form only. When citronellal cyanohydrin is distilled in a vacuum, hydroxycitronellal, b. p. 116°/5 mm., d^{15} 0·931, n_D^{20} 1·456, α^{20} +8·3°, results. This compound is also obtained by treating citronellal-enolacetate with

dilute alkali. When hydroxycitronellal is heated in a vacuum with 0·05 part of kieselguhr there is obtained a mixture of β-*iso*pulegol (pulegol) and rhodinal, together with a product, $C_{10}H_{24}O$. Rhodinal (semicarbazone, m. p. 75·5°) has b. p. 83°/2 mm., d_{20}^{20} 0·8709, $[\alpha]_D$ +1° 10′, when purified through its hydrogen sulphite compound and is also homogeneous. Oxidation of rhodinol with sodium dichromate gives resinous products together with rhodinal, which is transformed immediately into β-*iso*pulegol, b. p. 90°/10 mm., d_{20}^{20} 0·9275, and finally oxidised to pulegone. The menthone-like odour of this ketone is probably the reason for the statement that rhodinol can be transformed into menthone (Barbier and Bouveault, A., 1896, i, 491). H. Burton.

Rearrangement of ozonides. A. Verley (Bull. Soc. chim., 1928, [iv], **43**, 854—857).—The ozonides of citronellal, citral, and geraniol undergo considerable transformation from the α- to the β-form, probably during decomposition of the ozonides (cf. A., 1925, i, 406). The following rules are postulated to explain the author's work on the action of ozone on unsaturated compounds: (*a*) when the double linking is "privileged" (*e.g.*, cinnamic acid) decomposition is normal; (*b*) in compounds containing an "indifferent" double linking (*e.g.*, oleic acid) the changes $\cdot CH\cdot CH\cdot CH_2\cdot CH_2\cdot$ (with O_3 bridge) $\longleftarrow$ $CH_2\cdot CH\cdot CH\cdot CH_2$ (with O_3 bridge) $\longrightarrow$ $CH_2\ CH_2\ CH\ CH$ (with O_3 bridge) may take place and numerous by-products result; (*c*) if the ozonide is formed on a double linking bordering on a "privileged" position (*e.g.*, citronellal), a partial transformation takes place. H. Burton.

Production of inactive menthol. Rheinische Kampfer Fabr.—See B., 1928, 691.

Complete resolution of externally compensated acids and bases. A. W. Ingersoll (J. Amer. Chem. Soc., 1928, **50**, 2264—2267; cf. A., 1925, i, 814).—In the method previously described (*loc. cit*), after separation of the less soluble salt, *e.g.*, *l*-B,*d*-A, from the mixture of *dl*-B and *d*-A, the residual mixture of bases *dl*-B and *d*-B was combined with the *dl*-form of the same acid and *d*-B,*l*-A, for instance, separated from the mixture of salts *dl*-B,*dl*-A, *d*-B,*d*-A, and *d*-B,*l*-A. Alternatively, the half-racemic salt *d*-B,*dl*-A may be formed, and be less soluble, and the application of this process to the separation of the second component of an externally compensated base, *iso*-diphenylhydroxyethylamine, has now been accomplished. *d*-Camphor-10-sulphonic acid yielded d-*iso-diphenylhydroxyethylamine* d-*camphor*-10-*sulphonate* (+H_2O), m. p. 207—208° (anhydrous), from which the *d*-base was obtained (cf. Read and Steele, A., 1927, 557). The base recovered from the mother-liquors of the *d*-base–*d*-acid salt was treated with *dl*-camphorsulphonic acid, and the l-*base*–dl-*acid* salt (+H_2O), m. p. 206—207° (anhydrous), was separated, and yielded the pure *l*-base. The l-*base*–d-*acid* salt (+H_2O), m. p. 205—206° (anhydrous), d-*base*–dl-*acid* salt (similar to the *l*-base–*dl*-acid salt), and dl-*base*–dl-*acid* salt (+H_2O), m. p. 198—199° (anhydrous), were also prepared. R. K. Callow.

"Furylangelic" acid. A. S. Carter (J. Amer. Chem. Soc., 1928, **50**, 2290—2305).—"Furylangelic" acid, m. p. 95·5—97° (cf. Baeyer and Tonnies, A., 1877, ii, 746; Tonnies, A., 1879, 915), was prepared in 80% yield by heating furfuraldehyde with sodium butyrate and butyric anhydride. Ozonolysis yielded carbon dioxide, propionic acid, and possibly α-keto-butyric acid, whilst oxidation by acid or alkaline permanganate yielded acetic and propionic acids. These facts support the assumption of the structure of β-2-furyl-α-ethylacrylic acid for "furylangelic" acid which would be expected from the known course of the Perkin reaction. Tönnies' preparation of azelaic acid from "furylangelic" acid (*loc. cit.*) is not in accord with this, and his work was repeated. Reduction of "furylangelic" acid by sodium amalgam yielded α-furfurylbutyric acid, b. p. about 174°/46 mm., which, by the action of bromine water and silver oxide, yielded butyrofuronic acid (Δ^{α}-hepten-γ-one-αε-dicarboxylic acid), m. p. 149—150° (Tönnies gives 140—142°). Reduction of butyrofuronic acid by red phosphorus and hydriodic acid yielded no product similar to that obtained by Tönnies, but α-ethylpimelic acid, m. p. 41—43°, and a small amount of *heptan-γ-one-αε-dicarboxylic acid*, m. p. 83—84·5°, which appeared to be an intermediate product. The latter acid was prepared from "furylangelic" acid by the action of hydrogen chloride in alcohol and hydrolysis of the *ethyl* ester, b. p. 198—200°/25 mm., thus obtained. It was reduced by red phosphorus and hydriodic acid to ethylpimelic acid.
R. K. Callow.

Styrylpyrylium salts. X. Anhydropyrylium bases and *spiro*pyrans derived from dibenzyl ketone. R. Dickinson, I. M. Heilbron, and F. O'Brien (J.C.S., 1928, 2077—2082; cf. A., 1927, 884; also Dilthey and Wubken, this vol., 767).—Salicylaldehyde and dibenzyl ketone readily condensed in the presence of piperidine, giving 2-*hydroxy-α-phenylstyryl benzyl ketone* (I), m. p. 177° (*semicarbazone*, m. p. 196°; *methyl ether*, m. p. 140—141°), but in the presence of hydrogen chloride 2-*benzylidene*-3-*phenyl*-Δ^3-*benzopyran* (II), m. p. 115°, and (in small quantities) 3 : 3′-*diphenyldibenzo*spiro*pyran*, $\begin{matrix} CH{:}CPh \\ C_6H_4{-}O \end{matrix} \!>\! C \!<\! \begin{matrix} CPh{:}CH \\ O{\cdot}C_6H_4 \end{matrix}$ m. p. 197°, were obtained. The *spiro*pyran was obtained directly as the sole product of the action of hydrogen chloride on mixtures of (*a*) salicylaldehyde (2 mols.), dibenzyl ketone (1 mol.); (*b*) salicylaldehyde (1 mol.), I (1 mol.); or (*c*) salicylaldehyde and II (cf. Decker and Fellenberg, A., 1909, i, 950; Ruhemann and Levy, J.C.S., 1913, **103**, 551). Dibenzyl ketone and β-naphthol-1-aldehyde yielded, in the presence of piperidine, only 2-benzylidene-3-phenyl-Δ^3-β-naphthapyran, but with hydrochloric acid both this substance and smaller quantities of 3 : 3′-diphenyldi-β-naphtha*spiro*pyran (*monohydrate*, m. p. 248°) were formed. The latter was prepared in better yield by the action of hydrogen chloride on a mixture of dibenzyl ketone (1 mol.) and naphthol-aldehyde (2 mols.). Observations of colour formation on heating in inert solvents and on styrylpyrylium salt formation with acids in the cases of 3′- and 3-methylbenzo-β-naphtha*spiro*pyrans showed that, contrary to the expressed opinion of Dilthey and

Wübken (*loc. cit.*), the two processes were not analogous. R. J. W. LE FÈVRE.

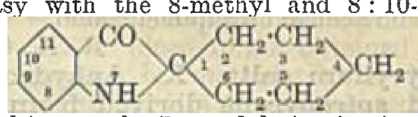
Ethylene ethers by cyclisation of chloromethyl ethers. S. SABETAY and G. SANDULESCO (Bull. Soc. chim., 1928, [iv], 43, 904—906).—When *cyclo*hexane-1 : 2-diol di(chloromethyl) ether is treated with finely-divided sodium in presence of benzene there is obtained the *dioxan*, $C_6H_{10}{<}{}^{O\cdot CH_2}_{O\cdot CH_2}$ b. p. 65·5—66·5°/20 mm., d^{18} 1·035, n_D^{18} 1·4585, together with undistillable products (cf. Palfray and Sabetay, this vol., 1130).

When piperonalsemicarbazone is heated with sodium ethoxide in an autoclave (cf. Wolff, A., 1912, i, 988) 3 : 4-methylenedioxytoluene, b. p. 80—81°/14 mm., n^{13} 1·533, is obtained. H. BURTON.

Manufacture of condensation products derived from thionaphthen-2 : 3-dicarboxylic acid. I. G. FARBENIND. A.-G.—See B., 1928, 635.

Manufacture of 2 : 3-phthaloylthionaphthen and derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1928, 635.

Derivatives of ψ-indoxyl*spirocyclo*hexane. R. L. BETTS and S. G. P. PLANT (J.C.S., 1928, 2070—2074; cf. A., 1927, 765).—Alkali fusion of the appropriate alkylated 1-anilino*cyclo*hexane-1-carboxylic acids gave 10-*methyl*-, m. p. 164°, 8-*methyl*-, m. p. 197°, 4-*methyl*-, m. p. 189°, and 8 : 10-*dimethyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 190°. Acetylation (least easy with the 8-methyl and 8 : 10-dimethyl



compounds) gave the 7-*acetyl* derivative in each case (m. p. 144°, 226°, 102°, and 96°, respectively). By the action of dilute nitric acid the following nitro-compounds were obtained: (?)8-*nitro*-10-*methyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 158°, (?)10-*nitro*-8-*methyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 273—274°, (?)10-*nitro*-4-*methyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 198°, (?)10-*nitro*-4 : 7-*dimethyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 141°, and (?)-*nitro*-8 : 10-*dimethyl*-ψ-*indoxyl*spiro*cyclohexane*, m. p. 183—184° (decomp.), all giving characteristic sparingly soluble sodium derivatives with aqueous sodium hydroxide.

The following compounds were prepared incidentally: 1-p-*toluidino*-1-*cyano*cyclo*hexane*, m. p. 76°; 1-p-*toluidino*cyclo*hexane*-1-*carboxylamide*, m. p. 156°; 1-p-*toluidino*cyclo*hexane*-1-*carboxylic acid*, m. p. 172°; 1-o-*toluidino*-1-*cyano*cyclo*hexane*, m. p. 72°; 1-o-*toluidino*cyclo*hexane*-1-*carboxylamide*, m. p. 143°; 1-o-*toluidino*cyclo*hexane*-1-*carboxylic acid*, m. p. 117°; 1-2′ : 4′-*dimethylanilino*-1-*cyano*cyclo*hexane*, m. p. 115—116°; 1-2′ : 4′-*dimethylanilino*cyclo*hexane*-1-*carboxylamide*, m. p. 133°; 1-2′ : 4′-*dimethylanilino*cyclo*hexane*-1-*carboxylic acid*, m. p. 125°; 1-*anilino*-1-*cyano*-4-*methyl*cyclo*hexane*, m. p. 107°; 1-*anilino*-4-*methyl*cyclo*hexane*-1-*carboxylamide*, m. p. 161°; 1-*anilino*-4-*methyl*cyclo*hexane*-1-*carboxylic acid*, m. p. 179°; 1-p-*nitroanilino*-1-*cyano*cyclo*hexane*, m. p. 134°; 1-p-*nitroanilino*cyclo*hexane*-1-*carboxylamide*, m. p. 217°; 1-p-*nitroanilino*cyclo*hexane*-1-*carboxylic acid*, m. p. 201°; 1-p-*aminoanilino*cyclo*hexane*-1-*carboxylic acid*, m. p. 216—217°.

The anilino*cyclo*hexanecarboxylic acids described dissociated on distillation into the corresponding alkylated aniline and Δ^1-*cyclo*hexene-1-carboxylic acid (cf. A., 1925, i, 1271). R. J. W. LE FÈVRE.

Reduction of pyridine hydrochloride and pyridinium salts by means of hydrogen and platinum oxide platinum-black. XVIII. T. S. HAMILTON and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 2260—2263).—Hydrogen and platinum-black from platinum oxide (cf. Adams and Shriner, A., 1923, ii, 773; Adams, Voorhees, and Shriner, this vol., 600) may be used for the reduction of pyridine hydrochloride and pyridinium salts, although pyridine itself is a catalyst poison. Absolute alcohol is the best solvent. Traces of ferrous salts do not affect the reaction. The following compounds are reduced quantitatively to the corresponding hexahydro-derivatives: pyridine hydrochloride and phenyl-, *n*-butyl-, ethyl-, benzyl-, carbethoxymethyl-, β-hydroxyethyl-, and γ-hydroxypropyl-pyridinium chlorides. The pyridinium salts are more readily reduced than pyridine hydrochloride. R. K. CALLOW.

Action of magnesium phenyl bromide on methyl *o*-cyanobenzoate. 1 : 3-Diphenyldihydro*iso*indole. D. R. BOYD and D. E. LADHAMS (J.C.S., 1928, 2089—2093).—Methyl *o*-cyanobenzoate was quantitatively converted by magnesium phenyl bromide in ethereal solution into 1-*hydroxy*-1 : 3 *diphenyl*iso*indole hydrobromide*, decomp. 220°; this with sodium carbonate gave the free *base*, m. p. 192·5° (decomp.), the reactions of which in solution are best explained by the equilibrium: $COPh\cdot C_6H_4\cdot CPh{:}NH \rightleftharpoons C_6H_4{<}{}^{CPh\cdot OH}_{CPh=N}$. Hydrolysis (dilute sulphuric acid) easily gave *o*-dibenzoylbenzene; reduction (zinc dust and acetic acid) yielded only small quantities of (probably *trans*, racemic) 1 : 3-*diphenyldihydro*iso*indole*, m. p. 109° [*hydrochloride*, m. p. 270—280° (decomp.); *nitroso*-derivative, m. p. 175—175·5°, *monobenzoyl* derivative, m. p. 236°; p-*toluenesulphonyl* derivative, m. p. about 225° (decomp.)], and much diphenylbenzfuran formed owing to reduction of *o*-dibenzoylbenzene produced by hydrolysis.

R. J. W. LE FÈVRE.

Manufacture of 4-alkylquinolines and derivatives thereof. SCHERING-KAHLBAUM A.-G.—See B., 1928, 730.

Quinoline derivatives. R. HUPE and A. SCHRAMME [with A. WINDAUS] (Z. physiol. Chem., 1928, 177, 315—320).—Reduction of the *oxime*, m. p. 201°, of 2-quinolylacetaldehyde with hydrogen in presence of platinum-black and acetic acid gives β-2-*quinolylethylamine*, m. p. 174° (*hydrochloride*, m. p. 212°; *picrate*, m. p. 209° after sintering), but with sodium and alcohol as the reducing agent β-1 : 2 : 3 : 4-*tetrahydroquinolylethylamine*, b. p. 188°/16 mm. when purified through the *dihydrochloride*, m. p. 230°, is formed. Reduction of 4-nitropyrogallol trimethyl ether with stannous chloride yields the corresponding *amino*-derivative (I), b. p. 150°/2 mm. (*hydrochloride*, m. p. 200°; *chloroacetyl* derivative, m. p. 85°). When (I) undergoes the Skraup reaction 6 : 7 : 8-*trimethoxyquinoline*, m. p. 80° (*picrate*, m. p. 181°), results. 6 : 7 : 8-*Trimethoxy-2-methylquinoline* (*picrate*, m. p.

142 ; *oxalate*, m. p. 148°) has m. p. 73° and condenses with chloral, giving *ααα-trichloro-γ-6 : 7 : 8-trimethoxy-2-quinolylpropan-β-ol*, m. p. 114°. When a mixture of (I), pyruvic acid, benzaldehyde, and a small amount of alcohol is heated on the steam-bath 6 : 7 : 8-trimethoxy-2-phenylcinchoninic acid (trimethoxyatophan), m. p. 174—175°, is produced.

H. BURTON.

Antiseptic compounds : further derivatives of anilquinoline. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1928, B, **103**, 404—411).—In continuation of previous work (A., 1924, i, 990) a number of new anils have been prepared by condensing the appropriate nitroso-compound with a derivative of 2-methylquinoline, and the antiseptic action of these new anils has been investigated. The following new intermediate compounds are described : *methyl 2-methyl-6-quinolylcarbamate* (m. p. 182—183°) from methyl chloroformate and 6-amino-2-methylquinoline; *ethyl 2-methyl-6-quinolylcarbamate* (m. p. 150·5°); *8-acetamido-2-methyl-β-naphthoquinoline methochloride* derived from *8-acetamido-2-methyl-β-naphthoquinoline*, m. p. 235—237°, which is prepared by the acetylation of *8-amino-2-methyl-β-naphthoquinoline*, m. p. 169—170°, itself obtained by the reduction of the previously known 3-nitro-2-methyl-β-naphthoquinoline, m. p. 166—167° ; *6-phenylcarbamido-2-methylquinoline*, decomp. above 220° (*methosulphate* and *methoacetate*) ; *p-nitrosocyclohexylaniline*, m. p. 91—93°.

W. O. KERMACK.

Metabolism of tryptophan. II. Synthesis of 6- and 8-methylkynurenic [4-hydroxyquinoline-2-carboxylic] acids. W. ROBSON (Biochem. J., 1928, **22**, 1157—1164).—*p*-Toluidine and ethyl acetoacetate were converted into 4-hydroxy-2 : 6-dimethylquinoline. This, with phosphorus oxychloride and pentachloride, gave *4-chloro-2 : 6-dimethylquinoline*, b. p. 119°/3·5 mm., m. p. 69—70°. On treatment with sodium methoxide this compound gave *4-methoxy-2 : 6-dimethylquinoline*, m. p. 106·5—107°, which with benzaldehyde gave *4-methoxy-2-styryl-6-methylquinoline*, m. p. 140—141° (*hydrochloride*, m. p. 204°). This compound, when oxidised in acetone solution with potassium permanganate, afforded *4-methoxy-6-methylquinoline-2-carboxylic acid*, m. p. 228°, converted by boiling hydrobromic acid into *4-hydroxy-6-methylquinoline-2-carboxylic acid* (*6-methylkynurenic acid*), m. p. 279° (decomp.) (*barium* salt).

The synthesis of 8-methylkynurenic acid followed similar lines : *o*-toluidine ⟶ 4-hydroxy-2 : 8-dimethylquinoline ⟶ *4-ethoxy-2 : 8-dimethylquinoline*, m. p. 55° (by the action of ethyl *p*-toluenesulphonate on the preceding compound) ⟶ *4-ethoxy-2-styryl-8-methylquinoline*, m. p. 115—116°, ⟶ *4-ethoxy-8-methylquinoline-2-carboxylic acid* ⟶ *4-hydroxy-8-methylquinoline-2-carboxylic acid* (*8-methylkynurenic acid*), m. p. 266° (*barium* salt).

S. S. ZILVA.

Preparation of quinoline derivatives. I. G. FARBENIND. A.-G.—See B., 1928, 691.

Manufacture of derivatives of substituted quinolinecarboxylic acids. SOC. CHEM. IND. IN BASLE.—See B., 1928, 730.

1-*o*-Chlorophenyl-3-methyl-5-pyrazolone and its derivatives. Z. TOMASIK (Rocz. Chem., 1928, 8, 345—348).—*o*-Chlorophenylhydrazine condenses with ethyl acetoacetate to yield *1-o-chlorophenyl-3-methyl-5-pyrazolone*, m. p. 199° (*4-benzylidene* derivative, m. p. 157° ; *4-o-nitrobenzylidene* derivative, m. p. 160°), which when condensed with *o*-nitrobenzaldehyde yields *o-nitrophenylbis-(1-o-chlorophenyl-3-methyl-5-pyrazolonyl)methane*, m. p. 249°.

R. TRUSZKOWSKI.

Replaceability of certain methylene groups and relation of constitution to stability of a C : C linking. H. V. MOYER and F. B. DAINS (J. Amer. Chem. Soc., 1928, **50**, 2293—2297).—The reaction which occurs between diphenylformamidine and the benzylidene derivative of methyl*iso*oxazolone, in which the benzylidene group is replaced by the anilinomethylene group, has now been found to take place in the case of aldehyde derivatives of certain heterocyclic compounds, particularly those in which the benzylidene group is readily removed by hydrolysis with dilute acids or heating with phenylhydrazine. Thus 4-benzylidene-3-phenyl*iso*oxazolone yielded 4-anilinomethylene-3-phenyl*iso*oxazolone when heated with diphenylformamidine, and the same reaction occurred with the piperonylidene, anisylidene, *m*-nitrobenzylidene, and cinnamylidene derivatives, but not with the furfurylidene derivative. The benzylidene and piperonylidene derivatives of 1-phenyl-3-methylpyrazolone yielded similarly the 4-anilinomethylene derivative. 1 : 3-Diphenyl-benzylidenepyrazolone yielded the 4-anilinomethylene derivative, but 1 : 3-diphenylpyrazolone yielded both this and bisdiphenylpyrazolone. 3-Hydroxy-1-phenyl-4-benzylidenepyrazolone or the 4-anisylidene derivative yielded the *4-anilinomethylene* derivative, m. p. 272—273°, also obtained from 3-hydroxy-1-phenylpyrazolone. 3-Phenyl- and 3-methyl-4-benzylidenepyrazolones did not react, and 3-methylpyrazolone reacted with difficulty to give the *4-anilinomethylene* derivative, m. p. 204°. The benzylidene derivative of 3-phenylrhodanine, m. p. 192°, yielded the 5-anilinomethylene derivative, m. p. 247°, but the cinnamylidene derivative did not react. Benzylidene-*o*-tolylthiazolidone did not react. Benzylidene derivatives in which the methylene carbon was not part of the ring, α-phenylcinnamonitrile, *m*-nitrobenzylideneacetylacetone, cinnamylideneacetylacetone, and acetylcoumarin, did not react. Phenyl styryl ketone yielded the *anil*, m. p. 168°, which was also prepared by heating the ketone with aniline and sodium acetate; the *p-chloroanil*, m. p. 167°, and *p-tolil*, m. p. 170°, were obtained in a similar way.

R. K. CALLOW.

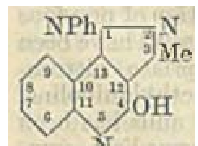
Aromatic derivatives of substituted acetamidoacetones. H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, **78**, 757—764 ; cf. this vol., 874).—*α-Acetamido-α-phenylacetoxime* has m. p. 152°; α-amino-α-phenylacetone hydrochloride gave, with potassium cyanate, *4-phenyl-5-methylglyoxalone*, m. p. 287—289°, and, with potassium thiocyanate, *2-thiol-4-phenyl-5-methylglyoxaline*, m. p. 290—295°. *α-Amino-α-benzylacetone hydrochloride*, m. p. 130°, gave *4-benzyl-5-methylglyoxalone*, m. p. 270° (darkening at 250°)

and 2-*thiol*-4-*benzyl*-5-*methylglyoxaline*, m. p. 279—280°; with ammonia it gave 2 : 5-*dibenzyl*-3 : 6-*dimethylpyrazine*, m. p. 92—94°. α-*Acetamido*-α-p-*hydroxybenzylacetoxime* has m. p. 189—190°; α-amino-α-p-hydroxybenzylacetone hydrochloride gave 4-p-*hydroxybenzyl*-5-*methylglyoxalone*, m. p. 243—244°, and 2-*thiol*-4-p-*hydroxybenzyl*-5-*methylglyoxaline*, m. p. 273—275°. C. R. Harington.

Glyoxaline-4 : 5-dicarboxylic acids. C. A. Yllner (Arkiv Kemi, Min., Geol., 1928, **9**, No. 41, 1—20).—The following glyoxaline-4 : 5-dicarboxylic acids have been prepared by interaction of the requisite aldehyde, dinitrotartaric acid, and ammonia: glyoxaline-4 : 5-dicarboxylic acid (ammonium $+H_2O$, *lithium hydrogen* $+3H_2O$, potassium hydrogen $+H_2O$, m. p. 281°, *potassium* $+3H_2O$, *sodium hydrogen* $+H_2O$, *sodium* $+2H_2O$, *barium*, and *magnesium* salts); 2-methylglyoxaline-4 : 5-dicarboxylic acid $+H_2O$ (*potassium hydrogen*, m. p. 271°, and *sodium hydrogen* $+H_2O$, salts); 2-*ethylglyoxaline*-4 : 5-*dicarboxylic acid* $+H_2O$ (*potassium hydrogen*, m. p. 265°, and *sodium hydrogen* $+3H_2O$ salts); 2-n-*propylglyoxaline*-4 : 5-*dicarboxylic acid* [*potassium hydrogen* $+1{\cdot}5H_2O$, m. p. 263° (decomp.), and *sodium hydrogen* $+1{\cdot}5H_2O$, m. p. above 300°, salts]; 2-iso*propylglyoxaline*-4 : 5-*dicarboxylic acid* $+H_2O$ (*potassium hydrogen* $+3H_2O$, m. p. 271°, and *sodium hydrogen* $+1{\cdot}5H_2O$, m. p. above 300°, salts); 2-iso*butyl*-, and 2-n-*hexyl-glyoxaline*-4 : 5-*dicarboxylic acids*. The solubilities of the above acids in water at 12—18° increases with ascent of the homologous series, whilst the molecular conductivities of the sodium salts decrease slightly. Titration curves of 2-*iso*propylglyoxaline-4 : 5-dicarboxylic acid, sodium hydrogen glyoxaline-4 : 5-dicarboxylate, and sodium 2-methylglyoxaline-4 : 5-dicarboxylate, with $0{\cdot}005N$-, $0{\cdot}005N$-, and $0{\cdot}1N$-sodium hydroxide solutions, respectively, show the existence of a small third constant in addition to first and second dissociation constants. The conception that one carboxyl group in these acids is neutralised by nitrogen is thus regarded as erroneous. H. Burton.

Curtius rearrangement of carbamyl azides. Formation of benzpyrazolones and bimolecular carbonylhydrazines. III. R. Stollé [with M. Merkle] (J. pr. Chem., 1928, [ii], **119**, 275—278).—The products of decomposition of benzaldehyde-phenylhydrazone-*N*-carbonyl azide (I) and of the *o*-chlorobenzaldehyde analogue (II) (cf. Stollé, A., 1927, 1203) are not now regarded as benzpyrazolones, since the benzylidene residue cannot be removed. The product from (I) is now identified as 5-hydroxy-1 : 3-diphenyl-1 : 2 : 4-triazole (cf. Wheeler and Statiropoulos, A., 1905, i, 721; Backer and Mulder, A., 1926, 182). The product from (II) is, however, regarded as 4-*hydroxy*-2-*phenyl*-5-o-*chlorophenyl*-1 : 2 : 3-*triazole*, since the action of alcoholic anhydrous ferric chloride on 2-*phenyl*-1-o-*chlorobenzylidenesemicarbazide*, $C_6H_4Cl{\cdot}CH{:}N{\cdot}NPh{\cdot}CO{\cdot}NH_2$, m. p. 181° (obtained by treating *o*-chlorobenzaldehydephenylhydrazone-*N*-carboxyl chloride with aqueous ammonia), gives rise to 5-*hydroxy*-1-*phenyl*-3-o-*chlorophenyl*-1 : 2 : 4-*triazole*, m. p. 188°, different from the above-described substance. E. W. Wignall.

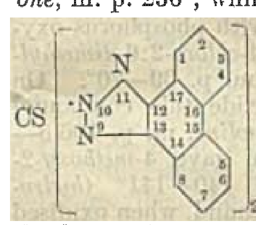
Condensation of o-aminobenzaldehyde with 1-phenyl-3-methyl-5-pyrazolone and with 1-o-chlorophenyl-3-methyl-5-pyrazolone. A. Musierowski, S. Niementowski, and Z. Tomasik (Rocz. Chem., 1928, **8**, 325—344).—Fusion in equimolecular quantities at 140° of *o*-aminobenzaldehyde with 1-phenyl-3-methyl-5-pyrazolone produces the *phenylhydrazone* of 2-*hydroxy*-3-*quinolyl methyl ketone*, m. p. 236°, which when heated with benzaldehyde yields 2-*hydroxy*-3-*quinolyl styryl ketone*, m. p. 269°. Among the products of the original condensation (carried out at 265°) is 4-*hydroxy*-1-*phenyl*-3-*methylquinpyrazole* (I), m. p. 273° (*hydrochloride*, m. p. 273°; *methiodide*, m. p. 273°), together with 2′-*hydroxy*-2 : 3′-*diquinolyl*, m. p. 313° [*nitrate*, m. p. 325°; *sulphate*, m. p. 299°; *hydrochloride*, m. p. 256° (decomp.); *methiodide*, m. p. 295°].



(I.)

Fusion at 150° with 1-*o*-chlorophenyl-3-methyl-5-pyrazolone yields the o-*chlorophenylhydrazone* of 2 : 4-*dihydroxy*-3 : 4-*dihydro*-3-*quinolyl methyl ketone*, m. p. 184°, the o-*chlorophenylhydrazone* of 2-*hydroxy*-3-*quinolyl methyl ketone*, m. p. 280° (*hydrochloride*, m. p. 280°; O-*acetyl* derivative, m. p. 262°; N-*acetyl* derivative, m. p. 236°; *monobromide*, m. p. 230°; *dibromide*, m. p. 208°), and 4-*hydroxy*-1-o-*chlorophenyl*-3-*methylquinpyrazole*, m. p. 281°. R. Truszkowski.

Action of hydrazides. II. Synthesis of bistriazoles from thiocarbo- and carbo-hydrazides. S. C. De (J. Indian Chem. Soc., 1928, **5**, 373—378).—2-Bromophenanthraquinone and thiocarbohydrazide hydrochloride react in presence of acetic acid, yielding *bis*-(2-*bromophenanthraquinone*)*thiocarbohydrazone*, m. p. 236°, whilst the monoxime of the diketone affords under similar conditions 2 : 2′-*dibromo*-10 : 10′-*bis*-10 : 9 : 11-*phenanthratriazolyl thioketone* (annexed formula), m. p. 145°. The following di-(substituted phenanthraquinone)thiocarbohydrazones are described: 2 : 7-*dibromo*-, m. p. 260° 2-*nitro*-, m. p. 220°; 4-*nitro*-, m. p. 155°; 4 : 5 *dibromo*-, m. p. 270° after blackening at 260°; 4 : 5-*dinitro*-, m. p. 162°, and 2 : 7-*dinitro*-, m. p. above 300°. The corresponding *carbohydrazones* are prepared similarly and the following are described: *diphenanthraquinone*, m. p. 285°; *di-2-bromo*-, m. p. 275°; *di-2-nitro*-, m. p. 280°; *di-4-nitro*-, m. p. 240°; *di-2 : 7-dibromo*-, m. p. 295°; *di-2 : 7-dinitro*-, m. p. above 300°; *di-2 : 5-dinitro*-, m. p. 295°, and *di-4 : 5-dibromo-phenanthraquinone*, m. p. above 300°.

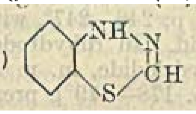
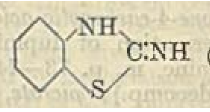


From the requisite phenanthraquinone monoximes the following 10 : 10′-*bis*-10 : 9 : 11-*phenanthratriazolyl thioketones* were obtained: 2 : 7-*dibromo*-, m. p. 210°; 2-*nitro*-, m. p. 200°; 4 : 5-*dibromo*-, m. p. 235°; 4 : 5-*dinitro*-, m. p. 160°, and 2 : 7-*dinitro*-, blackens at 250° and does not melt at 295°. Substituted 10 : 10′-*bis*-10 : 9 : 11-*phenanthratriazolyl ketones* are obtained similarly and the following are described: 2-*bromo*-, m. p. 245°; 2-*nitro*-, m. p. 192°; 4-*nitro*-, m. p. 200°; 2 : 7-*dibromo*-, m. p. 210°; 2 : 7-*dinitro*-, m. p. 230°; 4 : 5-*dinitro*-, m. p. 160°, and 4 : 11(5 ?)-

dibromo-, m. p. 273°. 10 : *-Bisphenanthratriazolyl ketone* has m. p. 272°. The colours of the sulphur derivatives are red, whilst the oxygen-containing compounds are mostly yellow. H. BURTON.

Bromoporphyrin I and tetramethylhæmatoporphyrin iron salt. (Addendum.) H. FISCHER and G. HUMMEL (Z. physiol. Chem., 1928, **177**, 321; cf. this vol., 659).—Bromoporphyrin I and dibromodeuteroporphyrin ester are identical. H. BURTON.

Silver and mercury salts of 1-aminobenzthiazole. F. FEIGL and A. DEUTSCH (Monatsh., 1928, **49**, 413—416).—The compound $C_7H_6N_2S$ obtained by Fischer and Besthorn (A., 1882, 1094) by heating phenylthiosemicarbazide with hydrochloric acid and later by Hugershoff (A., 1903, i, 865) by the action of bromine on phenylthiocarbamide was regarded by Harries and Lowenstein (A., 1894, i, 305) as (I) and by Hugershoff as (II). In addition to the known

(I.)  (II.) 

compound, $C_7H_5N_2SAg$, the *compounds* $C_7H_4N_2SAg_2$ and $C_7H_4N_2SHg$, corresponding with (II) but not with (I), have been obtained. The following *compounds* are also described: $C_7H_6N_2S,HgCl_2$; $C_7H_5N_2S,HgCl$; and $C_7H_5N_2S,Hg_2O(NO_3)$. No metals other than silver and mercury form insoluble precipitates with the aminobenzthiazole, a fact which may be made use of for the detection and determination of these two metals.

The aminobenzthiazole, acting as a base, forms the *periodide*, $C_7H_6N_2,HI,I_2$, its tautomerism thus being established. R. A. PRATT.

Manufacture of carbazolequinones. I. G. FARBENIND. A.-G.—See B., 1928, 635.

Oxidation. I. Action of ferric chloride and hydrogen peroxide on thiosemicarbazones. Synthesis of thiodiazoles and triazoles. S. C. DE and S. K. ROY-CHOUDHURY (J. Indian Chem. Soc., 1928, **5**, 269—278).—When benzaldehyde thiosemicarbazone is oxidised with ferric chloride the sole product is 2-amino-5-phenyl-1 : 3 : 4-thiodiazole (cf. Young and Eyre, J.C.S., 1901, **79**, 54), but if hydrogen peroxide is used the product is *5-phenyl-1 : 3 : 4-triazole*, m. p. 177°, thus demonstrating that thiosemicarbazones can react in either the *syn-* or *anti-*modifications. With ferric chloride as the oxidising agent the following substituted 1 : 3 : 4-*thiodiazoles* have been prepared: *2-amino-5-styryl-*, m. p. 260—261°, from cinnamaldehyde thiosemicarbazone; *2-anilino-5-o-hydroxyphenyl-*, m. p. 190—191°, from salicylaldehyde 4-phenylthiosemicarbazone; *2-anilino-5-m-nitrophenyl-*, m. p. 249—250° (*acetyl* derivative, m. p. 246°); 5(2?)-p-*toluidino*-2(5?)-*phenyl-*, m. p. 198—199° (*acetyl* derivative, m. p. 155°), from benzaldehyde 4-*p*-tolylthiosemicarbazone; 2-p-*toluidino*-5-p-*nitrophenyl-*, m. p. 197—198° (*acetyl* derivative, m. p. 243°); 2-p-*toluidino-5-styryl-*, m. p. 184°; *2-allylamino-5-phenyl-*, m. p. 114—115° (*acetyl* derivative, m. p. 120°), from benzaldehyde 4-allylthiosemicarbazone; *2-allylamino-5*-m-*nitrophenyl-*, m. p. 170—171°; 2-m-*toluidino*-5-p-*nitrophenyl-*, m. p. 257°; 2-m-*toluidino-5-phenyl-*, m. p. 176°; 2-o-*toluidino*-5-m-*nitrophenyl-*, m. p. 247°; *2-methylamino*-5-m-*nitrophenyl-*, m. p. 201° (*acetyl* derivative, m. p. 225—226°; *methyl* derivative, m. p. 209°), from *m*-nitrobenzaldehyde 4-methylthiosemicarbazone; *2-methylamino-5*-p-*nitrophenyl-*, m. p. 262° (*acetyl* derivative, m. p. 279°; *methyl* derivative, m. p. 203°); 2-m-*xylidino-5*-o-*nitrophenyl-*, m. p. 229°; 2-m-*xylidino*-5-m-*nitrophenyl-*, m. p. 205° (*acetyl* derivative, m. p. 197—198°); 2-β-*naphthylamino-5*-o-*nitrophenyl-*, m. p. 202°, and *2-ethylamino-5-phenyl-*, m. p. 238—240°.

Oxidation of thiosemicarbazones with hydrogen peroxide gives either a disulphide derived by oxidation of a thioltriazole (cf. Young and Eyre, *loc. cit.*), or a sulphur-free triazole, probably formed through further oxidation of the disulphide. The following 1 : 3 : 4-*triazole 2-disulphides* are described: 5-o-*nitrophenyl*-1-m-*xylyl-*, m. p. 201—203°; *5-phenyl-1-allyl-*, m. p. 90°; *5-phenyl*-1-p-*tolyl-*, m. p. 155—156°; *5-phenyl-1-ethyl-*, m. p. 88°; 1 : *5-diphenyl-*, m. p. 232° (decomp.), and 5-m-*nitrophenyl-1-allyl*, m. p. 173°. 5-m-*Nitrophenyl-1-allyl-1 : 3 : 4-triazole* has m. p. 194—195°.

Oxidation of acetone thiosemicarbazone with hydrogen peroxide gives 2 : *5-diisopropylidenehydrazino-1 : 3 : 4-thiodiazole*, m. p. 260° (decomp.), hydrolysed by hot concentrated hydrochloric acid to hydrazine hydrochloride. Similarly, acetone 4-phenyl- and 4-*p*-tolyl-thiosemicarbazones yield the *diisopropylidene* derivatives of 2 : *5-diketo-3 : 4-diphenyl-* and 2 : *5-diketo-3 : 4-di*-p-*tolyl-1 : 3 : 4-thiodiazoledihydrazones*, having m. p. 168° (decomp.) and 124°, respectively. H. BURTON.

Synthetic homologues of *dl*-ephedrine. J. F. HYDE, E. BROWNING, and R. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 2287—2292).—A series of compounds of the type OH·CHPh·CHR·NHR′ was prepared by the method used by Eberhard (A., 1915, i, 834; cf. Fourneau and Kanao, A., 1924, i, 978) for the synthesis of *dl*-ephedrine (R and R′ = Me), viz., the condensation of alkylamines with phenyl α-bromoalkyl ketones. The amino-ketone hydrochlorides COPh·CHR·NHMe,HCl were best purified by extraction from the excess of alkylamine hydrochloride by chloroform. In other cases the amine was removed from the basified mixture by distillation. The *dl*-amino-alcohol was obtained by reduction with hydrogen and platinum oxide-platinum-black. The following compounds are described: *α-bromo*-n-*valerophenone*, b. p. 150°/2·5 mm., d_4^{20} 1·3993, n_D^{20} 1·5600; hydrochlorides of ω-methylaminoacetophenone, m. p. 219°, and α-methylaminopropiophenone, m. p. 176—177°; *hydrochlorides* of *α-methylamino*-n-*butyrophenone*, m. p. 190—192°; *α-methylamino*-n-*valerophenone*, m. p. 183·5—184·5°; ω-n-*butylaminoacetophenone*, m. p. 214—215°; α-n-*butylamino*-n-*butyrophenone*, m. p. 138—140°; *hydrochlorides* of substituted *propiophenones*: *α-ethylamino-*, m. p. 183°; *α-propylamino-*, m. p. 180°; α-iso*propylamino-*, m. p. 213—213·5° (*base*, b. p. 105—110°/3 mm.); α-n-*butylamino-*, m. p. 158—159° (*base*, b. p. 140—142°/8 mm.); *α-dimethylamino-*, m. p. 167—168°; the following hydrochlorides of α-phenyl-substituted alcohols: -β-methylaminoethyl, m. p. 105—106°

(base, m. p. 75—76°); -β-methylaminopropyl, m. p. 189—190° (base, m. p. 76—77°); -β-*methylamino*-n-*butyl*, m. p. 201—202° (*base*, m. p. 89—90°); -β-*methylamino*-n-*amyl*, m. p. 224—225° (*base*, m. p. 76—77°); -β-n-*butylaminoethyl*, m. p. 218—220°) (*base*, m. p. 58—59°); -β-*di*-n-*butylamino*-n-*butyl*, m. p. 114—116°; -β-*ethylaminoethyl*, m. p. 190—191°; -β-*propylaminoethyl*, m. p. 218°; -β-iso*propylaminoethyl*, m. p. 193°; -β-n-*butylaminoethyl*, m. p. 220—221°; -β-n-*amylaminoethyl*, m. p. 219°; -β-*diethylaminopropyl*, m. p. 205—206°.

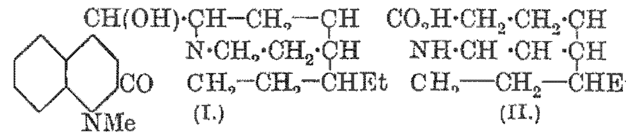
The blood-sugar level on injection of both ketones and alcohols increased as the *N*-alkyl group was made larger, and decreased as the alkyl group on the β-carbon atom was increased in size. The dialkylamino-compounds produced no physiological action. α-Phenyl-β-methylaminoethyl alcohol alone gave a dependable increase in blood pressure.

R. K. Callow.

Alkaloids of lupins. C. Schöpf (Annalen, 1928, **465**, 97—147). **I. Isomeric lupinic esters and lupinans.** [With O. Thoma.]—Lupinic acid, $(C_8H_{15}N)$:CH·CO_2H, gives two series of derivatives, (−) and (+)-epi-, according to the configuration of the terminal :CH·CO_2H group; the $C_8H_{15}N$ residue, which contains at least one asymmetric atom, remains the same in both series. Lupinic acid, obtained by chromic acid oxidation of lupinine, $(C_8H_{15}N)$:CH·CH_2·OH (Willstätter and Fourneau, A., 1902, i, 557), is isolated as the *methyl* ester, b. p. 120—122°/10 mm., $[\alpha]_D$ −19·4° to +5·8° in different preparations. The (−)-ester gives a soluble, resinous *picrate*, $[\alpha]_D^{18}$ −41·8°, but the more (+)-preparations yield an insoluble *picrate*, m. p. 185°, $[\alpha]_D$ +61·8°, from which the pure (+)-*epi*-ester, b. p. 126°/11 mm., $[\alpha]_D$ +54·8°, is obtained. Corresponding with the two methyl esters are the crystalline (−)-lupinic acid hydrochloride, m. p. 275°, of Willstätter and Fourneau (*loc. cit.*), and a non-crystalline (+)-*epimeride*. The (−)-ester is converted by a little sodium methoxide into the (+)-epi-ester; it is not attacked by methyl-alcoholic ammonia at 100°, but at 140° undergoes isomerisation to the (+)-epi-ester, followed by racemisation to an inactive (±)-*epi*-ester, b. p. 128—130°/11 mm. (*picrate*, m. p. 208°), which is more readily obtained in a similar manner from the (+)-epi-ester. By the action of phosphorus pentachloride in benzoyl chloride suspension (−)-lupinic acid hydrochloride is converted into an *acid chloride* (not isolated), from which by treatment with methyl alcohol the (+)-epi-methyl ester is obtained. The acid chloride reacts with ammonia to give, in small yield, the (+)-*epi-amide*, m. p. 228°, subliming at 250° (bath temperature)/11 mm., $[\alpha]_D^{18}$ +41·3°, together with the (+)-*epi-nitrile*, b. p. 120°/11 mm. (*hydrochloride*, $[\alpha]_D$ +52·9°).

The only definite oxidation product obtainable from Willstätter and Fourneau's anhydrolupinine, $(C_8H_{15}N)$:C:CH_2 (*picrate*, m. p. 94°), is the *glycol*, b. p. 165—167°/11 mm., but reduction with hydrogen and palladium yields two epimeric *lupinans*, b. p. 75—77°/11 mm. (*picrates* α-, m. p. 187°; β-, m. p. 163°; cf. G.P. 396,508, A., 1925, i, 294), together with a trace of a lupinine, b. p. 110°/11 mm., which, since it gives a crystalline *picrate*, m. p. 163°, is probably an isomerised or a racemised compound.

II. Possible relations between lupinine and the cinchona alkaloids. [With E. Schmidt.]—Attempts to correlate the $(C_8H_{15}N)$:CH· residue of lupinic acid with the quinuclidine residue of the hydrogenated cinchona alkaloids are unsuccessful. Dihydrocinchonine methiodide hydriodide (von Arlt, A., 1899, i, 962), m. p. 242—243°, is oxidised quantitatively by alkaline ferricyanide to a *quinolone* (I), m. p. 213—214° (hydrochloride, m. p. 301°), which is further oxidised by chromic acid to cincholoipone



(I.) (II.)

(methyl ester, b. p. 122—124°/12 mm.) and 1-*methylquinolone-4-carboxylic acid*, m. p. 246—247°, without any formation of lupinic acid. In dihydrodeoxycinchonine, m. p. 73—74° [hydriodide, m. p. 230—231° (decomp.); *picrate*, m. p. 178—179°], prepared by reduction of deoxycinchonine or of cinchen, the secondary alcohol group is absent; it gives an amorphous *methiodide hydriodide* (*dipicrate*, m. p. 170—171°) which reacts with sodium hydroxide to form an unstable *oil* (probably a methylenedihydroquinoline), from which by oxidation with permanganate in acetone only 1-methyl-4-quinolone, m. p. 142—143° (*picrate*, m. p. 229°), is obtained, the quinuclidine residue being lost. An attempt to cyclise the α-bromo-derivative of homocincholoipone (II) was unsuccessful, and no β-ethylquinuclidine could be obtained by decarboxylation of lupinic acid.

By the action of magnesium phenyl bromide on a methyl lupinate of $[\alpha]_D^{21}$ −7·4° there are obtained an oily *ketone*, $(C_8H_{15}N)$:CH·COPh, b. p. 126—218°/1 mm. (*picrate*, m. p. 185°, $[\alpha]_D^{21}$ +38·5°; *methiodide*, amorphous), and a *carbinol*, $(C_8H_{15}N)$:CH·CPh_2·OH, m. p. 170—171°, $[\alpha]_D^{21}$ +79·2° (*hydrobromide*, m. p. 205°), both belonging to the (+)-epi-series. The ketone shows no analogies with dihydrocinchoninone; it gives no oxime, and is oxidised with great difficulty with production of benzoic and acetic acids but no cincholoipone. The carbinol is even more resistant to oxidation. A quinuclidine structure for lupinine is therefore improbable. It is suggested that lupinine (C_{10}), sparteine (C_{15}), lupanine (C_{15}), oxylupanine (C_{15}), sarothamnine (C_{15}), spathulatine (C_{15} +Me), are built up from two, or three, isoprene molecules and ammonia [cf. galegine, CMe_2:CH·CH_2·NH·C(:NH)·NH_2 (Barger and White, A., 1924, i, 272; Späth and others, A., 1924, i, 502; 1926, 81)].

III. Sparteine. [With W. Braun.]—The further oxidation of oxysparteine (Ahrens, A., 1905, i, 917; Willstätter and Marx, *ibid.*, 544) throws no light on the constitution of sparteine. The exhaustive methylation of sparteine is investigated. The only product of the prolonged action of cold hydrogen peroxide on oxysparteine, m. p. 87° (picrate, m. p. 183°), is the N-*oxide*, m. p. about 220° (decomp.) [*picrate*, m. p. 221° (decomp.)]. Hot peroxide gives acid products (W. Braun, Diss., Munich, 1928), which, however,

contain no lupinic acid. Sparteine α-methiodide, m. p. 234°, $[\alpha]_D^{18}$ −48·5°, is converted by Hofmann degradation under special conditions into α-de-*N*-methylsparteine, b. p. 173·5—174°/10 mm., $[\alpha]_D^{21}$ −47·6° (cf. Moureu and Valeur, A., 1912, i, 210, 296), which is isolated as mercurichloride, m. p. 270—271°, together with two new *bases*, $C_{16}H_{28}N_2$, b. p. 160—161°/10 mm., $[\alpha]_D^{18}$ −21·3° [*dihydriodide*, m. p. 223—225° (decomp.), $[\alpha]_D^{18}$ −37·5°; *mercurichloride*, m. p. 182—185° (decomp.)], and $C_{16}H_{30}ON_2$, b. p. 183—189°/10 mm., $[\alpha]_D^{18}$ +16·0° [*mercurichloride*, m. p. 154—156° (decomp.)]. α-De-*N*-methylsparteine dihydriodide, m. p. 236—237°, $[\alpha]_D^{19}$ −37·6°, is isomerised by water at 130—135° or by boiling alcohol, giving a *compound* (probably a quaternary salt), $C_{16}H_{28}N_2,3HI$, m. p. 206—207°, $[\alpha]_D^{18}$ +19·5°, which with alkali yields the *dihydriodide*, m. p. 182—184°, $[\alpha]_D^{18}$ +41·7°; no corresponding base is obtained, but the mother-liquors from the trihydriodide contain a *compound*, $C_{16}H_{28}N_2,HI,H_2O$, m. p. 206—208°, $[\alpha]_D^{18}$ −13·3°. α-De-*N*-methylsparteine gives a *dibromide* (*perchlorate*, m. p. 267°), and by methylation a *mono-methiodide*, m. p. 135° (+H_2O) or 239° (anhyd.), and a *dimethiodide*, m. p. 266° (decomp.), together with a *product*, m. p. 75°. It is reduced by hydrogen and platinum oxide to a *dihydro*-derivative, m. p. 64° (*dihydriodide*, m. p. 267—268°), and is oxidised by permanganate to a *glycol*, m. p. 200°. C. Hollins.

Histamine derivatives. P. van der Merwe (Z. physiol. Chem., 1928, **177**, 301—314).—When αβδ-tribenzamido-Δ^{α}-butylene is heated with acetic anhydride for 14 hrs. at 145° and a further 2 hrs. at 160°, excess of the anhydride removed by evaporation in a vacuum, and the residual oil heated with concentrated hydrochloric acid at 160°, there is obtained 2-*methylhistamine* [*dipicrate*, m. p. 237°, or (+$2H_2O$) m. p. 208°; *dihydrochloride*, m. p. 217°]. Using propionic, benzoic, and phenylacetic anhydrides, 2-*ethylhistamine* (*dipicrate*, m. p. 219°; *dihydrochloride*, m. p. 209°); 2-*phenylhistamine* (*dipicrate*, m. p. 230°; *dihydrochloride*, decomp. gradually above 240°), and 2-*benzylhistamine* (*dipicrate*, m. p. 195°; *dihydrochloride*, decomp. 245°), respectively, are obtained. The following substituted histamines are described: N-*acetyl*-, m. p. 143°; N-iso*butyryl*-, m. p. 123°; *carbamido*-, m. p. 148° (*picrate*, m. p. 150°; *oxalate*, m. p. 153°), from histamine hydrochloride and potassium cyanate; *phenylcarbamido*-, m. p. 178°; α-*naphthylcarbamido*-, m. p. 193°, and the corresponding *guanidino*-derivative [*dipicrate*, m. p. 245° (decomp.); *dihydrochloride*, m. p. 208° (decomp.)], from histamine and cyanamide or from histamine hydrochloride and silver cyanamide.

Anisylidenehistamine, m. p. 186° (*dipicrate*, m. p. 222°), is reduced by sodium and amyl alcohol to N-p-*methoxybenzylhistamine* (*dipicrate*, m. p. 213°). When the *dihydrochloride* of this base is treated with benzoyl chloride and sodium hydroxide the glyoxaline ring undergoes fission and δ-N-p-*methoxybenzyl*-αβδ-*tribenzamido*-Δ^{α}-*butylene*, m. p. 205°, is obtained. *Piperonylidenehistamine*, m. p. 180° (*dipicrate*, m. p. 217°), is reduced to N-3 : 4-*methylenedioxybenzylhistamine* (*dipicrate*, m. p. 195°; *dihydrochloride*, decomp. 245°). When a mixture of histamine and ε-chloroamylbenzamide is heated on the water-bath for 1·5 hrs. and an alcoholic solution of the reaction product treated with hydrogen chloride at 0° for 24 hrs. and the residue from this heated with concentrated hydrochloric acid at 160° N-ε-*aminoamylhistamine* (*tetrapicrate*, m. p. 215°; *tripicrate*, m. p. 169°) is produced.

H. Burton.

Synthetical experiments on the aporphine alkaloids. IV. Synthesis of morphothebaine dimethyl ether. J. M. Gulland and R. D. Haworth (J.C.S., 1928, 2083—2088).—2′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-3-*methoxyphenylethylamide*, m. p. 107—108° (from 2-nitro-3 : 4-dimethoxyphenylacetyl chloride and 3-methoxy-β-phenylethylamine), gave, on interaction with phosphorus pentachloride, 2′-*nitro*-6 : 3′ : 4′-*trimethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 121—123° [*hydrochloride*, m. p. 217—218° (decomp.); *sulphate*, m. p. 237° (decomp.); *methiodide*, m. p. 220° (decomp.); the methiodide gave under conditions for alkaline fission only 2′-*nitro*-6 : 3′ : 4′-*trimethoxy*-1-*benzylidene*-2-*methyltetrahydro*iso*quinoline*, m. p. 108—109°], and small quantities of 2′-*nitro*-6 : 3′ : 4′-*trimethoxy*-1-*benzoyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 164° (decomp.) (*oxime*), formed by atmospheric oxidation of the previous compound.

The above methiodide was reduced by zinc dust and hydrochloric acid to 2′-*amino*-6 : 3′ : 4′-*trimethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline* (*dihydrochloride* +$1CHCl_3$, has m. p. 155°, softening at 135°), which was converted by diazotisation and heating into dl-3 : 4 : 6-*trimethoxyaporphine*, an oil [*hydrochloride*, m. p. 227° (decomp.)]. Resolution of this base with *d*-tartaric acid gave a *d*-tartrate identical with *l*-morphothebaine dimethyl ether hydrogen *d*-tartrate, m. p. 208—209° (decomp.) (Klee, A., 1914, i, 1086, gives 205°). Similarly, the *l*-base, an oil, $[\alpha]_D$ −173·5°, was identical with natural morphothebaine dimethyl ether, $[\alpha]_D$ −172·7° (lit. −184·8°) (*methiodides*, both m. p. 195° with softening at 190°, $[\alpha]_D$ −87·1°, −88·2°, respectively).

d-*Morphothebaine dimethyl ether hydrogen* l-*tartrate*, m. p. 208—209° (decomp.), $[\alpha]_D$ +75·5°, gave the d-*base*, $[\alpha]_D$ +174·2°. R. J. W. Le Fèvre.

Colour reactions of atropine and some related compounds. L. Ekkert (Pharm. Zentr., 1928, **69**, 529—531).—The colorations obtained by addition of the commoner phenols in presence of sulphuric acid are described. S. I. Levy.

Determination of morphine. L. David (Ber. ungar. pharm. Ges., 1926, **2**, 103—111; Chem. Zentr., 1928, i, 1560).—Debourdeaux' method, which is preferred, has a constant error of −1·5%. Other methods give too low results. A. A. Eldridge.

Determination of morphine with barium hydroxide. G. P. Scholtz (Ber. ungar. pharm. Ges., 1927, **3**, 435—437; Chem. Zentr., 1928, i, 1560).—In Debourdeaux' method calcium hydroxide is preferably replaced by barium hydroxide, the barium being removed with ammonium oxalate or sulphate.

A. A. Eldridge.

Sensitive modification of colour reaction for quinine. H. W. van Urk (Pharm. Weekblad, 1928, **65**, 847—849).—The green colour is developed with

much more certainty, and is more stable, if the oxidation is carried out with sodium hypochlorite instead of with chlorine or bromine water. With this modification, the test will detect 1 part of quinine in 40,000 parts. S. I. LEVY.

Thalleioquinine reaction of quinine salts. G. MIKÓ (Ber. ungar. pharm. Ges., 1927, 3, 205—207; Chem. Zentr., 1928, i, 1559—1560).—The quinine salt (0·5—1 g.) is preferably boiled with $5N$-hydrochloric acid (5 drops) and 3% hydrogen peroxide solution (3 drops) until a yellow coloration is obtained; the mixture is then diluted with water and 1 c.c. of $5N$-ammonia solution is added, a green coloration appearing at the interface. A. A. ELDRIDGE.

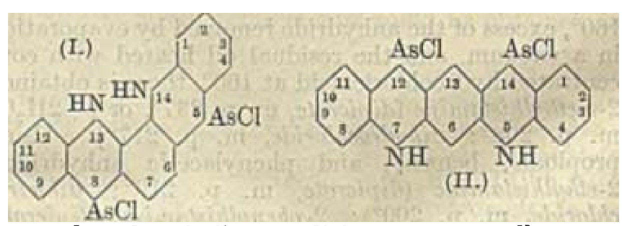
Isomerism of *p*-hydroxyphenylarsinic acid. G. GILTA (Bull. Soc. chim. Belg., 1928, **37**, 253—262; cf. this vol., 189).—The two isomeric forms of *p*-hydroxyphenylarsinic acid are described: (I), pinkish monoclinic crystals, $a:b:c=0·4483:1:0·4936$, obtained by diazotising *p*-arsanilic acid, and (II), yellowish monoclinic crystals, $a:b:c=2·465:1:0·7968$, obtained by fusion of phenol with arsenic acid. Spontaneous conversion of (II) into (I) proceeds slowly in aqueous solution, more quickly on boiling and seeding with a crystal of (I). The sodium and barium salts derived from (II), however, are more stable than the corresponding isomeric salts derived from (I). B. W. ANDERSON.

Condensation of 4-chloro-3-nitrophenylarsinic acid with amines, in particular ethylenediamine and piperazine. Reduction of the nitro-derivatives to amines. E. FOURNEAU and A. FUNKE (Bull. Soc. chim., 1928, [iv], **43**, 889—895).—When 4-chloro-3-nitrophenylarsinic acid is heated with ethylenediamine at 135—140° in presence of anhydrous sodium acetate, *3-nitro-4-β-aminoethylaminophenylarsinic acid* is obtained. When condensation is effected using an aqueous solution of the diamine the product is *NN'-di-o-nitrophenylethylenediamine-4 : 4'-diarsinic acid*, $[AsO_3H_2·C_6H_3(NO_2)·NH·CH_2·]_2$, reducible by ferrous hydroxide to the corresponding *amino-acid*. Reduction of *3-nitro-4-β-acetamidoethylaminophenylarsinic acid* with ferrous hydroxide below 50° affords the corresponding *3-amino-acid*, which has C/T=1/6. Piperazine reacts with 4-chloro-3-nitrophenylarsinic acid in presence of sodium hydroxide, yielding *3-nitro-4-piperazinophenylarsinic acid* (*acetyl* derivative); when condensation is effected with piperazine hydrate at 110° in presence of sodium acetate the product is *1 : 4-di-o-nitrophenylpiperazine-pp'-diarsinic acid*, $[AsO_3H_2·C_6H_3(NO_2)·N\colon(CH_2·)_2]_2$. *3-Amino-4-acetylpiperazino-*, *3-nitro-4-p-carbethoxyphenylamino-*, and *3-amino-4-p-carboxyphenylaminophenylarsinic acids* are described. The majority of the above amino-acids have no trypanocidal action. H. BURTON.

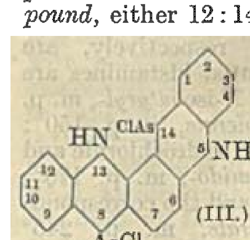
Arsenical quinoline derivatives. S. BERLINGOZZI (Annali Chim. Appl., 1928, **18**, 333—336; cf. A., 1927, 675; this vol., 434).—When coupled with various aminoquinolines, the diazo-derivative of arsanilic acid yields the following compounds: *3-amino-2-methylquinoline-4-azo-p-phenylarsinic acid*, decomp. 150—152°; *3-amino-2-phenylquinoline-4-azo-p-phenylarsinic acid*, decomp. about 100°; *3-amino-2-p-methoxyphenylquinoline-4-azo-p-phenylarsinic acid*, decomp. about 145°; *8-aminoquinoline-5-azo-p-phenylarsinic acid*, not appreciably altered below 250°; *5-aminoquinoline-8-azo-p-phenylarsinic acid*, not appreciably altered below 250°. T. H. POPE.

Manufacture of organo-arsenic compounds. R. W. E. STICKINGS, and MAY & BAKER.—See B., 1928, 691.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. VI. Compounds containing two nitrogen and two arsenic atoms in six- and five-ringed systems. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 2204—2215).—Condensation of benzidine with *o*-bromophenylarsinic acid gave *4 : 4-bis(diphenylamine-2'-arsinic acid)*, readily converted into *2 : 2'-bis-(10-chloro-5 : 10-dihydrophenarsazine)*, also formed from *NN'*-diphenylbenzidine and arsenious chloride. Oxidation of the above chloro-compound gave *2 : 2'-bis(phenarsazinic acid)* (*disodium* salt), from which was obtained *2 : 2'-bis-(10-bromo-5 : 10-dihydrophenarsazine)*. *NN'*-Di-*p*-tolylbenzidine similarly led to *2 : 2'-bis-(10-chloro-8-methyl-5 : 10-dihydrophenarsazine)*, *2 : 2'-bis-(8-methylphenarsazinic acid* (*disodium* salt), and *2 : 2'-bis-(10-bromo-* and *10-iodo-8-methyl-5 : 10-dihydrophenarsazines)*. *o*-, *m*-, and *p*-Phenylenediamines and *o*-bromophenylarsinic acid gave 1 : 2-, 1 : 3-, and *1 : 4-phenylenediaminodi-o-phenylarsinic acid*, respectively, the last two only being obtained pure. The 1 : 2-compound was reduced in presence of hydrochloric acid to *5 : 8-dichloro-13 : 14 : 5 : 8-tetrahydroisobenzarsazinephenarsazine* (I), whilst the 1 : 3-com-



pound under similar conditions gave a yellow *compound*, either *12 : 14-dichloro-5 : 7 : 12 : 14-* or *8 : 14-dichloro-5 : 13 : 8 : 14-tetrahydrobenzarsazinephenarsazine* (II) or (III), which differed from the red condensation product from *NN'*-diphenyl-*m*-phenylenediamine (1 mol.) and arsenious chloride (2 mols.). Both apparently yielded the same *diarsinic acid* (*5 : 7 : 12 : 14-* or *5 : 13 : 8 : 14-benzarsazinicphenarsazinic acid*; *disodium* salt) on oxidation and the same *dibromo-* and *di-iodo*-compounds on reduction in presence of the required halogen acid.



NN'-Diphenyl-*p*-phenylenediamine condensed with arsenious chloride, giving *7 : 14-dichloro-5 : 12 : 7 : 14-* (or 13 : 14-dichloro-5 : 8 : 13 : 14-)*tetrahydrobenzarsazinephenarsazine*, converted by oxidation into *5 : 12 : 7 : 14-* (or *5 : 8 : 13 : 14-*)*benzarsazinicphenarsazinic acid*, m. p. above 320°, darkening at 290° (*disodium* salt), from which the analogous dichloro- and *dibromo*-compounds were obtained by reduction.

All italicised compounds had m. p. above 320°.

R. J. W. LE FÈVRE.

Quadrivalency of selenium. I. 4-Carboxydiphenyl and *p*-carboxyphenyl methyl selenoxides. II. Simple halogen derivatives and dihydroxide of 4-acetamidodiphenyl selenide. W. R. GAYTHWAITE, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 2280—2287, 2287—2293).—I. *Phenyl* p-*tolyl selenide* (I), b. p. 175—178°/20 mm., obtained by the interaction of selenium with phenyl *p*-tolyl sulphone, m. p. 127—128° (lit. 124·5°), yields a *dibromide*, m. p. 149—150°. Oxidation of (I) with potassium permanganate or trituration of its dibromide with sodium hydroxide solution yields *phenyl* p-*tolyl selenoxide* (II), m. p. 131—133°. Oxidation of (I) with excess of potassium permanganate gives 4-*carboxydiphenyl selenoxide* (III), m. p. 253—255° (decomp.) [*brucine* salt, m. p. 130° (decomp.); *strychnine* salt; l-*menthylamine* salt, m. p. 220—222° (decomp.); d-α-*phenylethylamine* salt, m. p. 194—195° (decomp.)], in addition to (II). Reduction of (III) with zinc dust and acetic acid gives 4-*carboxydiphenyl selenide*, m. p. 182—184° (*dibromide*, m. p. 208—210°). 4 : 4′-*Dicarboxydiphenyl diselenide* (IV), m. p. 297°, is obtained by treatment of the diazo-solution from *p*-aminobenzoic acid with potassium selenocyanate and subsequent treatment of the mixed precipitate of *p*-carboxyphenyl selenocyanate and (IV) thus obtained with boiling sodium hydroxide solution.

Reduction of (IV) with alkaline sodium hyposulphite, followed by treatment with methyl sulphate, gives p-*carboxyphenyl methyl selenide* (V), m. p. 174° (*dibromide*, m. p. 198—199°). Oxidation of (V) or treatment of the dibromide with sodium hydroxide solution gives p-*carboxyphenyl methyl selenoxide* (VI), m. p. 183—184° (*brucine* salt, m. p. 105—110°). Attempts to resolve compounds (II), (III), and (VI) were unsuccessful, and these substances could not be oxidised to selenones. It is concluded that the double linking between the oxygen and selenium atoms of a selenoxide may be symmetrical instead of unsymmetrical, as in the case of the corresponding double linking in sulphoxides.

II. Benzeneseleninic acid reacts with aniline, giving 4-*aminodiphenyl selenide*, m. p. 93—94° (*hydrochloride*, m. p. 159°). 4-*Acetamidodiphenyl selenide* (I), m. p. 169—170°, is converted by treatment with hydrogen peroxide into 4-*acetamidodiphenyl selenide dihydroxide* (II), m. p. 147—148° (decomp.). When the dihydroxide is heated under reduced pressure, it loses water, giving 4-*acetamidodiphenyl selenoxide* (III), m. p. 144—146°; when it is fused at the ordinary pressure, the selenoxide first formed is decomposed by further heating, giving 4-acetamidodiphenyl selenide and oxygen. Addition of concentrated solutions of hydrochloric, hydrobromic, or hydriodic acid to a warm solution of (III) in glacial acetic acid gives, respectively, 4-*acetamidodiphenyl selenide dichloride*, m. p. 131—132°, *dibromide*, m. p. 135—136°, and *di-iodide*, m. p. 144—145° (decomp.). The dibromide and di-iodide are alternatively prepared by the action of bromine and iodine, respectively, on an acetic acid solution of (I). Chlorine reacts with (I) under these conditions, giving a *compound*, m. p. 186—187°, containing chlorine, which is not displaced by the action of aqueous alkali. The dibromide is converted by heat into a *compound*, m. p. 167°, containing nuclear bromine (3 : 5-dibromo-4-acetamidodiphenyl selenide ?). The dichloride suffers a similar change, whereas the di-iodide evolves iodine, reverting to the selenide. Gradual dissociation of the di-iodide takes place at the ordinary temperature, as well as in ethereal solution. The dichloride and dibromide are converted by the action of water or dilute alkalis into the dihydroxide. Boiling water, however, is without action on the di-iodide, which with sodium hydroxide yields its parent selenide. 4-*Aminodiphenyl selenoxide*, m. p. 188—189° (decomp.), obtained by treatment of (II) with sodium hydroxide solution, is unstable in the presence of acids. Its resolution was therefore impracticable.

M. CLARK.

Quadrivalency of selenium. III. Instability of the compounds of quadrivalent selenium derived from phenyl methyl and phenyl ethyl selenides, and phenyl- and *p*-tolyl-selenoglycollic acids. O. K. EDWARDS, W. R. GAYTHWAITE, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 2293—2303).—*Phenyl methyl selenide dibromide*, m. p. 115—116° (decomp.), prepared by the addition of bromine to phenyl methyl selenide, decomposes quantitatively at 100° into methyl bromide and bromoselenobenzene. The dibromide is converted by trituration at 40° with potassium iodide solution into the corresponding *di-iodide*, m. p. 69—71°. Trituration in the cold yields *phenyl methyl selenide bromoiodide*, m. p. 85° (decomp.), which is decomposed by heat into methyl iodide and bromoselenobenzene. *Phenyl ethyl selenide dibromide*, m. p. 84°, is decomposed by heat into ethyl bromide and bromoselenobenzene. *Phenyl methyl selenide dihydroxide*, a viscous oil, obtained by treatment of an aqueous solution of the dibromide with silver oxide and concentration of the filtrate in a vacuum, is decomposed by heat, yielding phenyl methyl selenide, diphenyl diselenide, and formaldehyde. *Phenyl ethyl selenide dihydroxide* is less stable and decomposes spontaneously, yielding mainly diphenyl diselenide. Phenylmethylselenetine bromide is decomposed at the m. p. into methyl bromide and phenylselenoglycollic acid, m. p. 36—37°, b. p. 197—198°/10 mm. (lit. m. p. 40°, b. p. 160°/750 mm.). *Phenylselenoglycollic acid dibromide*, m. p. 126°, is decomposed by heat into bromoselenobenzene and bromoacetic acid. p-*Tolylmethylselenine bromide*, obtained from *p*-tolyl methyl selenide and bromoacetic acid, is converted by heat into *p*-tolylselenoglycollic acid, and by treatment with a molecular proportion of bromine in cold carbon tetrachloride solution into *p*-tolylselenoglycollic acid dibromide, which is decomposed by heat into *p*-bromoselenotoluene and bromoacetic acid. Interaction of *p*-tolylselenoglycollic acid and excess of bromine yields p-*bromoselenotoluene dibromide*, m. p. 113—114° (decomp.), alternatively prepared by trituration of *p*-tolueneseleninic acid with concentrated aqueous hydrobromic acid or by reaction of bromine with di-*p*-tolyl diselenide. This substance is erroneously described by Morgan and Porritt (A., 1925, i, 1196) as *p*-tolylselenoglycollic acid tetrabromide. The sole product isolated from the interaction of phenyl ethyl selenide and bromoacetic acid was phenylselenoglycollic acid, owing presumably to the great instability of phenylethylselenetine bromide.

All the decomposition reactions described above support the contention that the withdrawal of aliphatic groups from their combination with quadrivalent selenium may be facilitated by their ability to provide a proton.

Diphenyl selenide dibromide, m. p. 154° (lit. 140°), is decomposed at the m. p. into *bromodiphenyl selenide* (?), m. p. 32—33°, and hydrobromic acid. Dibromodiphenyl selenide is obtained as a by-product (cf. Krafft and Lyons, A., 1894, i, 448). An improved method of preparation of diphenyl selenoxide, obtained by oxidation of diphenyl selenide with hydrogen peroxide, is described. M. CLARK.

Organo-antimony compounds. II. Constitution of *p*-amino[phenyl]stibinic acid and its amine salts. S. C. NIYOGY (J. Indian Chem. Soc., 1928, **5**, 285—291).—The following *salts* of *p*-aminophenylstibinic acid are described: *dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine,* iso*amylamine,* and *allylamine.* These salts dissolve in water to a red solution which becomes opaque after a few min., and are insoluble in all organic media except glycerol. Three mols. of the stibinic acid are combined with 1 mol. of base (cf. Schmidt, A., 1920, i, 900; 1922, i, 482). H. BURTON.

Isolation of pure *l*-proline. B. W. TOWN (Biochem. J., 1928, **22**, 1083—1086).—The hydrolysis products of gliadin are separated into three fractions by means of their copper salts, *i.e.*, copper salts soluble in water and in methyl alcohol, copper salts soluble in water but insoluble in methyl alcohol, and copper salts insoluble in both water and methyl alcohol. The proline is obtained from the first fraction, which also contains valine, hydroxyvaline, and phenylalanylproline, by dissolution in absolute alcohol and precipitation as the picrate, m. p. 148°. The proline thus obtained has a higher rotation ($[\alpha]_D^{18}$ $-86{\cdot}7°$) than those previously recorded. The phenylhydantoin, m. p. 143—144°, and *dl*-proline-phenylhydantoin, m. p. 118°, have also been prepared. There is also in the first fraction a product soluble in alcohol but giving no picrate and a product giving a picrate soluble in ether.

The second fraction contains glutamic acid as well as glycine, alanine, and serine, whilst phenylalanine, leucine, and aspartic acid are found in the third fraction. S. S. ZILVA.

Behaviour of polypeptides and their derivatives towards dilute alkali and acid. VII. *N*-Substituted polypeptides. E. ABDERHALDEN and P. MOLLER (Z. physiol. Chem., 1928, **176**, 207—216).—The fission of *N*-substituted *dl*-leucylglycines, $X{\cdot}NH{\cdot}CH(C_4H_9){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, where X=β-naphthoyl, phenylmethanesulphonyl, *p*-toluenesulphonyl, phenylacetyl, β-phenylpropionyl, phenylcarbamyl, and α-naphthylcarbamyl, by alkali is followed by Van Slyke's method, the products being an acyl-leucine and glycine. The rate of hydrolysis is greatly accelerated by the introduction of carboxylic acyl groups, but arylsulphonyl derivatives show no appreciable acceleration. In the carbamyl compounds particularly the peptide linking seems to be loosened. The preparation of β-*naphthoyl*- (m. p. 193—194°), *phenylmethanesulphonyl*- (m. p. 90°), p-*toluenesulphonyl*- (m. p. 120°), *phenylacetyl*- (m. p. 170°), and β-*phenylpropionyl*- (m. p. 187°) -dl-*leucylglycines* is described. C. HOLLINS.

Preparation of the unchanged modification of oxyhæmin and chlorohæmin. A. HAMSIK (Z. physiol. Chem., 1928, **176**, 173—186; cf. A., 1925, i, 845, 1476).—Details of the method previously outlined (coagulation of defibrinated blood with acetone, removal of chlorides, extraction with acetone and oxalic acid, and precipitation with sodium acetate or dilute hydrochloric acid) are given. Success depends on the rapidity of separating the precipitate from the mother-liquor. C. HOLLINS.

Iron porphyratins. The reversible side-chain reaction of hæmatin and the behaviour of hæmin and hæmatins towards acids. Preparation of hæmateric acid from hæmin and organic acids. O. SCHUMM and E. MERTENS (Z. physiol. Chem., 1928, **177**, 15—33; cf. A., 1927, 685, 798, 886; this vol., 80).—The four-stage reversible cycle of transformations of α-hæmatin is confirmed and extended to β-hæmatin and hæmin. The conversion into hæmateric acid (phase III) proceeds either in boiling hydrochloric acid or, better, in glacial acetic acid containing a little sulphuric acid. The partial saturation of the unsaturated side-chain of hæmin by boiling with 1% methyl-alcoholic hydrogen chloride is confirmed by analysis; the product ("dimethoxyhæmin dimethyl ester") is the tetramethyl compound of the iron complex salt of Nencki's hæmatoporphyrin. The cycle may be shortened to two phases, the product of phase I being reconverted directly by boiling glacial acetic acid into the original hæmatin. "Dimethoxyhæmin dimethyl ester" and the iron salt of Nencki's hæmatoporphyrin, when boiled with hydrochloric acid, yield a hæmatin-like substance distinguished from hæmatin by its greater stability towards hydrazine–acetic acid. The same or a similar compound is obtained from hæmatin and from hæmin by prolonged boiling.

The action of organic acids on hæmin and hæmatins varies considerably. Glacial acetic acid produces no structural change; 10% oxalic acid gives two different porphyrins, together with hæmateric acid; 70% lactic acid gives mainly hæmateric acid; pyruvic acid very readily converts pure hæmin into porphyrins, whilst with hæmin dissolved in aniline no removal of iron is observed; 10% solutions of malonic, succinic, tartaric, and citric acids have no effect; 98% acetic acid and 100% formic acid yield hæmateric acid. Hæmatins prepared by different methods differ in their resistance towards the action of boiling hydrochloric acid or 25% sulphonic acid. C. HOLLINS.

Preparation of hæmin derivatives. I. O. SCHUMM (Z. physiol. Chem., 1928, **176**, 122—126).—Hæmin is converted into mesohæmin by heating for a short time with a mixture of aniline and pyruvic acid, or with excess of aniline and acetic acid (reduced iron being added later), or with a mixture of hydrazine hydrate and aniline, *p*-toluidine, phenol, glycerol, glycol, amyl alcohol, olive oil, or liquid paraffin. With hydrazine hydrate alone heating under pressure

at 200° is necessary to bring about the change. By melting hæmin with resorcinol or pyrogallol some mesohæmin is first produced, and after 5—15 min. there is formed in good yield the iron complex salt of copratoporphyrin, the two stages being easily followed spectroscopically; stronger heating finally gives copratin, and by removal of iron with hydrazine and acetic acid copratoporphyrin and a yellow decomposition product are formed. Apparently no decarboxylation occurs. Nencki's hæmatoporphyrin behaves similarly. C. HOLLINS.

Resorption of copper and ferrocyanide ions by coagulated proteins. B. M. HENDRIX (J. Biol. Chem., 1928, **78**, 653—660).—From very dilute acid solutions copper is taken up almost completely by a suspension of coagulated egg-albumin, the proportion taken up increasing as the neutral point is approached. Similarly, the ferrocyanide ion is taken up in increasing amounts as the p_H decreases to 3·7. The constancy of the results obtainable with different preparations of protein at the same p_H indicates that the phenomenon is one of chemical combination rather than adsorption. C. R. HARINGTON.

Instability of serine–phosphoric acid chains and the general reaction of tyrins. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1928, **187**, 313—316).—Treatment of ovotyrin (1 mol.) with boiling *N*-sodium hydroxide yields pyruvic acid (2 mols.) and ammonia (4·2 mols.). Lactotyrin behaves in a similar way and in both cases the phosphorus is completely mineralised by alkali at the ordinary temperature. It is suggested that the first stage of the reaction is the fission of phosphoric acid groupings with the resultant production of a polypeptide, containing aminoacrylic acid chains, which is then hydrolysed to ammonia and pyruvic acid.

G. A. C. GOUGH.

Action of carbon monoxide on the autoxidation of thiol compounds. M. DIXON (Biochem. J., 1928, **22**, 902—908).—Carbon monoxide has no effect on the rate of the autoxidation of cysteine or reduced glutathione induced by the addition of iron, copper salts, or freshly-dissolved hæmatin. The last compound breaks up into a mixture of simpler compounds after keeping for several days. This mixture although retaining the catalytic power of the original hæmatin becomes susceptible to inhibition by carbon monoxide. S. S. ZILVA.

Characterisation of small quantities of proteins by Van Slyke's method. N. NARAYANA and M. SREENIVASAYA (Biochem. J., 1928, **22**, 1135—1137).—A description of a micro-method requiring 0·1—0·15 g. of protein. S. S. ZILVA.

Elementary organic analysis for carbon and hydrogen without the use of catalysts. I. MAREK (Bull. Soc. chim., 1928, [iv], **43**, 910—912).—See this vol., 82.

Electrically-heated furnace for organic combustions. M. PHILLIPS and R. HELLBACH (J. Assoc. Off. Agric. Chem., 1928, **11**, 393—396).—Five electrically-heated units of suitable dimensions are mounted on a parallel bar stand for the purpose of preheating the stream of oxygen, and for heating the oxidised copper coil, the boat containing the substance, the wire-form copper oxide, and the lead peroxide. The first four units are wound with asbestos-covered nichrome wire on mica-covered copper tubes to ensure an even temperature throughout. To control the temperature of the lead peroxide, the last unit consists of two concentric tubes of brass, of which the outer is suitably wound with nichrome wire, the annular space containing *p*-cymene and connecting to a pyrex reflux condenser.

F. R. ENNOS.

Determination of reducing sugars. N. SEMIGANOVSKY (Z. anal. Chem., 1928, **74**, 400—402).—A modification of Bertrand's method (A., 1907, ii, 136). The precipitated cuprous oxide is dissolved in the minimum amount of a solution containing 150 g. of sodium chloride, 27 g. of hydrochloric acid (*d* 1·19), and 5 g. of manganous sulphate tetrahydrate per litre. Potassium permanganate solution is added until a pink colour persists for a few seconds. The resulting cupric salt is determined iodometrically. J. S. CARTER.

Rapid determination of small quantities of phenol in glycerol solution. G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1927, **65**, 118—120; Chem. Zentr., 1928, i, 1558).—The solution (1 c.c.) is heated with Millon's reagent (2 c.c.) and acetic acid (0·2 c.c.) on a boiling water-bath for 5 min., and the red coloration compared with that of controls.

A. A. ELDRIDGE.

Biochemistry.

Blood-gases of the carp. H. WASTL (Biochem. Z., 1928, **197**, 363—380).—The oxygen content is 9·51 vol.-% and the carbon dioxide content is 44·86 vol.-% (mean values). The oxygen dissociation curve is much steeper and the carbon dioxide curves are much lower and flatter than the corresponding curves for warm-blooded animals.

The alkali reserve of the fish-blood is much smaller than that of warm-blooded animals.

H. W. DUDLEY.

Determination of carbon monoxide in blood. W. M. M. PILAAR (Chem. Weekblad, 1928, **25**, 509—513).—The various methods so far proposed are criticised. That of Tervaert (A., 1925, i, 710) gives fairly accurate results, but is open to objection. A micro-method of carrying out this determination is described, by which the carbon monoxide content may be determined in 1 c.c. of blood with an accuracy within 1%. S. I. LEVY.

Gasometric determination of hæmoglobin by the carbon monoxide capacity method. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1928, **78**, 807—819).—Blood is shaken in an atmosphere of carbon monoxide at 25 mm. pressure; the gases are expelled, the carbon monoxide–hæmoglobin

is decomposed with acid ferricyanide, and the carbon monoxide determined gasometrically; the whole operation is conducted in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to 0·1—2·0 c.c. of blood.

C. R. HARINGTON.

Gas and electrolyte equilibria in the blood. X. Solubility of carbon dioxide at 38° in water, salt solution, blood-serum, and corpuscles. D. D. VAN SLYKE, J. SENDROY, jun., A. B. HASTINGS, and J. M. NEILL. **XI. Solubility of hydrogen at 38° in blood-serum and corpuscles.** D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1928, **78**, 765—799, 801—805).—X. For distilled water at 38° the solubility coefficient of carbon dioxide is 0·5452, for blood-serum 0·509, and for red blood-corpuscles 0·45, the last value being determined by extrapolation from observed values for aqueous solutions of the cells. The reduction of the solubility in serum is due to a combination of the depressant effects of the salts and proteins and the augmenting effect of the lipins. The effect of mixtures of salts on the solubility of carbon dioxide is the additive effect of the individual ions. Neither blood-serum nor solutions of blood-corpuscles showed any deviations from Henry's law.

XI. Coefficients of 0·01620, 0·01559, 0·01533, and 0·01454 were found for the solubility of hydrogen in water, 0·15*M*-sodium chloride, ox-blood-serum, and ox-blood-corpuscles, respectively, at 38°; consideration of the relative amounts of water present in the various cases indicates that the organic constituents of the blood dissolve appreciable amounts of hydrogen.

C. R. HARINGTON.

Relation of copper to hæmoglobin content of rat blood. J. S. MCHARGUE, D. J. HEALY, and E. S. HILL (J. Biol. Chem., 1928, 78, 637—641).—Dried blood-serum of cows contains 0·0044% of copper and dried calf liver 0·0125%. Increase in the hæmoglobin of the blood of rats on a milk diet was observed on administration of the ash of calf liver; no such effect was obtained after removal of copper from the ash (cf. Hart and others, this vol., 790).

C. R. HARINGTON.

Reversible transformation of cathæmoglobin. B. JIRGENSONS (Biochem. Z., 1928, **198**, 206—208).—Cathæmoglobin changes reversibly at about 70° into hæmatin and globin.

P. W. CLUTTERBUCK.

Hæmochromogen, reduced hæmatin, and carboxyhæmatin. C. DHERÉ (Compt. rend. Soc. Biol., 1927, **97**, 1660—1663; Chem. Zentr., 1928, i, 1675).—An alcoholic (50—60%), slightly acid solution of reduced hæmatin, when sealed, acquires a red colour, and the absorption bands (564—528 μμ) are equivalent to those of ordinary hæmochromogen. The pigment is named "acid carboxyhæmatin" or "acid carboxyhæmochromogen."

A. A. ELDRIDGE.

The spleen as the regulator of the amino-acid equilibrium of the blood. I. Influence of splenectomy on the amino-acid content of the blood, red corpuscles, and plasma. II. Influence of denervation of the spleen on the amino-acid content of the blood, red corpuscles, and plasma. L. TUTKEVITSCH (Biochem. Z., 1928, **198**, 47—59, 60—64).—I. Intravenous injection of amino-acids brings about within the first 10 min. a decrease of the amino-acid content of the corpuscles. Splenectomy in dogs and rabbits causes the disappearance of this phenomenon, and injection of amino-acids is then always accompanied by an increase in both corpuscles and plasma. The spleen is therefore responsible for the power of the erythrocytes to adsorb amino-acids and splenectomy causes the disappearance of this power, the amino-acids being displaced by some other nitrogenous substance of the plasma.

II. Differences in the amino-acid content of the blood of animals after splenectomy and after denervation of the spleen are indicated and discussed in correlation with the non-penetration of the spleen by carbon monoxide in Barcroft's experiments.

P. W. CLUTTERBUCK.

Fractionation of serum-proteins by ammonium sulphate. A. MUSCHEL (J. Biol. Chem., 1928, **78**, 715—718).—Blood-serum is diluted and the total nitrogen determined in one portion; the globulin is removed from a second portion by half saturation with ammonium sulphate and the albumin+non-protein nitrogen determined in the mother-liquor after removal of ammonia by treatment with magnesium oxide and aeration. Finally, the non-protein nitrogen of the serum is determined in the usual manner.

C. R. HARINGTON.

Relation of the viscosity of blood-serum to temperature and the hydration of the proteins. L. DU NOUY (Ann. Inst. Pasteur, 1928, **42**, 742—769).—The viscosity of the blood-serum of rabbits, determined from the moment exerted on a cylinder suspended in a larger, rotating cylinder containing the liquid, is least at 57°. Heating for 1 hr. at 55° does not increase the viscosity, but heating above 56° causes an irreversible increase. Under these conditions the viscosity may be increased threefold, and by an application of the principles of Einstein (Ann. Physik, 1911, [iv], **34**, 591) to the results, the degree of hydration of the protein micelles may be calculated.

G. A. C. GOUGH.

Refraction differences [of serum and plasma]. I—IV. F. HOGLER and K. UEBERRACK (Z. ges. exp. Med., 1927, **58**, 22—39, 40—50, 51—75, 76—80; Chem. Zentr., 1928, i, 1541—1542).—A study of the changes in the difference in refractivity between plasma or serum and the value calculated for the protein in various physiological and pathological conditions. There is no parallelism between refractivity and fibrinogen content.

A. A. ELDRIDGE.

Effect of sodium citrate, acetate, and lactate on ultrafiltrability of serum-calcium. D. H. SHELLING and H. L. MASLOW (J. Biol. Chem., 1928, 78, 661—669).—Injection of 1 c.c. of a 30% solution of sodium citrate causes convulsions and death in normal rabbits; the blood of rabbits so treated contains a normal amount of calcium, but the latter can be filtered almost entirely through collodion membranes. No such effects were observed after injections of sodium acetate and lactate. Apparently, therefore, the citrate acts by the formation of a diffusible undissociated compound with the calcium.

C. R. HARINGTON.

Modification of the Widmark micro-method for the determination of alcohol in blood. A. Galamini and L. Bracaloni (Arch. Farm. sperim., 1928, **45**, 97—112).—The apparatus of Widmark (cf. A., 1922, ii, 789) is modified in order to include a micro-pipette. E. W. Wignall.

Modified Salkovski reaction for the determination of cholesterol in blood-serum. D. Abramsohn (Biochem. Z., 1928, **198**, 233—240).—Krastalevski's modification (A., 1924, ii, 127) of the Salkovski reaction is adapted for use at the ordinary temperature, when the yellowish-orange phase lasts 20—40 min., according to the amount of cholesterol present. P. W. Clutterbuck.

Colorimetric determination of lævulose in blood by the diphenylamine method. P. Radt (Biochem. Z., 1928, **198**, 195—203).—A colorimetric method for determining small amounts of lævulose in aqueous solution and in blood is elaborated and the normal variation in the blood of a fasting animal is investigated. P. W. Clutterbuck.

Action of glycine on blood-sugar. G. Paasch (Biochem. Z., 1928, **197**, 460—466).—Glycine, intravenously or subcutaneously administered to dogs and rabbits, produces only slight increases in the amount of blood-sugar. If hyperglycæmia is caused this may not be due to the action of the amino-acid itself. W. McCartney.

Distribution of bismuth in the blood. S. Lomholt (Biochem. Z., 1928, **198**, 98—102).—The predominating amount of bismuth, after absorption, is found attached to plasma-protein and may be precipitated in three fractions, the first with 37%, the second with 50% ammonium sulphate, and the third by boiling. A small amount is associated with the leucocytes, but the red cells contain either no bismuth or a very small amount. The ultrafiltrate of the plasma contains no detectable amount of bismuth nor do the lecithins of the plasma when precipitated with absolute alcohol at about 15°. P. W. Clutterbuck.

Absorption and solubility coefficients of chloroform vapour in water, blood, serum or plasma, and milk. M. Nicloux and L. Scotti-Foglieni (Compt. rend. Soc. Biol., 1927, **97**, 1720—1724; Chem. Zentr., 1928, i, 1493).—Henry's law is followed for a chloroform vapour pressure of 10 mm. The solubility of chloroform vapour in water does not increase regularly with rise of temperature, the anomaly being comparable with the irregular solubility of liquid chloroform in water. For whole blood the solubility is greater than for serum or plasma, and for serum or plasma greater than for water. It is greater for pig's than for human or ox blood, which give almost identical values. For milk the coefficient is 3—4 times as great as for blood. A. A. Eldridge.

Non-protein serum-colloids and their biological significance. K. Nikaido (Biochem. Z., 1928, **198**, 175—194).—A substance is present in the serum of rabbit, horse, and man which inhibits the agglutination of red cells by jack-bean extracts, the activity being greater when the agglutinin is purified and gradually added to the serum, than when serum is added to the agglutinin. The inhibition is best obtained at p_H 7. The active substance is salted out of serum by 60% saturation with ammonium sulphate. Edestin also has a slight agglutinating action and inhibits to some extent the jack-bean agglutination, but caseinogen neither agglutinates nor inhibits. The inhibitory substance is insoluble in ether, alcohol, acetone, and chloroform, and is not injured by these solvents. When serum is deproteinised with potassium dihydrogen phosphate, a highly active, protein-free inhibiting solution is obtained. Before deproteinisation, the substance is only slightly adsorbed by kaolin, but after deproteinisation it is completely adsorbed. It is only slightly adsorbed by cholesterol either before or after deproteinisation and is neither dialysable nor electrodialysable, but in the latter case is carried down as precipitation proceeds. It is retained on the ultrafilter. Glycogen, colloidal copper and iron, and silicic acid do not inhibit jack-bean agglutination. The substance is resistant to putrefaction and fairly resistant to boiling with acids and alkalis. It does not appear to be present in normal human urine or saliva. P. W. Clutterbuck.

Alleged acceleration of taurocholate hæmolysis by normal serum. K. C. Sen and N. K. Sen (J. Indian Chem. Soc., 1928, **5**, 261—268).—Sucrose appears to have an inhibitory effect on the hæmolysis, by sodium taurocholate, of human and sheep's erythrocytes, and normal serum inhibits hæmolysis in both normal saline and isotonic sucrose solutions. No acceleration of hæmolysis was observed (cf. Ponder, A., 1923, i, 975), except in experiments using small amounts of corpuscles. Serum inhibits the hæmolytic action of potassium oleate in isotonic sucrose solution. Inhibition is not due entirely to the sensitising action of serum on the membrane constituents (Sen and Basu, this vol., 663), but also to the large adsorption of serum on the surface of the stroma, where it displaces the adsorbed hæmolyte from the cell surface. H. Burton.

Hæmolysis. II. K. Klinke (Biochem. Z., 1928, **197**, 381—403).—The hæmolysin (amboceptor) is adsorbed on the erythrocytes and modifies the structure of the membranes in such a way that the actual lysis is enabled to take place. This consists in the adsorption of the modified constituents of the membranes on the serum-euglobulin. H. W. Dudley.

Permeability. I. Traube and F. Dannenberg (Biochem. Z., 1928, **198**, 209—224).—A critical examination of the existing theories of permeability is carried out and the "pore" theory as applying to gels is dismissed. Permeability, *e.g.*, of the vascular system, depends to a large extent on the material of the wall and on the substances in the body fluids which become concentrated on the wall in virtue of their surface activity. P. W. Clutterbuck.

p_H of fish muscle. C. C. Benson (J. Biol. Chem., 1928, **78**, 583—590).—The resting muscle of haddock has an alkaline reaction, which, after death, becomes acid; if the fish be killed after struggling, however, the muscle is already acid at death and does not change much afterwards. Hake muscle remained alkaline long after death, whilst cod muscle remained

near the neutral point. The onset of *rigor mortis* cannot therefore be due to increasing hydrogen-ion concentration. C. R. HARINGTON.

Vaccenic acid. A fatty acid from beef, mutton, and butter fats. S. H. BERTRAM (Biochem. Z., 1928, **197**, 433—441).—The acid, which occurs in quantities varying from about 0·01% (butter fat) to about 1·0% (beef fat) was shown to be a $\Delta^{11:12}$-*elaidic acid*. The purest sample obtained, crystallised from cooled acetone, had m. p. 39°, solidif. pt. 35·5°, iodine value (Hübl) 86·5°, d^{70} 0·85601.
W. McCARTNEY.

[Normal and pathological] human fat. A. HEIDUSCHKA and C. HANDRITSCHK (Biochem. Z., 1928, **197**, 404—409).—Small amounts of a higher unsaturated fatty acid, possibly arachidic acid, were found in one sample. Acids other than oleic, palmitic, and stearic acids were not encountered. The physical and chemical constants of normal and pathological fats were determined, but no appreciable distinctions could thus be made.
W. McCARTNEY.

Histological use of formaldehyde as preservative. J. MILLOT and A. GIBERTON (Compt. rend. Soc. Biol., 1928, **97**, 1674—1675; Chem. Zentr., 1928, i, 1443).—Formaldehyde does not inhibit changes in fat, which take place after 3 weeks, with disappearance of lipins and production of fatty acids. The rapidity of the change varies with the origin; fish liver changes most rapidly. The decomposition is attributed to a lipase which is active in the presence of formaldehyde, and is more rapid at 35—40° than at the ordinary temperature. A. A. ELDRIDGE.

Reversible crystallisation in tendons and its functional significance. J. H. CLARK (Proc. Nat. Acad. Sci., 1928, **14**, 526—532).—*X*-Ray pinhole diagrams have been investigated in the case of moist tendons and ligaments. The results show that collagen exists normally in skin and tendons as liquid crystals. The molecules are so arranged that *X*-ray reflexion takes place from planes with a spacing of approximately 6·2 Å. On stretching a living tendon some of the liquid crystals change to solid crystallites, arranged in fibre formation, the crystal units being one half the size of the molecules in the liquid crystal form. Depolymerisation thus occurs on stretching. The liquid crystals also change to the solid crystal form on dehydration. The formation of solid crystals in collagen probably increases its cohesion. Elastin also exists normally in the liquid crystal state, but does not form solid crystals on moderate stretching, although they may appear at the limit of extension. The *X*-ray diagram for elastin gives a different spacing from that for collagen.
A. J. MEE.

Artefacts as a guide to the chemistry of the cell. C. E. WALKER (Proc. Roy. Soc., 1928, **B**, **103**, 397—403).—When methyl myristate, or methyl laurate, in which yellow phosphorus has been dissolved, is added in the form of an emulsion to certain colloidal mixtures and kept at a temperature of 30°, the microscopical appearances presented on fixation and treatment with osmic acid show that in about 2 hrs. a large proportion of the lipins is distributed over the globules, whilst after about 24 hrs. most of the fatty acids of the lipins have become saturated or oxidised. W. O. KERMACK.

Copper content of milk. G. N. QUAM and A. HELLWIG (J. Biol. Chem., 1928, **78**, 681—684).—Cow's and sheep's milks contain 0·4—0·5 mg. per litre, goat's milk 0·2 mg. per litre, of copper. Pasteurised and condensed milks contain considerably greater amounts of copper which must have been introduced artificially. C. R. HARINGTON.

Biochemical studies of iodine. K. SCHARRER (Z. angew. Chem., 1928, **41**, 980—982).—No ill effects followed the administration of iodine to milking goats even in doses of 60—180 mg. (as sodium iodide) per animal daily. Temporary increases in milk yields were observed, and at these periods the fat yield increased although the actual fat percentage declined. Very brief increases in the iodine content of milk occurred. Small doses of iodine (as iodide) tended to delay the decline of milk yield in the later stages of lactation. Following the use of iodised rations increases in the iodine content of the liver and kidneys, but in no other organs, were noted. The milk of cows feeding on the marsh lands of the North Sea coast had a higher iodine content than those of southern Germany.

Iodine in small amounts (as potassium iodide) accelerated the reproduction of yeasts without any notable increase in the total weight of yeast produced. Yeast appears in hold iodine to some form of loose combination. Toxicity of iodine compounds to yeast varied in the order iodide>iodate>periodate. The combined base exerts considerable effect on the toxicity of these compounds. A. G. POLLARD.

Determination of minute quantities of metals in biological material. I. Determination of lead in urine. H. B. TAYLOR (J. Proc. Roy. Soc. New South Wales, 1927, **61**, 315—336).—An accurate method for the determination of small quantities of lead in urine is described, based on the fact that it is completely adsorbed on calcium oxalate in solutions of 4—5. The lead is then determined nephelometrically after addition of sodium hydrogen sulphite.
C. W. GIBBY.

Role of biocatalysts in carbohydrate metabolism of carcinoma. H. VON EULER and H. JOHANSSON (Svensk Kem. Tidskr., 1928, **40**, 209—218).—Cancerous tissue (liver) has been tested for its content of the activator *Z* (cf. Euler and Swartz, A., 1925, i, 209) using extracts of the tissue, finely-divided tissue, or dry tissue, and when compared with normal tissue it is deficient in the *Z* factor. The results are somewhat complicated by the presence in the tissue of inhibiting factors. It has been found possible to effect considerable concentration of the *Z* factor from tumour tissues by means of a method dependent on precipitation by salts of the heavy metals. Extract from cancerous tissues increases the consumption of oxygen by yeast, but apparently not quite as markedly as does a similar extract of the corresponding normal tissue.
W. O. KERMACK.

Cholesterol content of blood-serum after irradiation with *X*-rays. E. HUBERT (Klin. Woch.,

1928, **7**, 208—211; Chem. Zentr., 1928, i, 1677).—After irradiation of carcinomatous tissue a marked fall in serum-cholesterol is observed.

A. A. ELDRIDGE.

Genesis of diabetic hyperglycæmia. E. J. LESSER (Klin. Woch., 1928, **7**, 25—26; Chem. Zentr., 1928, i, 1540—1541).—Polemical. The speed of glycogenolysis in the isolated frog's liver does not depend on the sugar content. Glycogenolysis is inhibited by products thereof in sufficiently high concentration. An extract of these products does not alone raise the sugar value in the liver cells, since ferment and substrate must be brought together.

A. A. ELDRIDGE.

Insulin resistance in diabetes. F. DEPISCH and R. HASENOHRL (Z. ges. exp. Med., 1927, **58**, 110—116; Chem. Zentr., 1928, i, 1540).—The serum of a patient (paranephritic abscess) refractory towards insulin, when administered intravenously or subcutaneously to rabbits, diminished the action of insulin. The pus decomposed insulin after being heated for 2 hrs. at 80° or in presence of phenol.

A. A. ELDRIDGE.

Employment of dihydroxyacetone ("oxantin") in diabetes. M. GROSSMANN and S. POLLAK (Klin. Woch., 1928, **7**, 211—213; Chem. Zentr., 1928, i, 1677).—The blood-sugar falls after a short rise; acidosis is favourably affected. A. A. ELDRIDGE.

Primula idiosyncrasy. B. BLOCH and P. KARRER (Vierteljahrsschr. naturforsch. Ges. Zurich, 1927, **72**, Beibl. No. 13, 1—26; Chem. Zentr., 1928, i, 1535).—From the ethereal extract of the green leaves of *Primula obconica* was obtained a small yield of the toxic principle, *primin*, $C_{14}H_{18}O_3$ or $C_{14}H_{20}O_3$, golden-yellow, m. p. 62—63 , volatile with steam; one oxygen atom is present as hydroxyl, and the others apparently as lactone groups. Primin immediately decolorises potassium permanganate in acetic acid, and reduces ammoniacal silver nitrate solution at the ordinary temperature; in cases of primula idiosyncrasy it causes eczematous dermatitis clinically identical with spontaneous primula dermatitis.

A. A. ELDRIDGE.

Nitrogen balance and the urinary C : N coefficient in experimental scurvy, without complication by hunger. N. JARUSSOVA (Biochem. Z., 1928, **198**, 128—137).—By maintaining an animal on a scorbutic diet which is sufficient to maintain its body-weight, the nitrogen balance passes during development of scurvy from positive to negative values. The change in nitrogen secretion is insignificant. Increased decomposition of protein therefore does not, but impairment of the utilisation of food-nitrogen does, occur. The absolute amount of urinary carbon, and therefore the urinary C : N ratio also, is increased. P. W. CLUTTERBUCK.

Total chloride concentration and acidity of the gastric contents. F. D. GORHAM, C. M. STROUD, and M. HUFFMANN (Arch. Int. Med., 1928, **42**, 106—116).—The total chloride concentration and acidity of the contents of the stomach after fasting and after oral administration of water and phenolsulphonphthalein show wide variations under pathological conditions (increase in cases of pyloric stenosis and duodenal ulcer), but approach the same value (in many instances similar to that of the normal blood-plasma) in normal subjects. The relation between the total acidity and the chloride concentration during fasting and of the gastric chyme after a test meal varies in normal subjects and even more under pathological conditions where the total acidity shows the greatest fluctuation (cf. Guy's Hosp. Rep., 1924, **74**, 40). G. A. C. GOUGH.

Alkalosis in patients with peptic ulcer. W. E. GATEWOOD, O. H. GAEBLER, E. MUNTWYLER, and V. C. MYERS (Arch. Int. Med., 1928, **42**, 79—105).—At a certain period a third of these cases showed uncompensated alkalosis, and alkalosis accompanied by high carbon dioxide content occurred in the remainder. Treatment with sodium hydrogen carbonate leads often to an increase in the alkalæmia and generally to a rise in the blood hydrogen carbonates and a fall in the chloride content of the plasma, whilst calcium carbonate or magnesium oxide seldom increases alkalæmia. G. A. C. GOUGH.

***Post mortem* increase of lactic acid in the brain substance of animals.** M. E. MAYER (Arch. exp. Path. Pharm., 1928, **134**, 218—224).—Dogs and calves subjected to various experimental procedures show an increase in the lactic acid in the brain after death as compared with the normal content, this increase being more marked in the grey substance than in the white. Similar results are also obtained with cats. W. O. KERMACK.

Clinical calorimetry. XLII. Effect of dextrose and of dihydroxyacetone on metabolism. W. S. MCCLELLAN, A. BIASOTTI, and R. R. HANNON (J. Biol. Chem., 1928, **78**, 719—744).—Ingestion of dihydroxyacetone caused a rise in the respiratory quotient due to increased elimination of carbon dioxide. Heat production was increased to about the same extent as by dextrose. In normal individuals the blood-sugar fell; in diabetics it rose, but to a less extent than after dextrose. Acid phosphomolybdate-reducing substances (including dihydroxyacetone) were not increased in the blood of normal or diabetic individuals after ingestion of dihydroxyacetone or of dextrose; they were slightly increased in the urine in the former case. C. R. HARINGTON.

Mineral metabolism of the growing chick. F. E. MUSSEHL, M. J. BLISH, and C. W. ACKERSON (Poultry Sci., 1927, **6**, 239—242).—The addition of bone meal, calcium carbonate, or a mixture of these materials with sodium chloride, to a basal ration which was complete for vitamins, proteins, and mineral substances retarded the growth and increased the mortality of chickens. CHEMICAL ABSTRACTS.

Phosphorus metabolism. II and III. A. J. CHARIT (Arch. Sci. Biol., 1928, **28**, 145—147, 148—154).—I. Blood leaving the spleen of dogs is richer in inorganic phosphorus than that entering, when the animal has performed muscular work, has been fed with substances containing phosphorus in organic combination, or is under the influence of insulin, the difference amounting in the first two cases to about 1 mg. %, on the average. This difference is apparently due to the elimination of phosphoric acid from organic

compounds containing phosphorus by an agent present in the spleen.

II. The subcutaneous injection of adrenaline into dogs and rabbits reduces the inorganic phosphorus content of the blood by 28—30%. No further diminution can be produced by administration of dextrose or insulin during adrenaline hypophosphæmia. The inorganic phosphorus of the blood would hence appear to consist of two types: one capable of combining with carbohydrates, and the other not entering into this reaction. R. TRUSZKOWSKI.

Metabolism of the bile. II. Changes in blood and bile following intravenous injection of bile or of its constituents. C. H. GREENE and A. M. SNELL (J. Biol. Chem., 1928, **78**, 691—713).—Intravenous injection of bile acids or of bilirubin is followed by rapid elimination of the excess by excretion in the bile. The elimination is most rapid in the case of the bile acids which have a cholagogue action, and of which the excess is excreted by increase in the volume of bile; bilirubin, on the other hand, is eliminated more slowly and by means of increased concentration of the bile. Injections of whole bile give similar results except that the process is slower. C. R. HARINGTON.

Metabolism of tryptophan. II. Synthesis of 6-methyl- and 8-methyl-kynurenic acids. W. ROBSON.—See this vol., 1141.

Metabolism of tryptophan. III. Mode of formation of kynurenic acid from tryptophan. W. ROBSON (Biochem. J., 1928, **22**, 1165—1168).—*Bz*-3-Methyltryptophan or 8-methylkynurenic acid when injected into the rabbit is completely burnt. 6-Methylkynurenic acid, on the other hand, can be recovered from the urine of the animal almost quantitatively. In the formation of kynurenic acid from tryptophan, therefore, the pyrrole-nitrogen of the latter compound is eliminated and the side-chain with its amino-nitrogen forms the new pyridine ring. S. S. ZILVA.

Comparative nutrient value of the proteins of linseed meal and cotton-seed meal for different animals. R. M. BETHKE, G. BOHSTEDT, H. L. SASSAMAN, D. C. KENNARD, and B. H. EDINGTON (J. Agric. Res., 1928, **36**, 855—871).—The effect of these meals varied considerably with the type of animal used in nutrition experiments, and in the case of chickens with age. Cotton-seed meal showed toxic effects with pigs. In digestibility and biological value the two meals were equally valuable as supplementary protein foods for rats and calves. For young chickens cotton-seed meal was slightly superior. A. G. POLLARD.

Fate of foreign fats in the organism. L. SCHEFFER (Arch. exp. Path. Pharm., 1928, **134**, 66—73).—After the injection of "iodopin" (a fat containing iodine) into the jugular vein of a well-nourished dog very little or none is immediately deposited in the fatty tissue, but after 48 hrs. 98% and after 72 hrs. 70% is still found in the liver in an unaltered condition. W. O. KERMACK.

Fat metabolism after splenectomy. S. LEITES (Biochem. Z., 1928, **198**, 157—162).—After splenectomy, hydrolysis of fat, probably in the liver, is disturbed and partly transferred to the lungs, whilst decomposition of acetone substances is retarded, especially at the periphery. In splenectomised animals, feeding of fat leads to acetonæmia, which is not diminished by simultaneous administration of dextrose. The dextrose, however, does increase the hypercholesterolæmia accompanying fat feeding. P. W. CLUTTERBUCK.

Fat and lipin metabolism. VIII. Degradation of fat in the animal organism. S. LEITES (Biochem. Z., 1928, **197**, 357—362).—After administration of oleic acid to dogs an increase in the amount of ketonic substances in the blood of the right heart and arteries is observed. Olive oil or olive oil and cholesterol, orally administered, cause an increase in the amount of these substances in the blood of the right heart and of the femoral vein, and the increase in that vein is accompanied by a decrease in the amount of neutral fat. Administration of fat also results in the formation of ketonic substances in the liver and lungs and peripherally. The retention of neutral fat in the lungs of normal dogs is not accompanied by any degradation of the fat with formation of ketonic substances; these are apparently formed in the lungs from free higher fatty acids. Dextrose exerts its antiketogenic effect in the liver and peripherally, but not in the lungs. Dextrose given with oleic acid produces considerably greater hypercholesterolæmia than does the administration of oleic acid alone. The decomposition of the ketonic substances occurs in the lungs and peripherally. W. MCCARTNEY.

Lipins and metabolism. H. REITER and W. REISSMANN (Klin. Woch., 1928, 7, 306—307; Chem. Zentr., 1928, i, 1678).—In rats lack of lipins leads to increased degradation of protein; subsequent administration of lipin in the form of "Promonta" has a protein-sparing effect. A. A. ELDRIDGE.

Phosphatide content of organs after administration of large amounts of phosphatide. B. REWALD (Biochem. Z., 1928, **198**, 103—111).—Administration of large amounts of phosphatide over prolonged periods does not appear to affect the health of the animal and 90% is absorbed. After administration for one month, considerable storage occurs, particularly in the brain, kidney, and liver. The phosphatide content of the blood is also increased. P. W. CLUTTERBUCK.

Dehydrogenation processes with choroid membranes of albino and pigmented animals. A. CUCCHIA (Arch. Farm. sperim., 1928, **45**, 67—74).—Contrary to expectation on the oxidation theory of albinism and pigmentation, there is no distinct difference between the rates of reduction of *m*-dinitrobenzene by the choroid membranes of eyes of albino and of pigmented rabbits. E. W. WIGNALL.

Chemical factors which determine the deposition of colloids. G. SPAGNOL (Atti R. Accad. Lincei, 1928, [vi], 7, 667—670).—In continuance of previous work, experiments have been made on the effect of chloroform, ethyl ether, and carbon tetrachloride (applied to the skin) on the deposition in the tissues of numerous colloids, both electropositive and electronegative, after their intravenous injection into

various animals. The deposition occurs in the locality to which the reagent has been applied. With chloroform, after an application for 5—15 sec., the deposition occurred in the skin and in the subcutaneous tissue; with longer application (1—2 min.) a certain amount of deposition occurred also in the underlying muscles. Negative results were obtained if the application of the chloroform preceded the injection of the colloid by an hour. The optimum conditions were represented by the application of the chloroform for 15—20 sec., when the infiltration of the colloid into the tissues was manifest after 5—10 min., and was complete after 1 hr. Injections of dilute aqueous solutions of amylene hydrate and of ethylurethane gave similar results. This infiltration is attributed to an enhanced permeability of the blood capillaries.

F. G. TRYHORN.

Strengths of action of alkaloids and their degree of hydrolysis in buffered solutions as a function of hydrogen-ion concentration of the medium. S. MAYEDA (Biochem. Z., 1928, **197**, 410—417).—Mathematical and theoretical considerations led to the following conclusions which have been experimentally verified for the cinchona alkaloids. The degree of hydrolysis of a hydrolysable salt in a medium, the hydrogen-ion concentration of which is regulated, is a function of the p_H. For a salt from a strong acid and a weak base having a particular dissociation constant, the degree of hydrolysis can be calculated from an equation which is given. For the same dissociation constant the equation is identical with that for the dissociation curve of a weak base. The dependence of the biological action of the cinchona alkaloids on the p_H is to be traced solely to the base set free by hydrolytic dissociation; theoretically this should hold for other alkaloids also. The free quinine base alone is the bearer of the biological activity. Considered physicochemically, the action of the alkaloids on the free living micro-organisms is a process of adsorption.

W. MCCARTNEY.

Pharmacological differentiation of the *Solanaceæ* alkaloids. F. GARCIA (Arch. exp. Path. Pharm., 1928, **134**, 149—154).—The narcotic action of ether vapour on mice is increased by the administration of atropine, hyoscyamine, or scopolamine to the animals. These three alkaloids show this effect in different degrees and this circumstance is combined with a chemical method for the purpose of differentiating and determining the three alkaloids.

W. O. KERMACK.

Toxicology of certain chlorine derivatives of methane and ethane. G. A. HALOFF (Arch. exp. Path. Pharm., 1928, **134**, 168—172).—Chloroform and carbon tetrachloride produce fatty degeneration of the liver, whilst dichloromethane, ethylene dichloride, ethylidene chloride, and hexachloroethane have no such action.

W. O. KERMACK.

Transformation of benzene in the organism and a method for the determination of benzene. I. D. GADASKIN (Biochem. Z., 1928, **198**, 149—156).—A colorimetric method is described for the determination of benzene, depending on its nitration, reduction of the nitro-compound, and subsequent treatment with dimethyl-*p*-phenylenediamine. This test is sufficiently delicate to detect qualitatively sublethal amounts of benzene when present in blood. The toxic effect of benzene is the sum of its own toxicity and that of phenol arising by oxidation.

P. W. CLUTTERBUCK.

Solubility in stomach and duodenum of aluminium compounds found in baking powder residues. V. C. MYERS and J. A. KILLIAN (J. Biol. Chem., 1928, **78**, 591—594).—After administration to normal human subjects of 15—90 mg. of aluminium in the form of biscuits baked with aluminous baking powders, 2—20% of the aluminium was found in solution in the gastric contents and similar amounts in the duodenal contents.

C. R. HARINGTON.

Influence of administration of aluminium on aluminium content of tissues and on growth and reproduction in rats. V. C. MYERS and J. W. MULL. **Influence of aluminium on dogs.** V. C. MYERS and D. B. MORRISON. **Aluminium content of human autopsy tissue.** V. C. MYERS and J. W. MULL (J. Biol. Chem., 1928, **78**, 605—613, 615—624, 625—626).—Oral administration of 2 mg. of aluminium *per diem* had little or no effect on the aluminium content of the tissues or on the growth of rats. Intraperitoneal injection of aluminium was followed by an increase in the aluminium content of various tissues, particularly of the liver, of which the aluminium content rose to 8·22 mg.% as against the normal value of 0·14 mg.%. Similar results were obtained in dogs except that the aluminium content of the liver could be raised somewhat by oral administration of aluminium. The increased aluminium content of the tissues resulting from injection of aluminium was maintained for a considerable period after administration had ceased; excretion is therefore slow. Figures are given for the aluminium content of various human tissues determined at autopsy.

C. R. HARINGTON.

Determination of aluminium in animal tissues. V. C. MYERS, J. W. MULL, and D. B. MORRISON (J. Biol. Chem., 1928, **78**, 595—604).—The tissue is incinerated with a mixture of sulphuric and perchloric acids; a trace of iron is added and then iron and aluminium are precipitated together by ammonia solution; the precipitate is re-dissolved and the iron alone removed with sodium hydroxide and acetic acid; the aluminium in the mother-liquor is determined colorimetrically by means of aurintricarboxylic acid. The method is applicable to the determination of 0·01—1·0 mg. per 100 g. of tissue with an error of $\pm$10%.

C. R. HARINGTON.

Determination of arsenic in cadavers. R. FRIDLI (Ber. ungar. pharm. Ges., 1926, **2**, 84—87; Chem. Zentr., 1928, i, 1561).—The arsenic is separated as the element with Bettendorf's reagent, and weighed as such or as magnesium ammonium arsenate hexahydrate.

A. A. ELDRIDGE.

Detection of arsenic in ashes of cremated corpses. G. POPP (Z. angew. Chem., 1928, **41**, 856—858).—Three experiments carried out on dogs to which arsenic had been administered showed that the arsenic detected in the calcined bones is about one sixth of the amount found in the bones before cremation, and less than one thousandth of the total

amount in the whole body before cremation. In each case, the liver was incompletely calcined, although the calcined bone ashes were white, and in one case, in which morphine was injected before death, the alkaloid was detected in the charred liver remains.

S. I. LEVY.

Distribution of boric acid in human organs in six deaths due to boric acid poisoning. W. D. McNALLY and C. A. RUST (J. Amer. Med. Assoc., 1928, **90**, 382—383). CHEMICAL ABSTRACTS.

Distribution of gold in the organs of healthy and tuberculous rabbits following administration of gold preparations. I. Non-tuberculous rabbits. B. BRAHN and G. WEILER (Biochem. Z., 1928, **197**, 343—352).—A gold thiocarbamide compound ("lopion") containing 42% of gold, another organic compound ("preparation No. 2950"; 21·9% Au), and gold sodium thiosulphate, $(S_2O_3Au)Na,Na_2S_2O_3$ ("sanocrysin"; 37·35% Au), were the substances used, and the gold content of the kidneys, liver, lungs, spleen, heart, intestine, stomach, brain, bones, skin, and flesh was determined. The method adopted for the determination of the gold made it possible to determine accurately as little as 0·001 mg. In the experiments with "lopion" the chief amount of gold was found in the liver, whereas in those with the other two compounds by far the greatest amount was always found in the kidneys. The ratio of the amount of the element in the liver to that in the kidneys was about 3 : 1 when "lopion" was used, but when "preparation 2950" was used the ratio of the quantity of gold in the kidneys to that in the liver increased in proportion to the shortness of the time in which the animal died after injection. "Lopion" almost always caused high values for the gold content of the spleen, "sanocrysin" gave considerably lower figures, and with "preparation 2950" very low values were obtained. All three substances gave about the same, not very high, value for the content of the lungs. "Preparation 2950" gave lower amounts of gold in the heart than did the other two compounds. Almost throughout, the lowest values of all were for the brain. For the remaining organs very great variations were found. The toxicity of the three preparations used appeared to be proportional to the amount of gold which accumulated in the kidneys. Usually animals treated with "sanocrysin" lost weight considerably. The ratio of gold recovered from the organs to gold administered varied rather appreciably. The highest value found was 67·15%, "lopion" having been the compound used. W. McCARTNEY.

Mobilisation of mercury from sparingly soluble depots by halogen salts. F. GARCIA (Arch. exp. Path. Pharm., 1928, **134**, 142—148).—Rats to which a sparingly soluble mercury salt (calomel, mercuric oxide, di-iodide, or salicylate) had been administered in the form of a subcutaneous depot showed symptoms of mercury poisoning after they were given sodium chloride, potassium bromide, or potassium iodide. The halogen salts apparently facilitate the dissolution and dissemination of the mercury salts, the activities being in the order Cl<Br<I.

W. O. KERMACK.

Fatal thallium poisoning, and determination of thallium in cadavers as thallous iodide. R. FRIDLI (Ber. ungar. pharm. Ges., 1928, **4**, 43—49; Chem. Zentr., 1928, i, 1561—1562).—The thallium was determined titrimetrically with 0·1*N*-potassium iodide solution. Of 2·5 g. of thallium acetate taken *per os*, there were found 3·3 mg. in 100 g. of liver, 1·6 mg. in 98 g. of kidney, 5·0 mg. in 100 g. of urine, the greater part having already been eliminated in the urine. A. A. ELDRIDGE.

Fatty degeneration of the liver. A. GUBSER (Biochem. Z., 1928, **198**, 65—80).—The fat appearing in the liver during phosphorus poisoning and during decrease of atmospheric pressure is distinguished by its high phosphatide content, whereas that caused by overheating and chloroform poisoning has a normal phosphatide content. In the liver rich in phosphatide, the total phosphorus content is not greater than normal, but the phosphatide forms a much greater part of the total phosphorus. The conversion of nuclein- into phosphatide-phosphorus is regarded as a step in the formation of this phosphatide.

P. W. CLUTTERBUCK.

Absence of free aldehyde groups from enzyme solutions. F. LEHR (Biochem. Z., 1928, **198**, 204—205).—An attempt to detect the presence of free aldehyde groups in solutions of the following enzymes; 0·2% urease (jack bean), 0·5% taka-diastase, 1% pepsin and trypsin, freshly-prepared catalase, by means of the fuchsin–sulphurous acid method of Stepp, Feulgen, and Voit (A., 1927, 370) gave negative results. P. W. CLUTTERBUCK.

Specificity of intracellular dehydrogenases. I. Dehydrogenase of cunner muscle. M. E. COLLETT (J. Biol. Chem., 1928, **78**, 685—689).—The course of decolorisation of methylene-blue by a system consisting of washed muscle of the cunner together with one or more hydrogen donators in a vacuum was observed. Since decolorisation was no more rapid in presence of two donators than in presence of one, it is concluded that in the muscle of this fish there is only one dehydrogenase for which many substances may serve as hydrogen donators.

C. R. HARINGTON.

Potassium thiocyanate and diastatic action of saliva- and plant-diastases. L. R. JOHNSON and A. WORMALL (Proc. Leeds Phil. Soc., 1928, **1**, 318—324; cf. A., 1926, 1058).—Traces of potassium thiocyanate have a definite activating influence on the diastatic action of human saliva, which is significant at the concentration normally present. A similar effect is produced with malt diastase and with a diastatic preparation from potatoes. The effect is most pronounced when starch is used as substrate, but is still noticeable with dextrin or glycogen, or when sodium chloride is added to raise the concentration of this salt to the optimum value. The thiocyanate appears to accelerate only the first stages in the hydrolysis of starch and the rate of formation of reducing sugars is not markedly increased. The stimulating action of potassium thiocyanate on the germination of potatoes and barley is discussed in relation to the influence of the salt on diastatic action; preliminary experiments carried out with

barley indicate that potassium thiocyanate accelerates germination, although an excess retards or even destroys germinating power. C. W. SHOPPEE.

Hydrolysis of starch by salts. E. GLIMM and R. GRIMM (Biochem. Z., 1928, **197**, 445—459).—Provided precautions are taken to maintain sterile conditions, starch is never hydrolysed by solutions of salts, of amino-acids, of peptones, or of mixtures of these substances. The results obtained by Haehn (cf. A., 1923, i, 443) and by Biedermann (cf. *ibid.*, 655) are thus explained, since these workers did not use sterile materials. From Witte's peptone were isolated two organisms which convert starch into dextrin. W. McCARTNEY.

Hydrolysis of sucrose by enzymes. R. WEIDENHAGEN (Naturwiss., 1928, **16**, 654—655).—The hydrolysis of disaccharides can be brought about by the action of simple glucosidases. For the hydrolysis of a disaccharide of the maltose type, only one glucosidase will be necessary, whilst the non-reducing sugars provide a possibility of the action of two. According to this theory the hydrolysis of sucrose can be brought about by the action of two different enzymes which are called β-*l*-fructosidase and α-glucosidase. Some confirmation for the theory is to be found in the separation of maltase and invertase by Willstatter and Bamann, which may be regarded as a separation of β-*l*-fructosidase and α-glucosidase. If "invertase-free maltase" is allowed to act on sucrose at the optimum p_H of 7·0 the hydrolysis taking place is of the order of a maltose hydrolysis, whilst at p_H 4·6, which favours the fructosidase action, no hydrolysis can be proved. That no hydrolysis of raffinose occurs at p_H 7·0 is also in complete agreement with the theory. A. J. MEE.

Enzymic mutation and enzymic degradation of glycogen-lactic acid. H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1927, **39**, 287—295; Chem. Zentr., 1928, i, 1427).—The fission of aldehyde by liver juice takes place only in presence of co-zymase; the reaction velocity diminishes considerably during the reaction. The effect is not shown with preparations obtained by precipitation with acetic acid; inhibiting substances are apparently thereby removed. In this isoelectric precipitation the purity of the enzyme is not greatly increased, but it is increased tenfold by fractional precipitation with ferric hydroxide. Liver juice showed no formation of lactic acid from glycogen or zymophosphate. With muscle juice lactic acid was formed, the reaction velocity being of the same order as that of the action of mutase. A. A. ELDRIDGE.

Dry [enzyme] preparations from muscle. H. VON EULER and S. PROFFE (Svensk Kem. Tidskr., 1927, **39**, 295—297; Chem. Zentr., 1928, i, 1427).—The production of lactic acid and action of mutase by preparations from ox and rabbit muscle were studied. A. A. ELDRIDGE.

Reactions of hexoses in the animal organism. H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1928, **9**, No. 38, 1—6).—The extract made by grinding washed rat liver with sand and water decolorises methylene-blue in absence and presence of dextrose, lævulose, and rat's blood-serum. Mixtures of the serum with dextrose or lævulose do not cause decolorisation.

From experiments on the decolorisation of methylene-blue with yeast suspensions and sodium zymophosphate it is concluded that pure hexosediphosphate is not fermented in absence of co-zymase, and is of no use as a hydrogen donator. H. BURTON.

Properties of emulsin prepared 23 years ago. M. BRIDEL and (MLLE.) M. DESMAREST (J. Pharm. Chim., 1928, [viii], **8**, 201—205).—In a sample of emulsin prepared from almonds in 1905 β-glucosidase and lactase were still active but had lost more than 50% of their activity. Invertase was only very feebly active (cf. B., 1928, 729).

E. H. SHARPLES.

Stereochemical specificity of lipases. P. RONA and R. ITELSOHN-SCHECHTER (Biochem. Z., 1928, **197**, 482—490; cf. A., 1927, 377).—Pig-liver lipase preferentially hydrolyses the *d*-component in *r*-ethyl mandelate. As regards rate of hydrolysis, *l*-ethyl mandelate is most rapidly attacked by this lipase, whereas the *d*- and *dl*-forms and a mixture of equal parts of the *d*- and *l*-forms are hydrolysed more slowly but at equal rates. The action of the enzyme does not begin immediately after mixture with the substrate. An induction period, the extent of which depends on the degree of purity of the substrate, is observed (cf. Willstatter and others, A., 1927, 793). The degree of purity of the ferment has no influence on its specificity and it is concluded that the specificity is a property of the pure enzyme. The extent of the period of induction appears to increase with increasing purity of the ferment. When methyl mandelate is used similar results are obtained. Pig-pancreas lipase affects ethyl mandelate in the same way as it affects the methyl ester. W. McCARTNEY.

Kidney phosphatase and its activation. II. III. H. ERDTMAN (Z. physiol. Chem., 1928, **177**, 211—220, 231—236).—II. Investigation has been made of the fission of glycerophosphate solution by kidney phosphatase activated by meat extract (cf. this vol., 671). It is shown that the activator is not an enzyme protector, and that an excess of phosphate retards the reaction (cf. Martland and Robison, A., 1927, 699). Fission of sodium zymophosphate is effected with the activated phosphatase, but not as readily as that of glycerophosphate.

It is shown that the activator contains magnesium sulphate, and a comparison of glycerophosphate fission using pure magnesium sulphate and the sulphate from the activator shows their identity.

III. Activation of kidney phosphatase is not effected by calcium, zinc, or beryllium sulphates. Active enzyme preparations can be obtained by precipitation with alcohol. After further adsorption on aluminium hydroxide at p_H 5 and elution with Sørensen's secondary phosphate buffer an increased activity is manifested. The purest preparation obtained gives Millon's reaction, a negative Molisch's test, and an indistinct biuret reaction.

H. BURTON.

Purification of nucleosidases. H. VON EULER and E. BRUNIUS (Arkiv Kemi, Min., Geol., 1928, **9**,

No. 40, 1—14).—The reaction between nucleosidase (prepared by extraction of pig or ox kidney with water) and adenosine, measured by determination of the ribose liberated, is unimolecular and 73% fission occurs at infinite time. Partial purification of the nucleosidase is effected by dialysis or better by isoelectric precipitation combined with dialysis. Kaolin is unsuitable as an adsorbent, and although aluminium hydroxide *B* at p_H 6 effects 73% adsorption, subsequent elution yields only 10%. Alcohol and colloidal ferric hydroxide effect adsorption, but the enzyme is not recovered at p_H 6 or 9. Precipitation with alcohol is unsuitable, but fractional precipitation with acetone gives some improvement, whilst a further purification is effected by isoelectric precipitation. H. BURTON.

Pepsin. I. H. PENAU and J. PLE (Bull. Soc. Chim. biol., 1928, **10**, 779—783).—See this vol., 922.

Effect of fluorides and iodides on the clotting of milk by pepsin. W. M. CLIFFORD (Biochem. J., 1928, **22**, 1128—1132).—The clotting of milk by pepsin is inhibited by the addition of sodium, potassium, and ammonium fluorides and lithium, sodium, potassium, and ammonium iodides. This inhibitory action depends on the concentration of the halide. The inhibition of coagulation occurs suddenly at a definite molarity of the halide added, a difference of 0·0036*M* changing the rate from 5—13 min. to absence of change for 4—6 hrs. The inhibitory action of fluorides is greater than that of iodides. The concentration of ammonium iodide has to be six times that of sodium or potassium iodide and ten times that of lithium iodide to produce a similar inhibitory effect. S. S. ZILVA.

Action of fluoride on urease. M. JACOBY (Biochem. Z., 1928, **198**, 163—174).—Fluoride exerts its greatest action on urease when the enzyme is under optimal conditions of p_H, phosphate buffering, and cyanide activation, and the action cannot be replaced by that of oxalate or citrate. The action of fluoride is probably specifically on the urease, but no stoicheiometric relationship exists between fluoride and enzyme. Urease adsorbed on cholesterol is elutable by water. By decreasing the concentration of the urease, adsorption by cholesterol at first decreases to a minimum and then increases. P. W. CLUTTERBUCK.

Selective fermentation of dextrose and lævulose by brewer's yeast. R. H. HOPKINS (Biochem. J., 1928, **22**, 1145—1156).—Top and bottom types of brewer's yeast ferment dextrose faster than lævulose in mixtures of the two, both when the yeast is multiplying freely in the presence of various kinds of nutrients and when nutrients are absent. The relative specific rates of fermentation in such cases are dependent mainly on the species of yeast used and on the conditions of its nutrition. No lævulose could be detected in a solution of dextrose undergoing fermentation by living yeast. Zymin prepared from brewery yeast ferments dextrose faster than lævulose in a mixture of the two. A yeast trained by continual subculturing in a medium of lævulose and nutrients showed no change in its properties as regards selectivity. The temperature coefficients of esterification of dextrose and lævulose by zymin under conditions of phosphate concentration yielding the optimum esterification of dextrose are approximately the same, *i.e.*, v_{25}/v_1.—2·0. S. S. ZILVA.

Fermentation of hexoses racemised by dilute alkalis. A. FERNBACH, M. SCHOEN, and M. MORI (Ann. Inst. Pasteur, 1928, **42**, 805—826).—The course of fermentation of solutions of dextrose or mannose, rendered optically inactive by treatment with sodium hydrogen carbonate (0·8%) at 40°, with different yeasts is followed by measurement of the alcohol produced, the iodine value, the reducing power, and the optical activity. In all cases the alcohol formed is about 90% of the theoretical and the reducing power and the iodine value fall to a low figure. With brewer's yeast the curve of rotatory power first becomes negative and then rises to a small positive value, whilst with another variety (Sauterne) it becomes strongly positive and finally falls to a similar value (possibly representing a small amount of an unfermentable sugar). G. A. C. GOUGH.

Enzymic production of hexosephosphates. H. VON EULER, K. MYRBACK, and D. RUNEHJELM (Arkiv Kemi, Min., Geol., 1928, **9**, No. 49, 1—6).—Fermentation of the sodium hexosemonophosphate of Robison gives carbon dioxide and hexosediphosphate, no inorganic phosphate being produced. Fermentation of dextrose with a very active yeast in presence of phosphates and subsequent purification of the hexosemonophosphate produced through the *barium* salt, $[\alpha]_D$ +33°, affords a new *hexosemonophosphoric acid* having $[\alpha]_D$ +63°. Fermentation of dextrose with dry yeast-*H* in presence of phosphates and some hexosediphosphoric acid gives, after removal of the diphosphate as the insoluble barium salt, a hexosemonophosphoric acid, $[\alpha]_D$ +15°, similar to Robison's. H. BURTON.

Co-zymase. XV. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1928, **177**, 237—247).—When partly purified co-zymase (A., 1927, 993) is treated with picric acid solution an inactive *picrate*, m. p. 183°, is obtained. The base, m. p. 209° (slight decomp.), obtained from this is adenylmethylthiolpentose, $C_{11}H_{15}O_3N_5S$ (cf. Suzuki, Odake, and Mori, A., 1925, i, 338). The picric acid liquors when treated by methods previously described (*loc. cit.*) give preparations with an increased activity, which contain only small amounts of sulphur (0·3—0·5%), and about 14—15% N, 40% C, and 5·5% H. Hydrolysis with dilute acids produces adenine and a reducing nitrogen-free carbohydrate. The original co-zymase does not reduce alkaline copper solution. The carbohydrate contains pentose, since distillation with acid affords furfuraldehyde. It is concluded that the purest preparation yet obtained contains but a small proportion of co-zymase.

Co-zymase is very stable towards oxidising agents. A rapid air current at p_H 4 and 7 at 25° for 24 hrs. has no effect. Acid permanganate has no action, but at p_H 8 a slow decomposition occurs. Bromine water does not affect the co-enzyme during 15 min. even when the bromine is expelled at 50°.

H. BURTON.

Co-zymase and enzymic carbohydrate metabolism. H. von Euler and K. Myrback (Arkiv Kemi, Min., Geol., 1928, **9**, No. 37, 1—6).—Highly-purified co-zymase preparations are obtained from fresh yeast extracts by precipitating twice with lead (acetate ?), then with silicotungstic acid, and finally with ammoniacal silver nitrate. Other methods of purification are also given. The pure preparations contain only a trace of phosphorus and do not exhibit protein or ninhydrin reactions. Molisch's test and the phloroglucinol reaction for pentoses are strongly positive. When heated with copper sulphate and hydrogen sulphite considerable inactivation of the co-zymase occurs. H. Burton.

Purification of yeast co-zymase. R. Nilsson (Arkiv Kemi, Min., Geol., 1928, **9**, No. 31, 1—22).—Dialysis of co-zymase preparations affords a convenient method of purification. Precipitation of the co-enzyme with lead acetate and subsequent adsorption on lead hydroxide effects purification, but further treatment with lead acetate causes inactivation. Precipitation with colloidal iron hydroxide is not advantageous, although the co-zymase is remarkably free from ash and does not give a precipitate with lead acetate. Careful adsorption on lead hydroxide also effects purification. Adsorption on aluminium hydroxide at p_H 10, subsequent elution with an acetate mixture at p_H 5, and further adsorption on lead hydroxide at p_H 10 gives an improved preparation. No adsorption on silicic acid was effected at p_H 4·7 or 10. H. Burton.

Co-zymase in respiring organs of plants. H. von Euler and E. Nordenfeldt (Arkiv Kemi, Min., Geol., 1928, **9**, No. 35, 1—6).—An aqueous extract of green malt root-tips possesses a small co-zymase value. Malt embryo extract has a low co-zymase content and progressive germination causes a diminution of the enzyme. The oxygen consumption of fresh malt embryo is in large excess over the amount necessary to oxidise completely the sugar which is lost during the process. H. Burton.

Biological oxido-reductions. H. von Euler and R. Nilsson (Arkiv Kemi, Min., Geol., 1928, **9**, No. 29, 1—6).—The addition of dihydroxyacetone to a mixture of washed yeast and co-reductase causes a retardation in the time taken to decolorise methylene-blue both in absence and presence of dextrose. Insulin and a mixture of insulin and dextrose have no effect on the time factor (yeast-enzyme preparation only), but decolorisation is more rapid with added dextrose. Washed rabbit heart-muscle contains no donator, but it decolorises methylene-blue in presence of dihydroxyacetone, dextrose and dihydroxyacetone, and dextrose. Decolorisation is slowest in the last case. Zymophosphate has a powerful donator action causing decolorisation in presence of washed yeast in 10 min., whilst the yeast alone caused no reduction in 12 hrs. Methylene-blue is rapidly decolorised in presence of sodium succinate by washed yeast to which is added blood extract, thus demonstrating the presence of co-reductase in blood. H. Burton.

Mutase. H. von Euler and E. Grabe (Arkiv Kemi, Min., Geol., 1928, **9**, No. 50, 1—6).—A partial transformation of furfuraldehyde is brought about by ordinary dried yeast or washed yeast to which has been added a boiled yeast extract or purified co-zymase (cf., A., 1927, 175, 484). Dismutation of formaldehyde occurs rapidly during the first hour and then ceases after 30% change, presumably owing to the inactivation of the enzyme by the aldehyde. The presence of a small amount of potassium cyanide does not affect the transformation of acetaldehyde, but 0·003N-cadmium and -zinc chlorides cause considerable retardation. A very slight retardation is caused by 0·1N-calcium and -potassium chlorides, and potassium iodide and fluoride.

Mutase is found to occur in fresh and dried wheat seedlings and extracts therefrom. H. Burton.

State of combination of nucleic acid in yeast. N. Ishiyama (Z. physiol. Chem., 1928, **177**, 295—297).—When dried yeast is extracted with 10% copper chloride solution, the extract treated with sodium picrate solution, the precipitated picrates purified and finally converted into sulphate, 0·5% of a solid is obtained which when treated with a hydrochloric acid–pepsin solution is completely hydrolysed. It is concluded that there is no protamine-like substance in yeast and that yeast-nucleic acid is not in the same state of combination as the nucleic acids from fish sperm and the thymus gland. H. Burton.

Enzymic nitrogen metabolism. H. von Euler (Arkiv Kemi, Min., Geol., 1928, **9**, No. 47, 1—6).—*B. coli* effects a 15—20% conversion of alloxan into alloxanic acid, but has little action on barbituric acid and none on uric acid and uracil. Prolonged action of *B. prodigiosus* on Witte's peptone solution causes the disappearance of tryptophan (cf. A., 1926, 1177). Mandelonitrile is hydrolysed by expressed calf-liver juice in presence of calcium or sodium hydrogen carbonate to mandelic acid. H. Burton.

Theory of the production of zymase by the living cell. E. C. Grey (Proc. Roy. Soc., 1928, **B**, **103**, 302—311).—Experiments are described demonstrating that the first anaerobic mode of decomposition of dextrose by *B. coli communis* (cf. following abstract) is exhibited by the bacterium after a period of aerobic activity. The enzymes responsible for the zymase type of fermentation are considered to be derived from the enzymes responsible for aerobic respiration. W. O. Kermack.

Enzymes of *Bacillus coli communis*. VI. Alternative modes by which *B. coli* may bring about anaerobic decomposition of dextrose. E. C. Grey (Proc. Roy. Soc., 1928, **B**, **103**, 312—320).—*B. coli communis* decomposes dextrose anaerobically according to two mechanisms in the first of which carbon dioxide, alcohol, formic acid, and succinic acid are produced and in the second of which lactic acid is the characteristic product. Under disadvantageous conditions, *e.g.*, as the result of age or in presence of chloroacetate, the second type of decomposition tends to persist longer than the first. W. O. Kermack.

Behaviour of "β-lysin" with lipin solvents. A. Pettersson (Z. Immunitatsforsch., 1928, **54**, 292—302; Chem. Zentr., 1928, i, 1538).—The highly

thermoresistant bactericidal component of serum ("β-lysin") does not lose its activity towards *Bacillus subtilis*, *B. putrificus*, or *B. coli* by treatment with ether, chloroform, or light petroleum, whilst the thermolabile serum-alexin is thereby destroyed. Acetone and serum afford a non-bactericidal precipitate. A. A. ELDRIDGE.

Spirochæticidal properties of elemental vanadium. Asterogenesis around vanadium particles. C. LEVADITI, P. LEPINE, and (MLLE.) R. SCHOEN (Compt. rend., 1928, **187**, 434—436).—The anti-syphilitic properties of vanadium compounds are shared by the element itself, which, when injected as fine particles in suspension in oil, has a definite curative action on rabbits. Radiating masses are formed round the particles, resembling those formed by *Actinomyces*. E. W. WIGNALL.

Female sex hormone in yeast. E. GLIMM and F. WADEHN (Biochem. Z., 1928, **197**, 442—444).—The presence of the hormone in yeast has been confirmed. Brewer's yeast, probably because it grows in a medium rich in organic nitrogen, has a higher content of "feminin" than pressed yeast which is derived from a medium half of the nitrogen of which exists in the form of ammonium salts. When yeasts are preserved in the cold no change takes place in the content of hormone. W. MCCARTNEY.

Influence of adrenaline on formation of sugar. E. GEIGER and E. SCHMIDT (Arch. exp. Path. Pharm., 1928, **134**, 173—184).—Administration of adrenaline to fasting phloridzinised dogs does not increase the D/N ratio of the urine unless mobilisation of muscle glycogen occurs. The fat content of the liver is not decreased as a result of the administration of adrenaline. It therefore appears that adrenaline does not facilitate formation of dextrose from fat. The protein metabolism, which is raised as the result of phloridzin, and the excretion of acetone compounds in the urine, are both lowered during the process of glycogen mobilisation. W. O. KERMACK.

Cardaissin, a new cardiac accelerator extracted from the suprarenal gland. H. G. CAMERON (Endocrinol., 1926, **10**, 577—601).—*Cardaissin*, differing from adrenaline, was obtained by fractional precipitation of a de-fatted neutral acetone extract of ox adrenals. CHEMICAL ABSTRACTS.

Crystalline insulin. VI. An adsorption product? V. DU VIGNEAUD, E. M. K. GEILING, and C. A. EDDY (J. Pharm. Exp. Ther., 1928, **33**, 497—509).—Crystalline insulin (from beef pancreas) adsorbed from its solution in 0·01*N*-hydrochloric acid on charcoal and eluted with phenol exhibits no change in activity. When, in accordance with the method of Dingemanse, the product is extracted with 0·06*N*-disodium hydrogen phosphate solution no differential solubility of the material could be detected, both the soluble fraction and the residue possessing the same activity, whilst the charcoal–phenol powder was reconverted into crystalline insulin identical in all respects with the original product. When crystalline insulin is heated with 0·1*N*-hydrochloric acid for 1 hr. at 100°, a precipitate, insoluble in hydrochloric acid and disodium hydrogen phosphate solution, is obtained which, however, dissolves in dilute alkali and by acidification of this solution can be regenerated in its original acid-soluble form with only a slight loss of activity. The activity of solutions of insulin in disodium hydrogen phosphate decreases on keeping. J. W. BAKER.

Crystalline insulin. VII. Acetylation and behaviour of insulin towards alkali. H. JENSEN and E. M. K. GEILING (J. Pharm. Exp. Ther., 1928, **33**, 511—520).—Crystalline insulin (activity 45 units/mg.) treated with acetic anhydride for 15 hrs. at 0° yields acetylinsulin (4·5% Ac), which in 0·06*N*-disodium hydrogen phosphate solution has a very much smaller activity (8 units/mg.). The acetylinsulin is hydrolysed by 0·01*N*-sodium hydroxide at 0°, hydrolysis being almost complete in the first few minutes, the regenerated insulin having an activity of 25 units/mg., the whole of the activity being in the precipitate produced by adding excess of acetic acid to the alkaline solution. The lowered activity of the regenerated insulin is probably due to the loss of hydrogen sulphide, since even the dilute sodium hydroxide employed eliminates some hydrogen sulphide from acetylinsulin, whilst the original crystalline insulin is unaffected by the same concentration of alkali for 15 hrs. at 0°. The sulphur in acetylinsulin, therefore, appears to be much more labile than in insulin itself. Contrary to Freudenberg and Dirscherl (this vol., 675), it is found that acetylinsulin loses 30% of its activity by treatment with 0·03*N*-sodium hydroxide for 15 hrs. at 0°, and the much lower activity of the regenerated insulin of these authors is probably due to the greater amount of decomposition which occurs with the more concentrated alkali. J. W. BAKER.

Influence of diet on the physiological assay of insulin. A. STASIAK (J. Lab. Clin. Med., 1926, **12**, 256—258).—The actual range through which the blood-sugar is lowered by insulin is approximately the same in fed and starved rabbits. CHEMICAL ABSTRACTS.

Influence of a lipoid pituitary hormone on the deamination process in organs. R. AGNOLI (Arch. exp. Path. Pharm., 1928, **134**, 74—87).—A definite quantity of glycine (3 g.) was administered intravenously to a dog and the concentration of the compound left in the circulating blood was determined at intervals by measuring the amino-acid content of the protein-free filtrate. The rate of disappearance of the glycine was not sensibly altered by the administration of extracts of the posterior lobe of ox pituitary nor by certain commercial preparations of pituitrin, but was slightly accelerated by an extract of the whole ox pituitary, whilst the lipoid extract of the whole dried ox pituitary or of fresh pig pituitary had a marked accelerating action. W. O. KERMACK.

Influences of substances of the thyroid gland on fat metabolism. I. ABELIN and P. KURSTEINER (Biochem. Z., 1928, **198**, 19—46).—Considerable loss of fat is found in animals 24—72 hrs. after administration of thyroid substances (powdered gland, thyreoidea, etc.), although during this time only a slight increase in combustion has taken place.

Striated muscle shows the greatest, and liver and lung a smaller loss. The chief characteristic of this action is the almost complete inhibition of the resynthesis of cellular from nutritive material. A glycogen-free liver stores much fat and can ordinarily form glycogen from suitable material. Administration of thyroid substances causes the liver not only to become free from glycogen but also poor in fat. This loss of fat disturbs the synthesis of glycogen, but injection of adrenaline causes a partial recovery of the power of the liver to form glycogen.

P. W. CLUTTERBUCK.

Determination of vitamin-*A*. H. C. SHERMAN and M. P. BURTIS (J. Biol. Chem., 1928, **78**, 671—680).—The larger the weight of the test animal the less is its gain in weight with a given intake of vitamin-*A*; in testing for this vitamin male and female rats may be used equally well. It is considered best to adhere to an 8-week period for the test and to a weekly gain in weight of 3 g. as a standard; shortening of the period tends to give variable and higher results for the vitamin-*A* content of the material under test, whilst adoption of a higher standard rate of gain in weight decreases the delicacy of the test.

C. R. HARINGTON.

Fat-soluble growth factors. H. VON EULER (Arkiv Kemi, Min., Geol., 1928, **9**, No. 28, 1—6).—Rats fed on a vitamin-*A*-deficient diet supplemented by an irradiated 1% solution of cholesterol in ivory-nut oil show a normal blood-phosphorus content (A., 1925, i, 1515). Cholesteryl acetate and palmitate do not promote growth. Extracts of wheat seedlings and top yeast-*R* have a remarkably high antirachitic action. Betulin shows a doubtful antirachitic action.

H. BURTON.

Irradiated vitamin-*B* and automatin action. H. ZWAARDEMAKER (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 258—260).—The beating of an eel's heart which has been arrested by washing out potassium salts is restored by the addition of vitamin-*B*, previously irradiated for 15 hrs., to the circulating fluid in a manner similar to that produced by the addition of automatin from another irradiated heart, the contractions continuing regularly for 13—16 hrs. The latent period before the contractions recommence depends only on the time required for washing out the potassium salts, whilst the frequency depends on the concentration of the stimulating substance. Addition of non-irradiated vitamin-*B* causes only spasmodic single beats which cease after a period of about 2 hrs.

J. W. BAKER.

Nitrogenous metabolism during unbalanced nutrition. II. Nitrogenous metabolism in hens during avitaminosis-*B*. B. A. LAVROV and S. N. MATZKO (Biochem. Z., 1928, **198**, 138—148).—When hens are fed on polished rice, the early damage to the motor function of the crop leads to an avitaminosis complicated by starvation, and this method is therefore unsuitable for investigating the effect of avitaminosis on nitrogenous metabolism. When hens are fed on oats and starch and then transferred to rice, the body-weight at first remains steady and then slowly declines. The nitrogen balance is positive, but after 7 days becomes negative and the uric acid excretion may increase 280%. It would appear therefore that in the initial stages of avitaminosis-*B*, a more intensive decomposition of nitrogenous body substances takes place, followed a week later by the usual symptoms.

P. W. CLUTTERBUCK.

Content of vitamin-*C* in Japanese sand pear (*Pyrus serotina*, Rehder), kaki (*Diospros kaki*, L.), and Satsuma orange (*Citrus unshiu*). Y. IWASAKI (J. Okitsu Hort. Soc., 1927, No. 22, 1—10).

CHEMICAL ABSTRACTS.

Colour reactions of substances containing vitamin-*D*. W. A. SEXTON (Biochem. J., 1928, **22**, 1133—1134).—From the examination of a number of substances it is concluded that the colour tests of Shear and Kramer (Proc. Soc. Exp. Biol. Med., 1926, **23**, 546) and Bezssonoff (A., 1925, i, 107) are not specific for vitamin-*D*.

S. S. ZILVA.

Action of *X*-radiation on vitamin-*D* in activated ergosterol. R. R. MORRISON, P. R. PEACOCK, and S. WRIGHT (Biochem. J., 1928, **22**, 1138—1141).—A dose of 0·0002 mg. of ergosterol activated under the conditions described will partly protect against and cure experimental rickets. *X*-Rays when applied to a dry sample of activated ergosterol exposed to the air exert a destructive effect on vitamin-*D*.

S. S. ZILVA.

Respiration of beans (*Phaseolus multiflorus*) grown on an iron-deficient medium. H. VON EULER and S. STEFFENBURG (Arkiv Kemi, Min., Geol., 1928, **9**, No. 48, 1—6).—Seeds of *Phaseolus multiflorus* were grown on artificial media and the oxygen consumption of normal and chlorotic leaves was compared. Although the chlorotic leaves contain more iron than the green leaves, the intensity of respiration per mg. of iron is higher for the latter. A similar relation holds per g. of dry leaf. It is suggested that the cytochromic iron will be found to be higher in the green leaves.

H. BURTON.

Relations between pigment formation, leaf area, and dry weight of maize grown in sand cultures. H. B. SPRAGUE (New Jersey Sta. Rep., 1925, 332—337).—The chlorophyll content was more closely related to the area than to the weight of the leaf, whilst the reverse held for carotin and xanthophyll.

CHEMICAL ABSTRACTS.

Changes of fluorescent colours in ultra-violet light. M. HAITINGER and V. REICH (Z. angew. Chem., 1928, **41**, 982—983).—The slow decrease in intensity of the fluorescent colours of ethereal extracts of wines and plant juices in daylight is traced to the effect of ultra-violet rays. Exposure to a mercury-vapour lamp produces notable colour changes in 1 hr.

A. G. POLLARD.

Cause of blueing in red roses. G. S. CURREY (J. Proc. Roy. Soc. New South Wales, 1927, **61**, 307—314).—The blueing of red roses is traced to insufficiency of tannin in the petals, and does not appear to depend on the nature of the anthocyanin pigment. There is a direct relationship between the quantities of tannin and of anthocyanin pigment present.

C. W. GIBBY.

Cell-wall substances of plants; chemical changes taking place during lignification. E. J. CANDLIN and S. B. SCHRYVER (Proc. Roy. Soc., 1928, B, **103**, 365—376).—The action of dilute sodium hydroxide solution on pectic acid prepared from onion or citrus effects decarboxylation with the formation, amongst other products, of hemicellulose.

W. O. KERMACK.

Composition and structure of the cell-wall of wood. G. J. RITTER (Ind. Eng. Chem., 1928, **20**, 941—945; cf. B., 1925, 985).—Examination of sections of the wood of the Western yellow pine, elm, and red alder shows that the lignin is distributed almost equally between the middle lamella and the cell-wall, that present in the former being more soluble in alcohol. Changes in the structure of the fibre on swelling have been examined microscopically. The optical phenomenon observed when the bordered pits are examined between crossed Nicols may be explained if it is assumed that the longitudinal chains of cellulose molecules in the cell-wall are continuous and are bent around either side of the circular pit orifice. When lignified and delignified fibres are treated with swelling agents (15% sodium hydroxide or concentrated acids) the walls thicken both outwardly and inwardly, the general angular cross-section of the former being unaltered, whilst that of the latter is changed to a circular form in which the circumference is limited by the outer layer of fibrils which are oriented at 90° to the axis of the fibre. Alternate swelling and shrinking of delignified fibres by treatment with alkali followed by neutralisation with acids separates the several layers of which the cell-wall is composed. These layers can, by more drastic alkali–acid treatment, or better by treatment with 68% phosphoric acid, be separated into fibrils, those in the outer layer extending at approximately 90°, and in the remaining layers at 0—30°, to the axis of the fibre.

J. W. BAKER.

Acidity of root secretions. E. G. MININA (Bull. inst. rech. biol. Univ. Perm, 1927, **5**, 233—258).—Roots of bean, lupin, buckwheat, and cereals, in a soil of low buffering power, cause the soil solution to become more acid, then more alkaline, and finally more acid as the plant develops. Roots in distilled water excrete non-volatile organic acids.

CHEMICAL ABSTRACTS.

Formation of starch in the needles of the pine. M. A. BARGUES (Bull: Inst. Pin, 1928, 1—3; Chem. Zentr., 1928, i, 1537).—Starch is present in all cells of pine needles except those of the epidermis and the innermost tissue. Variations with season of the starch content are traced. Daily variations occur only in the peripheral green tissue. Branches which by being kept in the dark have lost much of their starch rapidly regain it when 5% dextrose solution is used as nutrient.

A. A. ELDRIDGE.

Role of phosphorus in the intermediate carbohydrate metabolism of plants. H. K. BARRENSCHEEN and W. ALBERS (Biochem. Z., 1928, **197**, 261—277).—In plants during assimilation there is an increase in the amount of acid-soluble organic phosphorus due to the intermediate formation of carbohydrate-phosphoric esters. In germinating rye and wheat grains the variations in the amounts of inorganic phosphorus, acid-soluble phosphorus, and acid-soluble organic phosphorus appear to depend on the time of year at which germination takes place, on the origin of the material used, and on other factors. The embryonic parts of the seeds exhibit the alterations in the way in which the phosphorus is combined most clearly and from those parts a *substance* which has the properties of a hexosemonophosphoric acid can be obtained. This acid, which forms an amorphous *barium* salt, probably $(C_{12}H_{20}O_{10})_4,PO_3Ba,2BaO$, and a crystalline *brucine* salt, m. p. 168—169° (uncorr.), is believed to be an intermediate product in the synthesis or degradation of starch.

W. McCARTNEY.

Colorimetric determination of the phosphoric acid requirement of soils. A. NEMEC (Biochem. Z., 1928, **198**, 112—127).—The author's previous work (this vol., 95) on the influence of the soluble silicic acid content of soil on the absorption of phosphoric acid is extended using a variety of plants and soils. The phosphoric and silicic acid contents of the soils are tabulated and the phosphate requirement is thus determined indirectly.

P. W. CLUTTERBUCK.

Current mineral nutrient content of the plant solution as an index of metabolic limiting conditions. B. E. GILBERT, F. T. McLEAN, and W. L. ADAMS (Plant Physiol., 1927, **2**, 139—151).—In a study of the expressed plant solution from various tissues of spinach, beet, turnip, maize, cabbage, and carrot, three types of inhibited metabolism were noted, due to (1) a decreased supply of available manganese in a neutral soil, (2) limiting amounts of phosphate and nitrogen applied to the soil, and (3) unfavourable weather conditions.

CHEMICAL ABSTRACTS.

Calcium and magnesium content of some plants of the Mediterranean area. E. CANALS and (MLLE.) G. DAUCAN (Bull. Soc. chim., 1928, [iv], **43**, 779—784).—Except in *Salicornia fruticosa* and *Suaeda fruticosa*, among the Phanerogams, the magnesium content is higher in the leaf than in the stem. Among herbaceous plants the xerophytes contain less magnesium than the hygrophiles. Plants grown on saline soils are low in magnesium, the non-halophile *Sedum altissimum* and *Opuntia ficus* being the richest. The variations in the magnesium content of leaves with age are less significant than those of calcium, except in the case of *S. altissimum*, the magnesium content of this plant being in October only about a third of its content in March. In woody shrubs and trees (halophiles and xerophytes), the calcium/magnesium ratio is higher in the stems than in the leaves, except in the case of *Phyllirea angustifolia*. In the hygrophile order the reverse is the case. The ratio may vary from year to year in the same plant examined at the same season and grown on the same soil. With the halophiles, *e.g.*, *Salsola soda*, the ratio may be less than unity and in general it increases with the age of plant.

R. BRIGHTMAN.

Distribution of calcium oxalate crystals in plant tissues; their probable role in plant metabolism. G. P. MAJUMDAR (Indian Sci. Cong. Proc. Calcutta, 1925, **12**, 187).—Excess of calcium is

supposed to be used in precipitating oxalic acid and soluble oxalates. It appears that calcium oxalate is re-introduced into the metabolic cycle, and that a limited supply of calcium may be sufficient for the life of plants. CHEMICAL ABSTRACTS.

Nitrogen metabolism of *Pyrus malus*, L. III. Partition of nitrogen in the leaves and one and two year branch growth and non-bearing spurs throughout a year's cycle. W. THOMAS (Plant Physiol., 1927, **2**, 109—137).—The total water-soluble nitrogen, non-protein nitrogen, and amino-nitrogen are parallel with the total nitrogen in all tissues throughout the cycle, but the amide nitrogen and the residual nitrogen tend to vary inversely with the total and amino-nitrogen. Amino-nitrogen is probably connected with protein synthesis and residual nitrogen with protein degradation, but amino-acids show no catalytic effect in accelerating growth. Nitric nitrogen was found only as the buds opened. CHEMICAL ABSTRACTS.

Cress grown on adrenaline. J. H. THOMPSON (Nature, 1928, **122**, 401).—Cress, when grown in adrenaline solution, appears to synthesise adrenaline or a similar compound from the products of oxidation of adrenaline. A. A. ELDRIDGE.

Manganese content of plants affording officinal drugs. O. WILLMANN (Ber. ungar. pharm. Ges., 1927, **3**, 29—53; Chem. Zentr., 1928, i, 1533—1534). —The manganese content of a large number of drugs of the Hungarian Pharmacopœia (3rd ed.) has been determined. Aquatic plants contain more than others; young plants contain more than old, and the aerial more than the subterranean portions. The manganese is present chiefly in the cell plasma.

A. A. ELDRIDGE.

Nitrogenous constituents of the leaves of kuzu (*Pueraria hirsuta*, Matsum). R. SASAKI (Bull. Agric. Chem. Soc. Japan, 1928, **4**, 1—5).—After precipitation of the protein, adenine, asparagine, glutamic and butyric acids, and a base (chloroaurate, m. p. 117—118°) were isolated.

CHEMICAL ABSTRACTS.

Localisation of alkaloid in the seed of *Colchicum autumnale*, L. P. LIPTAK (Ber. ungar. pharm. Ges., 1927, **3**, 346—351; Chem. Zentr., 1928, i, 1534—1535).—Colour reactions indicate that the alkaloid is contained in the endosperm and in the third layer of the seed coat. A. A. ELDRIDGE.

Variation in composition of althæa root. J. KABAY (Ber. ungar. pharm. Ges., 1928, **4**, 19—23; Chem. Zentr., 1928, i, 1537).—Ash, sugar, starch, galactose, and mucilage determinations for the period April to October are recorded. A. A. ELDRIDGE.

Mucilage of the rhizome of *Polygonatum officinale*, All. B. GAAL (Ber. ungar. pharm. Ges., 1927, **3**, 133—139; Chem. Zentr., 1928, i, 1534).—Arabinose, dextrose, and *d*-lævulose (81·7%) are present. When oxidised by Tollens' method the mucilage did not afford mucic acid.

A. A. ELDRIDGE.

Gum extracted from cotyledons of *Anagyris fœtida*. P. CONDORELLI and A. CHINDEMI (Annali Chim. Appl., 1928, **18**, 313—317).—This gum contains a paragalacto-araban, $C_6H_{10}O_5,C_5H_8O_4,8H_2O$, on which potassium and calcium silicates and phosphates are adsorbed. It differs from the podalirin contained in the seeds (cf. Condorelli, A., 1926, 210) in being much less soluble in water, and in containing no ketonic sugars. E. W. WIGNALL.

Formation of methyl alcohol in the autolysis of fresh tobacco leaves. C. NEUBERG and B. OTTENSTEIN (Biochem. Z., 1928, **197**, 491—501; cf. A., 1927, 385; this vol., 201).—Tobacco pectase is able to hydrolyse tobacco pectin. Under the conditions of experiment about 50% of the methyl alcohol present in the form of esters was eliminated in 2 hrs. by autolysis. Then the hydrolysis continued slowly until, after 5 weeks, the amount was 90%. Control experiments showed that the liberation of the alcohol was actually due to enzymic processes. Air-dried, unfermented tobacco leaf still contains considerable amounts of both firmly-combined and loosely-combined methyl alcohol, because rapid removal of water prevents hydrolysis of the pectin. The ribs contain more methoxyl than the remaining parts of the leaves, but since these contain more pectic methyl alcohol than the ribs, it follows that the ribs are richer in lignin. W. MCCARTNEY.

Photocapillary reaction of plant phosphatides. I. Influence of salts on the reaction. II. The photocapillary reaction in presence of iron. F. HERCIK (Biochem. Z., 1928, **198**, 81—87, 88—97).—I. The plant (pea) phosphatides dialysing into saline solutions show a characteristic positive or negative photocapillary reaction (the surface tension increases or decreases), cations promoting the reaction and anions being almost inactive. Most of the common ions are placed in series according to the extent of their activity.

II. The type of reaction obtained on dialysing plant (pea) phosphatides into ferric nitrate solutions varies with the concentration of the latter, higher concentrations giving a positive and lower concentrations a negative reaction. The largest reaction is obtained with 0·01M-ferric nitrate.

P. W. CLUTTERBUCK.

Diurnal variation of the gaseous constituents of river waters. R. W. BUTCHER, F. T. K. PENTELOW, and J. W. A. WOODLEY (Biochem. J., 1928, **22**, 1035—1047).—This investigation (cf. A., 1927, 899; this vol., 87) is now extended to the autumn months. The maximum and minimum values of oxygen saturation from the months of September to November are lower than at any previous time in the river Lark. In the river Itchen there is a progressive lowering of the maximum value and a progressive increase in the minimum value in the oxygen saturation curves during the months of August to December. The ammoniacal nitrogen values in the river Lark for September to November vary roughly in inverse ratio to those of dissolved oxygen, whilst in the river Itchen, as in the spring and summer, no diurnal variation of ammoniacal nitrogen was observed. The p_H curves are again similar in structure and in general follow the oxygen curves, the range in the winter being less than that in the spring and summer. The temperature curves show the

expected diurnal similarity but over different ranges according to the month of the year and the prevailing weather conditions. S. S. Zilva.

Characterisation of strains of *Aspergillus niger* on the basis of their biochemical behaviour. I. Acid formation by different strains. K. Bernhauer (Biochem. Z., 1928, **197**, 278—286); cf. A., 1926, 978).—Of the five strains used two, under all conditions, produced mainly gluconic acid with only inconsiderable amounts of citric acid. One strain was a relatively good producer of citric acid and the two remaining strains, which produced, under favourable conditions, approximately equal amounts of the two acids, could be regarded as intermediate types. W. McCartney.

Acid production by *Aspergillus niger*. IV. Importance of mycelium development. K. Bernhauer (Biochem. Z., 1928, **197**, 287—308).—For the growth of moulds and for their capability for acid production the nature of combination and the quantity of the nitrogen used as a source are of the greatest importance. It is shown that, under the conditions of experiment chosen, the amounts of gluconic and citric acids formed vary according to the amount of nitrogen used and to the form in which it is combined in the medium. The various compounds which are used as sources of nitrogen seem to influence the formation of enzyme complexes or enzyme activators which stimulate production of citric acid. W. McCartney.

Citric acid production by fungi. I. Acid production from various carbon compounds. II. Production of citric acid from gluconic acid. K. Bernhauer (Biochem. Z., 1928, **197**, 309—326, 327—342).—I. Only carbohydrates or closely-related compounds can be caused to yield citric acid by the action of *Aspergillus niger*, and important differences are observed in the amounts of the acid obtainable from different compounds. The yields also vary greatly according to the strain of the organism used. Although gluconic acid is also a product of the bacterial action in some cases and is one of the substances which yield citric acid, the former acid cannot be regarded as a necessary intermediate product in the formation of citric acid. The formation of citric acid is preceded by the breaking down of carbon chains so as to yield C_3 chains. The readiness or otherwise with which the various hexoses are attacked greatly affects the yields obtained. The yield of citric acid from the lævulose portion of the sucrose molecule is estimated to be much higher than that from lævulose itself and the significance of this fact is pointed out.

II. During the process of conversion of dextrose, first into gluconic acid, then into citric acid, there are formed, apparently, enzymes or enzyme activators which facilitate the transformation of gluconic acid into citric acid. Hence dextrose gives better yields of citric acid than does gluconic acid itself. An explanation of the chemistry of citric acid production and of similar processes is thus provided. It is also shown that a particular strain of an organism may, for reasons unknown, lose its power to produce citric acid and that, in addition to citric acid, another acid (or acids) such as saccharic acid or glyceric acid, is formed. W. McCartney.

Loss of fermenting power and change in acid produced by *Aspergillus fumaricus*. Fermentation giving gluconic acid in place of fumaric acid. C. Wehmer (Biochem. Z., 1928, **197**, 418—432).—*A. fumaricus* gradually loses completely its power to produce fumaric acid and produces in its place chiefly gluconic acid. The possible reasons for this change in behaviour are discussed and it is concluded that one and the same species of organism may exist in more than one physiological form. Various tests for and methods of determining fumaric, citric, malic, and gluconic acids are discussed. W. McCartney.

Use of monochromatic indicators in the double-wedge colorimeter. H. Kroepelin (Biochem. Z., 1928, **198**, 225—232).—A rule facilitating the determination of p_H by the double-wedge colorimeter is discussed and details are given for the use of nitrophenol dyes for this purpose. P. W. Clutterbuck.

Preparation of potassium "pyrogallate" solution for metabolic rate determinations. F. F. Schwentker (J. Lab. Clin. Med., 1926, **12**, 287—288).—Hot potassium hydroxide solution, *d* 1·517, is added to the pyrogallol and the mixture kept for a month. Chemical Abstracts.

Micro-determination of glycogen. A. Slosse (Compt. rend. Soc. Biol., 1927, **97**, 1810—1812; Chem. Zentr., 1928, i, 1443).—0·5 g. of the finely-pulped organ is rapidly weighed in a centrifuge tube, 1 c.c. of hot 60% potassium hydroxide solution added, and the whole kept in a boiling water-bath for 3 hrs., after which 4 c.c. of water are added and the mixture is cooled. The glycogen is precipitated with 10 c.c. of 95% ethyl alcohol, and centrifuged after 12 hrs. After treatment with 60% alcohol it is again centrifuged, washed twice again with 95% alcohol, dissolved in 10 c.c. of water and 0·67 c.c. of hydrochloric acid (*d* 1·175), kept in a boiling water-bath for 1 hr., neutralised with 0·45 c.c. of 60% sodium hydroxide solution, diluted to 15 c.c., and the dextrose determined in an aliquot portion by Hagedorn and Jensen's method. A. A. Eldridge.

Determination of iron [in organic substances]. G. Dominici (Folia Clinica, 1928, **3**, 65—82).—A critical review of the methods for determining iron in blood, urine, etc. The most satisfactory method with regard to rapidity and accuracy of results is considered to be the colorimetric method using thiocyanate. O. J. Walker.

Determination of sodium in biology. Laudat (Bull. Soc. Chim. biol., 1928, **10**, 757—768).—Determinations in biological fluids by the pyroantimonate method (Kramer and Tisdall, A., 1922, i, 1087) and by the uranium method (Blanchetiere, A., 1923, ii, 579) give similar results. The latter method is probably the most convenient if the recorded precautions are observed. G. A. C. Gough.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1928.

General, Physical, and Inorganic Chemistry.

The aurora and its spectrum. J. C. McLennan (Proc. Roy. Soc., 1928, **A**, **120**, 327—357).—Wave-lengths of the band heads in the band spectrum of nitrogen are given and compared with those of the aurora. The green auroral line λ 5577·341 Å. is shown to be due to the excitation of oxygen in the presence of rare gases, and could be caused by electrons given off by the sun and entering our atmosphere. The line was produced in an apparatus which is described and its Zeeman effect observed longitudinally. From this it is concluded that the green line has its origin in atomic oxygen and is due to a transition between low metastable energy states, being represented by $\nu={}^1D_2-{}^1S_0$. The intensity of the light of the night sky has been measured at various times of the night, and it has been shown that there is a variation in the intensity of that green light which gives rise to the auroral line. It shows a maximum about 1½ hrs. after midnight. The height of the ozone layer has also been measured.

J. L. Buchan.

Spectrum of singly-ionised carbon (C II). A. Fowler and E. W. H. Selwyn (Proc. Roy. Soc., 1928, **A**, **120**, 312—326; cf. A., 1924, ii, 285).—Methods for the production and observation of the spectrum are described. Most of the C II terms can be considered as arising from the addition of an electron in various orbits to a C III core. The lines have been classified and lists are given showing those of C II between λ 7236 and 2137 and also between λ 1760 and 534. Certain lines between λ 2137 and 1894, possibly due to C II or C III, are recorded.

J. L. Buchan.

Variations in the fine structure of H_α. G. E. Harrison (Proc. Physical Soc., 1928, **40**, 300—306).—The intensity changes taking place in the fine structure of H_α with alteration of the bore of the discharge tube at constant gas pressures and current densities were examined. The large variations in the electric field surrounding an emitting particle are held to account for the observed changes in the intensity distribution, which amounted to 100%. The doublet separation appeared to be independent of these changes, the mean value obtained being 0·304 cm.$^{-1}$

C. J. Smithells.

Structure of the induction spectra of the rare gases; arc spectra of argon, krypton, and xenon. A. T. Williams (Proc. Physical Soc., 1928, **40**, 312—315).—The value of the excitation by induction method to separate different orders of the spectra of the rare gases is emphasised. The arc spectra of argon, krypton, and xenon are examined, constant separations and groups of lines being deduced from Bloch and Dejardin's results. The regions occupied by different series are established and also the correspondence between theoretical terms and Meissner's terms in the arc spectrum of argon.

C. J. Smithells.

Regularities exhibited between certain multiplets for elements in the second long period. R. C. Gibbs and H. E. White (Proc. Nat. Acad. Sci., 1928, **14**, 559—564).—The regular displacement of multiple levels and of multiplets which holds for iso-electronic systems in the first long series has been found to hold also for elements in the second long period. In this period the strong lines in the spectra are due to electron transitions $5p$ to $5s$ in the presence of 0, 1, 2, 3 . . . 10 $4d$ electrons. In each case a single line was chosen from all those radiated in order to represent the position in the spectrum of each electron transition. The transition chosen was that taking place between two levels involving the highest R, L, and J values. The diagram between radiated frequency and atomic number shows marked similarity to that for the first long period. A. J. Mee.

Degree of association of sodium vapour. D. S. Villars (Proc. Nat. Acad. Sci., 1928, **14**, 508—511).—By photographing the absorption spectrum of an alloy of sodium and potassium and obtaining the positions of the sodium bands, the convergence frequencies for the excited and unexcited states were determined. Using these values, the heat of dissociation of diatomic sodium was found to be 26·8 g.-cal. By means of the Sackur–Tetrode equation, the degree of association is calculated for various temperatures. Sodium vapour is very largely diatomic, especially at the lower temperatures. This conclusion does not agree with previous work. A. J. Mee.

Broadening of spectral lines by the Doppler effect. G. Polvani (Nuovo Cim., 1927, **4**, 365—370; Chem. Zentr., 1928, i, 1936).—At the absolute zero spectral lines should have a finite width.

A. A. Eldridge.

Dissociation energy of nitrogen. G. Herzberg (Nature, 1928, **122**, 505—506).—It is shown that, in agreement with Gaviola's result (this vol., 1075), the dissociation energy of the neutral nitrogen molecule is probably about 9 volts; hence Sponer's interpretation of the afterglow requires modification.

A. A. Eldridge.

Interpretation of the atmospheric oxygen bands. Electronic levels of the oxygen mole-

cule. R. S. MULLIKEN (Nature, 1928, **122**, 505).—The upper, ^1S, level of the atmospheric oxygen bands, at 1·62 volts above the ^3S normal level, is identified with the predicted ^1S level. The low absorption coefficient for the transition $^3S \longrightarrow {}^1S$ is in agreement with the expected metastability of the ^1S level. A ^1D level of O_2 should exist between the ^3S and ^1S levels, and a new system of atmospheric absorption bands in the infra-red corresponding with the transition $^3S \longrightarrow {}^1D$ may be found.

A. A. ELDRIDGE.

Wave-lengths in the secondary spectrum of hydrogen. H. G. GALE, G. S. MONK, and K. O. LEE (Astrophys. J., 1928, **67**, 89—113).—Wave-lengths of 3064 lines between 3394 and 8902 Å. have been measured with precision. A. A. ELDRIDGE.

Width of the *D* absorption lines in sodium vapour. A. S. FAIRLEY (Astrophys. J., 1928, **67**, 113—122).—Between 180° and 380° the mean width varies from 0·11 to 3·78 Å. (for D_1) and 0·09 to 3·12 Å. (for D_2). For lines wider than 0·25 Å. the results support Stewart's view that the width can be ascribed to "radiation resistance." It is indicated that the Fraunhofer *D*-lines are due to only about 4×10^{14} non-ionised sodium atoms in a column 1 cm. square above the photosphere.

A. A. ELDRIDGE.

Effect of pressure on the spectrum of the iron arc. H. D. BABCOCK (Astrophys. J., 1928, **67**, 240—261).—The pressure effect for 130 lines in the arc spectrum of iron between 3895 and 6678 Å. has been measured for pressures below 1 atm. Empirical expressions make it possible to predict the pressure effect for both terms and lines. No connexion between term displacements and azimuthal or inner quantum numbers was observed. Theories attributing the pressure effect to coupling forces between adjacent similar atoms are rejected.

A. A. ELDRIDGE.

Normal state of helium. J. C. SLATER (Physical Rev., 1928, [ii], **32**, 349—360).—An approximate wave function for normal helium is calculated, and the charge density obtained agrees well with Hartree's independent result. The calculated diamagnetism of normal helium agrees with the observed value. The repulsive forces between two helium atoms and the van der Waals attractive forces are determined, and thence the "molecular diameter" is calculated. Approximately correct values are deduced for the density and the b. p. of the liquid. R. A. MORTON.

Origin of the helium spectrum. L. S. ORNSTEIN and H. C. BURGER (Physica, 1928, **8**, 111—118).—The intensity of the helium spectrum, excited in a capillary by a hot or cold cathode, was studied. Curves show the intensity of $^3P^3S$ as a function of pressure and current density. At sufficiently low pressures the triplet spectrum would probably be absent. At higher pressures the duration of the mean free path of an excited atom will become of the order of the radiation period, 10^{-8} sec.

CHEMICAL ABSTRACTS.

Band spectra in the extreme ultra-violet excited by active nitrogen. H. P. KNAUSS (Physical Rev., 1928, [ii], **32**, 417—426).—Gaseous hydrogen, oxygen, nitrogen, carbon monoxide, or nitric oxide was mixed with glowing nitrogen activated by means of an oscillatory discharge. The two oxides showed bands in the region (1000—2500 Å.) accessible to a vacuum spectrograph. In addition to the β and γ bands of nitric oxide characteristic of the afterglow, a new system (δ band) was found with the same final levels, *i.e.*, levels associated with the normal electronic state of the molecule. The initial level is an electronic state with zero vibration (level *C*) and the 0—0 δ-band is at 1915·7 Å. (6·44 volts). A few bands of the fourth positive group of carbon monoxide were obtained in the afterglow. The total energy of the levels affected was 8·2—9·0 volts. The conclusion is reached that the excitation of spectra in the afterglow is caused by a nitrogen molecule in one of a series of metastable states carrying the corresponding energy. The experiments support the view that atoms of nitrogen combine to form an excited molecule responsible first for the emission of α bands and later for the excitation of other spectra.

R. A. MORTON.

Electronic states and band spectrum structure in diatomic molecules. VII. $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2P$ transitions. R. S. MULLIKEN (Physical Rev., 1928, [ii], **32**, 388—416; cf. this vol., 105).—The empirical structure types for $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2P$ bands are discussed. The arrangement of the rotational levels in the ^2P state changes continuously with the parameter $\Delta E/B$ (ΔE=electronic doublet separation), the changes accounting largely for observed variations in band structure. Examples are given, and it is shown that the views of Hill and Van Vleck are supported. A consistent notation is applied to the branches of MgH, CaH, OH, ZnH, CdH, HgH, and NO bands, and has already been used for BO and CH λ 3900. The detailed discussion of band structure, missing lines, and intensity relationships indicates close agreement between the later formulæ and the experimental data. R. A. MORTON.

Fluorescence and absorption of a mixture of mercury and zinc vapours. J. G. WINANS (Physical Rev., 1928, [ii], **32**, 427—434).—Shorter rays than 2000 Å. (aluminium spark) excite vapour distilling from slightly amalgamated zinc, the first triplet of the sharp series of zinc being emitted. Neither the non-distilling vapour nor that distilling from pure zinc is excited. The same kind of mercury–zinc mixture shows continuous absorption from <1850 to 2050 Å. in distilling but not in stagnant vapour. The stagnant vapour and the zinc vapour show, in addition to the absorption lines of zinc, three bands, two of which correspond with absorption bands in cadmium. The absorption spectrum of mercury differs from that of the amalgam. The fluorescence is emitted by 2^3S zinc atoms produced possibly through absorption by HgZn molecules and dissociation into excited zinc and normal mercury atoms, or else through collisions of the second kind between normal zinc atoms and excited HgZn molecules. R. A. MORTON.

Absorption bands in the spectra of mixtures of metallic vapours. R. K. WARING (Physical Rev., 1928, [ii], **32**, 435—442).—At a given temperature, the amount of thallium in the vapour state is

increased by adding mercury vapour, indicating that thallium–mercury molecules are formed. A number of absorption bands are attributed to HgTl, but the resolving power was not sufficient to disclose structure. Asymmetric broadening of atomic thallium lines and the 2288 Å. line of cadmium, due to mercury vapour, has been observed; this may be due either to a superimposed molecular band or to transfer of kinetic energy by collisions. Mixtures of indium and cadmium vapours at 400°, 500°, and 800° show absorption bands due to InCd molecules. The short wavelength limits are given. The degree of resolution used disclosed traces of structure. R. A. MORTON.

Polarisation of resonance radiation in mercury. H. F. OLSON (Physical Rev., 1928, [ii], 32, 443—446).—The line $1^1S_0-2^3P_1$ of mercury excited by plane polarised light shows incomplete polarisation with and without a weak field parallel to the electric vector. The initial polarisation depends on the relative intensities of the hyperfine structure lines in the exciting light. A successful interpretation of data is supplied on the basis of a semi-classical model. The damping constant is found to be $1{\cdot}02(\pm0{\cdot}02)\times10^7$ sec.$^{-1}$ R. A. MORTON.

Comparison of measurements of critical potentials of mercury vapour. J. C. MORRIS, jun. (Physical Rev., 1928, [ii], 32, 447—455).—A special tube has been designed for comparing the different methods for determining the critical potentials of mercury vapour. For critical potentials other than those of ionisation the Hertz method is the best: of the 13 critical potentials below ionisation, 10 have spectroscopic significance, whilst 3 are probably due to mercury molecules. The partial current method (Franck and Hertz) gave concordant results but less resolution, whilst the method of Franck and Einsporn gave results indicating that it serves to detect photoelectric effects and not metastable atoms. Compton's method gave satisfaction. Three ultra-ionising potentials at 10·65, 11·34, and 11·78 volts occur, but an attempt to test the molecular origin of these high ionising potentials failed. R. A. MORTON.

Spark spectra of mercury vapour. J. VALASEK (J. Opt. Soc. Amer., 1928, 17, 102—106).—The critical potentials necessary for the excitation of the E_3 spectrum of mercury vapour (cf. Bloch and Bloch, A., 1924, ii, 78) have been found to be 108 and 118 volts. W. E. DOWNEY.

Time interval between the appearance of spectral lines in the spectra of alkali and alkaline-earth metals. G. L. LOCHER (J. Opt. Soc. Amer., 1928, 17, 91—101).—Using the method of Beams (A., 1926, 1069), the time intervals between the appearance in spark discharge spectra for fifty lines of the above metals have been found to vary between zero and 2×10^{-8} sec. W. E. DOWNEY.

Second spark spectrum of cadmium, Cd III. J. C. MCLENNAN, A. B. MCLAY, and M. F. CRAWFORD (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 45—54). —The spark spectrum of cadmium in air has been measured between 2250 and 1850 Å., and in hydrogen between 1850 and 1450 Å. The chief wave-lengths correspond with a d^9p-d^9s transition in Cd^{++}. A new multiplet $^2P(d^{10}s)-^2D(d^9s^2)$ has been discovered. C. W. GIBBY.

Arc spectrum of germanium. C. RICHTER (Z. wiss. Phot., 1928, 25, 380—393; cf. this vol., 99).—The arc lines of the spectrum of germanium have been schematically arranged in relation to five ground terms. The strongest lines show satellites. The Zeeman effect of a number of lines has been examined. W. E. DOWNEY.

Regularities in the spark spectrum of hafnium (Hf II). W. F. MEGGERS and B. F. SCRIBNER (J. Opt. Soc. Amer., 1928, 17, 83—90).—The wave-lengths of some 1500 hafnium lines have been accurately measured. Attempts to classify Hf I lines have not been successful, but 206 lines ascribed to Hf II have been arranged. W. E. DOWNEY.

Structure of the first spark spectrum of silver, Ag II. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 1—13; cf. Beals, A., 1926, 1071).—The spectrum Ag II is similar to Cu II and Zn II, and is in agreement with the structure predicted by the Hund theory. The deep-lying $^2D(d^9s^2)$ term of Ag I has been separated, and the screening constants for orbits of the 4_3 type have been calculated. C. W. GIBBY.

First spark spectrum of gold, Au II. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 103—115).—The first spark spectrum of gold has been measured from 2225 to 1390 Å. The $^{3,1}D(d^9s)$, $^{3,1}F,D,P(d^9p)$, and $^{3,1}D(d^9,s)$ terms of Au II corresponding with those most easily recognised in Cu II and Ag II have been identified. C. W. GIBBY.

Influence of argon on the spectrum of sulphur. J. C. MCLENNAN, R. RUEDY, and L. HOWLETT (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 79—86).—The influence of argon on the spectrum of sulphur from sulphur dioxide has been investigated. At low pressures the spark lines are suppressed and the arc lines enhanced. Similar results were obtained with an electrodeless discharge. With increasing current in the primary the intensity of the argon lines reached a maximum, whilst that of the sulphur lines increased steadily. C. W. GIBBY.

Spark spectra of [sulphur and of] selenium and tellurium. L. BLOCH and E. BLOCH (Compt. rend., 1928, 187, 562—564).—Extension of earlier experiments (A., 1927, 1117) led to the identification of three successive degrees of excitation of tellurium, Te II (3374·10—2304·29), Te III (3365·17—2239·50), and Te IV (3345·93—2226·07), corresponding with singly-, doubly-, and triply-ionised atoms, respectively, the arc spectrum being designated Te I. No new rays were found on repetition of experiments with sulphur, but an additional selenium spectrum, Se IV (3360·36—2446·96), was identified. The wave-lengths of the new rays are given. J. GRANT.

Absorption in excited krypton and xenon and the spectra of the inert gas type I. J. C. MCLENNAN and R. RUEDY (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 15—26).—In krypton the component of shorter wave-length of pairs of constant frequency-

difference is absorbed, these lines representing the transition $^3P_2-p$. The unabsorbed component originates in the $^1P_1$ level. Separation occurs between the $^3P_1$ and $^1P_1$ levels (4930) for a few lines; also the $^3P_2{}^1P_1$ separation for the strongest ultra-violet lines. Intercombination lines between triplet and singlet systems occur in all the rare gases except helium. The Na^+ spark lines in the violet correspond with the red neon lines $2p_j-S_i$. C. W. GIBBY.

Fine structure of the scattered radiation from graphite. B. DAVIS and D. P. MITCHELL (Physical Rev., 1928, [ii], 32, 331—335).—Experiments with a double *X*-ray spectrometer on the " undisplaced " scattered radiation from graphite indicate that the broadening of the spectral line is due to fine structure and a small displacement. Using a molybdenum target, four lines were observed: (*a*) the undisplaced line Mo-$K\alpha_1$ scattered from the whole atom; (*b*), (*c*), and (*d*) displaced 0·0012, 0·002, and 0·0113 Å., respectively, from $K\alpha_1$, in the direction of longer wave-lengths. The line (*d*) agrees with $h\nu'-h\nu-Ve$, where Ve is the energy level (287 volts) of the carbon atom. The relation does not hold for (*b*) and (*c*). No evidence of scattered radiation was obtained on the short-wave side of the Mo-$K\alpha_1$ position.

R. A. MORTON.

At. wt. of silver. O. HONIGSCHMID (Z. Elektrochem., 1928, 34, 625—627).—The determinations in the Munich laboratories gave (N=14·008) Ag=107·880, 107·879 (A., 1927, 806). Recent experiments on the ratio barium perchlorate/barium chloride/silver give Ag=107·880 (O=16).

S. K. TWEEDY.

Progression relation in the molecular spectrum of oxygen occurring in the liquid and in the gas at high pressure. O. R. WULF (Proc. Nat. Acad. Sci., 1928, 14, 609—613).—In gaseous oxygen at moderate and high pressures, and also in liquid oxygen, several investigators have observed a number of bands in the visible and ultra-violet up to 2400 Å., where continuous absorption begins. These are shown to constitute a progression of bands and are quite distinct from the Schumann–Runge system and the atmospheric bands. The intensity of the bands increases rapidly to shorter wave-lengths for any one length of light path and concentration of oxygen. The behaviour observed may be explained by supposing that polymerised molecules of oxygen, O_4, decompose into normal ozone molecules and either excited or unexcited oxygen atoms. The effect of dissociation into a normal oxygen atom and an excited ozone molecule cannot be calculated, since nothing is known about the electronic levels of the O_3 molecule.

M. S. BURR.

Time lag in the emission of spectral lines excited in a vacuum. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1928, 4, 361—363).—Previous work on the retardation of the emission of spectral lines has been extended by photographing the spectra on a moving photographic film. In the oscillatory discharge from copper and aluminium at diminished pressures it is found that although the spark lines are emitted immediately there is a lag of at least 10^{-5} sec. before the arc lines appear. As the emission of the arc lines proceeds their intensity first increases to a maximum and then gradually fades away. Many of the lines show much stronger reversal in air than in a vacuum. It is suggested that whilst the emission of spark lines is a consequence of the discharge process, some time must elapse before the evacuated space contains a sufficient number of electrons for the excitation of the arc lines. The change in intensity is attributed to the recombination and subsequent re-excitation of the ionised atoms.

A. E. MITCHELL.

Relative intensities of the Stark effect components of the Balmer H_β and H_γ lines. H. MARK and R. WIERL (Naturwiss., 1928, 16, 725—726).—The intensities of Stark effect components calculated according to Schrodinger's wave mechanics are in numerous instances the reverse of those found by Stark. For H_β and H_γ, Stark's data have been confirmed by maintaining the canal rays parallel to the lines of force of the resolving field; if, however, the canal rays proceed vertically to this direction, the conditions being otherwise unchanged, the results are in agreement with Schrodinger's theory. R. A. MORTON.

Absorption coefficient of slow electrons in mercury vapour. T. J. JONES (Physical Rev., 1928, [ii], 32, 459—466).—The absorption coefficient α in mercury vapour for electrons with energies of 0·5—400 volts has been determined by two methods. In the first, a homogeneous electron beam was obtained by bending electrons through a series of slits suitably arranged in a magnetic field, whilst the second method gave a fairly homogeneous beam without the use of a magnetic field. The values of α obtained by the two methods agree fairly well. The absorption coefficient increases continually as the electron energy decreases to 0·5 volt. No evidence was obtained for the sharp decrease in α for electrons slower than 3 volts as reported by Beuthe (this vol., 213). The results agree fairly well with those of Maxwell (A., 1926, 989) over the whole range of electron energies and with those of Brode (A., 1925, ii, 1020) at the lower energies. R. A. MORTON.

Oscillations in ionised gases. I. LANGMUIR (Proc. Nat. Acad. Sci., 1928, 14, 627—637).—Theoretical. Electrons accelerated from a hot cathode, and originally forming a beam of cathode rays with uniform translational motion, rapidly acquire a random or temperature motion (A., 1926, 3; this vol., 342). This scattering appears to be due to oscillations of the electrodes of less than 0·2 volt and frequencies up to $1{\cdot}2\times10^9$. The oscillations must be regarded as compressional electric waves, probably analogous to sound waves. The mathematical theory of these oscillations in the "plasma," or neutral regions containing approximately equal numbers of ions and electrons, is discussed.

M. S. BURR.

Element of time in the photo-electric effect. E. O. LAWRENCE and J. W. BEAMS (Physical Rev., 1928, [ii], 32, 478—485).—The time variation of the photo-electric emission from a metal surface illuminated by light flashes of 10^{-8} sec. duration has been studied. Photo-electric emission begins in less than

3×10^{-9} sec. after the beginning of the illumination of a potassium hydride surface. The time during which the photo-electric emission persists after cessation of irradiation is less than 10^{-8} sec. A wave travelling along a wire resulting from the sudden change of potential of one end by a spark discharge is so steep that the time necessary for about half the wave front to pass a point 6 m. along the wire is $4 \cdot 5 \times 10^{-9}$ sec. The short flashes of light were obtained by the Kerr cell electro-optical shutter (Proc. Nat. Acad. Sci., 1927, **13**, 207), the speed of operation of which has now been determined. R. A. Morton.

Scattering of positive ions from a platinum surface. R. W. Gurney (Physical Rev., 1928, [ii], **32**, 467—477).—The velocity distribution, angle distribution, and critical energy of potassium, cæsium, and lithium ions scattered from a platinum surface have been determined. R. A. Morton.

Condition of radium salts after storage in sealed glass tubes. A. G. Francis and A. T. Parsons (Nature, 1928, **122**, 571).—Considerable quantities of radium salts (*e.g.*, 171·8 and 54·9 mg. of radium as 92% chloride and 50% bromide, respectively), sealed in glass tubes, can be safely kept unopened for at least 7 years, provided the drying has been thorough. Labels or other foreign materials should not be attached directly to the glass of tubes containing radium, and the tubes should be stored out of contact with organic matter.

A. A. Eldridge.

γ-Rays from potassium salts. W. Kolhörster (Naturwiss., 1928, **16**, 28; Chem. Zentr., 1928, i, 1746).—Measurements of γ-radiation at Stassfurt are recorded. A. A. Eldridge.

Ionisation curve of pure oxygen for α-rays from polonium. T. Onoda (J. Phys. Radium, 1928, [vi], **9**, 185—186).—The ionisation curve of pure oxygen for α-rays from polonium has been determined. The gas used was prepared by an electrolytic method. From the curve the extrapolated range of the rays was found to be $3 \cdot 63 \pm 0 \cdot 01$ cm. at 15° and 760 mm., whilst at 0° and 760 mm. it was found to be $3 \cdot 49 \pm 0 \cdot 01$ mm. The range in air under the first conditions of temperature and pressure was $3 \cdot 87 \pm 0 \cdot 01$ cm., so that the stopping power of the oxygen molecule relative to air is $1 \cdot 066 \pm 0 \cdot 01$. A. J. Mee.

Attempt to accelerate the rate of radioactive transformation. H. Herszfinkiel and L. Wertenstein (Nature, 1928, **122**, 504).—The unexpected apparent stability of uranium atoms under bombardment by radium α-rays might be due to the formation of an atom of uranium-II, and not of uranium-X_1; the period of uranium-II, however, is too long to permit its detection, although with thorium the product formed after one α- and two β-transformations would be radiothorium with a period of only 2·02 years. On bombardment of thorium dioxide with radon α-rays, however, no change in α-ray activity was observed. It is computed that the upper limit of the probability of an α-ray collision producing an explosion of this type in the α-satellite is less than 1 in 8×10^6.

A. A. Eldridge.

Apparent evidence of polarisation in a beam of β-rays. R. T. Cox, C. G. McIlwraith, and B. Kurrelmeyer (Proc. Nat. Acad. Sci., 1928, **14**, 544—549).—An experiment is described in which β-particles are twice scattered at right angles and then enter a Geiger counter. The relative numbers entering are noted as the angle between the initial and final segments of the path is varied. Readings were taken for angles between 90° and 270°. The results show a marked asymmetry which can be explained most easily on the assumption that there is a true polarisation due to the double scattering of asymmetrical electrons. A. J. Mee.

Existence of meso-products in the disintegration series of actinium. J. von Weszelszky and L. Imre (Z. anorg. Chem., 1928, **175**, 141—160).—A quantitative separation of radioactinium from the other disintegration products of actinium is shown to be effected by heating the oxide mixture containing the actinium in radioactive equilibrium with its disintegration products in a current of dry chlorine saturated with the vapour of sulphur chloride, whereby radioactinium chloride alone sublimes. It may be further purified by precipitation with ammonia or hydrogen peroxide after addition of a small quantity of thorium nitrate to the chloride solution. The activity of the purified product rises to a maximum in about 14 days, whereas according to the Geiger–Nuttall theory maximum activity should not be reached until the twentieth day. It is shown that this variation from the theory is not due to the presence of an inactive product which further disintegrates into a very active product, nor to the greater homogeneity of the volatilised radioactinium as compared with that obtained by other methods, and the suggestion is made that the anomalies found in this series are of a similar nature to those found in other parts of the periodic system where the atomic weights do not increase with the atomic number.

A. R. Powell.

Angular scattering of electrons in hydrogen and helium. G. P. Harnwell (Proc. Nat. Acad. Sci., 1928, **14**, 564—569).—Experiments were made to determine the possibility of selective angular scattering of electrons in atomic hydrogen in order to extend the work on scattering by crystals, and to test the observations of Dymond on the scattering of electrons by helium. The apparatus is described in detail. It was found that there were no favoured angles for scattering from hydrogen or from helium. Dymond's experiments were repeated, but his results could not be reproduced. A. J. Mee.

Isotopes of neon. T. R. Hogness and H. M. Kvalnes (Nature, 1928, **122**, 441).—The existence of Ne^{21} is confirmed. Atmospheric neon is estimated to be composed of Ne^{22} 10, Ne^{21} 2, Ne^{20} 88%.

A. A. Eldridge.

Polarisation of the resonance radiation from degenerate systems. F. C. Hoyt (Physical Rev., 1928, [ii], **32**, 377—387).—The polarisation of radiation excited by light in resonance with the principal absorption frequency of a gas has been discussed on the basis of wave mechanics. Calculation of the electric moment of the perturbed atom

on the Schrodinger density hypothesis shows that when the incident light is linearly polarised the radiation has the same degree of polarisation as though the atom were in a weak magnetic field parallel to the electric vector of the light. With circular polarisation this fictitious field is perpendicular to the plane of polarisation. Heisenberg's rule, deduced from the correspondence principle, is confirmed. R. A. MORTON.

Quantum theory of electronic impacts. J. R. OPPENHEIMER (Physical Rev., 1928, [ii], **32**, 361—376).—Earlier mathematical treatment of electronic collisions has erroneously neglected terms in the solution corresponding with an interchange of the colliding electron with one of those in the atom. The corrected first-order cross-section for elastic collisions with atomic hydrogen and helium has been calculated by Dirac's method. Using Born's method for hydrogen, the complete solution indicates that the elastic cross-section becomes infinite, for low velocities with the reciprocal of the velocity. For hydrogen, the first-order cross-section is a monotonically increasing function; for atoms with completely paired electrons the monotonic increase is broken by a minimum at velocities corresponding with about 1 volt, and the higher the azimuthal quantum number of the paired valency electrons the more marked is the minimum and the lower the voltage at which it occurs. R. A. MORTON.

Recent theories of the atom. W. F. G. SWANN (J. Opt. Soc. Amer., 1928, **17**, 163—197).—A lecture.

Wave mechanics and radioactive disintegration. R. W. GURNEY and E. U. CONDON (Nature, 1928, **122**, 439).—Radioactive disintegration is regarded as a natural consequence of the laws of quantum mechanics. A. A. ELDRIDGE.

Interpretation of Dirac's theory of the electron. G. BREIT (Proc. Nat. Acad. Sci., 1928, **14**, 553—559).—Mathematical. Dirac's matrix-operators in wave-mechanics, α_1, α_2, and α_3, have not yet been given any physical significance. It is shown that α_1, α_2, and α_3 can be regarded as operational matrix-representations of the velocity-vector x/c, y/c, z/c, in the same way as the Pauli matrix-operators, s_x, s_y, s_z, represent the spin of the electron. A. J. MEE.

Properties of salt-like compounds and atomic structure. II. Influence of deformation of the electron sheaths. K. FAJANS (Z. Krist., 1928, **66**, 321—354; Chem. Zentr., 1928, i, 2046).

The self-consistent field and the structure of atoms. J. C. SLATER (Physical Rev., 1928, [ii], 32, 339—348).—Hartree's method (this vol., 216, 933) for the solution of problems in atomic structure has been examined in relation to Schrodinger's equation. Term values calculated by Hartree require correction because (*a*) electron distributions are not really spherical, (*b*) the resonant interactions between electrons are not allowed for, and (*c*) polarisation energy is neglected. The sizes of the corrections are of the same order as the errors occurring in Hartree's numerical examples. R. A. MORTON.

Fluorescence of fluorspars excited by light of different wave-lengths. H. NISI and K. MIYAMOTO (Proc. Imp. Acad. Tokyo, 1928, **4**, 357—360).—Fluorspars are found to be divisible into three classes according as they show both red and blue fluorescence, only blue fluorescence, or no appreciable fluorescence. The fluorescence spectrum of a specimen of the first class was found to comprise two main groups of lines. One group excited by wave-lengths in the region of 2300 Å. comprises lines in the red and yellow usually accompanied by others in the blue and green portions of the spectrum. The other group is excited by wave-lengths in the region of 2800 Å. The red and yellow lines of the 2300 Å. group are identified with samarium phosphor lines and it is suggested that those of the 2800 Å. group with the blue and green lines are due to europium and terbium phosphors. It is also suggested that the fluorescence phenomenon is due to the presence of traces of rare-earth phosphors. A. E. MITCHELL.

Raman effect in highly viscous liquids. S. VENKATESWARAN (Nature, 1928, **122**, 506).—Experiments with glycerol and mixtures of glycerol with water indicate that the transformation of the monochromatic incident radiation into general or white radiation is closely connected with the special state of molecular aggregation which gives rise to a high viscosity. A. A. ELDRIDGE.

Wave-length shifts in scattered light. W. H. MARTIN (Nature, 1928, **122**, 506—507).

Scattering of light by particles of metallic oxides dispersed in dry air. T. C. NUGENT and H. P. WALMSLEY (Proc. Physical Soc., 1928, **40**, 269—280).—The changes with time in the brightness of the Tyndall light from clouds of the oxides of zinc, copper, cadmium, and arsenic were measured, and can be accounted for by supposing that the particles disappear by aggregation and sedimentation. The curves obtained fluctuate in a similar way to the ionisation currents from the same cloud, suggesting that aggregation produces unstable complex particles which periodically break up in large numbers. A series of clouds vaporised from various masses, m, of arsenic trioxide gave values for the initial brightness of the Tyndall beam approximately proportional to $m^{2/3}$. In certain clouds the rapid fluctuations in brightness appear to form groups which succeed one another at intervals given by $t=Ar^n$, where A and r are constants and n is an integer. C. J. SMITHELLS.

Wave-lengths in the nitrogen peroxide absorption spectrum. L. C. K. CARWILE (Astrophys. J. 1928, **67**, 184).—Wave-lengths from 3978·67 to 6323·22 Å. in the absorption spectrum of nitrogen peroxide have been measured and the results published privately (University of Virginia, U.S.A.). A. A. ELDRIDGE.

Infra-red absorption spectra of the halogen derivatives of methane. M. A. EASLEY, L. FENNER, and B. J. SPENCE (Astrophys. J., 1928, **67**, 185—194).—Infra-red absorption spectra (0·8—3 μ) of methyl iodide, methylene chloride, bromide, iodide, and iodobromide, chloroform, bromoform, carbon tetrachloride and tetrabromide, and trichlorobromomethane were studied. Bands were not observed with compounds containing no hydrogen. A. A. ELDRIDGE.

Absorption spectra of water and ice, with reference to the spectra of the major planets. J. C. McLennan, R. Ruedy, and A. C. Burton (Proc. Roy. Soc., 1928, **A**, **120**, 296—302).—The absorption spectra of water and of ice have been photographed using long columns, and the bands obtained compared with those in the spectra of Uranus, Saturn, Neptune, and Jupiter. The strong band at 7200—7260 Å. given by these planets has been shown to be similar to that given by liquid water, whilst the band at 5430 Å. remains unidentified. The absorption of ice is different from that of water, the intensities being shifted towards longer wave-lengths. J. L. Buchan.

Light absorption and coloration of alkali halides. K. Przibram (Naturwiss., 1928, **16**, 27—28; Chem. Zentr., 1928, i, 1747).—The absorption maxima in the visible region of coloured alkali halides are in the order fluoride, chloride, bromide, iodide, and sodium, potassium, cæsium, rubidium for displacement towards the long wave-length side. The lability of the coloration increases in the order sodium, potassium, cæsium, rubidium chloride. A. A. Eldridge.

Luminescence of solid nitrogen under cathode-ray bombardment. J. C. McLennan, H. J. C. Ireton, and E. W. Samson (Proc. Roy. Soc., 1928, **A**, **120**, 303—311).—An apparatus for producing the luminescence emitted by solid nitrogen bombarded with high-speed electrons is described, and the spectrum of this luminescence has been photographed from 2000 to 8600 Å. The usual bands N_1, N_2, and N_4 are found and also bands at 6400 (probably N_3), 8535, 6725, and 6187 Å. Other bands are found at shorter wave-lengths and are tabulated. At the temperature of liquid hydrogen the bands N_1, N_2, and N_4 are all phosphorescence bands, but N_1 is thermoluminescent at a slightly higher temperature. Curves are given showing the rates of decay of the bands, each stage of which can be represented by an equation of the same form. The probable cause of the luminescence is discussed. J. L. Buchan.

Photo-electric emission of water and of aqueous solutions. L. Counson and A. Molle (Arch. Sci. phys. nat., 1928, **10**, 213—242).—Purified water is found to be photo-electric towards light of the region 2000—1300 Å. This effect is not due to accidental impurities on the surface of the water. Solutions of alkali halides are less photo-electric than pure water. Solutions of salts containing oxygen are more photo-electric than pure water. W. E. Downey.

Decomposition of ammonia by high-speed electrons. J. C. McLennan and G. Greenwood. —See this vol., 1197.

Chemical reactions of carbon monoxide and hydrogen after collision with electrons. A. Caress and E. K. Rideal. —See this vol., 1198.

Influence of disaggregation on the fluorescence of complex natural substances. H. Pringsheim and O. Gerngross (Ber., 1928, **61**, [*B*], 2009—2011).—The powdered polysaccharide is placed on non-fluorescent, porous plates and examined in filtered, ultra-violet light. Gelatin preparations are observed in solution or as films on glass plates. Disaggregation of lichenin, cellulose, glycogen, amylopectin, starch-amylose, inulin, inulin acetate, and gelatin appears to cause marked increase in fluorescent power. H. Wren.

Relationships between absorption spectrum and chemical constitution of azo dyes. II. Influence of position isomerism on the absorption spectrum of nitro-derivatives of benzeneazophenol, -*o*-cresol, and -*m*-cresol. W. R. Brode (Ber., 1928, **61**, [*B*], 1722—1731).—Determinations have been made of the absorption spectra of the nine possible mononitro-derivatives of benzeneazo-phenol, -*o*-cresol, and -*m*-cresol containing the nitro-group in the non-hydroxylated nucleus between 400 and 1300 f. in alcoholic and aqueous sodium hydroxide solution. The results, together with observations on the corresponding methyl compounds (to be published later), show that increase in mol. wt. is usually accompanied by decrease in the frequency of the absorption bands. Substitution of a nitro-group in the *p*′-position causes marked increase in intensity of the first main band and slight decrease of that of the second band. The frequency of the main band is displaced towards lower values in comparison with the isomeric compounds substituted in the *o*′- or *m*′-position. Introduction of a nitro-group in the *o*′-position, compared with the relationships of the *m*′-substituted isomerides, induces a general decrease in the intensity of absorption without altering the frequency of the bands. A subsidiary band on the side of higher frequency of the main band is shown by *o*′- and *m*′-substituted derivatives of benzeneazophenol. The main absorption band of all these compounds in aqueous sodium hydroxide appears to be formed of two components, although actually more than two are present. The equilibrium which appears to exist between the two components or bands depends on the position of the substituting group in the molecule. The same general effect is experienced with nitro- and methyl derivatives. Substitution in the *o*′-position causes an increase in intensity in the component of less frequency and a corresponding decrease in that of greater frequency. Substitution in *m*- or *o*′-position causes a weakening in the component of lower frequency; if a substituent is also present in the *o*′-position, a diminution of the sum of the intensities of both bands is induced. Introduction of a substituent in the *m*′-position does not cause a marked difference in the spectrum from that of the unsubstituted compound. Substitution in the *p*′-position causes a very decided increase in the intensity of the main band, a diminution in that of the second band, and a lowering of frequency of the middle of the main band. Mononitro-derivatives of benzeneazophenol in aqueous sodium hydroxide show the same general duplex structure and the same equilibrium in the second absorption band as in the first or main band, thus showing that the former is a harmonic of the latter and similarly influenced by position or substitution effects.

o-*Nitrobenzeneazo*-o-*cresol*, m. p. 105°, m-*nitrobenzeneazo*-o-*cresol*, m. p. 132—133°, o-*nitrobenzene*-

azo-m-*cresol*, m. p. 162°, and m-*nitrobenzeneazo*-m-*cresol*, m. p. 164—166°, are incidentally described.
H. WREN.

Structural relationships of silicates. B. GOSSNER (Ber., 1928, **61**, [*B*], 1634—1638).—Röntgen-spectrographic measurements of numerous silicates disclose the following regularities. A general structure with a definite number of oxygen atoms and definite sum of the numbers of other atoms can recur in spite of considerable variation in the nature of the latter. Such similar general structure is accompanied by a close similarity in volume and in length of the side of the elementary parallelepiped. Silicates are thus shown to be related to one another in a manner unsuspected from goniometric measurement. Data are recorded for the three groups (1) babingtonite, $CaFeSi_2O_6,SiO_2$, anorthite, $CaSi_2O_5,Al_2O_3$, and epididymite, $BeSi_2O_5,SiO_3NaH$; (ii) beryl, $3BeSi_2O_5,Al_2O_3$, and cordierite, $Mg_3Si_5O_{12},2Al_2O_3$; (iii) diopside, $MgCaSi_2O_6$, and tremolite, $Mg_3CaSi_4O_{12}$. H. WREN.

Dielectric constant and electric moment of carbon monoxide, carbonyl sulphide, carbon disulphide, and hydrogen sulphide. C. T. ZAHN and J. B. MILES, jun. (Physical Rev., 1928, [ii], **32**, 497—504).—Debye's equation $(\varepsilon-1)vT=AT+B$, in which ε is the dielectric constant, v is the specific volume referred to the ideal volume at S.T.P., T is absolute temperature, and A and B are constants, applies well to the above gases. Values for A and B are given and from the relation $\mu^2=1\cdot198\times10^{-36}B$, the electric moment μ is calculated, giving the values: carbon monoxide, 0·10; carbon disulphide, 0·326; carbonyl sulphide, 0·650; and hydrogen sulphide 0·931 in c.g.s. e.s. units $\times10^{18}$. Data by other workers and discrepancies are discussed. It seems likely that carbon disulphide and carbonyl sulphide, like carbon dioxide, possess a rectilinear structure.
R. A. MORTON.

Experimental proof of "negative dispersion." H. KOPFERMANN and R. LADENBURG (Nature, 1928, **122**, 438—439).

Ionising potentials of methane, ethane, ethylene, and acetylene. J. C. MORRIS, jun. (Physical Rev., 1928, [ii], **32**, 456—458).—The ionisation potentials of the pure gases determined in an ionisation tube of the Mackay type, calibrated against mercury and helium, are: methane 14·4, ethane 12·8, ethylene 12·2, acetylene 12·3 volts, correct within 0·2 volt.
R. A. MORTON.

Structure of thin films. XII. Cholesterol and its effect in admixture with other substances. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1928, **A**, **120**, 473—482; cf. this vol., 937).—The action of cholesterol on unimolecular films of fatty acids and of other substances on water or dilute hydrochloric acid has previously been studied. It is found that the presence of cholesterol contracts the film, and curves are given showing this effect on films of myristic and oleic acids, nonylphenol, and ethyl palmitate. A similar effect is given by cholesteryl formate and acetate. The effect is less on vapour-expanded films than on liquid-expanded films. From measurements of the surface vapour pressures of these films it is concluded that the contraction given by cholesterol is probably not due to its attraction of the smaller molecules. The effect of other large molecules has also been studied, and similar results have been obtained, so it is thought that the large molecules offer a mechanical obstruction to the tilting of the small molecules, thus preventing them from covering so large an area. J. L. BUCHAN.

Height of ozone in the upper atmosphere. F. W. P. GÖTZ and G. M. B. DOBSON.—See this vol., 1209.

Internal field of polarisation [of the molecules of a substance under the action of an external field]. R. DE MALLEMANN (Compt. rend., 1928, **187**, 536—538).—Mathematical. In the case of a regular assembly of molecules, such as a cubic crystal, the field is zero. The field in the case of a fluid is essentially due to the irregularity of the molecular arrangement. W. E. DOWNEY.

Method for determining the Kerr constant of poor insulating materials by means of alternating electric fields. W. ILBERG (Physikal. Z., 1928, **29**, 670—676).—An improved method for determining the Kerr constant is described and applied to nitrobenzene. The constant is given for a range of wave-lengths in the visible and a dispersion curve constructed. The results are in agreement with Havelock's formula. R. A. MORTON.

Liquid crystals. L. S. ORNSTEIN (Physikal. Z., 1928, **29**, 668—670).—Largely explanatory. The tendency of liquid crystalline substances to form parallel "swarms" can be explained equally well by the aggregate swarm hypothesis and by the crystal hypothesis. R. A. MORTON.

Rotation dispersion and spatial configuration in complex salts of cobalt and of rhodium containing ethylenediamine and *trans*-1 : 2-diamino*cyclo*pentane. F. M. JAEGER and H. B. BLUMENDAL (Z. anorg. Chem., 1928, **175**, 161—230).—Reduction with metallic sodium of an absolute-alcoholic solution of *cyclo*pentanedionedioxime affords r-trans-1 : 2-*diaminocyclopentane* as a colourless liquid, b. p. 170°, with a faint ammoniacal odour [*diacetyl* derivative, monoclinic prisms, m. p. 219—220° (corr.)]. The *r*-base may be resolved into its optical antipodes by fractional crystallisation of the hydrogen *d*- or *l*-tartrate. The *l*-base has b. p. 166° (corr.), d_4^{15} 0·9463, and $[\alpha]_{5463}^{15}$ −64° [*diacetyl* derivative, m. p. 248° (corr.); *chloride*, $[\alpha]_D^{15}$ −22°; *sulphate*, $[\alpha]_D^{15}$ −12°; *hydrogen* d-*tartrate*, m. p. 143°, $[\alpha]_D^{15}$ +10·5°]. On boiling a solution of cobalt chloride and hydrogen peroxide or a solution of sodium chlororhodite with the racemic base co-ordination complexes of the triethylenediamine type, $[M(C_5H_{12}N_2)_3]X_3$, are obtained, which can be resolved into their optical antipodes by means of *d*- or *l*-tartaric acid. The cobalt and the rhodium salts with the same direction of rotation have similar spatial configurations, the dextrorotatory ions containing 3 mols. of the *l*-base and the lævorotatory ions 3 mols. of the *d*-base; no compounds with 2 mols. of one base and 1 mol. of the other could be prepared. The following salts of the *r*-cobalt base were prepared: *chloride*, $[Co(C_5H_{12}N_2)_3]Cl_3,3H_2O$, triclinic blood-red prisms;

iodide ($1H_2O$), yellowish-brown precipitate; *nitrate* (anhyd.), red needles; *perchlorate* (anhyd.), red needles, and *chlorate* ($3H_2O$), blood-red monoclinic prisms. The following salts of the corresponding *r*-rhodium base have also been prepared: *chloride* ($2H_2O$), triclinic prisms; *bromide* ($1H_2O$), fine needles; *iodide* ($1H_2O$); *nitrate* ($2H_2O$); *chlorate* ($2H_2O$), monoclinic prismatic tablets; *perchlorate* (anhyd.), long, hair-like needles; *sulphate* and *nitrite*. The perchlorates of the *r*-cobalt and rhodium bases spontaneously decompose into their optical antipodes, the former above $-1\cdot5°$ and the latter above 48°. The optically active perchlorates of both bases crystallise with $12H_2O$, the chlorides with $4H_2O$, and the chlorates with $12H_2O$, all in the pentagonal icositetrahedral class of the cubic system; the nitrates and chlorides also crystallise with $3H_2O$ in hexagonal bipyramids and the perchlorates in rhombic crystals with $1H_2O$. The molecular dispersion of all the above salts is extraordinarily great; in the case of the cobalt salts it is three times as great as that of the corresponding triethylenediamine compounds for light of short wave-length and up to ten times as great for light of long wave-length, whilst in the case of the rhodium compounds the diamino*cyclo*pentane derivatives have seven to eight times as great a molecular dispersion as the corresponding ethylenediamine derivatives. Digestion of dichlorodiethylenediamine-cobaltic chloride with *r*-, *l*-, or *d*-*trans*-1 : 2-diamino*cyclo*pentane affords a new series of co-ordination complexes of the type $[Co\ en_2\ (C_5H_{12}N_2)]Cl_3$, the racemate of which is resolvable by means of *d*- or *l*-tartaric acid into two optical antipodes $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_DCl_3$ and $[Co\ en_2\ d\text{-}(C_5H_{12}N_2)]_LCl_3$. The following salts derived from the *r*-base are described: *diethylenediamine*-r-trans-1 : 2-*diamino*-cyclo*pentanecobaltic chloride* ($3H_2O$), *bromide* ($1H_2O$), and *iodide* (anhyd.), *nitrate* ($1H_2O$), and *perchlorate* ($4H_2O$). The values of $[\alpha]$ for the d- and l-*bromides* ($+2H_2O$) from the resolution of the *r*-bromide are as follows $[\alpha]^{18}_{4357}$ $\pm 835°$, $[\alpha]^{18}_{5185}$ $\pm 0°$, $[\alpha]^{18}_{5320}$ $\pm 162°$, $[\alpha]^{18}_{5875}$ $\pm 0°$, and $[\alpha]^{18}_{\cdot 4}$ $\pm 87\cdot5°$. The complexes derived from the *d*- and *l*-bases in the above way are partly racemic, optically active compounds which can be resolved into components which are not mirror images of one another, as they have formulæ of the type: $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_DX_3$ and $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_LX_3$. By treating cobalt chloride with diamino*cyclo*pentane and hydrogen peroxide and heating the solution with hydrochloric acid, bright green crystals of trans-*dichlorodi*-trans-1 : 2-*diamino*cyclo*pentanecobaltic chloride*, $[Cl_2(C_5H_{12}N_2)_2Co]Cl,2H_2O$, are obtained; this salt, when boiled with water, is converted into the *cis*-form (anhyd.). Attempts to convert these compounds into the corresponding ethylenediaminedi-*trans*-diamino*cyclo*pentane compounds failed, decomposition taking place into the triethylenediamine and tri-*trans*-diamino*cyclo*pentane compounds. Compounds derived from 2 mols. of one optical isomeride and 1 mol. of the other were also unstable, decomposing as follows: $3[Co(d\text{-}C_5H_{12}N_2)_2l\text{-}C_5H_{12}N_2]X_3 = [Co(d\text{-}C_5H_{12}N_2)_3]X_3 + 2[Co(l\text{-}C_5H_{12}N_2)_3]X_3$. A. R. POWELL.

Present position of the strain theory. W. HÜCKEL (Fortschr. Chem. Phys. u. physikal. Chem., 1928, **19**, 1—101; Chem. Zentr., 1928, i, 2037).—A critical discussion. A. A. ELDRIDGE.

Vacuum grating spectrograph for ultra-violet and soft *X*-rays. J. THIBAUD (J. Opt. Soc. Amer., 1928, **17**, 145—154).—A vacuum grating spectrograph using the tangential incidence method is described. It has been used to measure various soft *X*-rays of wave-lengths varying from 17·7 Å. ($L\alpha$ of iron) to 65 Å. (M of molybdenum). Absorption spectra of carbon, nitrogen, and oxygen have been obtained. W. E. DOWNEY.

Effect of chemical combination on the structure of the *K* absorption limit. B. DAVIS and H. PURKS (Physical Rev., 1928, [ii], **32**, 336—338).—The structure and shift of position in the *K* absorption limits of silver, molybdenum, and copper and the compounds Ag_2S, Ag_2O, MoO_3, MoS_2, and Mo_2O_3 have been determined by means of the double *X*-ray spectrometer. The width for a pure element decreases with increasing atomic number. In the compounds, the absorption limit is broadened, but little displacement occurs. There is marked evidence of fine structure in Mo_2O_3. Apparently the readjustment of energy which occurs with chemical combination extends throughout the whole atomic system and is not confined to the outer layers of the atom. The position and form of the *K* limit of molybdenum are independent of temperature. R. A. MORTON.

Velocity distribution of photo-electrons produced by soft *X*-rays. E. RUDBERG (Proc. Roy. Soc., 1928, **A**, **120**, 385—422).—An apparatus for studying the velocity of photo-electrons produced by soft *X*-rays on solid conductors is described. Curves showing the variation of photo-electric current with magnetic field strength are given for silver, copper, aluminium, and carbon, two curves for each, one before and the other after heating in a vacuum at 400°. From the shape of the curves it is concluded that the emission is made up of two parts: (1) a group of electrons of the low energy corresponding with only a few volts, and (2) a group of fast electrons of between 200 and 280 volts. Baking the electrode, *i.e.*, removing the adsorbed gas, reduces the emission, but this influence is confined to the low-velocity electrons. Curves are also given showing the distribution of energy over the field. The nature of the two groups in the emission is discussed. It is also suggested that some of the conclusions reached from experiments on soft *X*-rays should be modified. J. L. BUCHAN.

Reflexion and refraction of electrons by a crystal of nickel. C. J. DAVISSON and L. H. GERMER (Proc. Nat. Acad. Sci., 1928, **14**, 619—627).—The analogy between the reflexion of a homogeneous beam of electrons from a crystal face, previously observed (this vol., 683), and *X*-ray reflexion is discussed. The Bragg formula for the intensity maximum of *X*-rays does not, however, hold in the case of electrons at speeds due to bombarding potentials at least up to 600 volts. It is probable that the analogue of a given electron beam is the adjacent *X*-ray beam of shorter wave-length. This leads to values of the refractive index greater than unity. This is in agreement with the view that electron refraction in the

optical sense is a property of the crystal. Refraction in the case of electrons does not appear to arise from the same cause as for X-rays and light rays, since the trend of what may be regarded as the normal dispersion curve of nickel for the former is opposite to that of the normal dispersion curves of materials for the latter. M. S. BURR.

Diffraction of cathode rays by mica. S. KIKUCHI (Proc. Imp. Acad. Tokyo, 1928, **4**, 354—356).—An explanation is offered of the diffraction patterns obtained when a beam of cathode rays is passed through mica plates of different thickness (*ibid.*, 271). An electron in passing through a mica plate of appreciable thickness will be scattered more than once, so that during its passage through the plate a cathode-ray beam will become progressively more divergent. The energy losses must be small in comparison with the total energy, so that there will be no appreciable change in wave-length, the effect being the production of a point source of homogeneous rays in the crystal itself. Then if in the crystal there is a net plane of strong reflecting power this will reflect regularly all the rays giving rise to the reflexion and absorption lines observed (*loc. cit.*). Variation of the angle of incidence of the ray to this net reflecting plane and of the thickness of the crystal will then produce all the diffraction patterns observed. A. E. MITCHELL.

Spectrum and state of polarisation of fluorescent X-rays. A. H. COMPTON (Proc. Nat. Acad. Sci., 1928, **14**, 549—553).—The spectrum of the fluorescent X-rays from silver, excited by X-rays from a tungsten target, shows the complete absence of any continuous spectrum. Absorption measurements indicate that the line radiation constitutes more than 99% of the total radiation, the results being in agreement with the work of Sadler. The relative intensity and positions of the spectrum lines are approximately the same in the fluorescent as in the primary X-rays. By using the method of Hagenow and Compton, the polarisation of fluorescent X-rays was tested. The fluorescent X-rays from silver are unpolarised, with a probable error of 0·5%. A. J. MEE.

Polarisation of characteristic radiation. J. A. BEARDEN (Proc. Nat. Acad. Sci., 1928, **14**, 539—542).—An apparatus is described for finding the extent of polarisation of characteristic X-rays. Characteristic X-radiation is probably unpolarised, a result in agreement with the usual ideas on X-ray production, and with Compton's work on the polarisation of fluorescent radiation. A. J. MEE.

Spectrum of X-rays from the back of a tungsten target. E. LORENZ (Proc. Nat. Acad. Sci., 1928, **14**, 582—588).—The spectral distribution of radiation from the back of a tungsten target was investigated in order to gain information about the electrons producing it. A special tube was designed in order to obtain radiation of sufficient intensity. Five voltages varying from 22,400 to 82,500 were used. The spectrum was obtained by measuring for each voltage the ionisation currents as a function of the crystal angle, an ordinary Bragg spectrometer with a calcite crystal, and an ionisation chamber containing methyl iodide being used. The spectrum appears to be produced at high voltages mainly by secondary electrons. No secondary electrons, however, appear from the N levels when the voltage across the X-ray tube is 22,400 volts, and neither N nor M electrons when the voltage is 83,350. In order to explain this it is necessary to assume that there is practically no absorption of primary electrons in any level in the tungsten anode if the energy of the primary electrons exceeds that of the level by about 40 times. The probability of absorption in any level is thus a function of the voltage across the tube, reaching a maximum and then decreasing to zero for energies of primary electrons which exceed the energy of the level by about 40 times. It is therefore to be expected that the intensity of any characteristic series due to the knocking out of electrons from an atom will also be a function of the voltage of the tube, increasing at first, and then decreasing. A. J. MEE.

Destruction of single crystals of aluminium by rolling. T. SAKAO (Mem. Coll. Sci. Kyōto, 1928, **11**, 279—282).—Single-crystal sheets of aluminium were reduced 10% in thickness by rolling in small steps, and Laue patterns obtained after each pass. From the progressive distortion of the Laue spots it appears that a rotation of the crystal fragments takes place about an axis parallel to the direction of rolling, irrespective of the orientation of the original crystal. C. J. SMITHELLS.

Crystallographic orientation of electrolytically deposited metals [copper and nickel]. G. TAMMANN and H. STRAUMANIS (Z. anorg. Chem., 1928, **175**, 131—140).—On a polished copper cathode the crystals of electrolytically deposited copper (from sulphate solutions) are small and their orientation bears no relation to that of the base metal. But if the surface of the cathode is previously etched with nitric acid, ammonia and hydrogen peroxide, or ammonium persulphate, the electrolytically deposited metal grows in the same orientation as the crystals of the base metal, provided that only a low current density is employed. This growth takes place only when the deposition of the copper is a primary reaction: copper deposits formed by a secondary reaction, *e.g.*, by electrolysis of cyanide solutions, have an irregularly oriented structure. From ammoniacal solutions nickel is deposited on coarsely crystallised, etched nickel cathodes in a finely crystalline form which bears no crystallographic relation to the cathode. A similar behaviour is shown by nickel deposited from sulphate solutions on etched copper cathodes and by copper deposited on etched nickel cathodes. The deposition of copper on etched spheres of single-crystal copper is illustrated diagrammatically; on the cube poles octahedral nodules are formed, on the octahedral poles tetrahedral nodules, and on the dodecahedral poles prismatically arranged ridges, and the field between the various poles can be divided into regularly shaped zones according to the structure of the deposit thereon. The value of these indications in determining the orientation of crystals in a metal sheet is discussed. A. R. POWELL.

X-Ray analysis of copper–tin alloys. A. WESTGREN and G. PHRAGMÉN (Z. anorg. Chem., 1928, **175**,

80—89; cf. A., 1926, 1084).—*X*-Ray analysis of alloys of the copper–tin system by the powder method has, in general, confirmed recent work on the equilibria in this system. The maximum solid solubility of tin in copper is 15%, the parameter of the α-lattice increasing from 3·608 to 3·693 Å. by the gradual addition of tin. The β-phase, stable only at high temperatures, has a body-centred cubic lattice (a=2·972 Å. with 5% Sn) in which the tin and copper atoms are irregularly distributed at the lattice points. The γ-phase has a face-centred cubic lattice (a= 17·91 Å.) the elementary cube of which contains 416 atoms; the phase is homogeneous when the composition corresponds with $Cu_{31}Sn_8$. The concentration of valency electrons in this formula is the same as in those ascribed to the compounds which Bradley and Thewlis (A., 1926, 1084) investigated in the copper–zinc and copper–aluminium systems, viz., Cu_5Zn_8 and Cu_9Al_4. The ε-phase has an hexagonal structure with the densest sphere packing, the constants for which increase from a=2·747, c=4·319 Å. to a=2·755, c=4·319 Å. (c/a=1·572—1·568) with increasing tin concentration; the tin and copper atoms in this phase also are irregularly distributed at the lattice points, hence the formula Cu_3Sn generally ascribed to ε is not admissible. Alloys containing more than 60% Sn have the nickel arsenide lattice with a=4·190, c=5·086 Å. The tetragonal tin lattice has a base of 5·818 Å. and a height to top of the prism of 3·174 Å. A. R. POWELL.

X-Ray analysis of silver–cadmium alloys. H. ÅSTRAND and A. WESTGREN (Z. anorg. Chem., 1928, **175**, 90—96).—The work of Natta and Freri (this vol., 223) is confirmed and amplified. The parameter of the α-face-centred cubic lattice increases from 4·078 to 4·170 with increase of cadmium from 0 to 44 at.-%. The β-phase contains 49—51 at.-% Cd; the body-centred cubic lattice contains only 2 atoms in the elementary cube (a=3·327 Å.). The region of pure γ extends from 57 to 66 at.-% Cd; the body-centred cubic lattice contains 52 atoms in the elementary cube (a=9·935—9·980 Å.). The γ-phase contains 69—83 at.-% Cd and consists of an hexagonal lattice of densest packing (c/a=1·582—1·559). Above 400° the β-phase undergoes a polymorphic change to β′, the lattice of which resembles that of ε (c/a=1·615). The change point in the cooling curve found by Petrenko and Fedorov (A., 1911, ii, 281) at 200° is not due to a change of phase. A. R. POWELL.

Fibrous structure in metals deposited by the difference of electrolytic solution pressures. S. TSUBOI (Mem. Coll. Sci. Kyoto, 1928, **11**, 271—277).—Silver deposited on copper from silver nitrate solutions forms flat, acicular crystals which have a fibrous structure. The fibre axis lies in the [110] direction, and makes an angle of 30° with the acicular axis, the direction of growth being nearly parallel to the [112] direction. The (111) plane is nearly parallel to the flat surface of the crystal in most of the fibres. C. J. SMITHELLS.

Recrystallisation of aluminium. K. TANAKA (Mem. Coll. Sci. Kyoto, 1928, **11**, 229—232).—The orientations of 192 single crystals of aluminium were determined and the crystals then extended 4—20% and annealed for 5 hrs. at 600°. No relation between the orientation of the grains formed on recrystallisation and that of the original crystal could be found. C. J. SMITHELLS.

Arrangement of micro-crystals in the banded "supposed aragonite (Arareishi)." H. FUKUSHIMA (Mem. Coll. Sci. Kyōto, 1928, **11**, 223—227).—*X*-Ray analysis shows that the banded mineral "arareishi," previously supposed to be aragonite, consists of calcite crystals, the principal axes of which are perpendicular to the surfaces of the layers. C. J. SMITHELLS.

X-Ray analysis of copper–magnesium alloys. A. RUNQVIST, H. ARNFELT, and A. WESTGREN (Z. anorg. Chem., 1928, **175**, 43—48).—Rontgenographic examination of alloys of the copper–magnesium series proves the existence of two compounds only, namely, Cu_2Mg and $CuMg_2$. The former has a face-centred cubic lattice containing 24 atoms in the elementary cube; the parameter varies from 7·021 to 7·036 Å. within the homogeneous region, which extends at the most through only 1 at.-%. The second compound has a face-centred rhombic lattice the parameters of which are as follows: a=5·273, b=9·05, c=18·21 Å., the axial ratios being 0·295 : 0·497 : 1; the elementary parallelepiped contains 48 atoms. A re-measurement of the constants of the lattice of very pure magnesium gave a=3·203, c=5·196 Å., whence c/a=1·622. A. R. POWELL.

Laue photograph taken with convergent X-rays. T. FUJIWARA (Mem. Coll. Sci. Kyoto, 1928, **11**, 283—301).—Some of the spots in the Laue pattern from a tungsten crystal, obtained by using white radiation from a molybdenum target, show the spectrum of the *K* radiation of molybdenum, from which the orientation of the crystal can be determined. By using a convergent beam of white *X*-rays the sharpness of the Laue spots is destroyed but the chance of obtaining the spectrum lines is increased. The method is developed for determining the reflecting planes and orientation of the crystal. C. J. SMITHELLS.

Examination of the micro-crystals of calcium carbonate in molluscan shells by means of X-rays. I. J. TSUTSUMI (Mem. Coll. Sci. Kyoto, 1928, **11**, 217—221).—The shell of *Atrina japonica* consists of three layers, the middle or prismatic one having a columnar structure. This layer is shown by *X*-ray analysis to consist of calcite crystals the principal axes of which coincide with those of the columns. C. J. SMITHELLS.

Crystal structure of carbamide and the molecular symmetry of thiocarbamide. S. B. HENDRICKS (J. Amer. Chem. Soc., 1928, **50**, 2455—2464).—The unit of the carbamide structure contains 2 mols. and has d_{001} 4·77 Å. and d_{100} 5·73 Å. The space-group is V_d^3; the oxygen atoms are probably at (0, ½, 0·57), (½, 0, −0·57), the carbon atoms at (0, ½, 0·32), (½, 0, −0·32), and the nitrogen atoms at (0·13, ½−0·13, 0·20), (½−0·13, −0·13, −0·20), (−0·13, 0·13+½, 0·20), and (0·13+½, 0·13, −0·20).

Thiocarbamide has a simple orthorhombic lattice; the unit contains 4 mols. and has d_{001} 8·57 A.,

d_{010} 7·68 Å., and d_{100} 5·50 Å., the suffixes referring to the crystallographic axes. The space-group is V_h^{16}, the sulphur and carbon atoms being at $(0, u, v)$, $(\frac{1}{4}, \frac{1}{4}-u, v)$, $(0, u+\frac{1}{4}, v)$, and $(\frac{1}{4}, u, v+\frac{1}{2})$, and the nitrogen atoms occupying the general positions. The crystallographic evidence favours a symmetrical formula for thiocarbamide. S. K. Tweedy.

Crystal structure of topaz. L. Pauling (Proc. Nat. Acad. Sci., 1928, **14**, 603—606).—With the help of the co-ordination theory of ionic crystals a structure for topax has been predicted which agrees satisfactorily with the experimental *X*-ray data obtained by Leonhardt (Z. Krist., 1924, **59**, 216). The fundamental polyhedra for topaz are assumed to be an octahedron of oxygen and fluorine anions about each aluminium ion and a tetrahedron of oxygen ions about each silicon ion. The anion–anion distance determining the length of a polyhedron edge is taken to be 2·72 Å. throughout (A., 1927, 399). Assuming the polyhedra to be regular, the edges of the unit structure are d_{100} 4·72, d_{010} 8·88, and d_{001} 8·16 Å. The unit contains 4 mols. of $Al_2SiO_4F_2$. Each aluminium octahedron shares two edges with adjoining octahedra, and the four corners occupied by oxygen ions, and defining these edges, are shared with tetrahedra. The other two corners, occupied by fluorine ions, are shared with octahedra. The oxygen ions, although crystallographically of three kinds, are, from the point of view of the co-ordination theory, alike, for each is attached to two aluminium octahedra and one silicon tetrahedron. Each fluorine ion is shared between two octahedra. The arrangement of the oxygen and fluorine ions is that of double hexagonal close packing. It is probable that a consideration of the effect of deformation will give values for the edges of the unit of structure in still better agreement with those observed. M. S. Burr.

Constitution of tungsten carbides. K. Becker (Z. Elektrochem., 1928, **34**, 640—642).—The carbides were prepared by burning a tungsten wire in a mixture of hydrogen with suitable quantities of acetylene or methane. The conductivities of such carburetted wires are recorded. The carbide stable above 2400° (Skaupy, this vol., 381) is a modification (β-form) of the carbide W_2C; it forms crystals which break down noisily to a crystalline powder above the transition point. This form may be supercooled to the ordinary temperature, but if pulverised it changes into α-W_2C. *X*-Ray photographs show that the α-variety forms hexagonal closest-packed crystals, the structure being of the cadmium iodide type. The carbon atoms are at $(0, 0, 0)$ and the tungsten atoms at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4}+p)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4}-p)$, where $p=0{\cdot}02$ approximately. The *X*-ray data for the carbide WC agree with those of Westgren and Phragmen (A., 1926, 1084). In these carbides the domain of the carbon atom is the same as in diamond. The mean coefficients of linear expansion of the carbides were determined in two axial directions by *X*-ray methods; the carbide W_2C exhibits greater anisotropy than the carbide WC. S. K. Tweedy.

Structure of acetylene. J. K. Morse (Proc. Nat. Acad. Sci., 1928, **14**, 645—649).—Regarding acetylene as an ethane molecule from which four hydrogen atoms have been removed, the co-ordinates of the dynamic isomerides of acetylene, in terms of *R*, the radius of the carbon atom, have been determined as previously for ethane (this vol., 351) and methane (this vol., 461), and the moments of inertia of these structures compared with the moments of inertia obtained from band-spectra analysis (Levin and Meyer, this vol., 570). The value obtained by the latter method is $2{\cdot}4\times10^{-39}$ g. cm., which is in close agreement with that calculated for the largest number of dynamic isomerides. The method of investigation employed appears to be of wide application. In connexion with acetylene itself it might prove a convenient starting point for (1) the interpretation of *X*-ray diffraction effects from solid acetylene and the determination of the lattice structure, (2) the study of the relative abundance of the various dynamic isomerides by an analysis of the effect of temperature on the intensities of these bands, and (3) a study of the possible electron configurations in the acetylene molecule and the physical effects to be expected from them. M. S. Burr.

***X*-Ray investigation of long-chain compounds.** A. Müller (Proc. Roy. Soc., 1928, **A**, **120**, 437—459; cf. A., 1927, 503).—The hydrocarbon from supa oil, believed to be triacontane by Robertson and others (cf. B., 1927, 172), is now shown by determination of crystal structure to be the *hydrocarbon* $C_{29}H_{60}$, the $C_{30}H_{62}$ hydrocarbon having been synthesised and examined alongside for comparison. The dimensions of the unit cell are $a=7{\cdot}45$, $b=4{\cdot}97$, $c=77{\cdot}2$ Å., and the angles between its faces are all 90°. The other constants have been determined and are summarised. J. L. Buchan.

Crystal structure of monomethylammonium chlorostannate and chloroplatinate. R. W. G. Wyckoff (Amer. J. Sci., 1928, [v], **16**, 349—359). —The atomic arrangement of monomethylammonium chlorostannate, $(NH_3Me)_2SnCl_6$, is a distortion of the fluorspar structure. The unit cell contains a single molecule; $\alpha=50°\ 14'$, $a_0=8{\cdot}42$ Å. Monomethylammonium bromostannate and chloroplatinate have similar structures. In the latter $\alpha=48°\ 46'$, $a_0=8{\cdot}31$ Å. C. W. Gibby.

Crystal structure of solid methane. J. C. McLennan and W. G. Plummer (Nature, 1928, **122**, 571—572).—In an *X*-ray "powder" investigation of methane at a temperature between those of liquid air and liquid hydrogen, only a cubic form was observed, the structure being based on a face-centred lattice; the unit cell of edge 6·35 Å. contained 4 mols. of methane, whence $d_{calc.}$ is 0·413. A. A. Eldridge.

Crystal structure of cinnabar and covellite. B. Gossner and F. Mussgnug (Zentr. Min. Geol., 1927, *A*, 410—413; Chem. Zentr., 1928, i, 2049). —Cinnabar has *a* 4·17, *c* 9·50 Å.; space-group D_3^4 or D_3^6. Covellite, CuS, has *a* 3·81, *c* 16·46 Å.; space-group D_{6h}, with six molecules in the unit cell. A. A. Eldridge.

Crystal structure of pyrargyrite. B. Gossner and F. Mussgnug (Zentr. Min. Geol., 1928, *A*, 65—73; Chem. Zentr., 1928, i, 2049—2050).—Rhombohedral

pyrargyrite, Ag_3SbS_3, has r 7·07 Å., α 104° 1′; space-group C_{3v}^6. The unit cell contains two molecules. The positions of the atoms are discussed.

A. A. ELDRIDGE.

Structure of β-corundum. C. GOTTFRIED (Z. Krist., 1928, **66**, 393—398; Chem. Zentr., 1928, i, 2050).—The unit cell, containing 12 mols., has a 5·63, c 22·63 Å.; space-group

A. A. ELDRIDGE.

Crystal structure of pentaerythritol. A. NEHMITZ (Z. Krist., 1928, **66**, 408—416; Chem. Zentr., 1928, i, 2050).—Evidence is adduced for the view that pentaerythritol has no polar axis; hence the space-group is S_4^2.

A. A. ELDRIDGE.

Crystal structure of pentaerythritol tetra-acetate and tetranitrate. A. GERSTACKER, H. MOLLER, and A. REIS (Z. Krist., 1928, **66**, 355—392; Chem. Zentr., 1928, i, 2050).—Pentaerythritol tetra-acetate has a 12·18, c 5·58 Å., with two molecules in the unit cell; space-group C_{4h}^3; the tetranitrate has a 9·38, c 6·(9 Å., with two molecules in the unit cell; space-group V_d^4.

A. A. ELDRIDGE.

***X*-Ray study of some triclinic-pinacoidal crystals.** A. GERSTACKER, H. MOLLER, and A. REIS (Z. Krist., 1928, **66**, 421—433; Chem. Zentr., 1928, i, 2047).—*r*-Tartaric acid monohydrate has (100) 8·3, (001) 4·95, (111) 11·2 Å.; anhydrous, (100) 14·6, (010) 9·6, (001) 4·9 Å. Malonic acid has (010) 11·2, (001) 5·2, (110) 5·3 Å. Potassium persulphate has (100) 7·4, (010) 6·55, (001) 7·4, (101) 5·11 Å.

A. A. ELDRIDGE.

Structure of triclinic-pinacoidal crystals and racemate formation. A. REIS (Z. Krist., 1928, **66**, 417—420; Chem. Zentr., 1928, i, 2047).—A discussion.

A. A. ELDRIDGE.

Form of organically deposited calcium carbonate, and influence of the medium. F. ULRICH (Z. Krist., 1928, **66**, 513—515; Chem. Zentr., 1928, i, 2072).—The calcium carbonate deposited at 15—22° by *Cyanophyceæ* from nutrient solutions containing calcium is rhombohedral, the habit varying with the concentration of the agar-agar.

A. A. ELDRIDGE.

Crystal structures of the alkaline-earth metals. G. L. CLARK, A. J. KING, and J. F. HYDE (Proc. Nat. Acad. Sci., 1928, **14**, 617—618).—Calcium, strontium, and barium, of a purity greater than 99·9%, have been prepared, and the crystal structures examined by the Hull powder method of *X*-ray spectrography. The results are in full agreement with those of Hull (Physical Rev., 1921, **17**, 42). Barium crystallises in the cubic system with a unit cell of two atoms and constant 5·04 Å., forming a body-centred cubic lattice; $d_{calc.}$ 3·52. Sharp spectra could not be obtained for strontium. At the most only seven ill-defined diffraction lines were observed. Simon and Vohsen (this vol., 694), from the results of crystal analyses, assign a face-centred cubic lattice to strontium, with the constant 6·03 Å., but consider that a hexagonal modification may be possible at high temperatures. Two of the seven lines might be made to agree with the structure given by Simon and Vohsen. The fact that strontium is a transition step between calcium and barium may account for its anomalous behaviour. It is predicted that radium probably crystallises as a body-centred cubic lattice.

M. S. BURR.

Light figures of copper and iron. G. TAMMANN and A. A. BOTSCHWAR (Z. anorg. Chem., 1928, **175**, 121—130).—When a fine ray of light is passed through a pin-hole in a piece of photographic paper on to an etching pit in a deeply etched crystal surface of copper or iron a light figure is reflected on to the paper in a form characteristic of the orientation of the crystal and of the angle of incidence of the light. When the incident ray is perpendicular to the reflecting surface an octahedral plane produces a figure composed of three intersecting lines of equal length at an angle of 120° to one another, a cube plane gives a "webbed" cross and a rhombic dodecahedral plane a straight line. The value of light figures in determining the orientation of the crystal faces on a metal surface is illustrated with reference to a copper single-crystal sphere deeply etched with ammonium persulphate.

A. R. POWELL.

Etching phenomena on copper single crystals. G. TAMMANN and F. SARTORIUS (Z. anorg. Chem., 1928, **175**, 97—120).—When a single-crystal copper sphere is etched with a suitable reagent, small, bright surfaces of regular shape joined by bright lines appear regularly disposed over the surface of the sphere. The bright lines form the boundaries of a series of circular planes intersecting at the centre of the sphere. Along two of these circles in planes at right angles to one another are arranged alternately cube faces and rhombic dodecahedral faces. If one of the cube faces is considered as the north pole, another will be at the south pole and four others arranged equidistantly round the equator, whilst one of the twelve dodecahedron faces will be midway between every pair of cube faces and one of the eight octahedron faces in the middle of the four quadrants of each hemisphere. If the sphere is etched with ammonium persulphate twenty-four (201) faces will also appear regularly oriented over the surface, whereas etching with ammoniacal persulphate develops only the octahedron faces together with bright lines joining these to the points at which the cube faces normally appear. Etching with nitric acid and mercurous nitrate produces a diamond network of bands joining the (111) to the (100) poles, and etching with 50% nitric acid containing 0·5% of silver nitrate develops the octahedron poles and lines joining them to one another. The rate of dissolution of the metal is greatest at the bright spots in the etching figures developed by the attack of the solvent. If a single-crystal cylindrical rod is allowed to remain for some hours in a solution of ammonium persulphate the cylinder becomes a twelve-sided prism, the indices of the sides being (two opposing sides having the same index) successively (111), (052), (353), $(\bar{9}91)$, (301), and $(\bar{3}12)$, the length of the sides and hence their rate of dissolution increasing in the order given. The changes in reflexion of etched copper spheres and the shapes of the etching figures developed by different reagents are discussed at some length.

A. R. POWELL.

Electrons and symmetry. P. VINASSA (Nuovo Cim., 1927, 4, 981—998; Chem. Zentr., 1928, i, 1931—1932).—An application of the view that electron arrangement obeys the laws of crystallographic symmetry to considerations of valency, polyatomicity, photographic phenomena, and phosphorescence. A. A. ELDRIDGE.

Theory of crystal growth. I. N. STRANSKI (Z. physikal. Chem., 1928, **136**, 259—278).—It is assumed that the surface layer of a crystal is essentially similar to the inner layers and that units in the surface take up mean positions forming a continuation of the inner lattice, and, further, that these positions correspond with minimum energy values. On this basis it is possible to express quantitatively the growth or dissolution of a crystal in terms of the work necessary to remove to infinity from their mean positions of rest the various units of the surface layer. Calculations made for a crystal of the sodium chloride type are in fair accord with experimental results. F. G. TRYHORN.

Structure of quenched carbon steel. G. KURDUMOV and E. KAMINSKY (Nature, 1928, **122**, 475—476).—*X*-Ray examination of quenched carbon steels containing 0·64—1·44% C shows that the tetragonal structure exists not only at the surface but also at a depth of 5 mm. The length of the *c* axis increases, whilst that of the *a* axis diminishes, with increasing carbon content. In steel containing 1·03% C the ratio *c*/*a* is constant (1·041—1·045) for initial temperatures of 900°, 1100°, and 1300°; in steel containing 0·91% C the diminution of the ratio commences at 850°. Inhomogeneity of the tetragonal structure causes diffusibility of the lines of the *X*-ray photograms. Austenite was present in all specimens. Honda's β-martensite is probably a mixture of tetragonal crystals with different small ratios of the axes. Sekito's results (cf. B., 1928, 713) are criticised. A. A. ELDRIDGE.

Existence of an isomorphism, forbidden by the strict structure theory, of crystals of hexammine, aquopentammine, and diaquotetrammine complexes of high elements of symmetry. O. HASSEL (Norsk. geol. Tidsskr., 1927, 9, No. 1, 6 pp.; Chem. Zentr., 1928, i, 1360).—It is considered that crystallographically equivalent positions in crystals of complex cobalt compounds are not always occupied by chemically identical groups. The lattice structure of the compounds $[Co(NH_3)_6SO_4]Br$, $[Co(NH_3)_6]SO_4I$, $[Co(NH_3)_5H_2O]SO_4I$, $[Co(NH_3)_5H_2O]SO_4Br$, the corresponding chromium compounds, and compounds in which the sulphur was substituted by selenium or chromium is discussed. A. A. ELDRIDGE.

Crystals of 5-methylamino-3-methylhydantoyl-5-methylamide. J. J. P. VALETON (Z. Krist., 1928, **66**, 516; Chem. Zentr., 1928, i, 2075).—The crystals, m. p. 187°, are triclinic holohedral. $a:b:c$—1·2493 : 1 : 1·0012, α 90° 38′, β 93° 52′, γ 107° 39′. A. A. ELDRIDGE.

Theory of the meso-structure of organic compounds. I. KOTUKOV (Bull. Siberian Inst. Tech., 1927, **48**, No. 1, 35 pp.; Chem. Zentr., 1928, i, 1944—1945).—The strength of linkings is considered to change quite gradually in the series methane, hexahydrobenzene, benzene, ethylene, acetylene; the stronger is the affinity claim of one carbon atom for others, the smaller is the affinity remaining for the neighbouring hydrogen atom. If the carbon-hydrogen linking is weak, the hydrogen possesses a residual affinity called "mesovalency." The view is applied to the explanation of *cis-trans*-isomerism, ease of hydrolysis, polymorphism, etc. A. A. ELDRIDGE.

Magnetic susceptibility of sodium and potassium. C. T. LANE and E. S. BIELER (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 117—123; cf. McLennan, Ruedy, and Cohen, A., 1927, 1017).—The magnetic susceptibilities of sodium and potassium are found to be $0·67\times10^{-6}$ and $0·60\times10^{-6}$, respectively. The metals were distilled three times, and the iron content was too small to affect the accuracy of the results. C. W. GIBBY.

Mol. wt. of saturated vapours by the effusion method. H. E. EYRING (J. Amer. Chem. Soc., 1928, **50**, 2398—2401).—The liquid, of vapour pressure p_1, is allowed to evaporate in an evacuated glass apparatus and the time necessary for the pressure in a receiving chamber beyond the glass orifice (0·1 sq. mm.) to reach some predetermined value, p_2, is measured. The time taken by air at p_1 to produce a pressure p_2 beyond the orifice is also measured. The apparatus is simple and the method is rapid and accurate to 1%. The measurement with air may be dispensed with if the times taken by liquids to set up a pressure equal to some definite fraction (*e.g.*, one half) of p_1 are always measured. Theoretical considerations show that these times are independent of p_1 and so the apparatus may be calibrated permanently. No appreciable association of saturated water vapour, of the vapour from constant-boiling hydrochloric acid, or of organic vapours was detected with the apparatus. S. K. TWEEDY.

Electrical resistance of alloys under pressure. C. W. UFFORD (Physical Rev., 1928, [ii], **32**, 505—507).—Average pressure coefficients to 12,000 kg./cm.^{2} of electrical resistance for lithium-tin, bismuth-tin, and calcium-lead alloy series, and for a 10% magnesium in calcium alloy are given. The variation of the pressure coefficient with concentration, the temperature coefficient, and the relative change of the latter with pressure is comparable with structural variation as given by equilibrium diagrams. The conductivity and the pressure coefficient of a dilute solid solution of bismuth in tin are the same as those of pure tin under pressure. As hydrostatic pressure and impurities have the same effect on the pressure coefficient, electric conduction probably depends on the geometrical properties of the conductor. R. A. MORTON.

Change of resistance of lead by the action of radium. K. PRASAD and S. BASU (Nature, 1928, **112**, 610).—A temporary change in the resistance of lead takes place when a thin plate of the metal is exposed to the action of β-particles and γ-rays from radium. A. A. ELDRIDGE.

Electrical conductivity of vaporised potassium chloride. T. PECZALSKI and J. CHICHOCKI (Compt.

rend., 1928, **187**, 534—536).—The measurements were made by means of copper electrodes in a glass tube heated in a furnace. The resistance of the vapour increased with the length of time of heating from $0{\cdot}7\times10^{-5}$ to $2{\cdot}8\times10^{-5}$ ohm. The electrodes became polarised. The conductivity is due to the dissociation of the potassium chloride.

W. E. DOWNEY.

Isotherms of monatomic substances and their binary mixtures. XXVI. Isotherms of helium at −183·0° and −201·5° and 3—8 atm. G. P. NIJHOFF and W. H. KEESOM. **XXVII. Isotherms of helium between −103·6° and −259·0° and 1·5—14 atm.** G. P. NIJHOFF, W. H. KEESOM, and B. ILIIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 404—409).—The construction of two closed manometers for use between pressures of 2 and 6 atm. is described. The required isotherms of helium have been determined by the method previously given (A., 1926, 463). Values of B_A have been calculated and plotted against temperature along with those of other investigators.

M. S. BURR.

Isotherms of diatomic substances and their binary mixtures. XXXIV. Isotherms of hydrogen at 0° and 100°. XXXV. Isotherms of hydrogen at −225·5° to −248·3° and 1·6—4·2 atm. G. P. NIJHOFF and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 410—414).—Values of B_A and C_A have been calculated from the experimental data obtained at the higher temperatures and of B_A from those at the lower temperatures. M. S. BURR.

Effect of magnetic fields on thermal conductivity of iron, copper, gold, silver, and zinc. H. M. BROWN (Physical Rev., 1928, [ii], **32**, 508—514).—In a longitudinal field of 10,000 gauss iron showed a 1·14% decrease in heat conductivity, whilst a transverse field of 4000 gauss caused a 0·4% decrease. For copper, the 10,000 gauss field caused a 0·23% decrease. The remaining metals showed no change greater than 0·04%. The values of electrical and thermal conductivity were higher in crystal bars than in the ordinary cast form, but magnetic fields produced no change in either case.

R. A. MORTON.

Generalised Gibbs-Boltzmann equation. F. R. BICHOWSKY (Physical Rev., 1928, [ii], **32**, 494—496).—Mathematical. A generalised form of the Gibbs–Boltzmann canonical equation is derived without the assumption of the Maxwell distribution law. The equation allows a treatment of statistics of the most generalised type of systems.

R. A. MORTON.

Chemical equilibrium in the vapour of a mixture of paraffins and unsaturated hydrocarbons. H. A. WILSON.—See this vol., 1190.

Steam tables and equations, extended by direct experiment to 4000 lb./sq. in. and 400°. H. L. CALLENDAR (Proc. Roy. Soc. 1928, **A**, **120**, 460—472).—The densities of water and steam have been investigated near the critical point. It is found that they are not equal at this point, 374°, but at about 380°, there being an unstable region of equilibrium between these temperatures. This is illustrated by curves, which do not agree with those calculated from a formula of the Thiesen type. The total heat has also been measured for water and for steam, and it is shown that air-free water gives values for H and h which are different from those given by ordinary distilled water, and the curves so obtained agree with those found by the previous method. The equations for the total heat, the entropy, and the saturation pressure have been extended, and are discussed. Extended steam tables for the equilibrium states of steam up to 4000 lb. pressure have been calculated. J. L. BUCHAN.

Entropy and vibration frequency of solid inorganic compounds. W. HERZ (Z. anorg. Chem., 1928, **175**, 245—248).—It is shown for 44 compounds of the type AB and for 41 compounds of the type AB_2 that the product $S\nu^{1/2}$ is approximately a constant, where S is the entropy of the compound calculated by Latimer's formula (A., 1921, ii, 380) and ν is the vibration frequency. The recorded values of $S\nu^{1/2}$ for the first-named type of compounds vary from 3·49 to 5·94 with a mean value of about 4·5, and for the second type from 5·59 to 8·55 with a mean value of nearly 7. A. R. POWELL.

Volume studies. III. Calculation of limiting values. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 435—438; Chem. Zentr., 1928, i, 1492).—Limiting values of d_4^0 are computed for various classes of hydrocarbons. A. A. ELDRIDGE.

Volume chemistry. III. Oxygen compounds. Carbonyl group. F. WRATSCHKO (Pharm. Presse, 1928, **33**, 36—39, 61—63; Chem. Zentr., 1928, i, 1833).—"E-values" for various classes of compounds are calculated. A. A. ELDRIDGE.

Vapour pressure of barium oxide. M. DE K. THOMPSON and W. G. ARMSTRONG (Amer. Electrochem. Soc., Sept., 1928. Advance copy. 4 pp.).—The vapour pressure of barium oxide between 1280° and 1470° has been determined by Wartenberg's method (A., 1912, ii, 1137).

H. J. T. ELLINGHAM.

Characteristic density and the properties of liquids. W. HERZ (Z. anorg. Chem., 1928, **175**, 277—280).—Values of the quantity $\gamma^{1/3}/(d-d_\kappa)$, where γ is the surface tension, d the density, and d_κ the critical density, have been calculated for a number of organic liquids, and are shown to be approximately constant for any one liquid over a wide temperature range. If the viscosity be employed in place of the surface tension, a constant is again obtained, which, however, below the b. p. decreases slowly with rise of temperature. H. F. GILLBE.

Measurements on the equation of state for solid argon. F. SIMON and (FRL.) F. KIPPERT (Z. physikal. Chem., 1928, **135**, 113—128).—A method for the direct measurement of the thermal pressure of condensed gases has been devised and the following values of $\partial P/\partial T$ in atmospheres and degrees over temperature intervals from about 68° to 90° Abs. have been obtained: argon (solid), 38, argon (liquid), 25; methane (solid), 28; oxygen (liquid), 24; nitrogen (liquid), 24. The density of solid argon is 1·505 at

76° Abs. The compressibilities in the liquid state for argon at 86° Abs., oxygen at 82° Abs., and nitrogen at 75° Abs. are 180, 169, and 247×10^{-12} abs. units, respectively. The magnitude $\gamma=-d \log \nu/d \log V(=3\alpha V/KC_v)$ is 4·5 for solid argon, as against 2·3 for metals and 1·8 for ionic lattices. R. A. MORTON.

Periodic classification of the hardness and m. p. of the elements. S. A. KORFF (Science, 1928, 67, 370—371).—The classification of elements according to hardness and m. p. accords with an 18-period table based on spectroscopic similarities; hence these properties are related to the electronic configuration. A. A. ELDRIDGE.

Internal friction in metals. R. H. CANFIELD (Physical Rev., 1928, [ii], 32, 520—530).

Thermal conductivity of gas mixtures. H. GRUSS and H. SCHMICK (Wiss. Veroff. Siemens-Konz., 1928, 7, (i), 202—224).—The thermal conductivity (air=1) of mixtures of air with steam, ammonia, acetylene, methane, and carbon monoxide, and of mixtures of carbon monoxide with ammonia, has been determined at atmospheric pressure between 20° and 80°. The conductivity–composition curves for air–ammonia, carbon monoxide–ammonia, air–steam, and air–acetylene mixtures are concave to the composition axis, whereas those for air–methane and air–carbon monoxide are straight lines. The deviation of the first-named series from the mixture rule is ascribed to the presence of dipolar and quadripolar molecules, whereby the attractive force is appreciably reduced with a corresponding decrease in the number of impacts, *i.e.*, an increase in the thermal conductivity. The subject is discussed theoretically and mathematically and the curves derived from this treatment are shown to be in fair agreement with experiment. A. R. POWELL.

Determination of the concentration of solutions. G. JAEGER (Ber., 1928, 61, [*B*], 1654—1659).—The concentration of a comparison solution is adjusted until waves do not appear, when it is mixed with the solution under investigation. The maximum error is about 0·2%. The light from a small electric lamp, rendered parallel by passage through a convex lens, passes through a tube containing the comparison solution and is then brought nearly to a focus on a screen. The solution under investigation is added to the comparison solution from a burette fitted with a very narrow jet bent to a right angle beneath the liquid. The relative concentrations are indicated qualitatively by the production and movement of the waves and the comparison solution is adjusted in concentration until these no longer appear. In a second process, the comparison solution in the tube is stronger than that under investigation and is diluted with solvent from a burette until equality of concentration is attained. H. WREN.

Coefficient of expansion of binary liquid mixtures. K. M. STACHORSKI (Ukraine Chem. J., 1928, 3, 219—222).—The expression $\alpha=M_1v_1\alpha_1x+M_2v_2\alpha_2(1-x)/M_1v_1x+M_2v_2(1-x)$ is derived, where α, α_1, and α_2 are the coefficients of expansion of the mixture and of its respective components, M_1v_1 and M_2v_2 the gram-molecular volumes of the components, and x is the proportion of one component in the mixture. Values of α calculated from this expression are in good agreement with those found experimentally for mixtures of various organic liquids. R. TRUSZKOWSKI.

Dielectric constants of binary mixtures. VII. Electric moments of certain diphenyl derivatives. Their relation to the several structures. J. W. WILLIAMS and A. WEISSBERGER (J. Amer. Chem. Soc., 1928, 50, 2332—2336; cf. this vol., 355).—Dielectric constants and densities for benzene solutions of *p*-phenylenediamine, *p*-dichloro-, *p*-dinitro-, *p*-diethoxy-, and *p*-diamino-diphenyl at 25° are recorded. The calculated electric moments of the molecules indicate that in the dichloro-, dinitro-, and diethoxy-derivatives the benzene nuclei are coaxial, whilst in the diamino-derivative the nuclei cannot be extended (cf. Kuhn and Albrecht, A., 1927, 876). A modified apparatus for the accurate determination of dielectric constants is described. S. K. TWEEDY.

Dielectric constants of binary mixtures. VIII. Electric moment as a vector quantity. J. W. WILLIAMS (J. Amer. Chem. Soc., 1928, 50, 2350—2357; cf. preceding abstract).—Electric moments, calculated from the dielectric constants and densities of benzene solutions, are recorded for 11 benzene derivatives. A substituent in a molecule is characterised by a definite electric moment which can be considered to be a vector quantity, the electric character being assigned with reference to a standard group (*e.g.*, methyl group). Two substituents do not interact if they are of very simple type; in general, however, the vectors characterising such groups cannot be considered to act in the plane of the benzene ring. Thus, *s*-trinitrobenzene has a finite but small electric moment (cf. this vol., 355), so that interaction between the groups causes them to be extended slightly above the plane of the benzene nucleus. The data offer strong support for the planar structure of the benzene molecule. S. K. TWEEDY.

Application of Debye's dipole theory to binary liquid mixtures. II. J. W. WILLIAMS (Physikal. Z., 1928, 29, 683—688).—The electric moment has been calculated from the dielectric constant and density in benzene solutions at 25° for 33 different substances. It is shown that each atom or group substituted in the benzene ring is characterised by a more or less well-defined vectorial moment, *e.g.*, NO_2 −3·8; CHO −2·8; OH −1·7; Cl −1·5; Br −1·5; OMe −1·2; CO_2H −0·9; Me +0·4; NH_2 +1·5. When two or more atoms or groups are substituted in the benzene ring, the reciprocal effects of the substituents cannot in general be neglected. It is probable that the only possible structure for the benzene ring is the arrangement of all the carbon atoms in one plane. The structure of diphenyl and its derivatives cannot be depicted simply. The electric moment of an inorganic molecule can be determined by the method used for organic molecules. Judging from compounds of the type CA_4, there is no simple relation between the structure of a crystal and that of the molecules in solution. R. A. MORTON.

Association in liquid dielectrics. J. ROLINSKI (Physikal. Z., 1928, **29**, 658—667).—Benzene, carbon disulphide, and carbon tetrachloride are dipole-free liquids, whereas ethyl ether, chlorobenzene, and quinoline are typically dipolar. From the relation $P = M/c \,.\, [(\varepsilon-1)/(\varepsilon+2)d - (1-c)(\varepsilon_2-1)/(\varepsilon_2+2)d_2]$, P being the molecular polarisation of a solute of mol. wt. M, c the percentage concentration in grams, ε the dielectric constant of the mixture, d its density, and ε_2, d_2 the values for the solvent, the following values of P were obtained: carbon disulphide (in benzene) 21·1—22·0; carbon tetrachloride 27·3—28·2. In these cases P is independent of the concentration. The volume polarisation of carbon tetrachloride–carbon disulphide mixtures obeys the simple mixture rule. Mixtures containing a dipole-free and a dipolar liquid show that the molecular polarisation of the latter decreases with increasing concentration owing to molecular association. By assuming that the dipolar moments of associating molecules disappear, the degree of association in dipolar liquids is calculated, and it is found that the higher the concentration and the stronger the dipolar moment the greater is the tendency towards association. Binary mixtures of dipolar liquids do not obey the additivity law, the discrepancies being again due to association. R. A. MORTON.

Vapour pressures of binary systems; aqueous solutions of orthophosphoric acid, sodium hydroxide, and potassium hydroxide. U. NAKAYA (Trans. Faraday Soc., 1928, **24**, 543—544).—A continuation of the work of Porter (this vol., 710). For the above solutions calculations are tabulated, equations proposed, and curves are given showing the relation between the molar fractions and the vapour pressures at 100°. Deductions therefrom are discussed. N. M. BLIGH.

Physical properties of phenol in benzene. L. E. SWEARINGEN (J. Physical Chem., 1928, **32**, 1346—1353; cf. this vol., 703).—The densities, viscosities, and surface tensions of mixtures of benzene and phenol have been determined at 25°. The density–concentration curve is linear. The calculated partial molal volumes of the phenol in the various mixtures are practically constant, indicating that the two components form an ideal solution. It is stated that the viscosity–concentration and the surface tension–concentration curves show minima; that of the former is attributed to association of the phenol molecules in the more concentrated solutions followed by dissociation on dilution, whilst that of the latter is explained on the basis of negative adsorption of the phenol at the phenol–benzene interface. L. S. THEOBALD.

Electrical conductivity of tellurium and of liquid mixtures of tellurium and sulphur. C. A. KRAUS and E. W. JOHNSON (J. Physical Chem., 1928, **32**, 1281—1293).—The specific resistance of pure tellurium has been measured over the range 363—500°, and that of mixtures of tellurium containing up to 85 at.-% of sulphur over the range 382—477°. In all cases, the specific resistance decreases exponentially with rise of temperature, whilst at constant temperature the specific resistance of a liquid mixture increases rapidly with an increase in sulphur content. The specific resistance of liquid tellurium at its m. p. is approximately one fifteenth of that of the solid. Liquid tellurium is, comparatively, a good conductor, its specific conductance, at 500°, being one sixth of that of mercury at the ordinary temperature. Methods and apparatus, including a thermo-regulator giving trustworthy results over the range 200—600°, are described. L. S. THEOBALD.

***X*-Ray analysis of thallium-antimony alloys.** E. PERSSON and A. WESTGREN (Z. physikal. Chem., 1928, **136**, 208—214).—Four phases can be recognised in the X-ray analysis of the thallium-antimony system. The lattice of α-thallium is of the close-packed hexagonal type with unit cells of base 3·449 Å. and height 5·513 Å. A second phase, apparently a solid solution of antimony in β-thallium, which occurs in alloys moderately rich in antimony, contains about 7% Sb, and possesses a face-centred cubic lattice of edge 4·842 Å. A second intermediate phase, corresponding in composition with Tl_7Sb_2, has a complex cubic lattice in which the unit cell contains 54 atoms and has an edge of 11·59 Å. Antimony has a face-centred rhombohedral lattice, with an axial angle of 87° 24′ and an edge 6·226 Å. F. G. TRYHORN.

Recrystallisation of steel, cast but not further treated, after heat treatment. H. HEIKE and F. WESTERHOLT (Z. anorg. Chem., 1928, **174**, 244—256).—The microcrystalline structure and the fracture exhibited by various specimens of cast steel after heating at 700—900° for periods up to 12 hrs. have been studied. Apart from the more or less regular subdivision exhibited by ferrite, that which is not dissolved as mixed crystals up to 800° undergoes no regular orientation on working. The general law of recrystallisation, viz., that particle size is dependent on temperature and working, is valid to only a limited extent. H. F. GILLBE.

Solubility of aluminium bromide in carbon disulphide. H. H. KAVELER and C. J. MONROE (J. Amer. Chem. Soc., 1928, **50**, 2421—2426).—Aluminium bromide, m. p. 97·1°, was prepared by passing a mixture of hydrogen and bromine vapour over aluminium at 400°. The salt is very soluble in carbon disulphide, *e.g.*, 32·3 mol.-% at 25° and 87·8 mol.-% at 85°. This is in accordance with the principles laid down by Hildebrand. The saturated solutions are dark red in colour, possibly because of solvation. The experimental data show negative deviation from Raoult's law at low temperatures and practically no deviation at higher temperatures. The solutions have an appreciable conductivity. An electrically heated siphon is described for sampling saturated solutions at high, constant temperatures. A method of analysing aluminium bromide is given in which the salt is first converted into the compound $AlBr_3,2PhNO_2$, which is allowed to react with water, the resulting solution being titrated by the Volhard method. S. K. TWEEDY.

Solubility of diphenylamine in water, alcohol, and other organic solvents. L. DESVERGNES (Ann. Chim. analyt., 1928, [ii], **10**, 253—255).—Tables are given showing the solubility of diphenylamine in

water, alcohol, and other organic solvents at various temperatures. The solutions in organic liquids containing combined chlorine are deeply coloured, the coloration being due to the presence of a small quantity of free chlorine. Alcoholic solutions become coloured when exposed to light. A. J. MEE.

Solubility relations of isomeric organic compounds. VIII. Solubility of the aminobenzoic acids in various liquids. C. L. LAZZELL and J. JOHNSTON (J. Physical Chem., 1928, **32**, 1331—1341; cf. this vol., 579).—The solubilities in benzene, chloroform, ethyl alcohol, and ethyl acetate have been determined at 25° by the analytical method and at temperatures up to the respective m. p. by the synthetic method. Methyl and butyl alcohols were also used as solvents. The results are compared with similar data for the nitroanilines (Collett and Johnston, A., 1926, 237) and for the monosubstituted hydroxy-, chloro-, and nitro-benzoic acids (Sidgwick and Ewbank, J.C.S., 1921, **119**, 979). Corresponding curves, in many cases, are similar in shape, as is the case with the amino-acids in any one solvent, but the irregularities which occur indicate that the solubility even of closely-related compounds is influenced by the specific chemical nature of both solute and solvent. In the present case, no particular solvent offers any special advantage in the separation of the isomerides by crystallisation. Solubility data are given. L. S. THEOBALD.

Influence of salts on the solubility of other salts in non-aqueous solvents. C. A. KRAUS and R. P. SEWARD (J. Physical Chem., 1928, **32**, 1294—1307; cf. King and Partington, A., 1927, 1020).—Results previously summarised (A., 1927, 1020) are presented and discussed. The solubility of salts in non-aqueous solvents is influenced by the presence of traces of water. The solubility of sodium chloride in *iso*propyl alcohol containing varying amounts of water in the presence of sodium nitrate is recorded. The addition of 2% of water to the alcohol increases the solubility of sodium chloride approximately 2½ times. The diminution of the solubility in the pure solvents on the addition of a salt with a common ion is approximately one fourth that in water, whilst the increase on addition of a salt without a common ion is four times that in water as solvent. The divergence of the experimental results from the Debye–Hückel theory bears no apparent relationship to the dielectric constant and cannot be explained on the basis of a change in dielectric constant due to the added salts. It is suggested that the inter-ionic attraction theory must include factors which take account of the specific attractive forces between the ions and the solvent. L. S. THEOBALD.

Effect of one salt on the solubility of another in ethyl alcohol solution. III. F. S. HAWKINS and J. R. PARTINGTON (Trans. Faraday Soc., 1928, **24**, 518—530; cf. A., 1927, 1020).—The influence of sodium iodide and magnesium iodide on the solubility of potassium iodide in alcohol at 25° has been investigated. At concentrations below 0·5N the solubility in sodium iodide and alcohol solutions is given by Bronsted's equation $-\frac{1}{2}\log R=3\alpha(\sqrt{2\mu}-\sqrt{2\mu_0})+\beta c$; where R=activity product ratio$=C_{A_0}C_{B_0}/C_AC_B$= concentrations of ions A and B in pure solvent÷ their concentrations in a solution of another salt, α and β are constants, c=concentration of added salt, μ_0=ionic strength of salt AB in pure solvent, μ= ionic strength of a solution of the two salts. In the case of magnesium iodide+alcohol solutions evidence is given for the formation in solution of the complex MgI_2,KI. The viscosities and conductivities of the solutions have been measured, and values of the ionic radius were calculated. The conductivity of potassium iodide was also measured. N. M. BLIGH.

Wood charcoal as adsorbent for gases. A. MAGNUS, E. SAUTER, and H. KRATZ (Z. anorg. Chem., 1928, **174**, 142—144).—The anomalous curvature of the isotherms for the adsorption of carbon dioxide by charcoal at low pressures vanishes if the adsorbent be previously boiled with hydrochloric acid and washed thoroughly. It is probable that the impurity thus removed is alkali or alkaline-earth carbonate, which is converted into oxide when the charcoal is heated in a vacuum before use. H. F. GILLBE.

Adsorption of gases by graphitic carbon. II. X-Ray investigation of the adsorbents. H. H. LOWRY and R. M. BOZORTH (J. Physical Chem., 1928, **32**, 1524—1527; cf. A., 1925, ii, 1053).—An X-ray examination of three samples of graphite, graphitic acid, and natural graphite shows that carbon prepared by the explosion of graphitic acid is composed of small graphite flakes, averaging 50 atom diameters across and 10 atom layers thick. The apparent disagreement with the results of Ruff and co-workers (A., 1927, 1138) is explained, and it is reiterated that a graphitic carbon can be prepared which shows an adsorptive capacity of one fourth to one third that of the best adsorptive charcoal. L. S. THEOBALD.

Unimolecular character of the adsorption of gases by glass and wood-charcoal. H. ZEISE (Z. physikal. Chem., 1928, **136**, 385—418).—The adsorption of methane, nitrogen, oxygen, and hydrogen has been studied at pressures from 2×10^{-4} to 7×10^{-2} mm. and 90° Abs., using as adsorbent thin glass microscope cover-glasses separated from one another by means of glass threads. The results can be expressed by the adsorption isotherm $q=\sqrt{k_1k_2p/(1+k_2p)}$, where q=mols. of gas adsorbed/sq. cm., p=pressure, and k_1, k_2 are constants. This expression is also derived theoretically by reasoning similar to that used by Langmuir, assuming that two elementary spaces can adsorb one molecule. The Freundlich isotherm is a first approximation to this expression, which leads to a maximum adsorption at high pressures and is in qualitative agreement with the Langmuir unimolecular layer theory. Measurements of the adsorption of methane, nitrogen, and oxygen at higher pressures (4—307 mm.) support this view. Berényi's confirmation of the Polanyi multimolecular adsorption theory based on the results of other workers on the adsorption of gases by charcoal (A., 1920, ii, 591) is criticised. It is shown that the original Langmuir isotherm agrees better with the experimental results cited by Berényi. The theories of Williams and of Iliin are also discussed. O. J. WALKER.

Reversal of Traube's rule of adsorption. H. N. Holmes and J. B. McKelvey (J. Physical Chem., 1928, **32**, 1522—1523).—The adsorption of acetic, propionic, butyric, and octoic acids from toluene solutions by silica gel has been measured. Adsorption decreases as the series is ascended, showing the reversal of Traube's rule (cf. Freundlich, "Colloid and Capillary Chemistry," 1926).

L. S. Theobald.

Adsorption in solutions. XVI. Reversal of Traube's adsorption law. B. Nekrassov (Z. physikal. Chem., 1928, **136**, 379—384).—The adsorption of the normal fatty acids (C_1—C_9) by sugar charcoal from aqueous solution has been examined. Traube's adsorption law is completely reversed, probably on account of the strongly polar nature of the charcoal.

H. F. Gillbe.

Existence of Volmer's adsorption layer. F. Moll (Z. physikal. Chem., 1928, **136**, 183—185). —Positive evidence for the existence of adsorption layers on mercury has been obtained with phthalic anhydride, coumarin, and diphenylmethane. Paraffin and cetyl alcohol, which do not wet mercury, gave negative results. A new interference method for the detection of these layers gave satisfactory results with benzophenone and salol.

F. G. Tryhorn.

Adsorption and dissolution phenomena encountered in precipitations. F. R. Balcar and G. Stegeman (J. Physical Chem., 1928, **32**, 1411—1421).—The adsorption of thorium by barium sulphate when the latter is precipitated from solutions of thorium chloride has been investigated. The redissolving of the adsorbed thorium increases with time and stirring, and the particle size of the precipitated barium sulphate passes through a maximum and a minimum when the concentration of the thorium chloride solution increases. The solubility, S, of barium sulphate in thorium chloride of concentration C (mol./litre) can be represented by $\log S=0{\cdot}68 \log C+0{\cdot}0789$; the solubility of lead sulphate also can be similarly represented. The influence of barium chloride on the solubility of barium sulphate in the thorium chloride solution has also been investigated. The variations in the "constants" for the adsorption of thorium by barium sulphate are discussed.

L. S. Theobald.

Structure of salts adsorbed on cellulose. R. H. Aborn and R. L. Davidson (Nature, 1928, **122**, 440).—*X*-Ray examination of salts (sodium chloride and tungstate) adsorbed on cellulose shows that up to a certain saturation concentration the salt is molecularly or ionically dispersed throughout the cellulose units, whilst above that concentration it is probably held mechanically. No new structural arrangement was observed.

A. A. Eldridge.

Blue coloration given by iodine in presence of starch. E. Angelescu and J. Mircescu (J. Chim. phys., 1928, **25**, 327—342).—In the adsorption of iodine and potassium iodide by starch it would seem that the potassium iodide is adsorbed as potassium tri-iodide and that most of the iodine is taken up in this way. The blue colour formed is due to free iodine either directly adsorbed or liberated from the adsorbed potassium tri-iodide, and is not due to chemical combination between iodine and starch. This is also the case for starch in colloidal solution. With reference to the colour change blue — violet — red which may occur in iodine–starch solutions, observations on the influence of electrolytes on the colour changes in dextrin–iodine solutions and also on the viscosity of starch solutions lead to the conclusion that substances which increase the degree of dispersion of the colloidal particles tend to produce a red colour and conversely. These colour changes are interpreted in a similar manner to the colours of colloidal gold solutions.

L. F. Gilbert.

Reversible and irreversible chemical phenomena at interfaces. D. Deutsch (Z. physikal. Chem., 1928, **136**, 353—378).—Aqueous solutions of certain indicators when shaken with immiscible inert liquids such as hydrocarbons show a colour change at the interface. Acidic indicators show an apparent acidification and basic indicators the reverse. The change of colour vanishes as the two liquids separate. Air produces a similar effect, the foam on a yellow solution of thymolsulphonephthalein being violet in colour. Aqueous solutions of heavy metal salts of coloured acids, *e.g.*, the silver salt of eosin, undergo a colour change when shaken with inert liquids, and the salt is precipitated. It appears therefore that the ionisation at the interface between an aqueous solution and air or a liquid having a smaller dielectric constant than the solution is less than in the body of the solution. A colourless benzene solution of a dye exhibits at the interface between the solution and water a colour change which is ascribed to the disturbance of a lactoid–quinonoid equilibrium, whereas the corresponding phenomenon with rhodamine ester solutions is due to increased dissociation of the ester at the interface. The increased aggregation of colloidal particles in the surface of aqueous solutions is a result of the greater surface activity of the larger particles compared with that of the smaller, whilst the relatively small lowering of surface tension produced by hydrophobic colloids is due to the reduction of the number of particles present in the surface.

H. F. Gillbe.

Surface tension and solvation in salt solutions. P. P. Kosakewitsch (Z. physikal. Chem., 1928, **136**, 195—207).—Measurements of the surface tension of solutions of alkali halides in pyridine, acetone, methyl alcohol, formic acid, and in mixtures of ethyl alcohol and water show that the usual lyotrope series $Cl>Br>I$ and $K>Na>Li$ are reversed for solutions in these solvents. For mixtures of alcohol and water a minimum usually occurs in the surface tension as the amount of alcohol in the mixture is increased. It is suggested that the solutes in these solutions are bound partly to alcohol molecules (solvation) and partly to water molecules (hydration) and that inversion of the lyotrope series occurs as the extent of solvation diminishes.

F. G. Tryhorn.

Permeability of colloidal substances to gases. K. Kanata (Bull. Chem. Soc. Japan, 1928, **3**, 183—188).—The relative permeabilities of membranes of rubber, celluloid, and gelatin with respect to hydrogen,

oxygen, carbon dioxide, and ammonia were determined. The sorption is not an adsorption phenomenon. The mechanism of the permeability is discussed, and it is shown that viscosity flow is not the main cause, but that the permeability is probably due to the dissolution of the gas in the membrane.

A. J. MEE.

Osmosis of ternary liquids. III. F. A. H. SCHREINEMAKERS and B. C. VAN B. WALTER (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 560—568; cf. this vol., 702).—In extension of previous work, the directions in which substances will pass through membranes are investigated mathematically.

A. J. MEE.

Osmosis of ternary liquids. General considerations. V. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 459—468).—Preceding communications (cf. this vol., 583) have dealt with a "theoretical" membrane which does not contain any of the diffusing substances. The "real" membrane, containing some of the diffusing substances, is now considered. M. S. BURR.

Apparatus for the determination of electro-endosmosis. N. SCHONFELDT (Wiss. Veroff. Siemens-Konz., 1928, 7, (1), 301—303).—The apparatus comprises a central horizontal tube which carries the diaphragm and is bent upwards at right angles at both ends, the openings being ground to admit the shorter arms of two inverted U-tubes carrying the measuring capillaries. The longer arms of these U-tubes are joined by means of conical ground glass joints to the longer arms of the electrode U-tubes, the shorter arms of which are closed with rubber stoppers carrying zinc plate electrodes. The electrode tubes are filled with zinc sulphate solution (d 1·5), which, in the longer arms of the tubes, is covered with a layer of glycerin added in two portions, the lower portion mixed with a little zinc sulphate solution and the upper with a little of the solution to be tested. The remainders of the tubes on both sides of the diaphragm are filled with the solution to be tested; observations are made successively from both directions and the mean value is taken, so as to avoid variations in the concentration. A. R. POWELL.

Diaphragms. II. Porosity and endosmosis. K. ILLIG and N. SCHONFELDT (Wiss. Veroff. Siemens-Konz., 1928, 7, (1), 294—300).—Some results obtained with potassium chloride and copper sulphate solutions in a new apparatus for determining endosmotic processes (cf. preceding abstract) are recorded using diaphragms of varying porosity. Assuming the validity of the Helmholtz formula, the results show that the charge on the diaphragm decreases with increasing porosity, whereas this charge has always been considered to be a material constant dependent only on the nature of the substance of which the diaphragm is made and on the solution in which it is immersed.

A. R. POWELL.

Lyotropic properties of the nitrite ion. D. DEUTSCH and S. LOEBMANN (Kolloid-Z., 1928, **46**, 22—23).—Some physical properties of nitrite solutions have been examined with the view of assigning a place to the nitrite ion in the lyotropic series. Measurements of the surface tension of solutions of sodium nitrite show that the increase in surface tension bears a linear relation to the concentration over a wide range. Comparison of the curve with those obtained with other sodium salts gives the series F, Cl, NO_3, NO_2. Determination of the coagulation value of a positively-charged ferric oxide sol for potassium nitrite and for other potassium salts gave the series NO_3, Cl, CNS, NO_2, the value for the nitrite ion being very close to that for the thiocyanate ion. Experiments were also conducted on the influence of potassium salts on the partition of basic colouring matters between a benzene phase and a water phase. The following series was obtained: Cl, NO_3, I, SCN, NO_2. It is concluded that the position of the nitrite ion is in the neighbourhood of iodide and thiocyanate. E. S. HEDGES.

Influence of pressure on the temperature of maximum density of water and of solutions of varying concentration. G. TAMMANN and E. SCHWARZKOPF (Z. anorg. Chem., 1928, **174**, 216—224).—Isobars for aqueous solutions of lithium chloride, hydrogen chloride, and ethyl alcohol have been determined by the dilatometric method over the temperature ranges $-1°$ to $-72°$, $-1°$ to $-38°$, and $+0·4°$ to $-15·6°$, respectively. The temperature of maximum density of lithium chloride solutions decreases in a linear manner as the concentration increases from 0 to 27%, but thereafter the fall is much more rapid; for 22·5, 28·05, and 31·1% solutions the observed temperatures are $-26·5°$, $-42°$, and $-57·5°$, respectively. The corresponding values for 11·1 and 13·6% ethyl alcohol solutions are $-0·2°$ and $-2·8°$, and for 8·1% hydrogen chloride, $-12°$.

H. F. GILLBE.

Relation between the internal pressure of solutions and the nature of the dissolved substance. G. TAMMANN (Z. anorg. Chem., 1928, **174**, 231—243).—The change $\delta\kappa$ of the internal pressure of a liquid when a non-volatile substance is dissolved therein yields a measure of the molecular attraction between solvent and solute. The relation between this attraction and the nature of the solute is subject to three rules: (1) the attraction for strong electrolytes is additive, and suggests complete ionisation at concentrations up to N; that of the ions is specific and decreases with the ionic volume; (2) for weak electrolytes and non-electrolytes, which have an internal pressure greater than that of water, the attraction is not differentiated from that shown by strong electrolytes; (3) for volatile non-electrolytes the relation between molecular attraction and concentration is complex in character; in dilute solutions negative $\delta\kappa$ values are obtained which usually pass through a minimum as the concentration increases.

H. F. GILLBE.

Apparent hydration of ions. II. Densities and viscosities of mixed aqueous solutions of lithium chloride and hydrochloric acid. J. W. INGHAM (J.C.S., 1928, 2381—2388; cf. this vol., 948). —The densities of concentrated mixed aqueous solutions of lithium chloride and hydrochloric acid may be calculated with fair accuracy by means of the equation $d=K+k_1a+k_2b$. Scarpa's method (A., 1911, ii, 17) for the measurement of viscosities gives

results which agree well with those obtained by the Ostwald U-tube method. It is suggested that the decrease in viscosity which accompanies the replacement of lithium chloride by hydrochloric acid in these solutions is due to the greater hydration of the lithium ions as compared with the hydrogen ions. It is further shown that lithium ions are hydrated to a greater degree than sodium ions under the same conditions and that the degree of hydration decreases as the proportion of acid in the solution increases. From a consideration of the viscosities of mixed solutions of lithium, sodium, or potassium chlorides and hydrochloric acid it is apparent that variations of free space alone (cf. McLeod, Trans. Faraday Soc., 1926, **22**, 401) cannot account for the viscosity effects.

F. J. Wilkins.

Spectroscopic method of studying the formation of complex salts in dilute solution. II. Y. Shibata and T. Inoue (Japan. J. Chem., 1926, **2**, 109—115).—By a spectroscopic method previously described (*ibid.*, 1922, **1**, 1), the formation of complex mercuric salts has been studied. On plotting the wave-length corresponding with the end of the absorption spectrum for various mixtures of two salts a maximum is found when a complex salt is formed, the position of the maximum indicating the composition of the complex salt. The greater the dilution at which this maximum can be observed the more stable is the complex salt. Mixtures of mercuric chloride with a number of chlorides, bromides, iodides, and thiocyanates have been examined. The general similarity in the behaviour of these mixed solutions suggests a similarity of constitution. They probably all contain a mercury atom as the central metallic atom in a complex radical. In the case of mixtures of chlorides, the greater the number of chlorine atoms which are contained in the complex ion the more stable is the complex salt; *e.g.*, the salts obtained with chlorides of univalent metals, forming the ion $[HgCl_3]M^{\cdot}$ or $[HgCl_3(H_2O)_3]M^{\cdot}$, are less stable than those with chlorides of bivalent metals forming the ion $[HgCl_4]M^{\cdot\cdot}$ or $[HgCl_4(H_2O)_2]M^{\cdot\cdot}$, and so on. Those in which the second component is not a chloride are generally far more stable than those containing only chlorine atoms in the complex ion. In general the complex salts examined are far more stable in alcoholic than in aqueous solution.

M. S. Burr.

Spectrochemical studies on complex formations between mercuric salts and other metallic salts in dilute aqueous solutions. I. Formation of complex salts due to double decomposition of mercuric salts. II. Formation of complex salts in solution between mercuric cyanide and other metallic salts. T. Inoue (Japan. J. Chem., 1928, **3**, 131—146, 147—163).—I. The absorption spectrum method (cf. *ibid.*, 1922, **1**, 1; also preceding abstract) has been applied to the study of solutions containing mercuric salts and other metallic salts. The absorption curves for the systems mercuric nitrate–metallic chloride and mercuric sulphate–metallic chloride all show a minimum for the mixture containing two atoms of chlorine to one atom of mercury, indicating that the minimum is caused by the formation of mercuric chloride in solution by double decomposition. Maxima obtained with increasing quantities of metallic chloride indicate the formation of complex ions such as $[HgCl_3]'$, $[HgCl_4]''$, and $[HgCl_5]'''$ with chlorides of univalent, bivalent, and tervalent metals, respectively. Similarly, $[HgBr_4]''$, $[HgI_4]''$, $[Hg(SCN)_3]'$, and $[Hg(SCN)_4]''$ are obtained. It has also been shown that, although it is possible to have a complex thiocyanate ion containing cobalt, the complex thiocyanates produced between mercury and cobalt thiocyanates contain a mercury and not a cobalt atom as co-ordination centre in the complex ion. In mixtures of mercuric thiocyanate with metallic halides maxima are obtained only in the case of the iodides, and this is probably due to the initial formation of mercuric iodide by double decomposition and subsequent combination of this with more iodide to form a complex salt. No complex ion containing both halogen and thiocyanate appears to be formed. The tendency to the formation of complex ions appears to be in the order $Cl'<Br'<SCN'<I'$.

II. With chlorides, bromides, and thiocyanates mercuric cyanide produces the complex ions $[Hg(CN)_2Cl]'$, $[Hg(CN)_2Br_2]''$, and $[Hg(CN)_2(SCN)_2]''$. With alkali or alkaline-earth iodides the ion $[Hg(CN)_2I_2]''$ is first obtained, but double decomposition with the formation of the ion $[HgI_4]''$ then takes place. With zinc or cadmium iodide the $[HgI_4]''$ ion is obtained without any intermediate complex formation. The following order of stability was established: $[Hg(CN)_2Cl]'<[Hg(CN)_2Br_2]''<[Hg(CN)_2(SCN)_2]''<[Hg(CN)_2I_2]''<[HgI_4]''<[Hg(CN)_4]''$. The existence in solution of the compounds $[Hg(CN)_2S_2O_3]K_2$ and $[Hg(CN)_2(MeCO_2)]Na$ has been confirmed.

M. S. Burr.

Ebullioscopic determination of double salts and complexes in aqueous solution. F. Bourion and F. Rouyer (Ann. Chim., 1928, [x], **10**, 182—262).—A detailed account of the theoretical basis, experimental technique, and results of work previously published (A., 1927, 515, 729, 841; this vol., 233, 477).

J. W. Baker.

Modern colloid chemistry. H. R. Kruyt (Rec. trav. chim., 1928, **47**, 883—895).—A lecture.

Non-existence of the amorphous state. P. P. von Weimarn and T. Hagiwara (Japan. J. Chem 1926, **3**, 15—70).—See A., 1927, 410.

Human saliva as a reagent for preparing red dispersoid solutions and dispersible precipitates of gold. P. P. von Weimarn (Japan. J Chem., 1926, **2**, 123—128).—See A., 1926, 792.

Degree of dispersion of solutions of metals in molten salts (pyrosols). E. Heymann (Z. anorg. Chem., 1928, **175**, 241—244).—From considerations based on the thermodynamic theory of March (this vol., 235) it is shown that the particles of lead in the lead "fog" observed by other workers in molten lead chloride have a diameter of the order of 3×10^{-8}—8×10^{-8} cm., and those of cadmium in a "fog" of that metal in molten cadmium chloride a diameter of the order of 2×10^{-7} cm. Hence the lead particles have approximately atomic or molecular dimensions, but those of cadmium must be considered as amicronic colloid particles. These results agree with the

experimental facts observed by Eitel and Lange (this vol., 700). A. R. Powell.

Colloidal and elastic properties of polyvinyl acetate. G. S. Whitby, J. G. McNally, and W. Gallay (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 27—32; cf. Staudinger, Frey, and Starck, A., 1927, 1051).—Polyvinyl acetate is an organophilic colloid which exhibits elastic properties when swollen or heated. It dissolves and swells in polar organic liquids and in some liquids of very high dielectric constant. The elastic properties are shown in a comparatively low state of polymerisation. *X*-Rays give no fibre diagram. The viscosity relative to that of the solvent is almost unaffected by temperature changes. C. W. Gibby.

Alcosol of silicic acid. K. Inaba (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 92—93).—The alcosol of silicic acid is best prepared by hydrolysis of an alcoholic solution of ethyl orthosilicate with the calculated amount of water in the presence of sulphuric or hydrochloric acid ($<0\cdot04N$) which is subsequently removed by silver or lead oxide or by electrodialysis. The sol is a transparent, colourless, and viscous liquid $\kappa=2\cdot5-3\cdot0\times10^{-5}$ and $\eta=3\cdot35$ (at 25°) for a silica content of 17%. The concentration of silica (C) is related to the time required for spontaneous coagulation (t) by the expression $C-C_0/(1+at^n)$ where a and n are constants depending on the nature of the sol, and C_0 is the concentration when $t=0$. Electrolytes, particularly inorganic acids, decrease the stability slightly, whilst certain organic substances increase it. J. Grant.

Structure of the filaments obtained by the desiccation of colloidal ferric oxide solutions. P. Bary (Compt. rend., 1928, 187, 538—540).—The filaments were obtained by the evaporation of a solution of ferric oxychloride of the composition $10Fe_2O_3,Fe_2Cl_6$. On evaporation fine filaments with a parallel disposition are obtained at first; at a later stage thicker filaments are formed which are radially arranged. The former have the composition $20Fe_2O_3,Fe_2Cl_6$. An explanation of the formation of the two types of filaments is given. W. E. Downey.

Sol–gel systems with anisotropic particles. I. Dibenzoylcystine. II. Barium malonate. H. Zocher and H. W. Albu (Kolloid-Z., 1928, 46, 27—33, 33—36).—I. A microscopical examination has been made of gels of dibenzoylcystine at various concentrations. The particles are composed of positive doubly-refracting, needle-like particles, which exhibit a strong double refraction when under deformation. The diameter of the particles is below the limit of microscopic resolution. The weak double refraction shown in absence of deformation indicates that the gel is composed of spherical aggregates of radially disposed needles. When the gel is dried, there remains a varnish-like layer composed of needles oriented radially; these give negative double refraction, as does pure dibenzoylcystine crystallised from alcohol. The double refraction changes to positive when the substance is moistened with water or with salt solutions. From these observations, the existence of a hydrate in the gel is deduced. Unlike the higher alcohols, gels in a medium of ethyl alcohol do not show the presence of needles at first, but do so on ageing. At certain concentrations, sols are obtained which show visible streaming in reflected light and strong streaming-double refraction under the polarisation microscope. Marked dichroism is observed by colouring with methylene-blue or neutral-red.

II. The influence of various conditions on the formation of the malonate gels described by Flade (A., 1913, i, 824) has been investigated, and it is shown that by using anhydrous glycerol perfectly clear gels are produced, whereas the gels made with commercial glycerol described by Flade are turbid. The turbidity rises with increasing water content. These gels, especially those free from water, are thixotropic. Gels prepared with methyl alcohol in absence of glycerol are very stable so long as care is taken to exclude air. Sols exhibiting marked streaming-double refraction are produced by addition of water to gels free from glycerol. Attempts to produce dichroism by addition of various colouring matters met with failure. E. S. Hedges.

Regular micellar structure of caoutchouc. H. Mark and G. von Susich (Kolloid-Z., 1928, 46, 11—21).—*X*-Ray examination has shown that when natural caoutchouc is stretched, an orientation of particles takes place, not only in the direction of stretching, but also in a perpendicular direction. The stretched caoutchouc belongs to the rhombic crystal system and the identity periods of the elementary cell are $a=12\cdot3$ Å., $b=8\cdot3$ Å., and $c=8\cdot1$ Å. There are eight isoprene residues in the elementary cell. The crystal class is probably V or V_h. Caoutchouc was treated in the stretched state with various chemical reagents, and the derivatives were examined by the *X*-ray method. All the derivatives gave only an amorphous *X*-ray diagram. E. S. Hedges.

Micellar state of starch. G. Malfitano and M. Catoire (Kolloid-Z., 1928, 46, 3—11).—A comprehensive theory of colloids is outlined, which characterises and explains the micellar state of starch. The micelle is considered to consist of units of many grades of complexity, each unit being composed of polymerised molecules. The complexes may be of the Werner type, or polymerised polymerides, or crystals formed by the aggregation of micro-crystals. The colloid state is further characterised by a duality of composition involving an electrolytic part and a non-electrolytic part. A colloid is formed when both of the above conditions operate simultaneously. It is considered that the electrolytic part is present along with the non-electrolytic complexes in the central kernel of the micelle. The alternative hypothesis, that the electrolytic part is adsorbed at the surface of the particle, is not excluded, but is insufficient to explain all the facts. The dependence of the stability, flocculation, sedimentation, and formation of colloids on the nature and valency of added electrolytes is explained by the change in the degree of ionisation and consequently dispersion of the micellar ion. E. S. Hedges.

Effect of non-electrolytes on the stability of colloids. I. Arsenious sulphide sol. S. G. CHAUDHURY (J. Physical Chem., 1928, **32**, 1481—1487; cf. A., 1927, 413).—Adsorption experiments using arsenious sulphide sol in methyl and ethyl alcohols with barium chloride as coagulant indicate that adsorbability as measured analytically does not run parallel with the tendency towards coagulation. Measurements of the rate of migration of the sol with hydrochloric acid in substitution for barium chloride indicate that a diminution in ϵ sensitises the sol. Explanations are advanced, and it is suggested that the addition of a non-electrolyte may alter ϵ, which generally sensitises the sol, and also the interfacial tension which, in turn, influences the electrical potential below which coagulation takes place.

L. S. THEOBALD.

Stabilisation of colloids. V. KOULIKOV (Compt. rend. Soc. Biol., 1927, **97**, 1337—1339; Chem. Zentr., 1928, i, 1779).—A series of substances has been prepared which permit the formation of a colloidal solution from two mutually insoluble substances.

A. A. ELDRIDGE.

Ionic equilibrium, phagocytosis, and age of colloids. V. KOULIKOV (Compt. rend. Soc. Biol., 1927, **97**, 1335—1336; Chem. Zentr., 1928, i, 1779).

Viscosity theory of Sen, Dhar, and collaborators. P. C. VAN DER WILLIGEN (Kolloid-Z., 1928, **46**, 55-57).—Objections are raised against the viscosity theory proposed by Sen (A., 1926, 470) and Chakravarti and Dhar (*ibid.*, 677), for in presence of large amounts of electrolytes other phenomena besides viscosity play a part, and in presence of small quantities of electrolytes the supposed relation between charge and viscosity has not been proved either experimentally or theoretically. E. S. HEDGES.

Viscosity of glycogen and some dyes and the relation between gelatinisation and double refraction. S. N. BANERJI and N. R. DHAR (Kolloid-Z., 1928, **46**, 24—26).—Measurements of the viscosity of ponceau-red, Victoria-blue BA, dianil-blue B, Victoria-blue B, Bordeaux B extra, aniline-brown, and dianil-orange G showed that in each case the viscosity falls on addition of small quantities of electrolytes. The viscosity of a 5% solution of glycogen is higher than that of most hydrophobic colloids of equal concentration. The viscosity of glycogen and of Bordeaux B extra rises slightly on keeping. Methyl-orange, patent-scarlet, imperial-green, tropæolin D, theonine, mercury sulphosalicylate, orange III, orange N.R. II, and aniline-orange exhibit streaming-double refraction. Many of these substances can be obtained in the gel form. It is considered that high viscosity, strong hydration, tendency to form stable gels, and double refraction are factors connected with a non-spherical form of the particles. E. S. HEDGES.

Reactions in gelatin gels. S. M. KUZMENKO (Ukraine Chem. J., 1928, **3**, 231—235).—Liesegang rings are produced when the sulphides of manganese, iron, nickel, zinc, and cobalt are precipitated in gelatin gels. Where mixtures containing pairs of the above cations are used, the less soluble sulphide is precipitated from the pairs Co–Mn, Ni–Fe, Zn–Fe, and Co–Fe. From the pair Fe–Mn the more soluble sulphide separates, whilst the sulphides are precipitated in approximately equal amount from the pairs Zn–Mn, Zn–Ni, Co–Ni, Co–Zn, and Ni–Mn. The above results are in accordance with Ostwald's theory of the formation of Liesegang rings.

R. TRUSZKOWSKI.

Rhythmic formation of precipitates in gels. D. AVDALIAN (Ukraine Chem. J., 1928, **3**, 222—235).—The presence of neutral salts such as sodium chloride and potassium nitrate diminishes the distance between the Liesegang rings formed in gelatin gels by the reaction between silver nitrate and potassium dichromate to an extent which depends on the concentration of the substrates. This effect is explained by the lowering of the metastable boundary of supersaturated solutions, and supports Ostwald's interpretation of this phenomenon ("Lehrb. allgem. Chem," 1902, II, **2**, 782). R. TRUSZKOWSKI.

Denitration in artificial silk manufacture. A. NADAI (Z. physikal. Chem., 1928, **136**, 289—313).—Denitration of cellulose nitrates by hydrosulphides is analogous to the alkaline hydrolysis of esters. The kinetics of the reaction in a heterogeneous system, however, are those of a reaction of the first order. Increase of the temperature or of the hydrosulphide concentration, or the presence of substances such as alcohol, acetone, or certain inorganic salts at high concentration, which produce swelling of the cellulose nitrate, results in an increase of the velocity coefficient. During the reaction the hydrosulphide is oxidised to polysulphide, whilst the nitro-group eliminated is reduced to nitrite and ammonia; no nitrate appears to be produced. H. F. GILLBE.

Limiting condition "concentration=0" in diffusion problems. W. DE GROOT (Physica, 1928, 8, 23—34; Chem. Zentr., 1928, i, 1943).—Mathematical. A. A. ELDRIDGE.

Heat of vaporisation at absolute zero. J. E. VERSCHAFFELT (J. Chim. phys., 1928, **25**, 408—409).—Polemical against Kolosovski (cf. this vol., 241).

L. F. GILBERT.

Limiting value of the latent heat of vaporisation and the specific heat of the saturated vapour at absolute zero. N. DE KOLOSOVSKI (Z. physikal. Chem., 1928, **136**, 314—316).—Polemical. All attempts to evaluate the true limiting value of latent heat of evaporation, the entropy of a gas, or the specific heat of a saturated vapour at 0° Abs. from thermodynamical considerations are illusory.

H. F. GILLBE.

Formulæ for the internal energy and entropy of a substance or mixture. R. D. KLEEMAN (J. Physical Chem., 1928, **32**, 1396—1410).—Theoretical. From relations previously given (A., 1927, 520, 936), the more important formulæ for the controllable internal energy and the controllable entropy of a substance or mixture are derived. Both these quantities are additive for substances in the gaseous state. On mixing substances of the same type at infinite dilution, no change in internal energy or entropy takes place. Formulæ for the maximum work and free energy of a substance or mixture are also given. From the additive laws developed, it is

possible to calculate the entropy, free energy of formation, and the mass-action constant of compounds at present undiscovered. L. S. THEOBALD.

New mass-action law. VI. Interchange of the components in the equation of the mass-action law. R. LORENZ (Z. anorg. Chem., 1928, **175**, 257—269).—A discussion of alternative methods of expressing states of equilibrium in terms of the law of mass action. H. F. GILLBE.

Thermal dissociation of steam into hydrogen and free hydroxyl. K. F. BONHOEFFER and H. REICHARDT (Z. Elektrochem., 1928, **34**, 652—654).—The absorption spectrum of steam containing suitable amounts of oxygen shows at 1200° the presence of free hydroxyl. The heat of the reaction $2H_2O=H_2+2OH$ is determined as −125,000 g.-cal., or possibly higher, at about 1400°. The equilibrium constants for this reaction, calculated by Nernst's heat theorem, are very close to those determined experimentally for the reaction $2H_2O=2H_2+O_2$. S. K. TWEEDY.

Activity coefficients and mass-action law in electrolytes. L. ONSAGER (J. Physical Chem., 1928, **32**, 1461—1466).—The deductions of Soper (this vol., 24, 26), which lead to limiting formulæ for the activity coefficients of electrolytes other than those given by Debye and Hückel, have been analysed and shown to be in error. The Debye–Hückel theory is satisfactory in all points attacked by Soper, so far as the deductions are concerned. The agreement of Soper's formulæ with experiments on reaction velocity is attributed to the application of the limiting square root formulæ at concentrations which are too high. L. S. THEOBALD.

Theory of the acidic–basic function. J. N. BRONSTED (Ber., 1928, **61**, [*B*], 2049—2063).—The conception of an acid as a substance which can lose a proton and a base as a material which can add a proton is further developed (cf. A., 1926, 797). Since it is admitted that a proton cannot exist as such in aqueous or other solution, the acidic function can manifest itself only when a second molecule is present which can combine with the proton. The general scheme for the stoicheiometric acidic–basic function is therefore $A^1(acid_1)+B^2(base_2) \rightleftharpoons A^2(acid_2)+B^1(base_1)$. The production of hydrogen ions is not a necessity for the manifestation of acidic properties, but occurs in aqueous solution thus: $A(acid_1)+H_2O(base_2) \rightleftharpoons B(base_1)+H_3O^-(acid_2)$. The intimate connexion assumed previously between salt formation and the acidic–basic function is accidental, since salt formation from two electrically neutral molecules can occur by transference not only of a proton, but also of an electrically-charged particle of any kind from one to the other electrically neutral molecule. The behaviour of acids in indifferent solvents such as benzene illustrates the development of acidic and basic properties without participation of hydrogen or hydroxyl ions. The non-acidity of a solution of picric acid in benzene is due, not to low dielectric constant of the medium, but to absence of an acceptor for the proton. If, however, a base is added the colour of the picric ion is developed thus: $(NO_2)_3C_6H_2{\cdot}OH(acid_1) + PhNH_2(base_2) \longrightarrow (NO_2)_3C_6H_2{\cdot}O^-(base_1) + PhNH_3^+(acid_2)$. Similarly, the presence of the hydrogen ion is unnecessary for the development of the indicator equilibrium in benzene, but indicator reactions are possible, as the equilibrium is only a special case of the reaction $A(acid)+I_B(indicator\text{-}base) \longrightarrow B(base)+I_A(indicator\ acid)$. The acidity of a solution is defined in general as its proton activity, so that the basicity is the reciprocal of the acidity. Measurement of acidity is based on the expression $a \times C_B/C_A=K_{acid}$, in which C_A is the concentration of the acid A, C_B that of the corresponding base B, and a_H^+ the acidity of the solution as defined above. The basicity constant of the base is given by the formula $C_A/(a_H \times C_B)=K_{base}$. The values of K are constant only for a constant medium. In benzene, a direct determination of a_H is impossible and the relative magnitudes of the constants must be elucidated from measurements of equilibrium. By use of the equation $K_1/K=C_{1B} \times C_A/(C_{1A} \times C_B)$, the constants K and K_1 are compared by the indicator method. The following sequence is determined in benzene: hydrogen chloride, methyl-red, dimethyl-yellow, trichloroacetic acid, dichloroacetic acid, picric, *o*-nitrobenzoic, monochloroacetic, and salicylic acids, bromophenol-blue, β-dinitrophenol, *o*-chlorobenzoic acid, neutral-red, *m*-chlorobenzoic acid, bromocresol-green, benzyl-ammonium ion, formic, phenylacetic, benzoic, and acetic acids, *iso*amylammonium ion, bromocresol-purple, piperidinium ion, bromothymol-blue. H. WREN.

Effects of the spatial position of substituent groups on acidic strength. D. H. HEY (J.C.S., 1928, 2321—2323).—A criticism of the analogy drawn by Rule, Hay, and Paul (this vol., 765) between the influence of substituents on the acidity of geometrically isomeric acids and the effect of terminal alkoxyl and carboxyl groups on rotatory power. It is suggested that in the light of recent work on the configuration of the crotonic acids, this analogy is invalid. Further, the increase in the dissociation constants of these acids produced by the spatial proximity of the substituent group is in close conformity with the influence of *ortho*-substituents on the acidity of benzoic acid. F. J. WILKINS.

Superacid solutions. III. Titration and dilution curves of bases dissolved in acetic acid. N. F. HALL and T. H. WERNER (J. Amer. Chem. Soc., 1928, **50**, 2367—2386; cf. this vol., 129).—The influence exerted by the nature and concentration of the titrating acid (sulphuric, hydrochloric, perchloric) and the strength of the base being titrated on the shape of the titration curves is investigated for solutions with acetic acid as solvent. The first two factors have a much greater effect on the p_H of a mixture of a weak base and its salt in acetic acid than in water. The weaker bases give anomalous titration curves, whilst the curves for bases which act like strong bases in water conform to theory. The influence of dilution on acetic acid solutions of bases is studied by an *E.M.F.* method, using a chloranil electrode, in preference to the conductivity method. Anomalies which are often present when the latter method is used are not apparent with the former method. Bases which behave during titration in

acetic acid solution like strong bases are nevertheless weak electrolytes. The liquid junction potential between the solutions used and aqueous potassium chloride solution is practically constant. Factors are suggested which may explain certain minor anomalies. S. K. TWEEDY.

Hydrolysis measurements in solutions of stannous salts. M. PRYTZ (Z. anorg. Chem., 1928, **174**, 355—375).—The hydrolytic constants of stannous chloride, bromide, and perchlorate have been determined by potentiometric titrations, the results of which are recorded graphically. The values obtained indicate that hydrolysis takes place with the formation first of the ion $Sn(OH)^{\cdot}$, which then passes into the dimeric form $Sn_2(OH)_2^{\cdot\cdot}$ or its anhydride $Sn_2O^{\cdot\cdot}$. The value of $K=\alpha^2m/(1-\alpha)$ for $Sn^{\cdot\cdot}+H_2O=SnOH^{\cdot}+H^{\cdot}$ decreases with the dilution, whereas the value of $K'=\alpha^3m(1-\alpha)^2$ for $2Sn^{\cdot\cdot}+2H_2O=Sn_2(OH)_2^{\cdot\cdot}+2H^{\cdot}$ is independent of the dilution. In the presence of potassium salts the value of K' is considerably reduced owing to the formation of complexes. When the neutralisation point is passed in the titrations, a white precipitate is obtained; assuming this to be $Sn(OH)_2$, the results indicate that stannous hydroxide has a solubility product of 5×10^{-26} and that in feebly alkaline solutions it has no tendency to form stannites. A. R. POWELL.

Hydrolysis of solutions of zinc sulphate and the presence of univalent zinc ions. H. G. DENHAM and N. A. MARRIS (Trans. Faraday Soc., 1928, **24**, 510—515).—When the hydrolysis of zinc sulphate solutions is measured by the hydrogen electrode method anomalous values are obtained. Subsequent work with the allied element cadmium showed that the hydrogen electrode causes a reduction of the bivalent cadmium ion to a univalent state, suggesting a similar reduction in the case of zinc. A quinhydrone electrode was found to give a steady and normal value for the hydrolysis of zinc sulphate solutions. The authors' views are confirmed by the successful results of an attempt to reduce zinc sulphate by means of platinum-black kept vigorously stirred in the solution by a stream of hydrogen. It is suggested that the low hydrogen pressure peculiar to the quinhydrone electrode is incapable of setting up such reduction. N. M. BLIGH.

Hydrolysis of certain easily reducible metallic salts. H. G. DENHAM and N. A. MARRIS (Trans. Faraday Soc., 1928, **24**, 515—518; cf. preceding abstract).—The quinhydrone electrode has been successfully used in the determination of the hydrolysis of solutions of cadmium sulphate, lead chloride and nitrate, and thallous sulphate, all of which had previously been shown to be capable of reduction to a univalent or a subvalent condition. N. M. BLIGH.

Amphoteric nature of cadmium hydroxide. J. PIATER (Z. anorg. Chem., 1928, **174**, 321—341).—The solubility of cadmium oxide in water at 25° is $1{\cdot}7\times10^{-5}$ mol./litre and that of cadmium hydroxide $1{\cdot}11-1{\cdot}18\times10^{-5}$ mol./litre, according to its age and method of preparation. The solubility decreases on the addition of sodium hydroxide to a minimum of about $0{\cdot}13\times10^{-5}$ mol./litre in 0·01—0·1*N*-sodium hydroxide. In more strongly alkaline solutions the solubility increases rapidly, reaching 9×10^{-5} mol./litre in 5*N*-alkali, thus showing that cadmium hydroxide is an extremely weak acid. By the use of Bjerrum's theory of strong electrolytes the magnitude of the activity product of cadmic acid has been found to be of the order of 1×10^{-19}. A. R. POWELL.

Influence of intensive drying on inner equilibria. III. A. SMITS (J.C.S., 1928, 2399—2409).—A review is given of the present position of the problem of intensive drying and the apparent contradiction between the results of the author and Baker (*ibid.*, 1051) is discussed. It is pointed out that with the exception of his measurements of surface tension all Baker's experiments were carried out under conditions of rapid evaporation or distillation. The author suggests that neither Baker nor he has stopped the inner transformations in the liquid phase of a single substance and that, therefore, the differences between their results are to be expected, as his static methods are favourable to the establishment of equilibria in the gas phase, whilst Baker's methods are not. The results obtained from surface tension experiments are rejected on the ground that this property is not a trustworthy criterion for internal equilibria. Electric fields have no influence on either the vapour pressure or the b. p. of benzene. F. J. WILKINS.

Intensive drying of liquids. S. LENHER and F. DANIELS (Proc. Nat. Acad. Sci., 1928, **14**, 606—609).—After about 4 years' intensive drying with phosphoric oxide in sealed glass tubes at the ordinary temperature, no abnormal rise was observed in the b. p. of benzene and of carbon tetrachloride (cf. Baker, J.C.S., 1922, **121**, 568). M. S. BURR.

Glass. II. Transition between the glassy and liquid states in the case of dextrose. G. S. PARKS, H. M. HUFFMAN, and F. R. CATTOIR (J. Physical Chem., 1928, **32**, 1366—1379; cf. this vol., 115).—Crystalline dextrose when heated at 160° for 10—15 min. and cooled to the ordinary temperature under a pressure of 4 atm. in nitrogen yields a clear, colourless glass, which softens at 40° and becomes, at 60°, a thick, viscous liquid. The glass is stable in dry air or under xylene, but eventually crystallises, especially if traces of a solvent for dextrose are present. Water (10%) or sodium acetate (1%) with dextrose can form two-component glasses with modified properties. The specific heat, coefficient of thermal expansion, and refractive index of dextrose glass have been determined over the ranges 90—340°, 262—348°, and 7—77° Abs., respectively. Up to 275° Abs., the curve relating C_p and temperature for dextrose glass is slightly higher than the corresponding curve obtained by Simon (A., 1922, ii, 684) for crystalline dextrose, but over the range 275—287° Abs. there is a sharp, 62% increase in the values of C_p. The corresponding values of C_v have been calculated. The coefficient of thermal expansion, measured by a dilatometric method, shows a sharp, 200% increase over the range 293—303° Abs. Below this transition region the coefficient for the glass is somewhat greater than that for the crystalline form, which is uniform at the value $0{\cdot}84\times10^{-4}$ over the range 273—323° Abs.; above this region it is identical with that of the liquid. The

refractive index–temperature curve shows a change in slope over the interval 20—30°. L. S. THEOBALD.

Thermal decomposition of Bayer's alumina. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 970—975).—Arrest points were found at 190°, 270°, and 450° in a thermal analysis of an alumina of composition very close to $Al_2O_3,3H_2O$. From *X*-ray spectrograms of this alumina taken after heating to various temperatures it is inferred that decomposition occurs in stages, giving perhaps $Al_2O_3,2H_2O$, and certainly Al_2O_3,H_2O, the final product being anhydrous alumina of a high density, which therefore differs from Blanc's alumina.
F. G. TRYHORN.

Effect of gelatin on the polymorphic transformation of mercuric iodide. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1928, 3, 189—191).—The transition temperature of mercuric iodide (red ⟵ yellow) is made less sharp by the presence of gelatin. It is necessary to heat considerably above 127° to transform the red form into the yellow, whilst the yellow form will remain unchanged indefinitely at the ordinary temperature. The gelatin acts as a protective colloid in the solid phase. Light energy accelerates the change of mercuric iodide from the metastable to the stable form. A. J. MEE.

General theory of distillation of liquid mixtures of many components and its experimental verification. Y. TSUKAMOTO (Japan. J. Chem., 1926, 2, 129—147).—On the basis of the kinetic theory equations have been derived for the determination of the composition of the liquid and gaseous phases in the distillation of liquid mixtures. If N_1, N_2 . . . are the molecular quantities of each component in the original mixture, and n_1, n_2 . . . those in the residual liquid mixture, $n_2=N_2(1/N_1)^{K_1}n_1^{K_1}$, $n_3=N_3(1/N_1)^{K_2}n_1^{K_2}$, and so on, K_1, K_2 . . . being obtained from the expressions $K_1=\sqrt{m_1/m_2}\times e^{L_2/RT}/e^{L_1/RT}$, K_2— . . ., m_1, m_2 . . . being the mol. wts. and L_1, L_2 . . . the molecular latent heats of evaporation. If the solution is non-ideal the partial molecular latent heat of evaporation must be substituted for the molecular latent heat of the pure substance. The equations have been verified experimentally in the system benzene–chlorobenzene–bromobenzene and can also be applied to the calculation of the composition of the vapour phase in equilibrium with a given mixture. Such calculations have been carried out for the systems oxygen–nitrogen, nitrogen–argon, carbon tetrachloride–alcohol, chloroform–benzene, and chloroform–methyl alcohol. M. S. BURR.

Vapour pressure of water over sulphuric acid–water mixtures at 25°, and its measurement by an improved dew-point apparatus. J. R. I. HEPBURN (Proc. Physical Soc., 1928, 40, 249—260).—A critical study is made of the data used by Wilson (cf. B., 1921, 421) in the construction of a mean curve for the vapour pressure of water over sulphuric acid–water mixtures at 25°. Sorel's observations are shown to be inconsistent with calculated values and with determinations using an improved dew-point apparatus. The mean curve has been reconstructed and a table of the most probable values compiled.
C. J. SMITHELLS.

Vapour pressures of the heptahydrate and the saturated solution of sodium sulphite. K. ARII (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 83—84).—The vapour pressures of the systems $Na_2SO_3,7H_2O$–Na_2SO_3, $Na_2SO_3,7H_2O$–sat. solution, and Na_2SO_3–sat. solution were determined between 15° and 50° by the statical method, and good agreement with the calculated values was found. The transition point heptahydrate–anhydride, determined from the point of intersection of the three vapour pressure–temperature curves, is 33·6° (33·49° calc.). J. GRANT.

Chemical equilibrium in the vapour of a mixture of paraffins and unsaturated hydrocarbons. H. A. WILSON (Proc. Roy. Soc., 1928, A, 120, 247—251; cf. A., 1927, 1139).—Unsaturated hydrocarbons containing more than one double linking are considered and their partial pressures in the mixture calculated by making use of their heats of formation and chemical constants in Planck's approximate equation for the equilibrium constant. A table is given showing the percentage of unsaturated hydrocarbons at various temperatures and pressures. The equilibrium in the formation of coke from oil is discussed. J. L. BUCHAN.

Equilibrium in binary systems cresols–amines. N. A. PUSHIN and L. SLADOVIC (J.C.S., 1928, 2474—2483).—Equilibrium diagrams for *o*-, *m*-, or *p*-cresol paired with dimethylaniline, *p*-toluidine, quinoline, piperidine, 1 : 5-naphthylenediamine, or carbamide are described. These indicate the formation of the compounds $CO(NH_2)_2$,*o*-$C_6H_4Me{\cdot}OH$ (cf. Kremann, A., 1907, i, 912); $NPhMe_2$,*o*-$C_6H_4Me{\cdot}OH$, m. p. —6°; *p*-$C_6H_4Me{\cdot}NH_2$,*o*-$C_6H_4Me{\cdot}OH$, m. p. 38°; *p*-$C_6H_4Me{\cdot}NH_2$, -$C_6H_4Me{\cdot}OH$, m. p. 12·9°; *p*-$C_6H_4Me{\cdot}NH_2$,*p*-$C_6H_4Me{\cdot}OH$, m. p. 20·5°; C_9H_7N,*o*-$C_6H_4Me{\cdot}OH$, m. p. 34·2°; C_9H_7N,2*o*-$C_6H_4Me{\cdot}OH$, m. p. 34·5°; C_9H_7N,*p*-$C_6H_4Me{\cdot}OH$, m. p. 31·8°; C_9H_7N,2*p*-$C_6H_4Me{\cdot}OH$, m. p. 24·5°; $C_5H_{11}N$,2*p*-$C_6H_4Me{\cdot}OH$, m. p. 42·1°; 1 : 5-$C_{10}H_6(NH_2)_2$,2*p*-$C_6H_4Me{\cdot}OH$, m. p. 118°. Dimethylaniline and *p*-cresol do not combine.
F. J. WILKINS.

Binary systems cadmium–antimony and cadmium–lead. E. ABEL, O. REDLICH, and J. ADLER (Z. anorg. Chem., 1928, 174, 257—268).—Thermal and micrographical study of the system cadmium–antimony shows that the compound Cd_3Sb_2 does not exist in a stable region. The activities of the components in the cadmium–lead system have been calculated from the thermal diagram and are in agreement with *E.M.F.* measurements. Cadmium and lead are not soluble in one another to any appreciable extent in the solid phase. H. F. GILLBE.

Constitution of the iron–tungsten and iron–molybdenum alloys. H. ARNFELT (Iron and Steel Inst. Carnegie Schol. Mem., 1928, 17, 1—21).—Portions of the equilibrium diagrams for these systems have been investigated microscopically and by *X*-ray analysis. The crystalline compound Fe_2W has a hexagonal structure and when it is in equilibrium with the iron phase the dimensions of the lattice are $a_1=4{\cdot}727$ Å., $a_3=7{\cdot}704$ Å., four Fe_2W groups being present in the unit cell. This compound is un-

stable at higher temperatures and decomposes somewhere between 1000° and 1450°; it forms solid solutions to some extent, but their range is probably narrow. Direct determination gave the density as 13·0. A second compound, Fe_3W_2, is formed by a peritectic reaction at a high temperature, and has a trigonal lattice with parameters a_1=4·731 Å., a_3=25·7 Å., with 40 atoms in the unit cell, the density being 12·9. This also is associated with a short range of solid solutions. The iron–molybdenum system contains a trigonal compound, Fe_3Mo_2, analogous to Fe_3W_2; the lattice parameters are a_1=4·743 Å., a_3=25·63 Å., with 40 atoms to the unit cell. This compound also forms solid solutions to a small extent. There is no iron–molybdenum compound corresponding with the hexagonal iron–tungsten compound, but there is one compound and possibly two in addition to the trigonal Fe_3Mo_2, but these have not been isolated. W. HUME-ROTHERY.

Fluorine tension of metallic fluorides and the chemical constants of fluorine and hydrogen fluoride. K. JELLINEK and A. RUDAT (Z. anorg. Chem., 1928, **175**, 281—320).—The equilibrium conditions for the reduction of silver, cupric, lead, nickelous, cobaltous, ferrous and ferric, cadmium, zinc, chromic and chromous, and manganous fluorides by hydrogen at temperatures from 100° to 800° have been determined. The equilibrium $FeF_2+H_2 \rightleftharpoons Fe+2HF$ may be reached from either side, and the same is probably true of the reduction of manganous and chromous fluorides. In all other cases, however, equilibriun can be reached only from the hydrogen side; this is probably due to the small rate of diffusion of hydrogen fluoride through the film of fluoride which is first formed on the surface of the metal, that of hydrogen through the film of metal formed by reduction being relatively high. The calculated heats of formation of the metallic fluorides are in good agreement with calorimetric determinations. The ease of reduction of certain fluorides is discussed and compared with that of other halides. The chemical constants of hydrogen fluoride and of fluorine are $-1·0\pm0·3$ and $+0·7\pm0·3$, respectively.

H. F. GILLBE.

Ternary system lead–antimony–cadmium. E. ABEL, O. REDLICH, and J. ADLER (Z. anorg. Chem., 1928, **174**, 269—280).—The system has been thoroughly investigated, but no evidence has been obtained for the existence of mixed crystals.

H. F. GILLBE.

Equilibrium in the systems $ZnSO_4$–Na_2SO_4–H_2O at 0° and 25°; $MnSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 35°; and $CoSO_4$–K_2SO_4–H_2O at 25°. R. M. CAVEN and W. JOHNSTON (J.C.S., 1928, 2506—2514; cf. A., 1924, ii, 683; 1927, 1142).—The recorded solubility data show the range of existence of the double salts $ZnSO_4,Na_2SO_4,4H_2O$, $MnSO_4,Na_2SO_4,2H_2O$, and $CoSO_4,K_2SO_4,6H_2O$ at the various temperatures. The equilibrium relations in the third system are compared with those shown by the corresponding systems in which cobalt is replaced by copper and by nickel. F. J. WILKINS.

Equilibrium of the system barium carbide, barium oxide, carbon, and carbon monoxide. M. DE K. THOMPSON (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 16 pp.).—Equilibrium pressures for the system $BaO+3C \rightleftharpoons BaC_2+CO$ have been measured at three temperatures in an Arsem vacuum furnace. To ensure true equilibrium with carbon monoxide the charge was made in the form of a tube using a double-walled paper container. The pressures measured were corrected for the vapour pressure of barium oxide (see this vol., 1179). The equilibrium pressure was found to depend, not only on the temperature, but also on the percentage of carbide and on the ratio of barium oxide to carbon. This indicates that the three solid substances must form a solid solution. Consistent results were obtained at 1141° and 1295°, but at 1375° dissociation of the carbide or some other disturbing factor entered. H. J. T. ELLINGHAM.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1928, **50**, 419—424; cf. this vol., 955).—The influence of temperature and volume as independent variables in the thermodynamic equations of mixtures is examined. Further, the bearing of free energy, internal energy, and heat content on the equilibrium conditions for a mixture of two components is discussed. W. E. DOWNEY.

Derivation of the phase rule. O. REDLICH (Z. anorg. Chem., 1928, **174**, 281—284).—The derivation postulates that for two closed systems in equilibrium to be identical, the quantities of the independent phases, the total energy, and the total volumes must be equal; the procedure is applicable to all systems which are not acted on by any external force.

H. F. GILLBE.

Heat of combustion of benzoic acid. W. A. ROTH (Z. physikal. Chem., 1928, **136**, 317—320).—Various results are compared; the most probable value is 6323 g.-cal./g., weighed in air against platinum weights. H. F. GILLBE.

Heat of dissociation of oxygen as estimated from photochemical ozonisation. O. R. WULF (Proc. Nat. Acad. Sci., 1928, **14**, 614—616).—The heat of dissociation of oxygen in the photochemical formation of ozone was estimated by Warburg (Z. Elektrochem., 1920, **26**, 58) from the energy of the absorbed wave-length 2070 Å., and by Born and Gerlach (Z. Physik. 1921, **5**, 433) from the wave-length 2530 Å. It is supposed, however, that molecules are dissociated by light absorption only when such absorption lies in the continuous spectrum that stretches to shorter wave-lengths from the point of confluence of a band progression. There is no continuous spectrum in the Schumann–Runge band system, but in the absorption by gaseous oxygen under pressure, or by liquid oxygen, wave-length 2070 Å. lies in such a continuous spectrum. Apparently, however, it refers to the dissociation of the O_4 molecule and not of the O_2 molecule (cf. this vol., 1168) as supposed by Warburg (*loc. cit.*). The wave-length 2530 Å. does not lie in a continuous spectrum, and therefore cannot be used as a basis for the determination of the heat of dissociation. M. S. BURR.

Electronic thermochemistry of inorganic compounds. A. BERKENHEIM (Z. physikal. Chem.,

1928, **136**, 231—258).—The arithmetical relations existing among the heats of formation of analogous inorganic compounds are considered in the light of the accepted structure of atoms and molecules. It is shown that heats of formation may be calculated with considerable accuracy by the summation of terms due respectively to heats of sublimation, heats of ionisation or dissociation, and the work, mechanical and electrostatic, of bringing together the component atoms or ions of the compound. F. G. TRYHORN.

Method of conductivity determination. O. REDLICH (Z. physikal. Chem., 1928, **136**, 331—352).—An alternating-current compensation method has been developed for the measurement of the conductivity of solutions of electrolytes with uncoated electrodes. It is said that the error is about 0·02%. H. F. GILLBE.

Light-sensitivity of commercial selenium cells. G. P. BARNARD (Proc. Physical Soc., 1928, **40**, 240—248).—For commercial selenium cells the change in conductance C due to an intensity of illumination I is given by $C \propto I^x$, where x varies from cell to cell, depending on the construction. A sensitivity curve for a Fournier d'Albe type of cell is given. The change in conductance of selenium cells is shown to depend on the amount of radiant energy received, and not on the number of foot candles incident on the cell. For equal radiant energy the action of the infra-red is relatively much weaker than that of some shorter waves. The light-sensitivity of selenium is attributed to changes in crystalline structure. C. J. SMITHELLS.

Transport numbers of ions in solid sodium chloride at high temperatures. T. E. PHIPPS and R. T. LESLIE (J. Amer. Chem. Soc., 1928, **50**, 2412—2421).—Between 410° and 510° the transport number of the sodium ion in solid sodium chloride is unity; at 558° it is about 0·57 and it gradually increases, probably because of polarisation effects, to 0·72 at 655°. The change from uni-ionic to bi-ionic conductivity occurs in the temperature region in which the slope of the conductivity curve (log κ against $1/T$) is doubled. A reversible sodium electrode is described. S. K. TWEEDY.

Theory of electrical migration of ions. J. N. MUKHERJEE (Nature, 1928, **122**, 608).—The theory of moving boundaries as developed by Kohlrausch and Weber overlooks the unequal transfer of the common ion at the boundary, and rests on a misconception of the conditions on the "indicator" side of the boundary. A. A. ELDRIDGE.

Electrochemistry of the proteins. D. M. GREENBERG (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 12 pp.).—Transport numbers have been measured for solutions of casein and of A, B, and C fibrin in 0·1N-solutions of various acids and alkalis. These proteins are deposited on the cathode or the anode according as the solution is acid or alkaline, and the amounts deposited are found to be proportional to the quantity of electricity passed and inversely proportional to the amount of acid or alkali per g. of protein in the solution. For casein the weight of the deposit is very close to that calculated on the assumption that all the acid or alkali present is taken up by the protein, giving positive or negative "protein ions" which are discharged at 100% current efficiency; for the fibrins considerably lower weights are obtained. The transport number measurements indicate that the only carriers of the current are the negative protein ion and the alkali metal cation in alkaline solutions, and the positive protein ion and the acid anion in acid solutions. Thus, for casein in various alkali hydroxide solutions the equivalent ionic conductivity of the casein ion calculated on this assumption is practically independent of the nature of the cation, and has the high value of 44·5±2 at 30°. With casein in solutions of alkaline-earth hydroxides abnormally high transport numbers (sometimes >1) were obtained, indicating the formation of complex negative ions containing the alkaline-earth metal. This result agrees with the observation that milk and blood normally contain more dissolved calcium than would be expected from the solubility of the phosphate and carbonate, and only part of this calcium will diffuse through a parchment membrane. H. J. T. ELLINGHAM.

***E.M.F.* between copper and its amalgam and the reproducibility of the copper electrode.** M. OKU (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 84—86).—A reproducible copper electrode may be prepared by electrolysis of a 0·1M-solution of copper sulphate acidified with sulphuric acid, with a platinum cathode and a copper anode at a current density of 0·5—1·0 amp./cm.² The *E.M.F.* of the combination Cu|$CuSO_4$ solution|Cu amalgam (heterogeneous) at 25° were then found to be 0·00513±0·00005 volt and 0·00511±0·00003 volt for M- and 0·05M-copper sulphate solutions, respectively, and $dE/dT=-0{\cdot}0000737$ volt/1° between 0° and 40°. Both the electrode and amalgam should be protected from oxidation by the air. J. GRANT.

Oxidation potential of the quinquevalent–tervalent niobium system. II. S. J. KIEHL and D. HART (J. Amer. Chem. Soc., 1928, **50**, 2337—2345; cf. this vol., 846).—The above oxidation potentials were measured at 25° with a mercury electrode in an atmosphere of hydrogen, the niobium concentration, expressed as pentoxide, being 0·024M and 0·012M. Sulphuric acid was present at the concentrations 3·14, 5·91, and 9·87M and the corresponding normal electrode potentials were −0·3730, −0·3849, and −0·4261 volt. The results confirm the tervalent nature of reduced niobium. S. K. TWEEDY.

Lead–mercurous iodide cell. W. C. VOSBURGH (J. Amer. Chem. Soc., 1928, **50**, 2386—2394).—The *E.M.F.* at 15—40° of the following cells: Pb amalgam (10 or 12·7%)|xM-KI satd. with PbI_2|xM-KI+PbI_2+Hg_2I_2|Hg; Pb amalgam|soln. satd. with PbI_2+CdI_2|Hg_2I_2+soln. satd. with PbI_2+CdI_2|Hg; Cd amalgam|CdI_2 satd. soln.|CdI_2 satd. soln.+Hg_2I_2|Hg, where x=0·01—0·02, are given by $E=0{\cdot}31748+0{\cdot}000129(t-25)$ for the first two cells and $E=0{\cdot}41702+0{\cdot}000360(t-25)$ for the third. The following thermal data are calculated (at 25°): $Pb(s)+Hg_2I_2(s) \longrightarrow PbI_2(s)+2Hg(l)$, $\Delta F=-14{,}915$ g.-cal., $\Delta S=6{\cdot}69$ g.-cal./1°, $\Delta H=-12{,}920$ g.-cal.; $2Hg(l)+I_2(s) \longrightarrow Hg_2I_2(s)$, $\Delta H=-28{,}939$ g.-cal.; $Cd(s)+Hg_2I_2(s) \longrightarrow CdI_2(s)+2Hg(l)$, $\Delta F=-21{,}575$ g.-cal., $\Delta S=$0·30

g.-cal./1°, $\Delta H = -19{,}979$ g.-cal.; $Cd(s)+I_2(s) \longrightarrow CdI_2(l)$, $\Delta H = -48{,}918$ g.-cal. S. K. TWEEDY.

Capillary phenomena and film formation in liquid gallium. A. FRUMKIN and A. GORODETZKAJA (Z. physikal. Chem., 1928, **136**, 215—227).—Measurements have been made at 30° of the electrocapillary curves of liquid gallium in various solutions, chiefly of potassium chloride to which different amounts of acid or alkali had been added. The maximum surface tension of 592 absolute units occurs in *N*-potassium chloride+0·1*N*-hydrochloric acid solution, and corresponds with an interfacial potential of 0·9 volt between the gallium and a normal calomel electrode. The surface tension is markedly lowered in the presence of hydroxyl ions, the maximum value attained in *N*-potassium hydroxide solution being 519 absolute units. At a certain polarisation potential, which approaches the cathodic end of the curve as the alkalinity of the solution increases, a solid but elastic film forms on the surface of the gallium, which causes the surface tension to fall gradually to a very low value. Similar films may be produced on the surface of gallium drops by atmospheric oxygen or by nitric acid. F. G. TRYHORN.

Measurement of the electrokinetic potential on proteins by the streaming potential method. D. R. BRIGGS (J. Amer. Chem. Soc., 1928, **50**, 2358—2363).—Dilute egg-albumin solutions containing lithium chloride and hydrochloric acid and having a p_H range of 3·6—7·5 were forced through a diaphragm of quartz powder, the surface of which had previously been saturated with albumin so that the diaphragm behaved as though it were wholly composed of protein, and the electrokinetic potentials were measured in the manner previously described (this vol., 713). The results are in agreement with the cataphoretic experiments of Abramson (*ibid.*, 364) between p_H 3·8 and 5·2. The divergence beyond this range is primarily a concentration effect, although the nature of the ions present may have some effect. The method may be used to measure the isoelectric point of a water-soluble protein. S. K. TWEEDY.

Electrocapillary phenomena in amalgams. I. Thallium amalgams. A. FRUMKIN and A. GORODETZKAJA (Z. physikal. Chem., 1928, **136**, 451—472).—The electrocapillary curves of thallium amalgams of various concentrations in solutions of sodium sulphate and other salts and of thiocarbamide, *iso*amyl alcohol, and pyrogallol have been measured by the capillary electrometer method of Gouy. The curves do not coincide with those of pure mercury, the maximum being displaced in the direction of higher cathodic polarisation. In *N*-sodium sulphate solution the displacement of the maximum is 0·45 volt for a 41·5% thallium amalgam. The value of the maximum surface tension falls at first, then passes through a minimum, and finally increases with increasing thallium content. The curves are affected in the same way as the mercury curves by the electrolyte concentration and by the presence of capillary-active substances. The results are discussed from the point of view of the Gibbs theory of surface phenomena. The amount of thallium adsorbed is a function of ϕ, the *P.D.* at the boundary amalgam/solution. For small values of ϕ the adsorption is positive, but gradually becomes negative with increasing values of ϕ. O. J. WALKER.

Mechanism of homogeneous gas reactions. I. Effect of black-body radiation on a molecular beam of nitrogen pentoxide. F. O. RICE, H. C. UREY, and R. N. WASHBURNE (J. Amer. Chem. Soc., 1928, **50**, 2402—2412).—Reaction kinetics involve three simultaneous processes, viz., absorption and emission of radiation, intermolecular collision, and molecular collision with the walls of the vessel. Methods of separating these effects are outlined. Experiments are described in which a molecular beam of nitrogen pentoxide is passed through a furnace at 793° Abs. under such conditions that intermolecular collisions and collisions with the walls are eliminated. No decomposition occurs. The probability of absorption of radiation by a nitrogen pentoxide molecule is calculated; the experimental result is in agreement with the theory (cf. Mayer, this vol., 140). S. K. TWEEDY.

Homogeneous gas reactions at high concentrations. I. Decomposition of hydrogen iodide. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1928, **50**, 2315—2332).—The kinetics of the thermal decomposition of hydrogen iodide at 300° and 321° has been investigated at concentrations between 0·02 and 7 mol./litre. The results agree with those of Bodenstein (A., 1899, ii, 637) to within 4%, indicating that in each case a true homogeneous reaction rate has been measured. The reaction is strictly bimolecular, even when the gases are intensively dried; the increase in the "constant" at concentrations greater than 1 mol./litre is probably to be attributed to the number of bimolecular collisions not being proportional to the square of the concentration. Allowance for this is made with the aid of van der Waals' theory, whence the value $3{\cdot}33\times10^{-8}$ cm. is derived for the diameter of the hydrogen iodide molecule. Calculations based on activation data indicate that the cross-sections of effective reacting (activated) molecules are smaller than those of the normal molecules. A method of deciding the origin of the activation energy is outlined. S. K. TWEEDY.

Velocity of flame in complex gaseous mixtures of low inflammability in closed vessels. K. YUMOTO (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 93).—The velocity of flame, determined kinematographically in mixtures of carbon monoxide or hydrogen with a large excess of air is constant in the former but not in the latter case. The mean velocities are almost equal, but are less than those obtained for complex mixtures of both gases with air. J. GRANT.

Gaseous combustion at high pressures. XI. Influences of hydrogen and steam on the explosion of carbonic oxide-air etc. mixtures. W. A. BONE, D. T. A. TOWNEND, and G. A. SCOTT (Proc. Roy. Soc., 1928, **A**, **120**, 546—563).—A repetition and extension of the work of Bone and Haward (cf. B., 1921, 802) with isothermic $2(mH_2+nCO)+O_2+3{\cdot}76N_2$ mixtures (where $m+n=1$). The peculiar effect of successive replacements of carbon monoxide by hydrogen previously observed is confirmed, but it is found to require a hydrogen content

exceeding 0·65% in the mixture fired. It is of the nature of a "knock" effect, which may be eliminated by raising the bomb temperature to 100° without altering the charge density. Under these conditions, it is found that after the first 1% of hydrogen has definitely catalysed the carbon monoxide combustion up to a certain velocity (about twice that of the well-dried $2CO+O_2+3{\cdot}76N_2$ mixture), further amounts of hydrogen produce merely an "additive" accelerating effect. An investigation of the influence of steam on the rate of pressure development in theoretical carbon monoxide–air explosions at initial pressures of 32·2 and 64·4 atm., respectively, and with the bomb chamber at 100°, showed that, whereas the first small successive additions of steam markedly accelerated the rate of increase of pressure, optimum conditions were nearly reached in each case when about 1% of steam had been added. Evidence is cited which indicates that the role of the steam in such circumstances is not chemical, in the sense of its being continually decomposed and regenerated. The addition of a small quantity of hydrogen has a greater effect than its equivalent of steam in accelerating the explosion of a carbon monoxide–air mixture at high pressures, the purely catalytic effect of hydrogen probably exceeding that of steam under the same conditions. The progressively increasing lag in the pressure rise always observed in theoretical carbon monoxide–air explosions at high initial pressures, irrespective of the hygroscopic condition of the medium, is principally a nitrogen effect, since it is not observed at all when the nitrogen is replaced by its volume equivalent of either carbon monoxide or argon. L. L. BIRCUMSHAW.

Gaseous combustion at high pressures. XII. Influence of steam and temperature, respectively, on the "explosion limits" of carbonic oxide–air mixtures. W. A. BONE, D. M. NEWITT, and C. M. SMITH (Proc. Roy. Soc., 1928, A, **120**, 563—572; cf. this vol., 248).—Carbon monoxide–air mixtures were fired at a temperature of 100° at either 32·2 or 64·4 atm. initial pressure, either (1) in a "well-dried" condition (moisture content $<0{\cdot}02\%$), or (ii) in an 80% saturated condition (moisture content 2·24 or 1·12%, according to the initial pressure). The results show that the effect of drying is to lower the explosion range at the high initial pressures employed. In the case of "moist" mixtures, the effect of doubling the pressure is to shift each limit slightly downwards without narrowing the explosion range, but with the "dry" mixture, the explosion range is definitely narrowed by increasing the initial pressure. On comparison of the results with those of the previous "dry" experiments (*loc. cit.*), it appears that the influence of temperature is to widen the explosion range. L. L. BIRCUMSHAW.

Kinetics of the reaction between hydriodic and iodic acids. E. ABEL and K. HILFERDING (Z. physikal. Chem., 1928, **136**, 186—194; cf. Abel and Stadler, A., 1926, 1009).—The previous treatment of this reaction has been amended, since it is found that with very small iodine-ion concentrations the reaction velocity is proportional to the first and not to the second power of the concentration.
F. G. TRYHORN.

Mechanism of reactions between hydrogen peroxide, iodine, and iodine ions. E. ABEL (Z. physikal. Chem., 1928, **136**, 161—182; A., 1921, ii, 180).—The complete reactions occurring among these reactants can be expressed by the two independent and simultaneous reactions, $H_2O_2+2HI=2H_2O+I_2$ and $H_2O_2+I_2=2HI+O_2$. An analysis of earlier experimental results shows that an important part is played by the intermediate production of hypoiodous acid which functions, according to the concentrations of the main reactants, either as a reactant or resultant in a number of subsidiary and simultaneous reactions. The hypoiodous acid is formed primarily by the interaction of hydrogen peroxide and hydriodic acid; $H_2O_2+HI=HIO+H_2O$ and may then react either with additional hydrogen peroxide: $H_2O_2+HIO=HI+H_2O+O_2$, or with hydriodic acid: $HIO+HI=H_2O+I_2$. On the other hand, hypoiodous acid may be formed by a hydrolytic reaction from the free iodine: $I_2+OH'=I'+HIO$. The last two reactions are catalysed by hydrogen peroxide. The kinetics of this complicated series of reactions are considered and differential equations have been obtained which represent satisfactorily the experimental results.
F. G. TRYHORN.

Kinetics of nitrous acid. V. Nitrous acid–nitric acid–nitric oxide reaction. E. ABEL, H. SCHMID, and S. BABAD (Z. physikal. Chem., 1928, **136**, 419—429; cf. this vol., 374, 847).—The kinetic data for the two opposed reactions represented by $3HNO_2 \rightleftharpoons H^{\cdot}+NO_3'+2NO+H_2O$ have been applied in the interpretation of the kinetics of the reaction in which both are involved. The velocity equation $\mp d(HNO_2)/dt=\pm k_1[HNO_2]^4/P_{NO}{}^2\mp k_2[HNO_2][H^{\cdot}][NO_3']$ for the decomposition or formation of nitrous acid has been verified.
O. J. WALKER.

Kinetics of nitrous acid. VI. Relation between equilibrium and kinetics of the nitrous acid–nitric acid–nitric oxide reaction. E. ABEL and H. SCHMID (Z. physikal. Chem., 1928, **136**, 430—436; cf. preceding abstract).—From the velocity coefficients of the two opposed reactions the "equilibrium constant" $K_c=[H^{\cdot}][NO_3']P_{NO}{}^2/[HNO_2]^3$ is determined. K_c increases with increasing ionic concentration. Bronsted's theory of reaction velocity is applied to the reaction. O. J. WALKER.

Role of phosphates in oxidation of dextrose. A. N. KAPPANNA (J. Indian Chem. Soc., 1928, **5**, 387—396).—The reaction between dextrose (1 mol.) and iodine (1 mol.) takes place only at $p_H>7$, either in absence or in presence of phosphates. At constant alkalinity the rate of oxidation is independent of the concentration of phosphate, and increases with increase in p_H. The rate of decomposition of aqueous hydrogen peroxide solution at 60° has been studied in presence of phosphate buffers at p_H 7·6 and 7·8. This decomposition is also independent of the phosphate concentration and increases with increased alkalinity. It is concluded that no hexose-phosphate or hydrogen peroxide–phosphate complexes are formed in solution.
H. BURTON.

Rate of hydrolysis of some αβ-oxy-compounds in acid solution. G. WODE (Svensk Kem. Tidskr.,

1928, **40**, 221—226).—The hydrolysis of a solution of glycide at 25° by means of perchloric acid has been examined, the progress of the reaction being followed by employing a dilatometer, since a considerable contraction in volume occurs. The reaction is strictly unimolecular, the velocity coefficient being between that obtained for ethylene oxide and epichlorohydrin. The above method could not be used in the case of *cis*- and *trans*-ethyleneoxide-αβ-dicarboxylic acids, the rate of hydrolysis being too slow at the ordinary temperature, so that here the course of the reaction was followed by means of conductivity measurements, the solutions being contained in a special closed cell immersed in a thermostat at 97·7°. The results in the case of the *cis*-acid do not exhibit the customary parallelism between the hydrogen-ion concentration and the velocity coefficient, the latter increasing with the degree of dissociation. The *trans*-acid is hydrolysed more slowly than the *cis*-, yielding a mixture of tartaric and mesotartaric acids, whereas the *cis*-acid gives only the former. Measurements carried out at 25° showed that the above acids have larger primary dissociation constants than those obtained from the isomeric hydroxymaleic and hydroxyfumaric acids, and that these constants, unlike those of tartaric acid itself, diminish markedly with rise of temperature.

H. F. HARWOOD.

Velocity of reaction between amylene and trichloroacetic acid in different solvents. L. M. ANDREASOV (Ukraine Chem. J., 1928, **3**, 209—218).—The velocity of reaction between amylene and trichloroacetic acid is greatest in benzene, less in nitrobenzene, chloroform, carbon disulphide, and is least in carbon tetrachloride. The velocity coefficients of the reaction diminish steadily in all solvents, owing to the formation of a double compound between amyl chloroacetate and chloroacetic acid. R. TRUSZKOWSKI.

Velocity of esterification of amides in alcohol. H. A. TAYLOR and T. W. DAVIS (J. Physical Chem., 1928, **32**, 1467—1480; cf. Reid, A., 1909, ii, 650).—The velocity of esterification of formamide, acetamide, propionamide, and benzamide in dry and in aqueous solutions of ethyl alcohol, with hydrogen chloride as catalyst, has been measured. The reactions appear to be bimolecular, and formamide seems to contain a tautomeride which catalyses its esterification. Small concentrations of neutral salt are without marked effect on the velocity of reaction, but the addition of small quantities of water has an accelerating effect which reaches a maximum at 8—12%. Stieglitz's suggestion (J. Amer. Chem. Soc., 1910, **32**, 221) that the catalytic effect of an acid is due to the transformation of a weaker into a stronger base is extended to explain the inhibiting or accelerating effect of water in various reactions. L. S. THEOBALD.

Spontaneous and linear crystallisation velocity in binary mixtures. W. RAWITZER (Z. anorg. Chem., 1928, **175**, 321—334).—Parallel relationships exist for supercooled fused masses between the velocity of crystallisation and the velocity of nucleus formation on the one hand and the concentration on the other, in contradistinction to the differing relationships of the latter quantities. Application of this result to simple binary mixtures shows good agreement with the experimental determinations of Tammann and Botschwar (A., 1927, 196). Measurements with the binary system palmitic acid–stearic acid indicate that the relationship is accurately valid only for simple systems, and must be modified for complex systems. H. F. GILLBE.

Corrosion of chemical lead. D. W. JONES.—See B., 1928, 786.

Corrosion at discontinuities in metallic protective coatings. U. R. EVANS.—See B., 1928, 751.

Phenomena of corrosion of iron and steel. A. HERRERO and M. DE ZUBIRIA.—See B., 1928, 751.

Resistance of pure chromium–nickel–iron alloys to corrosion by acids. W. GUERTLER and W. ACKERMANN.—See B., 1928, 753.

Acid and basic catalysis. J. N. BRONSTED (Svensk Kem. Tidskr., 1928, **40**, 230—233).—The phenomena of acid and basic catalysis are discussed in the light of the author's conception of the nature of acids and bases, the view being taken that the catalytic effect is to be ascribed, not particularly to the hydrogen and hydroxyl ion, but to the action of acid and basic molecules in general (cf. J. Amer. Chem. Soc., 1927, **49**, 2554). H. F. HARWOOD.

Conversion of thiosulphates into polythionates with the aid of catalysts. A. KURTENACKER and A. CZERNOTZKY (Z. anorg. Chem., 1928, **175**, 367—382).—The quantity of polythionate produced during the decomposition of *N*-sodium thiosulphate solution by hydrogen chloride diminishes as the acid concentration is increased. Mercuric chloride, lead acetate, bismuth trichloride, sodium tungstate, or sodium sulphide solutions have no marked influence on the reaction. On acidifying a thiosulphate solution which contains a small quantity of arsenite or arsenate, a strong odour of hydrogen sulphide is produced, which is rapidly replaced by that of sulphur dioxide; after some minutes a precipitate of sulphur and arsenious sulphide commences to form. For constant arsenic content, approximately equal quantities of tetra- and penta-thionate are formed at low acid concentrations; at moderate concentrations pentathionate alone is produced, whilst with higher concentrations penta- and hexa-thionates are obtained. At constant acid concentration an increase of the quantity of arsenate in the solution results in the formation of more tetrathionate, probably on account of partial neutralisation of the acid present by the arsenite solution. Although an excess of arsenic acid should convert all the thiosulphate into tetrathionate, some pentathionate appears to be formed. Arsenious sulphide has no influence on the thiosulphate decomposition, and arsenic trichloride but little. Tervalent antimony has much less effect than has arsenious acid, whilst with molybdic acid the yield of polythionate is very small; in presence of stannic chloride considerable quantities of polythionate are produced.

H. F. GILLBE.

Oxidative catalytic action of iron. O. WARBURG (Biochem. Z., 1928, **195**, 241—242).—The theory of Handovsky (this vol., 718) that it is not iron but the hydrogen dissolved in it which combines with

atmospheric oxygen forming hydrogen peroxide, and thus effects the oxidation of amino-acids, is discredited.
P. W. CLUTTERBUCK.

Autoxidation and antioxygenic action. XXX. Autoxidation and polymerisation of chloral: action of light. XXXI. Autoxidation and polymerisation of chloral: action of various catalysts. C. MOUREU, C. DUFRAISSE, and G. BERCHET (Bull. Soc. chim., 1928, [iv], 43, 942—957, 957—962).—XXX. The autoxidation of chloral in presence of oxygen has been studied by following the increase in pressure resulting from the formation of the gaseous products hydrochloric acid, carbon dioxide, and carbonyl chloride. The process is autocatalytic and depends on the initial formation by the action of light of a catalyst, which is probably an oxidation product. The reaction can then proceed in the dark. Reaction with oxygen appears to take place in two ways, viz., $CCl_3{\cdot}CHO+O=CCl_3{\cdot}CO_2H$ and $CCl_3{\cdot}CHO+O_2=COCl_2+HCl+CO_2$, although the latter unusual type of reaction is not confirmed quantitatively. The mechanism of the formation of these gaseous products is discussed. Chloral hydrate does not undergo autoxidation unless it is first dehydrated.

XXXI. The autoxidation of chloral is inhibited by a large variety of substances, *e.g.*, phenols, aromatic amines, sulphur, iodine, etc. (antioxygenic catalysts). These substances also inhibit the spontaneous polymerisation of chloral to metachloral.
O. J. WALKER.

Thermal decomposition of ammonia on mixed surfaces of tungsten and platinum. R. E. BURK (Proc. Nat. Acad. Sci., 1928, 14, 601—602).—The catalytic effect on the decomposition of ammonia of a surface alloy of platinum and tungsten, prepared by evaporating one metal from a spiral on to a filament of the other metal mounted axially within it, is greater than that of an equal surface of either constituent. The temperature coefficient for the mixed surfaces is also smaller than for either of the metals alone, in agreement with the generally accepted view that the accelerating effect of a contact catalyst is due to a lowering of the heat of activation. The "promoter action" is considered to be due to the fact that tungsten adsorbs nitrogen more strongly than hydrogen, whilst the opposite is true for platinum. The strain exerted by the mixed surface on the ammonia linking is thus much greater than that produced by one metal alone. The results suggest that, in the catalysis of the decomposition of ammonia, no other action, *e.g.*, atomic distortion (cf. this vol., 27; A., 1926, 915), is concerned.
M. S. BURR.

Decomposition of hydrogen peroxide at surfaces. W. M. WRIGHT and E. K. RIDEAL (Trans. Faraday Soc., 1928, 24, 530—538).—Experiments were made to find an explanation for the varying effects of adding traces of acids or alkalis on the reaction rate for a number of different surfaces. Fair agreement was found between the amount of acid or alkali which must be added to give a maximum rate of decomposition and that required to neutralise the electrokinetic potential at the solid–liquid interface. This potential was determined by the electro-endosmotic method, and the reaction rate by measuring the rate of evolution of oxygen. Tungstic acid showed certain abnormalities, probably associated with the formation of soluble pertungstic acid. The alteration in reaction rate can likewise be effected by the addition of multivalent ions such as aluminium chloride. At high concentrations the effects of poisoning by the adsorbed salt can be observed. The fraction of the surface of charcoal capable of effecting the decomposition is much larger than that capable of effecting oxidation of organic acids.
N. M. BLIGH.

Thermal decomposition of hydrogen peroxide. W. M. WRIGHT (Trans. Faraday Soc., 1928, 24, 539—542).—The surface of glass treated with acids was known to be partly converted into silica gel. Since the rate of decomposition of hydrogen peroxide on glass in presence of silver nitrate is approximately proportional to the amount of silver adsorbed, investigation was made as to whether the silver which is catalytically active is in the form of silver silicate. The rate of decomposition of hydrogen peroxide on silica gel and on silver silicate was studied. The former has only slight catalytic activity, but this is greatly increased in presence of silver nitrate, and by further addition of a trace of alkali is increased several hundred times. Silver silicate caused a very rapid decomposition of the peroxide, probably through an intermediately formed silver oxide. The catalytic properties of glass in contact with silver nitrate are ascribed to the formation of traces of silver silicate.
N. M. BLIGH.

Catalysis of solid-phase reactions by solids. S. ROGINSKI and E. SCHULZ (Ukraine Chem. J., 1928, 3, 177—207).—Moles and Crespi's view that the thermal decomposition of solid potassium permanganate is of an autocatalytic nature (A., 1925, ii, 877) is confirmed, and shown also to apply to that of ammonium dichromate. Ostwald's equation is inapplicable to the kinetics of the former reaction, the velocity of which over the first section of the autocatalytic curve is better expressed by $K=(x_t^{1/3}-x_{t_0}^{1/3})/(t-t_0)$ where x is the mass of substrate decomposed at time t. This equation gives fair agreement with experiment where the permanganate is finely powdered, but not where whole crystals are taken, as in the latter case the number of active centres present is small, making the incubatory period comparatively long. An analogous equation is derived for the third section of the curve expressing diminishing velocity, which gives satisfactory agreement with experiment for powdered substrate, and fair agreement with crystalline substrate. The catalytic action of a number of metallic oxides on the decomposition of potassium permanganate is in the order of intensity $NiO>CuO>Al_2O_3>CdO$, and their action is most marked below 400°. At temperatures much above this, the catalytic action of the above substances undergoes inversion, the reaction being retarded in their presence, both for potassium permanganate and for ammonium dichromate. This effect is explained as being due to the high thermal capacity of these catalysts at high temperatures.
R. TRUSZKOWSKI.

Stationary nickel catalyst for a continuous hydrogenation process. A. SVIZUIN (Masloboino-Zhir. Delo, 1928, No. 3, 25—27).—Iron wire is coated

electrolytically with a smooth layer of nickel, on which, by increasing the current density, a layer of greater surface is produced. The nickel is oxidised in a hydroxide bath and washed; spirals of the wire are employed in the autoclaves.

CHEMICAL ABSTRACTS.

Catalytic oxidation of furfuraldehyde in the vapour phase. W. V. SESSIONS (J. Amer. Chem. Soc., 1928, 50, 1696—1698).—Furfuraldehyde was volatilised in a current of air at 40—50° and the mixture passed over a vanadic oxide–asbestos catalyst at 200—300°. The product contains up to 14·5% of the theoretical yield of maleic acid, m. p. 138·5—140°, together with maleic anhydride, formaldehyde, water, and carbon dioxide, but no fumaric acid (cf. Milas, A., 1927, 973). H. E. F. NOTTON.

Catalysts used in the synthesis of higher hydrocarbons from water-gas. A. ERDELY and A. W. NASH.—See B., 1928, 775.

[Catalytic preparation of] methyl alcohol from hydrogen and carbon monoxide. R. L. BROWN and E. A. GALLOWAY.—See B., 1928, 780.

Cathodic halogen. R. H. CLARK and R. H. BALL (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 6 pp.).—Solutions in various solvents of compounds containing so-called positive halogen, *i.e.*, halogen which on hydrolysis is replaced by hydrogen and appears as hypohalous acid, have been electrolysed between silver electrodes. *N*-Bromosuccinimide in acetonitrile yielded a deposit of silver bromide on the cathode, whilst at the anode silver succinimide free from bromide was deposited. *N*-Iodosuccinimide and *N*-bromoacetamide in acetonitrile yielded silver halide deposits on both electrodes. In other solvents no cathodic liberation of halogen was observed with these substances, but cyanogen iodide yielded iodine at the cathode when dissolved in pyridine.

H. J. T. ELLINGHAM.

Electrochemical reduction of solid electrodes. III. Chromites. IV. Sulphides. K. FISCHBECK and E. EINECKE (Z. anorg. Chem., 1928, **175**, 335—340, 341—342).—III. When chromite is employed as third electrode, chromic acid is formed by anodic oxidation and then diffuses through the mineral under the influence of the potential fall, to appear finally at the cathode. Chromite, which has a remarkably high resistance, exhibits a high degree of porosity to the sulphate ion, as shown both by analysis and by the increase of its conductivity after being placed between electrodes in dilute sulphuric acid solution. The variation of conductivity has been studied in its relationship to the direction and strength of current; in general it is lower during anodic polarisation than during cathodic, on account principally of changes in the electrolyte and in the quantity of gas in the pores of the mineral. Hysteresis effects are also to be observed. The porosity of chromite is estimated at 0·15—0·4 c.c./100 g., the lower figure being the more probable.

IV. Both cobaltous and nickelous sulphides undergo reduction when spread on a lead plate and subjected to cathodic polarisation in a dilute sulphuric acid solution; hydrogen sulphide is formed and the metal partly enters into solution. Zinc blende, despite its low conductivity, reacts under the same conditions in an analogous manner. H. F. GILLBE.

Experimental technique of photochemistry. VI. Energy distribution of the Uviol lamp. E. BEESLEY and H. N. RIDYARD (J. Physical Chem., 1928, **32**, 1342—1345; cf. this vol., 851).—The results of an investigation of the energy distribution of a Uviol lamp burning at 29·5 volts and 2·42 amp. are recorded, and are compared with those previously obtained by Allmand (J.C.S., 1915, **107**, 682), and with the energy distribution of the quartz–mercury lamp.

L. S. THEOBALD.

Phototropic compounds of mercury. S. V. R. RAO and H. E. WATSON (J. Physical Chem., 1928, **32**, 1354—1365; cf. A., 1923, i, 764).—Twenty mercury compounds of the types Hg(X)CNY and $HgX_2,2HgY$, where X is chlorine, bromine, iodine, hydrosulphide, hydroselenide, thiocyanate, or selenocyanate, and Y is oxygen, sulphur, or selenium, have been prepared and found to be phototropic. The times required for darkening in diffused daylight vary from <1 to 200 min., but the times for recovery in darkness are all of the same order, viz., from 1·5 to 3 days. The compounds with the probable formulæ Hg(HSe)CNS and Hg(HSe)CNSe are not phototropic. Spectroscopic examination of the more sensitive compounds showed them to be darkened by exposure to light of wave-length of the order of 5500 Å. and less, with slight sensitiveness extending into the ultra-violet to the limit of transmission of quartz. A broad, well-defined maximum of sensitivity occurs usually in the green; this maximum tends to move towards the red with an increase in mol. wt. for related compounds. In the case of compounds darkened by exposure, reversal is effected by exposure to red light. No maxima were observed, but there is a limiting wave-length beyond which no reversal occurs. Heat causes reversal in all cases. Darkening is accelerated by the presence of agar agar, gelatin, and collodion, but is retarded by that of gum arabic; all four substances retard the reverse reaction. In the case of the compound Hg(HS)CNS, the light-sensitive region is extended towards the red by dyeing the compounds with eosin, erythrosin, methyl-green, malachite-green, and methylene-blue. The temperature coefficients of the direct and reverse reactions approximate to 1·0 and 1·9, respectively, for the compounds Hg(HS)CNS and HgI·CNS, and the time of exposure necessary to produce a given change is inversely proportional to the intensity of the light. No induction period has been observed.

L. S. THEOBALD.

Decomposition of ammonia by high-speed electrons. J. C. McLENNAN and G. GREENWOOD (Proc. Roy. Soc., 1928, **A**, **120**, 283—295).—The electrons are produced by a Coolidge cathode-ray tube and pass into the reaction vessel through a window of "resistal" metal. Decomposition of the ammonia sets in suddenly when the voltage is high enough to drive the electrons through this window. Increase in the pressure of the ammonia decreases the percentage decomposition, but in the first stages of the decomposition the ratio of the number of ammonia molecules decomposed to the number of electrons causing

decomposition is independent of the pressure of the ammonia, and increases with the speed of the electrons. Excess of nitrogen increases the quantity of ammonia decomposed, whilst excess of hydrogen decreases the amount. Excess of nitrogen has no effect on the speed of the primary stage of the decomposition, which, however, is decreased by the addition of hydrogen. J. L. BUCHAN.

Chemical reactions of carbon monoxide and hydrogen after collision with electrons. A. CARESS and E. K. RIDEAL (Proc. Roy. Soc., 1928, A, **120**, 370—385; cf. A., 1927, 943).—The rate of reaction of carbon monoxide with hydrogen has been determined for various electron speeds. The reactions are followed by measuring the rate of decrease of pressure, dp/dt, in the reaction chamber. It is calculated that $n=-0{\cdot}0944\,v/c\times dp/dt$, where n is the number of molecules removed by one electron, v the volume of the system, and c the effective current. With carbon monoxide alone the reaction has been shown to be $2CO=C+CO_2$ and dp/dt varies with the electron speeds, the curves showing this exhibiting definite breaks. The combination of carbon monoxide with hydrogen atoms and with hydrogen molecules has also been studied, and the reactions show similar curves. The product in these cases is first formaldehyde which then polymerises at the ordinary temperature. The electron efficiencies for these reactions have been tabulated, and the mechanism of the reactions is discussed. J. L. BUCHAN.

Formation of a polymeride of carbon monosulphide by ultra-violet irradiation of carbon disulphide. Absorption spectrum of carbon disulphide in carbon tetrachloride. W. DORAN and A. E. GILLAM (J.S.C.I., 1928, **47**, 259—260T).—A polymeride of carbon monosulphide has been obtained as a reddish-brown solid by irradiation of mixtures of carbon disulphide and carbon tetrachloride by means of a vitaglass-screened mercury-vapour lamp. Its properties and analysis agree with those recorded by previous investigators for the same product obtained by different means. The absorption spectrum of carbon disulphide in carbon tetrachloride is discussed, and the possibility of the detection and determination of the former in the latter by this means is pointed out.

Mechanism of photosensitisation and photo-inhibition from the point of view of absorption spectra. B. K. MUKERJI and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 411—415).—The absorption spectra of the various constituents of a reacting system (*e.g.*, reduction of Fehling's solution in presence of uranyl nitrate and ferric chloride) and of sensitising or inhibiting substances have been determined for six reactions. The results show that in photosensitised systems there is a marked increase in the light absorption, whilst in inhibited systems no increase takes place. H. BURTON.

Photochemical studies. VII. Photochemical decomposition of formic acid liquid and vapour. W. N. HERR and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1928, **50**, 2345—2350).—Data for the quantum efficiency of the decomposition of formic acid liquid and vapour by radiation are recorded, the number of molecules of gas uncondensed by liquid air formed per quantum being determined and also the number of additional molecules uncondensed by carbon dioxide and ether. For the liquid the quantum efficiency rises with increasing frequency; the vapour absorbs at short wave-lengths only. The primary reaction in both the liquid and vapour state may lead to the formation of carbon dioxide (cf. Allmand and Reeve, A., 1927, 29). S. K. TWEEDY.

Influence of a change of intensity of the incident light on the velocity of certain photochemical reactions. A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1928, **175**, 357—366).—The velocities have been studied of nine inorganic photochemical reactions in sunlight and under illumination from a 1000-watt lamp at various intensities. The velocities of the reactions between chromic and oxalic acids and between potassium persulphate and potassium iodide are directly proportional to the intensity of the illumination, but for all the other reactions investigated the velocity is proportional to the square root of the intensity; it appears that this latter condition obtains for reactions in which atomic oxygen is formed. If the reactants exhibit marked absorption the velocity increases more rapidly with increase of intensity, or is directly proportional thereto; whilst for the systems having but slight absorption the square root law is valid. H. F. GILLBE.

Influence of the intensity of incident light on the velocity of some photochemical reactions. B. K. MUKERJI and N. R. DHAR (J. Physical Chem., 1928, **32**, 1308—1330).—Data on the influence of the intensity of light on the rate of reaction of 15 pairs of substances are submitted and discussed. The rate of reaction is proportional to (i) the square of the intensity of the incident light in the reactions between sodium formate and iodine (both in the presence of sodium acetate), Rochelle salt and bromine, and quinine sulphate and chromic acid in the presence of sulphuric acid, (ii) to the square root of the intensity in the reactions between potassium oxalate and iodine, ammonium oxalate and iodine, ammonium oxalate and mercuric chloride in the presence of eosin, and sodium nitrite and iodine in the presence of sodium acetate, and (iii) to the intensity of the light in the reactions between chromic and oxalic acids in the presence of manganese sulphate and sulphuric acid, sodium citrate and iodine, ferrous sulphate and iodine, sodium formate and mercuric chloride in the presence of sodium acetate, and in the bleaching of dicyanin, and in the oxidation of iodoform in benzene as solvent. In the reaction between potassium permanganate and oxalic acid, no relation between reaction velocity and intensity of the incident light is apparent. L. S. THEOBALD.

Quantum yield of the photochemical decomposition of light-sensitive diazo-compounds. EGGERT [with W. SCHRÖTER] (Z. Elektrochem., 1928, **34**, 602—605).—The photochemical decomposition of the diazo-compounds derived from 2-amino-α-naphthol-4-sulphonic acid and *p*-aminodiphenylamine was investigated by measuring the rate of liberation of nitrogen. The latter is evolved at a constant rate

which diminishes gradually when the illumination is withdrawn. The shape of the velocity curve depends on secondary phenomena and is altered, *e.g.*, by change in the force or rhythm with which the decomposition vessel is tapped (cf. Gleu, this vol., 601). The quantum yield (about 0·35) is independent of the intensity and wave-length of the light and of the temperature and concentration of the diazo-solution. The same quantum yield is obtained with the solid compounds. Under the influence of X-rays no nitrogen could be detected, although a perceptible colour change occurs.

S. K. TWEEDY.

Hydrolysis of sodium chloride. H. BRUCKNER (Z. physikal. chem. Unterr., 1928, **41**, 92—93; Chem. Zentr., 1928, i, 1833).—A small quantity of water, added to molten sodium chloride in a platinum crucible, is poured while in the spheroidal state into blue litmus solution after half has evaporated. The litmus solution becomes red, whilst a solution of the cooled mass reacts alkaline.

A. A. ELDRIDGE.

Sodium alum. H. LEFFMANN and L. W. STROCK (Bull. Wagner Free Inst. Sci., 1928, **3**, 19—22).—Crystals (octahedra modified by cubes, cubes, or monoclinic) of sodium alum are best obtained by evaporation of a solution at the ordinary or a moderate temperature; slow cooling of the boiling saturated solution is unsuitable.

CHEMICAL ABSTRACTS.

Decomposition of sodium thiosulphate in hydrochloric acid solution. E. H. RIESENFELD and G. SYDOW (Z. anorg. Chem., 1928, **175**, 49—73).—The decomposition products of thiosulphate in hydrochloric acid of varying concentrations in the presence and absence of arsenious acid have been studied by a new method of quantitative analysis which is given in detail. In hydrochloric acid solution alone thiosulphate may decompose according to either of the following schemes, depending on the acidity: (1) $S_2O + H^{\cdot} = HSO_3{}' + S$, and (2) $5S_2O_3{}'' + 6H^{\cdot} = 2S_5O_6{}'' + 3H_2O$. The sulphurous acid formed in (1) then reacts with the pentathionic acid formed in the second reaction, giving first tetrathionic, then trithionic acid, thus (3) $S_5O_6{}'' + SO_3{}'' = S_4O_6{}'' + S_2O_3{}''$, and (4) $S_4O_6{}'' + SO_3{}'' = S_3O_6{}'' + S_2O_3{}''$. Trithionic acid may also be formed by the direct action of sulphurous acid on thiosulphuric acid, thus: (5) $S_2O_3{}'' + 4HSO_3{}' + 2H^{\cdot} = 2S_3O_6{}'' + 3H_2O$. In strongly acid solutions, however, trithionic acid decomposes rapidly as follows: (6) $S_3O_6{}'' = S + SO_2 + SO_4{}''$. Addition of arsenious acid to the reaction mixture of hydrochloric acid and thiosulphate retards the reaction (1) and in the absence of sulphurous acid reactions (3), (4), and (5) cannot take place. Hence pentathionic acid formed according to (2) is practically the sole product of the reaction in the presence of arsenious acid (cf. Kurtenacker and Czernotzky (this vol., 1201).

A. R. POWELL.

Silver alkali thiosulphates. A. ROSENHEIM and G. TREWENDT (Ber., 1928, **61**, [*B*], 1731—1735).—Alkali silver thiosulphates are prepared by the gradual addition of aqueous silver nitrate to an ice-cold, well-agitated solution of the alkali thiosulphate. The sparingly soluble salts separate directly from the mixture, whereas the more freely soluble compounds are precipitated by addition of alcohol. The following *compounds* are described: sparingly and freely soluble *ammonium* salts, $NH_4AgS_2O_3$ and $(NH_4)_5[Ag_3(S_2O_3)_4]$; the *potassium* salt, $K[Ag(S_2O_3)]$, and also $K_5[Ag_3(S_2O_3)_4]$ and $K_3[Ag(S_2O_3)_2,H_2O$; sparingly soluble sodium salt, $Na[Ag(S_2O_3)]$, and the more freely soluble salt to which the structure $Na_5[Ag_3(S_2O_3)_4],3H_2O$, instead of $Na_4[Ag_2(S_2O_3)_3],2H_2O$, is ascribed; the last salt and technical rubidium sulphate (containing potassium sulphate) give an isomorphous mixture of the salts $K_5[Ag_3(S_2O_3)_4]$ and $Rb_5[Ag_3(S_2O_3)_4]$.

H. WREN.

Basic carbonates of beryllium. T. NISHIMURA and T. YAMAMOTO (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 89—90).—Beryllium carbonate is unstable in air, but in the dry state decomposition is slow and the salt attains a composition depending on the proportion of carbon dioxide originally present in the wet salt and on the degree of drying. The salt $3Be(OH)_2,CO_2,nH_2O$ is produced by double decomposition of a solution of beryllium chloride ($<1·0N$) saturated with carbon dioxide at 0°, by a saturated solution of a hydrogen carbonate of ammonium, or of an alkali metal. A suspension of this salt in excess of water is converted into a substance containing 0·047 mol. of carbon dioxide to 1 mol. of beryllium oxide by prolonged passage of air at the ordinary temperature. This and similar experiments with beryllium hydroxide indicate that the substance containing 5% of carbon dioxide is stable in contact with air or water.

J. GRANT.

Synthesis of sapphirin. E. DITTLER (Z. anorg. Chem., 1928, **174**, 342—354).—Natural sapphirin does not melt unchanged; at 1500° decomposition takes place with the formation of spinel, sillimanite, and a highly silicious glass containing a little alumina, thus: $Mg_5Al_{12}Si_2O_{27} = 5MgAl_2O_4 + Al_2SiO_5 + SiO_2$. Attempts to synthesise the mineral by heating magnesia, alumina, silica, and small quantities of ferrous oxide (added as oxalate) yielded at 1400—1500° mixtures of spinel, sillimanite, and silica glass. No better results were obtained in the presence of boron trioxide as mineraliser. As natural sapphirin usually contains small quantities of water as well as, occasionally, boron trioxide, it is suggested that synthesis can be effected only in the presence of water vapour at about 900—1000° under high pressure. This would account for the paragenesis of sapphirin with biotite at Fiskernas and other places, where the (001) face of mica has grown with the (010) face of sapphirin.

A. R. POWELL.

Crystalline aluminium hydroxide of von Bonsdorff. R. FRICKE (Z. anorg. Chem., 1928, **175**, 249—256).—The crystalline aluminium hydroxide precipitated from alkali aluminate solutions by hydrolysis or by the slow action of carbon dioxide is hydrargillite only when the precipitation takes place over a period of months. With more rapid precipitation a metastable hydroxide of the same composition, $Al_2O_3,3H_2O$, is obtained, which has a lattice structure identical with that of the aluminium hydroxide obtained by Bohm (A., 1926, 113) from acid solutions. This new form is named "bayerite," as it occurs in large quantities in the alumina precipitated by the Bayer process.

A. R. POWELL.

Efflorescence of carbon. P. H. Prausnitz (Naturwiss., 1928, **16**, 57—58; Chem. Zentr., 1928, i, 1841).—Efflorescence on carbon tubes heated at 1200° in illuminating gas contained 99% C and 1% of water, and was formed by the decomposition of hydrocarbons at the carbon surface. A. A. Eldridge.

Carbonyl bromide. II. Preparation and properties. H. J. Schumacher and S. Lenher (Ber., 1928, **61**, [*B*], 1671—1675; cf. this vol., 847).—Carbonyl bromide is prepared by heating a mixture of carbon tetrabromide and concentrated sulphuric acid (*d* 1·83) at 150—170°, whereby a distillate containing carbonyl bromide, bromine, hydrogen bromide, and sulphurous acid is obtained. The bulk of the free bromine is removed by cautious treatment with mercury followed by distillation. The product is cautiously mixed with powdered antimony and distilled from an all-glass apparatus, the process being repeated if necessary. Carbonyl bromide is thus obtained as a colourless liquid, d^{15} 2·52. Its physiological action is similar to that of the corresponding chloride. It is less readily hydrolysed than the latter compound by water. The vapour-pressure curve between −50° and +25° is given. The thermal equilibrium even at the ordinary temperature lies strongly towards the components and is attained very slowly from carbon monoxide and bromine. Homogeneous carbonyl bromide is moderately stable to heat and, at 200°, suffers scarcely appreciable decomposition. At higher temperatures, the reaction is one of the first order at the glass walls. Decomposition is unusually strongly accelerated by catalysts, particularly organic substances. H. Wren.

Formation of ammonia from active nitrogen and active hydrogen. B. Lewis (J. Amer. Chem. Soc., 1928, **50**, 2427; cf. this vol., 258).—The comparatively high pressures used and the long gas exit tube of the apparatus suffice to explain why the formation of ammonia was not detected in the experiments of Koenig and Elod (A., 1914, ii, 264, 266). S. K. Tweedy.

Ammonium polysulphides, hydrogen pentasulphide, and the thiocarbonic acids. H. Mills and P. L. Robinson (J.C.S., 1928, 2326—2332; cf. Bloxam. *ibid.*, 1895, **67**, 277; Thomas and Riding, *ibid.*, 1923, **123**, 1726; Walton and Whitford, A., 1923, ii, 315).—Suspensions of sulphur in aqueous ammonia on saturation with hydrogen sulphide yield only ammonium pentasulphide, which by refluxing with carbon disulphide gives ammonium thiocarbonate and ammonium perthiocarbonate. *Hydrogen pentasulphide*, d^{16} 1·67, is obtained by treating ammonium pentasulphide with anhydrous formic acid. Tetrathiocarbonic acid and trithiocarbonic acid, f. p. −30·5°, d_4^{10} 1·47, $\gamma^{12\cdot5}$ 48·3 dynes/cm., have been isolated. F. J. Wilkins.

[**Radical-like alkali salts of a new acid containing nitrogen and oxygen.**] E. Zintl and O. Kohn (Ber., 1928, **61**, [*B*], 2063).—The authors' compound, Na_2NO_2 (cf. this vol., 258), has been isolated previously by Maxted (J.C.S., 1917, **111**, 1016). H. Wren.

Hydrazine selenate. J. Meyer and W. Aulich (Ber., 1928, **61**, [*B*], 1839—1840).—Hydrazine hydrate and dilute selenic acid afford colourless *hydrazine hydrogen selenate*, which is not decomposed by boiling water. When dry, it is caused to explode with unusual readiness by heat, shock, or gentle trituration. It explodes violently on contact with hydrochloric acid vapour. In analytical practice, therefore, selenic acid and selenates should be reduced to selenites by hydrochloric acid before hydrazine hydrate is added. H. Wren.

Tetraphosphorus triselenide and phosphorus thioselenides. J. Mai (Ber., 1928, **61**, [*B*], 1807—1811; cf. A., 1926, 1113).—The preparation of tetraphosphorus triselenide, d^{22} 3·161, from its components in the presence of tetrahydronaphthalene and its subsequent purification are described in detail. The colour varies from yellow to orange-red, according to the thickness of layer. The substance is slowly decomposed by atmospheric moisture, but does not appear sensitive to light. It is slowly decomposed by water. Sodium or potassium hydroxide or sodium sulphide converts it into sodium selenide; sodium carbonate and calcium or barium hydroxides behave similarly but less energetically. It has m. p. 242—243° after becoming lighter at 200°. It exhibits distinct phosphorescence at about 160° which becomes very marked at 280°.

Attempts to prepare phosphorus thioselenides from the components in tetrahydronaphthalene or from varying proportions of tetraphosphorus triselenide and trisulphide do not lead to the isolation of chemical individuals and indicate that the so-called phosphorus thioselenides are, at most, isomorphous mixtures. H. Wren.

Phosphates and arsenates of quadrivalent manganese. V. Auger and A. Yakimach (Compt. rend., 1928, **187**, 603—605).—*Ammonium manganiphosphate*, $(NH_4)_2H_2MnP_2O_9$, has been prepared by heating a solution of a mixture of diammonium phosphate and permanganate; black, rhombic crystals separate on cooling. *Manganiarsenic acid*, $Mn(H_2AsO_4)$, can be prepared by dissolving hydrated manganese dioxide in concentrated arsenic acid solution, by the action of arsenic acid on a permanganate, or by the interaction of arsenic acid with a mixture of manganous nitrate and a permanganate. *Ammonium manganiarsenate* resembles the corresponding phosphate. C. W. Gibby.

Constitution of hydrogen disulphide. Action of hydrogen disulphide on compounds of tervalent phosphorus. J. Dodonov and H. Medox (Ber., 1928, **61**, [*B*], 1767—1770).—In the hope of establishing a constitutional similarity between hydrogen disulphide and hydrogen peroxide, the behaviour of the former towards tertiary amines and phosphines has been investigated. Dimethylaniline causes vigorous decomposition of the compound into hydrogen sulphide and sulphur. Triethylphosphine and triethylarsine afford the corresponding sulphides. With phosphorus trichloride in benzene the disulphide yields phosphoryl thiochloride, phosphorus pentasulphide, hydrogen chloride, and a little hydrogen sulphide. It appears probable that the compound $PCl_3(SH)_2$ is formed initially and that a similarity in constitution exists between hydrogen disulphide and hydrogen peroxide. H. Wren.

Compound of sulphur with sulphurous acid. A. KURTENACKER and A. CZERNOTZKY (Z. anorg. Chem., 1928, **175**, 231—240).—The yellow solution obtained by treating a thiosulphate solution with sulphur dioxide becomes colourless on keeping and then yields a precipitate of sulphur when treated with formaldehyde and sodium hydroxide or acetate, although no polythionate can be detected in the solution. Neutralisation of the colourless liquid with sodium hydroxide yields thiosulphate and sulphite, but no precipitate of sulphur. With ice-cold concentrated hydrochloric acid and thiosulphate a similar colourless solution is obtained without precipitation of sulphur; after 15 hrs. no thiosulphate can be detected. These reactions are ascribed to the formation of a loose compound of sulphur and sulphurous acid; thus, $[S_2O_3,SO_2]''+H_2O$ $[S_2O_3,SO_3H_2]''$; $[S_2O_3,SO_3H_2]''$ $[S(SO_3H)_2]''$. A. R. POWELL.

Higher polythionates. A. KURTENACKER and A. CZERNOTZKY (Z. anorg. Chem., 1928, **174**, 179—188).—The action of concentrated hydrogen chloride solution on sodium thiosulphate solutions in presence of small quantities of sodium arsenite at $-10°$ to $-15°$ has been studied. Although pure hexathionates have not been prepared, mixed crystals of penta- and hexa-thionates have been obtained, which in aqueous and dilute acetic acid solution decompose rapidly with separation of sulphur. The reaction between sodium carbonate and pentathionates does not yield quantitatively sulphur and tetrathionate, as assumed by Raschig, but goes far beyond this stage even in dilute solution, and cannot therefore be made the basis of a method of determination of pentathionate. H. F. GILLBE.

Action of ammonia on alkali chromichlorides and on chromiammines which contain more than six molecules of ammonia. F. EPHRAIM and W. RITTER (Helv. Chim. Acta, 1928, **11**, 848—864).—The action of ammonia on dipotassium aquochromic pentachloride gives a greyish-violet mass containing hydroxypentamminechromic chloride. This dissolves in water to give a cherry-red solution from which nitric acid precipitates first the purpureonitrate and finally the roseo-nitrate in 27% yield. Hydrochloric acid precipitates from the aqueous solution the purpureo-chloride in 40% yield. The action of ammonia on the ammonium salt gives the same products. The formation of the compound $(NH_4)_3[CrCl_5(OH)]$ as an intermediate is suggested. No evidence of the existence of ammines of double salts was obtainable.

The action of ammonia on a number of chromiammines has been studied at the ordinary temperature and at the temperature of a salt freezing mixture. Amounts of ammonia varying from 1 mol. to 12 mols. per g.-mol. of salt are taken up. Decomposition curves of the additive products are given. The following salts have been investigated: luteobromide and -nitrate; roseo- and purpureo-nitrates, chlorides and bromides; thiocyanato-pentammine nitrate, bromide, iodide, and thiocyanate; oxalotetrammine nitrate; hydroxypentammine chloride; hexacarbamido-chloride, -bromide, and -iodide.

A method of preparation of the roseo- and purpureo-chromiammines by acting on potassium or ammonium chromichloride with a solution of ammonia in ammonium nitrate is described; yields of 45% have been obtained. R. N. KERR.

Reduction of selenious acid. L. M. CLARK (J.C.S., 1928, 2388—2393; cf. Keller, A., 1898, ii, 638).—The composition of the precipitate obtained by the reduction of selenious acid by sulphurous acid in the presence of copper sulphate and hydrochloric acid varies from that of cuprous selenide in slightly acid solutions to that of pure selenium in solutions containing much hydrochloric acid. It is suggested that the selenious acid is under all conditions first reduced to selenium, which subsequently affords cuprous selenide. The extent of the formation of cuprous selenide depends on the hydrogen-ion concentration of the solution. F. J. WILKINS.

Preparation of a tungsten carbonyl by means of a [Grignard] magnesium compound. A. JOB and J. ROUVILLOIS (Compt. rend., 1928, **187**, 564—565).—Job and Cassall's method (A., 1926, 1017) has been used for the production of *tungsten carbonyl*, $W(CO)_6$, by the action of pure carbon monoxide for 6 hrs. at 0° on pure tungsten hexachloride in the presence of magnesium phenyl bromide (to fix the former), ether, and benzene. Colourless, laminated crystals, subl. 50°, were obtained, decomposed at 100° or by fuming nitric acid, but not by water or ordinary acids. J. GRANT.

Explosive properties of solid hypochlorites. J. WEICHHERZ.—See B., 1928, 783.

Iron [and tin]. L. G. KNOWLTON (J. Physical Chem., 1928, **32**, 1572—1595).—The subjects investigated include new methods for the determination of carbon in iron, tin–iron alloys, the effect of aniline on the rate of dissolution of iron in acid, the reduction of nitrobenzene by iron, and the passivity of tin in nitric acid.

The total carbon in iron can be determined electrolytically by making iron turnings in a platinum dish the anode, a copper strip the cathode, and a 10% solution of sodium sulphate, renewed several times to remove ferric hydroxide, the electrolyte. The carbon can then be determined by combustion in the usual way. Graphitic carbon cannot be determined by making iron the cathode in an ammoniacal solution of ammonium nitrate. The current does not cause the corrosion, and the total carbon is left. The amount of carbon left by the action of acids on iron is increased when depolarisers are added during dissolution. With potassium permanganate of the correct concentration and a white iron, the total carbon present is left, but with grey iron some of the graphitic carbon is oxidised. Chlorine and aqua regia also increase the amount of residual carbon.

The addition of 25% of tin to molten grey cast iron throws carbon out of the iron, but not the total graphitic carbon as claimed by Eyferth (Percy's "Metallurgy of Iron and Steel," 1864). The addition of tin beyond a certain amount has little effect owing to the formation of two layers. The condition of the carbon present in molten iron is discussed. The increased combined carbon content of the alloy is attributed to the dissolution of silicon by the tin.

The action of 10% sulphuric acid, saturated with aniline, on iron at 50—60° removes the mill scale, but the amount of hydrogen evolved is greatly reduced. Further, the hydrogen overvoltage on iron is raised by the presence of aniline.

Grey iron reduces nitrobenzene approximately to the same extent when boiled with either sodium chloride or sulphate solutions, but, owing to the kind of iron used, the results disagreed with those of Snowdon (A., 1912, i, 100). Iron is not rendered passive by sodium chloride solution.

Tin becomes passive in nitric acid, *d* 1·426, when wrapped with a platinum wire; when connected with a platinum electrode, it becomes passive only with a more concentrated solution of the acid, and when made the anode with a cathode of platinum, it becomes passive in an acid more dilute than that required in the case with the platinum wire. The results are discussed. L. S. THEOBALD.

[Nitric oxide and carbon monoxide compounds of so-called univalent iron and nickel.] W. MANCHOT and H. GALL (Annalen, 1928, **465**, 304—305).—Polemical against Reihlen (cf. this vol., 35, 1114). E. W. WIGNALL.

Reactions and derivatives of iron carbonyl. II. Compounds of iron halides and carbon monoxide. W. HIEBER and G. BADER (Ber., 1928, **61**, [*B*], 1717—1722; cf. this vol., 511).—Iodine reacts with a slight excess of iron pentacarbonyl in ether, giving the dark brownish-red *iodide*, $Fe(CO)_4I_2$. The analogous *bromide*, $Fe(CO)_4Br_2$, is prepared in light petroleum and is the sole compound even when the halogen is used in large excess. The less stable, yellow *chloride*, $Fe(CO)_4Cl_2$, is similarly obtained at −20°. Determinations of mol. wt. in indifferent solvents give normal values. The compounds do not appear preparable from ferrous halides and carbon monoxide. They are very sensitive to reagents containing oxygen and nitrogen. Water decomposes them rapidly into ferrous halide and carbon monoxide. Ammonia, amines, alcohols, and organic carbonyl compounds such as esters, ketones, and aldehydes behave similarly with varying readiness; the superior stability of the iodides is noteworthy. The bromide loses carbon monoxide completely in the presence of 2 mols. of pyridine. Under precisely similar conditions the iodide affords the *dicarbonyl* compound, $Fe(CO)_2I_2,2C_5H_5N$, which loses carbon monoxide completely when treated further with the base and decomposes spontaneously when preserved or exposed to light to the *monocarbonyl* derivative, $Fe(CO)I_2,2C_5H_5N$. With a large excess of pyridine, hexapyridine ferrous iodide is produced. Under the influence of light the chloride is rapidly and completely decomposed; the iodide is less readily affected than the chloride. The final products are the ferrous halides, which are thus readily prepared in the pure state. H. WREN.

Oxidation of ferrous hydroxide in air. A. KRAUSE (Z. anorg. Chem., 1928, **174**, 145—160).—Precipitation of ferrous hydroxide from ferrous sulphate solutions by an equimolecular quantity of sodium hydroxide yields a product which on atmospheric oxidation is converted completely into hydrated ferric hydroxide, whereas that produced in presence of a greater concentration of sodium hydroxide oxidises in the air to products which always retain ferrous iron; the highest FeO/Fe_2O_3 ratio, resulting from high alkali concentrations, is 0·3 : 1, increase of the ferrous ratio causing a change of colour of the product from yellow to black, with a decrease of the water content, which corresponds with a change from hydrated meta-ferric hydroxide to ferrous ferrite. The isoelectric point of the hydroxide, the composition of which approximates to $Fe_2O_3,2H_2O$, lies at p_H 5·2. Confirmation of the theory of ferrite formation has been obtained by oxidising ferrous hydroxide in the presence of magnesium hydroxide, whereby magnesium ferrite is obtained. The meta-form of the hydroxide differs from the brown ortho-form, having its isoelectric point at p_H 7·7, in its ease of peptisation by ammonia, and its greater particle size. The ortho-form is the less stable and under water is gradually transformed into the meta-form. H. F. GILLBE.

Carbonatocobaltammines. J. KRANIG (Bull. Soc. chim., 1928, [iv], **43**, 989—995).—The constitution of carbonatodecamminecobaltic sulphate, $[Co_2(NH_3)_{10}CO_3](SO_4),4H_2O$, has been confirmed. This is the only known salt of the series and is extremely unstable, giving by double decomposition salts of other series. Of the pentammine series the *chloride*, $[Co(NH_3)_5CO_3]Cl,H_2O$, and the *oxalate*, $[Co(NH_3)_5CO_3]_2C_2O_4,3H_2O$, have now been isolated. The bromide of this series described by Werner can be obtained more readily by double decomposition between the above chloride and potassium bromide. O. J. WALKER.

Multinuclear cobaltammines, and method of preparation of the non-electrolyte $[Co(NH_3)_3Cl_3]$. E. BIRK (Z. anorg. Chem., 1928, **175**, 405—412).—The complex $[\{Co(NH_3)_3\}_2(OH)_3]Cl_3,H_2O$ has been prepared from the compound $[Co(NH_3)_3(NO_3)_3]$ by conversion into triamminotriaquocobaltic nitrate, treating with concentrated hydrochloric acid at −20°, and then with potassium hydroxide and ammonium chloride. The compound $[Co\{Co(NH_3)_4(OH)_2\}]Cl_6,2H_2O$ may be obtained as a by-product. Better yields are obtained in the preparation of cobalt trichlorotriammine by Werner's method if hydrogen chloride saturated at the lowest possible temperature be employed. H. F. GILLBE.

Ruthenium [chlorides]. H. GALL (Z. angew. Chem., 1928, **41**, 1070—1071).—A reply to Krauss (this vol., 413). Evidence based on the work of other investigators and on Gall's earlier work is adduced in support of the bivalency of ruthenium in the blue chloride and its quadrivalency in the product obtained by the reduction of the tetroxide with concentrated hydrochloric acid. A. R. POWELL.

Compounds of osmium tetroxide. F. KRAUSS (Z. anorg. Chem., 1928, **175**, 343—346).—Polemical. Fritzmann's experiments confirm the author's opinion that Tschugaev has not prepared compounds of octavalent osmium. H. F. GILLBE.

Applicability of the analytical quartz lamp to mixtures of solid substances. F. HEIN and W. RETTER.—See B., 1928, 733.

Physical methods in chemical laboratories. VIII. Electrical methods of titration. E. THILO (Z. angew. Chem., 1928, **41**, 1057—1061).—An account of the principles and methods of electrometric titrations, both potentiometric and conductometric procedures being discussed. A. R. POWELL.

Importance and examination of standards for titration. N. SCHOORL (Chem. Weekblad, 1928, **25**, 534—537).—A *résumé* of the methods of examining the commoner reagents for volumetric analysis. S. I. LEVY.

Potentiometric titration using monometallic electrode pairs. E. MÜLLER and H. KOGERT (Z. physikal. Chem., 1928, **136**, 437—445).—A modification of the bimetallic electrode method (cf. A., 1923, ii, 33) of potentiometric titration using two electrodes of the same metal is described. The end-point is marked, not by the maximum change of *P.D.* between the electrodes, but by the maximum *P.D.* itself. The titration can therefore be performed more quickly. Smooth and platinised platinum are used as the electrodes, but the method is not restricted to these metals. The method is illustrated by means of permanganate, dichromate, and thiosulphate titrations. O. J. WALKER.

Two new potentiometric titration methods. E. MÜLLER and H. KOGERT (Z. physikal. Chem., 1928, **136**, 446—450).—Two electrodes of the same kind are placed not too close together in the solution to be titrated, which is stirred in a circular direction. The standard solution is allowed to drop in close to one of the electrodes, which is thereby momentarily in contact with a solution containing excess of the added reagent and therefore acquires a different potential from the second electrode, which is always in contact with the thoroughly mixed solution. The course of the titration near the end-point is followed by connecting a galvanometer across the two electrodes and measuring the temporary deflexion produced by the addition of each drop. At the end-point this deflexion is practically zero.

In a modification of the above method the positions of the two electrodes and the direction of stirring are so arranged that the change in concentration produced in the reaction vessel by the addition of each drop takes place sooner at one electrode than at the other. The temporary *P.D.* between the electrodes on the addition of each drop passes through a sharp maximum at the end-point.

These methods, particularly the second method, give good results with precipitation reactions, but are unsuitable for oxidation–reduction processes. O. J. WALKER.

Accuracy and practice of quantitative kinetic analysis in the case of bimolecular reactions. L. SMITH and J. LINDBERG (Ber., 1928, **61**, [*B*], 1709—1717).—The mathematical method developed previously (Smith, A., 1920, ii, 607) for ascertaining the composition of a mixture of two allied and difficultly separable substances when the reaction constants for the mixture and one component are known is examined experimentally. Mixtures of α- and β-glyceryl chlorohydrin or of the α-compound with barium β-chloro-α-hydroxybutyrate are hydrolysed with barium hydroxide under somewhat unusually careful conditions. Experiments are recorded under the conditions, $k_1/k_2=14\cdot9$ and $2\cdot7$. The accuracy obtained in the latter circumstances indicates that kinetic analysis is doubtless applicable even at $k_1/k_2=2$ with an error of a few %, provided only that and k_2 are well-defined and accurately determinable constants of the second order. H. WREN.

Use of simple metallic electrodes in the potentiometric titration of acids and bases. J. O. CLOSS and L. KAHLENBERG (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 24 pp.).—Preliminary experiments showed that the single potentials of the metals tungsten, molybdenum, arsenic, antimony, bismuth, aluminium, and tin in $0\cdot1N$-acids differed greatly from their potentials in $0\cdot1N$-alkalis. The possibility of using these metals as indicator electrodes in the titration of an acid with an alkali was therefore examined. From the numerous titration curves obtained with various strong and weak acids it is evident that all these metals yield sharp end-points in titrations with N-sodium hydroxide. In some cases, notably with aluminium, the change of potential at the end-point is much greater than with a hydrogen electrode. Except with tin electrodes in oxalic acid solutions and with cadmium electrodes the potential always changed towards baser values at the end-point. With tin electrodes a second discontinuity was generally observed in the alkaline region of the curve, but its position depends on the nature of the acid being titrated and is influenced by shaking the electrode. In most cases the potentials of the metals became constant within a minute after each addition of alkali, and, even in some instances where the potential tended to drift, the effect was not great enough to interfere with the determination of the end-point. Satisfactory results were also obtained with platinised platinum electrodes, but thallium, lead, and zinc electrodes give anomalous results. The theory of the method is discussed and it is concluded that the potentials observed arise from the adsorption of oxygen or hydrogen by the metal surface. H. J. T. ELLINGHAM.

p_H Value of distilled water. C. VAN DER HOEVEN (Collegium, 1928, 440—443).—The most accurate method is the colorimetric method using a dilute solution of methyl-red neutralised with sodium hydroxide. This gives p_H 6·7—6·6 for distilled water. There is always an error on the acid side with the quinhydrone electrode method for all p_H measurements, which diminishes in proportion to the amount of buffering. D. WOODROFFE.

Methods of expressing acidity of solutions. A. J. J. VANDE VELDE (Natuurwetensch. Tijdschr., 1928, **10**, 145—151).—The various methods of stating the concentration of hydrogen ion and hydroxyl ion in solutions are discussed, and a table is given in which the coefficients of Giribaldo, Derrien-Fontes, and Wherry are set out with the hydrogen-ion values, p_H values, normalities, and volumes containing 1 g. of hydrogen ion corresponding. S. I. LEVY.

Micro-determination of vapour pressure and water of hydration of solid compounds. F. E. E.

GERMANN and O. B. MUENCH (J. Physical Chem., 1928, **32**, 1380—1386; cf. Wilson, A., 1921, ii, 376).—The micro-method described consists in introducing solutions of sulphuric acid of known concentration in dishes into the tightly-closed case of a sensitive assay balance which bears the thin film of the sample painted from a saturated solution of the salt on a tared microscope cover-glass. Changes in weight and the equilibrium weight are ascertained by means of a system of riders of different weights. With thermostatic temperature control and other slight modifications of the method, the vapour pressure for a hydrate-pair can be found by a bracketing method from the concentrations of sulphuric acid used. Data for disodium phosphate and barium chloride show the method to be accurate and quick, and to require only small amounts of material which are recoverable. Methods for the preparation and preservation of pure hydrates, and for the determination of heat of hydration, are described. L. S. THEOBALD.

Determination of moisture by rapid drying. S. H. MEIHUIZEN.—See B., 1928, 696.

Gravimetric determination of fluorine as calcium fluoride, using a membrane filter. G. G. KANDILAROV (Ber., 1928, **61**, [*B*], 1667—1671).—For the determination of fluorine in sodium fluoride, the aqueous solution is heated nearly to its b. p. and a slight excess of calcium chloride solution is added very gradually and with continuous stirring. The precipitated calcium fluoride is filtered on a membrane filter and washed three times with cold and four times with warm water. The precipitate and filter are dried in a specially-designed vacuum desiccator. The precipitate is removed from the membrane and heated at about 500° for 30—40 min. An addition of 0·0016 g. per 100 c.c. of mother-liquor is made to the weight of the precipitate, but the effect of the wash water may be neglected. If alkali carbonate is present, the solution is treated with so much nitric acid that it is neutral to methyl-red after the dissolved carbon dioxide has been expelled; after addition of a further few drops of acid sufficient to produce a faint red colour, the determination is carried out as above. The presence of nitrate ions causes the precipitate to be filtered much more rapidly; if the added acid is insufficient for this purpose, alkali nitrate may be added. H. WREN.

Diffusion of oxygen through rubber and various other substances. S. E. HILL (Science, 1928, **67**, 374—376).—For the approximate evaluation of the amounts of oxygen diffusing through various materials, use is made of a tube containing luminous bacteria which give a perceptible glow at an oxygen pressure of 0·005 mm.; the lengths of the luminescent columns are compared. A. A. ELDRIDGE.

Gravimetric determination of sulphuric acid in presence of antimony. S. VON FINALY (Z. anal. Chem., 1928, **75**, 17—27).—The determination of the sulphur content of antimony sulphides involves oxidation of the sulphur to sulphuric acid and the precipitation of barium sulphate from media containing tartaric acid, etc. The results thus obtained are not always trustworthy. The conditions under which the precipitation of sulphuric acid as barium sulphate from media containing antimony, tartaric acid, hydrochloric acid, and chlorides is reproducible and the necessary corrections minimal and independent of the concentration of antimony have therefore been determined. J. S. CARTER.

Determination of polythionates. E. H. RIESENFELD and G. SYDOW (Z. anorg. Chem., 1928, **175**, 74—79).—For the determination of trithionate the solution is heated for 1 hr. to boiling with a mixture of 30 c.c. of 10% copper sulphate solution, 100 c.c. of 10% barium chloride solution, and 20 c.c. of hydrochloric acid (*d* 1·12), whereby the trithionate is quantitatively precipitated as barium sulphate, thus: $S_3O_6'' + 8Cu^{\cdot\cdot} + 6H_2O = 3SO_4'' + 8Cu^{\cdot} + 12H^{\cdot}$. Tetrathionate, thiosulphate, and sulphite interfere, but pentathionate is without action. All polythionates, except dithionate, are oxidised completely to sulphate by heating with iodine and sodium hydrogen carbonate in a closed tube for 1 hr. or by keeping the mixture for 48 hrs. at the ordinary temperature in a closed flask. Titration of the excess of iodine affords a means of determining the sum of the polythionates present. A. R. POWELL.

Detection of pentathionate in presence of sulphurous acid. A. CZERNOTZKY (Z. anorg. Chem., 1928, **175**, 402—404).—The pentathionate ion may be detected, even at a concentration of 0·004*M*, in presence of 25 times the quantity of sulphite ion by adding 5 c.c. of formaldehyde solution to 10 c.c. of the solution, rendering slightly alkaline, and observing the appearance of opalescence within 2—3 min.; opalescence after a longer period is no longer characteristic of pentathionate. H. F. GILLBE.

Elimination and determination of nitrogen in argon. C. LEU (Helv. Chim. Acta, 1928, **11**, 761—763).—The exact conditions for removing nitrogen from, and determining it in, argon by passing the gas over magnesium containing small quantities of lime and sodium are described. The most favourable temperature is 850—870°. The nitride formed is decomposed by passing air containing water vapour over the cooled mixture and the ammonia produced is collected. Experiments show that 98% of the nitrogen content of a mixture containing 5% of nitrogen can be removed and determined in this way. R. N. KERR.

Micro-Kjeldahl determination [of nitrogen]. B. SAIKO-PITTNER (Pharm. Presse, 1928, **33**, 60—61; Chem. Zentr., 1928, i, 1892).—In the determination of nitrogen in pyramidone, phenylhydrazine, or semicarbazide the evolution of nitrogen or oxides of nitrogen is largely prevented by the addition of selenium. A. A. ELDRIDGE.

Analysis of nitrates. P. RISCHBIETH.—See B., 1928, 745.

Assay of phosphoric acid. F. A. MAURINA.—See B., 1928, 709.

Use of liquid amalgams in volumetric analysis. XI. Determination of phosphoric acid by employment of zinc or cadmium amalgam. Note to part VII. Method of determining chromium in chromium steels. K. SOMEYA (Z. anorg. Chem.,

1928, **175**, 347—356).—Zinc and cadmium amalgams reduce sexavalent molybdenum quantitatively to the tervalent state. Phosphate ion may be determined by precipitating as ammonium phosphomolybdate, dissolving the precipitate in ammonia solution, evaporating to small volume, reducing with amalgam, and titrating the resulting solution with $0{\cdot}14N$-potassium permanganate.

Satisfactory results are obtained for the determination of chromium in chromium alloys only if clean amalgam is used and if the method of procedure be somewhat modified. H. F. GILLBE.

Picric acid as an artificial standard in the colorimetric determination of silica. E. J. KING and C. C. LUCAS (J. Amer. Chem. Soc., 1928, **50**, 2395—2397).—The addition of the reagents of Diénert and Wandenbuleke (A., 1923, ii, 507) to a silicate solution containing 50 mg. of silica per litre produces a yellow coloration which matches that of a solution containing 25·6 mg. of pure vacuum-dried picric acid per litre. The discrepancy between this and previous results may be due to previous workers not having dried the acid thoroughly before use.

S. K. TWEEDY.

Micro-elementary analysis. R. GOUBAU (Natuurwetensch. Tijdschr., 1928, **10**, 129—136).—An apparatus for micro-analysis in which the water formed in the combustion is collected in a U-tube immersed in a mixture of solid carbon dioxide and alcohol, and the carbon dioxide in a tube immersed in liquid oxygen is described. The limbs of the absorption tubes contain spirals of silver wire to bring the gases into contact with the cooled surfaces. The precautions described allow an accuracy of 0·2—0·5% with quantities of 5—10 mg. of material.

S. I. LEVY.

Accurate gas burette for the volumetric determination of carbon [in steel]. O. MEYER.—See B., 1928, 753.

Detection of carbon dioxide. G. ELTESTE.—See B., 1928, 709.

Improved Orsat apparatus for the analysis of flue gases. K. MÜNZER.—See B., 1928, 733.

Micro-determination of potassium as cobaltinitrite. A. LEULIER, L. VELLUZ, and H. GRIFFON (Bull. Soc. Chim. biol., 1928, **10**, 891—904).—The precipitate obtained by treatment of a solution of the sample with excess of sodium cobaltinitrite is separated and washed by centrifuging under standardised conditions. The precipitate is then decomposed by heating at 100° with a solution of sodium phosphate and acidified with sulphuric acid; potassium iodide is added, and the liberated iodine titrated with sodium thiosulphate solution. The error is below 3%. G. A. C. GOUGH.

Determination of potassium as perchlorate. A. T. DALSGAARD (Dansk Tidsskr. Farm., 1928, **2**, 257—273).—The perchlorate process for the determination of potassium has been critically examined and the following procedure is recommended. The solution is evaporated almost to dryness in a Pyrex dish after the addition of 1·5 times the theoretical amount of perchloric acid. After cooling, water and perchloric acid (1 c.c.) are added and the resulting solution is evaporated to complete dryness. The cold residue is crushed with a glass rod, 10 c.c. of absolute alcohol are added, and the whole is left for 30 min. with occasional stirring. The liquid is decanted through a glass filter crucible and the precipitate washed by decantation with 3—5 c.c. of 96% alcohol containing 0·2% of 70% perchloric acid. The remaining alcohol is carefully evaporated, water added, and the whole again evaporated to dryness. After cooling, the residue is treated with a special wash liquid (96% alcohol containing 0·2% of perchloric acid and saturated with potassium perchlorate) and the potassium perchlorate filtered, washed, and dried at 150—200°. If the redissolution of the precipitate after the first washing with alcohol be omitted, the results are invariably 2—3 mg. too high when considerable amounts (0·1 g. or more) of sodium are present, and a similar, although smaller, error occurs if the crystals of potassium perchlorate are not crushed finely before filtration. The method as given yields accurate results in the presence of sodium, barium, calcium, magnesium, and iron, and is recommended for technical purposes. A comprehensive summary of previous work on the perchlorate process accompanies the paper. H. F. HARWOOD.

Micro-determination of sodium. E. DI BENEDETTO and A. D. MARENZI (Rev. Centr. Estud. Farm. Bioquim., 1927, **16**, 592—595; Chem. Zentr., 1928, i, 1794).—In Nau's modification of Blanchetiere's method, the uranyl magnesium sodium acetate is precipitated, separated, and washed in the centrifuge tube. A. A. ELDRIDGE.

Electrometric determination of calcium by the use of secondary electrodes. M. H. CORTEN and L. ESTERMANN (Z. physikal. Chem., 1928, **136**, 228—230).—The chains $Ag|Ag_2C_2O_4|CaC_2O_4|Ca^{\cdot\cdot}$, and $Zn|ZnC_2O_4|CaC_2O_4|Ca^{\cdot\cdot}$ may be used as reversible secondary electrodes for the determination of calcium ions. The latter must be used for determinations in blood and serum, and gives reproducible results, maintaining a constant potential over considerable periods. F. G. TRYHORN.

Wolff's calcimeter for the continuous gasometric determination of calcium carbonate. A. HOCK (Chem. Fabr., 1928, 548).—An apparatus for the determination of the calcium carbonate content of fertilisers etc. by which series of determinations can be carried out in succession is described and illustrated. It comprises a number of reaction flasks coupled with an automatic shaking apparatus which permits of the continuous agitation of the sample with the acid for any desired period. The reaction flasks are each connected to a gas-measuring burette graduated in c.c., a manometer for adjusting the level of the liquid in the burette, and a reservoir containing the necessary acid. A. R. POWELL.

Quantitative separation of barium and calcium. M. LEMARCHANDS (Compt. rend., 1928, **187**, 601—603).—The solubilities of barium sulphate in water and in hydrochloric acid solutions have been determined at 100°, also its solubility in calcium chloride solution. C. W. GIBBY.

Differentiation of dolomite and magnesite. F. Feigl and H. Leitmeier (Zentr. Min. Geol., 1928, A, 74—87; Chem. Zentr., 1928, i, 1795).—Magnesite, but not dolomite, is coloured reddish-violet by alkaline-alcoholic diphenylcarbazide solution. Dolomites containing magnesium carbonate, brucite, and breunnerite give the reaction. A. A. Eldridge.

Identification of cadmium by the drop method. P. G. Popov (Ukraine Chem. J., 1928, 3, 158—160).—Two or three drops of the solution to be analysed, which may contain, besides cadmium, lead, bismuth, copper, mercury, and silver, are acidified by the addition of 2—3 drops of sulphuric acid, and the solution is evaporated until dense white fumes of acid are evolved, when it is diluted, and excess of iron powder added, and the whole immediately filtered. A solution of hydrogen sulphide is then added to the solution on a watch-glass, when, if cadmium is present, it will be precipitated as a yellow sulphide. R. Truszkowski.

Separation of cadmium from copper in qualitative analysis. P. G. Popov (Ukraine Chem. J., 1928, 3, 153—155).—The filtrate obtained in group II after the precipitation of bismuth by ammonia is slightly acidified by sulphuric or hydrochloric acid and zinc or iron powder is added. The mixture is shaken for 10—20 sec., and immediately filtered; the cadmium is precipitated as sulphide from the filtrate, which is free of copper. R. Truszkowski.

Determination of copper in molybdenite. M. G. Roeder.—See B., 1928, 787.

Volumetric determination of mercuric oxide. P. Ray and J. Das-Gupta (J. Indian Chem. Soc., 1928, 5, 483—485).—Mercuric oxide reacts with sodium thiosulphate according to the equation $HgO+2Na_2S_2O_3=Na_2[Hg(S_2O_3)_2]+2NaOH$. The liberated alkali is determined by titration. The method gives trustworthy results provided a large excess of sodium thiosulphate is avoided. H. Burton.

Confirmatory test for aluminium. E. H. Panganiban and (Miss) F. A. Soliven (J. Amer. Chem. Soc., 1928, 50, 2427—2428).—The solution obtained by Noyes' procedure ("Quantitative Chemical Analysis," 1923, 190) is passed through a filter-paper having a few asbestos fibres at the apex of the cone. The latter are withdrawn and burned on a platinum wire. This modification renders thorough washing unnecessary, and the ignition takes less time. S. K. Tweedy.

Electrometric iron–dichromate titrations. F. J. Watson (Chem. Eng. Min. Rev., 1928, 20, 396—399).—In the absence of a satisfactory indicator the electrometric method of titrating ferrous iron and dichromate is more successfully used. The non-reversibility of the reaction renders investigations empirical and prevents a quantitative application of electrode theory. The use of a calomel electrode and potassium chloride bridge was eliminated in favour of bimetallic electrodes. Bright platinum is used as the "indicator electrode" on account of the high *E.M.F.* change at the end-point. A large number of metals maintained practically a constant *E.M.F.* with respect to the solution over the end-point region and were suitable as "reference electrodes," although gold was a marked exception. Tungsten appeared to be most suitable. Silver was found suitable for the titration of iron with dichromate but not *vice versa*, owing to the rapid oxidation of the metal by chromic acid. C. A. King.

Determination and separation of chromium, iron, aluminium, and phosphorus. K. K. Jarvinen (Z. anal. Chem., 1928, 75, 1—16).—The oxidation of chromium in alkaline media is accomplished most rapidly and satisfactorily by bromine. Considerable occlusion of chromate is observed when aluminium and iron are precipitated as hydroxides from solutions containing chromate. No chromate is occluded when these metals are precipitated as phosphates. The constituents in a mixture of chromium, iron, aluminium, and phosphate are determined in the following manner. A portion of the solution is treated with bromine (1—2 c.c.) and a distinct excess of $2N$-sodium hydroxide added with constant shaking. After 15 min. the precipitate is dissolved in the minimum amount of hydrochloric acid and the solution again made alkaline. The solution is warmed for some time, acidified, and the excess of bromine removed by boiling. A sufficient amount of $2N$-ammonium phosphate is added to the hot solution and iron and aluminium are precipitated by careful addition of ammonia. The cooled solution is diluted to a suitable volume and chromate determined iodometrically in a portion of the acidified filtrate. The precipitate, which need not be washed, is dissolved in hydrochloric acid and any chromate reduced by sodium hydrogen sulphite. Iron is oxidised by bromine water and the excess of bromine removed by boiling. The solution is boiled with 1—2 g. of potassium iodide in a retort and the liberated iodine absorbed in dilute sodium hydroxide solution. Rubber etc. connexions are inadmissible and the retort end must be sealed in the receiving liquid. The latter is acidified and the iodine titrated with thiosulphate. If the phosphate content of the original solution is known all constituents may be precipitated by ammonia and aluminium determined from the weight of the ignited precipitate by difference. J. S. Carter.

Diphenylcarbazide as a test for chromium. N. M. Stover (J. Amer. Chem. Soc., 1928, 50, 2363—2366; cf. Brandt, A., 1906, ii, 309).—Diphenylcarbazide as a reagent for dichromate and chromium ions is much superior to a mixture of hydrogen peroxide and ether. It is more sensitive in presence of sulphuric acid than in the presence of either acetic or citric acids. Zinc and nitrate ions may be present. S. K. Tweedy.

Quantitative separation and determination by evaporation with gaseous hydrogen chloride. VII. Separation and determination of the components of tungstates. G. Jander and D. Mojert (Z. anorg. Chem., 1928, 175, 270—276).—The hydrogen chloride method has been applied to the analysis of sodium and barium tungstates. H. F. Gillbe.

Precise determination of thorium by precipitation as subphosphate. F. Hecht (Z. anal. Chem., 1928, 75, 28—39).—Thorium is precipitated quan-

titatively as subphosphate, $ThP_2O_6,11H_2O$, from boiling solutions containing about 10% of hydrochloric acid. Cerium is not precipitated alone under these conditions, particularly in presence of hydrogen peroxide. Conversion into pyrophosphate by ignition is, however, not quantitative. The precipitated subphosphate may be treated with sulphuric acid and sodium nitrate, and thorium precipitated as oxalate from the resulting solution. If sulphuric acid is not removed after the oxidation the solution obtained on dilution may be used for the precipitation. If sulphuric acid is removed, the suspension obtained on treating with water is made alkaline with ammonia and the precipitated phosphate (previously held to be a hydroxide) dissolved after filtration in hydrochloric acid. The oxalate is ignited and weighed as oxide. Alternatively, the subphosphate may be fused with sodium and potassium carbonates, the cooled mass treated with water, and the insoluble matter ignited. This ignited material is fused with potassium pyrosulphate, the cooled mass dissolved in hydrochloric acid, and thorium precipitated as oxalate.

J. S. Carter.

Determination of vanadium. B. S. Evans and S. G. Clarke.—See B., 1928, 786.

Determination of vanadium in steel. A. T. Etheridge.—See B., 1928, 714.

Ceric sulphate as a volumetric oxidising agent. VII. Determination of vanadium in presence of chromium, tungsten, and iron. H. H. Willard and P. Young (Ind. Eng. Chem., 1928, 20, 972—974).—Vanadyl salts may be titrated electrometrically with ceric sulphate in hot (70—80°) solutions containing 5—10 c.c. of sulphuric acid (*d* 1·83), nitric acid (*d* 1·42), perchloric acid (70—72%), or hydrochloric acid (*d* 1·18) per c.c. Conversely, ceric salts may be accurately determined by electrometric titration with vanadyl sulphate in hot solutions containing sulphuric, nitric, or perchloric acids. For the determination of vanadium in steel 4—5 g. of turnings are dissolved in 10 c.c. of sulphuric acid and 35—40 c.c. of water. The solution is boiled vigorously until salts begin to separate, diluted with 20 c.c. of water, and cautiously oxidised with nitric acid, avoiding excess. After diluting to 100 c.c., 2 c.c. of silver nitrate solution (2·5 g./litre) and 2 g. of ammonium persulphate are added; the solution is boiled for 15 min., cooled, treated with 40 c.c. of sulphuric acid (*d* 1·5) and 0·05*N*-ferrous sulphate solution in slight excess as indicated by a drop in the voltage, and set aside for 10 min. After a slight excess of permanganate has been added, the solution is cooled to 5—10°, titrated with ferrous sulphate until the reduction of vanadic acid to vanadyl sulphate is complete, diluted to 300 c.c., heated to 70—75°, and titrated with 0·05*N*-ceric sulphate to reoxidise the vanadium. If the steel contains tungsten, the tungstic acid precipitated by the nitric acid treatment is collected, washed, and dissolved in sodium hydroxide, the solution being returned to the main solution prior to titration. A. R. Powell.

Cerium salts in quantitative analysis. Determination of antimony in presence of arsenic. H. Rathsburg (Ber., 1928, 61, [*B*], 1663—1665).—Antimony is determined by titration with 0·05*N*- or 0·01*N*-ceric sulphate solution in presence of methylene-blue, Congo-red, methyl-orange, or methyl-red; alternatively, the end-point is measured electrometrically. After determination of antimony, arsenic may be determined in the same solution either by titration with potassium bromate or with ceric salt until a sudden alteration of potential is observed.

H. Wren.

Analytical chemistry of tantalum, niobium, and their mineral associates. XII. Pyrosulphate–hydrolysis method. XIII. Separation of zirconium and hafnium from tantalum and niobium. W. R. Schoeller and E. F. Waterhouse (Analyst, 1928, 53, 467—475, 515—520).—XII. An experimental investigation of the pyrosulphate–hydrolysis method shows that the earth acids cannot by any of the modifications of the method be quantitatively separated from zirconia or titania. The method is regarded as a balanced reaction in which a colloidal phase gradually flocculates with adsorption of almost any of the constituents of the solution, and should be disregarded. In mixtures of earth acids and titania no practical separation occurs at any stage preceding total precipitation; zirconia prevents hydrolytic precipitation of titania, and in the presence of titania the earth acids cannot be separated from ferric sulphate, but may be imperfectly separated from ferrous sulphate.

XIII. The term "zirconia" is used for the mixture $(Zr,Hf)O_2$. Small quantities of earth acids may be separated from much zirconia by fusing the mixed oxides with potassium hydrogen sulphate, dissolving the product in a saturated solution of ammonium oxalate containing as much salt as hydrogen sulphate taken, and treating the boiling liquid with 0·2 g. of tannin in hot water and dilute ammonia. The colour of the precipitate varies according to the ratio of oxides present. The precipitate is washed with 2% ammonium chloride solution and ignited. To precipitate zirconia-free pentoxide, the ignited precipitate is treated the same way as the mixed oxides, and the clear solution neutralised while boiling until cloudiness is perceptible; this is removed with the minimum amount of hydrochloric acid. The boiling solution is then treated with 1 g. of ammonium chloride and a freshly-prepared solution of tannin, which imparts a yellow, orange, or red colour, followed by flocculation of the coloured precipitate. After 1—2 hrs. at 50—70°, the liquid is filtered and the precipitate weighed as $(Ta,Nb)_2O_5$. Since the tannin and earth acid precipitate is very bulky, it is preferable to separate zirconia from quantities of earth acid exceeding 0·02—0·03 g. by first using the potassium carbonate fusion followed by the tannin process. The potassium fusion is carried out by fusing 6 parts of potassium carbonate with 1 part of the mixed oxides, digesting with 1 g. of potassium hydroxide and enough water to cover, stirring filter pulp into the diluted liquid, and filtering. The zirconia residue is washed with 2% potassium carbonate solution and ignited, and if heavy and derived from a mixture rich in tantalic oxide, fused again. The alkaline filtrate is acidified with hydrochloric acid, boiled with a small excess of ammonia, the precipitate mixed

with filter pulp, washed with dilute ammonium nitrate solution, ignited, digested with hot water acidulated with hydrochloric acid, again ignited strongly, and weighed as $(TaNb)_2O_5$. The zirconia residue from the carbonate fusion is ignited, moistened with dilute sulphuric acid, dried, fused with hydrogen sulphate, and the product dissolved in ammonium oxalate solution. After filtering to remove impurities such as silica it is submitted to the tannin process.

D. G. HEWER.

Wilson's ray-track apparatus. T. WULF (Z. physikal. chem. Unterr., 1928, **41**, 70—73; Chem. Zentr., 1928, i, 1832).—An improved apparatus is described. A. A. ELDRIDGE.

Light source devised by Auer von Welsbach. K. WARM (Z. wiss. Phot., 1928, **25**, 365—379).—The light source consists of a spark between two electrodes which alternately touch and separate as a result of the effect of an interrupted electromagnet. The source gives both arc and spark lines, and a continuous passage from one type of spectrum to the other can be made by increasing the current.

W. E. DOWNEY.

Physical methods in chemical laboratories. VII. Spectroscopy as an aid in chemical research. II. E. RABINOVITSCH (Z. angew. Chem., 1928, **41**, 1021—1028; cf. this vol., 728).—A review showing the value of spectroscopic methods in determining the state of molecular aggregation of elements, in distinguishing between polar and non-polar molecules in the gaseous state, in discovering new compounds, and in chemical analysis. A. R. POWELL.

Design of equipment for measuring the specific volume of carbon dioxide vapour. C. H. MEYERS (Refrig. Eng., 1928, **15**, 157—158).

CHEMICAL ABSTRACTS.

Friction coefficient for gas flow through small glass tubes. M. ELLIOTT (Ind. Eng. Chem., 1928, **20**, 923—924).—Small rates of gas flow can be conveniently measured by the pressure drop through a capillary tube. In order to obtain absolute results by this means determinations of the constant f in the equation $\Delta h=2fLu^2/gd$ (where Δh is the pressure drop, u the velocity, and L and d are respectively the length and diameter in feet) were made. The factor f is a function of $Du\rho/\mu$, where ρ and μ are the density and viscosity of the gas. The values of f found were plotted against this modulus on log–log paper, giving a curve which was nearly a straight line. For a known gas, therefore, the curve affords a means of obtaining the relation between f and u and thus plotting pressure drop against velocity. C. IRWIN.

Exact determination of the coefficient of internal friction of molten salts. R. S. DANTUMA (Z. anorg. Chem., 1928, **175**, 1—42).—An apparatus is described for the determination of the viscosity of molten salts by measuring the damping of a freely-swinging platinum sphere suspended in the liquid by means of a platinum strip carrying a mirror, the movements of which are registered photographically on a revolving drum which also acts as a time recorder. The whole apparatus is mounted above, and heat-insulated from, a well-lagged wire-wound resistance furnace, the temperature of which is automatically recorded by means of a thermocouple. The viscosities of sodium, potassium, and lithium nitrates and of sodium chloride have been determined for temperatures up to about 200° above their respective m. p., and the results are recorded graphically and in a series of tables. Except in the case of lithium nitrate, they agree well with the results of other workers. A. R. POWELL.

Precision pipette viscosimeter. S. W. FERRIS (Ind. Eng. Chem., 1928, **20**, 974—977).—The bulb of the pipette has a capacity of 4·5 c.c.; the tip is drawn out to an inside diameter of 2 mm. and this is further drawn out to 0·5 mm., the decrease in diameter throughout being kept gradual. The tip is then broken off at the narrow point and polished on a fine emery stone to obtain a smooth, circular orifice. The pipette is enclosed in a water-jacket provided with paddles driven by an air-jet paddle-wheel. Calibration graphs, in which Saybolt seconds (s) are plotted against pipette seconds (p), are always straight lines conforming to the equation $s=kp+4$; hence the instrument may be calibrated with any oil of known viscosity or, to an accuracy of about 1%, with water. The results obtained are more accurate than those from the Saybolt viscosimeter.

A. R. POWELL.

Measurement of [temperature with] a resistance thermometer. A. MICHELS and GEELS (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 485—491).—The relationship between the various factors concerned, necessary for the accurate measurement of temperature by the resistance thermometer, is discussed theoretically. A circuit with overlapping shunts is described. M. S. BURR.

Zambelli's vacuum evaporator. R. GIORDANO (Rev. Centr. Estud. Farm. Bioquim., 1927, **16**, 596—601; Chem. Zentr., 1928, i, 1793).

Continuous extraction apparatus. H. L. MAXWELL.—See B., 1928, 695.

Large-capacity laboratory extractor. F. E. HOLMES (Ind. Eng. Chem., 1928, **20**, 888).—The vaporised solvent is delivered through a vertical tube centrally placed within a bulb. An expansion in the bottom of the latter is packed with cotton wool on which the material to be extracted is placed. Above the bulb is a reflux condenser. C. IRWIN.

Mechanical agitator. G. N. QUAM (Ind. Eng. Chem., 1928, **20**, 922).—An agitator designed for determining rates of corrosion of metal samples by fluids was made of soft wood and mounted a number of test-tubes resting obliquely towards each side which contained the sample. These were fitted with bent breathing tubes to ensure aeration. The rocking (through 30°) is controlled by a hinge on the rocker arm and by the walls of the thermostat.

C. IRWIN.

Adjustable thermostat. B. NOYES, jun. (J. Opt. Soc. Amer., 1928, **17**, 127—131).—The *E.M.F.* of a thermocouple is used, by way of a potentiometer, galvanometer, photo-electric cell, and an amplifier, to actuate a series of relays which vary the current in the winding of the furnace which it is desired to keep at a constant temperature. W. E. DOWNEY.

Constant-rate aspirator. C. F. Hottes and A. L. Hafenrichter (Science, 1928, **67**, 320—322).—The aspirator is described and figured.

A. A. Eldridge.

Exclusion of atmospheric oxygen by superimposed surface layers. H. Schmalfuss and W. Peschke (Biochem. Z., 1928, **198**, 487—493).—Of 13 liquids investigated, amyl alcohol when floated on the surface of oxygen-free water was most and anisole least efficient in preventing oxygen from reaching the aqueous layer. The curve showing the degree of protection at different temperatures shows a sharp minimum. The influence of the thickness of the protective layer is strikingly small. Atmospheric oxygen penetrates into a fluid between the glass wall and the medium and not through the medium, the passage of oxygen being rendered visible by a colour reaction. Oxygen is excluded completely either by superimposing a layer of a liquid paraffin which by cooling can be quickly solidified or, in experiments at high temperatures, by covering with a layer of a fluid which at the temperature concerned boils very vigorously.

P. W. Clutterbuck.

Modified Hartmann diaphragm. J. R. Green (J.C.S.I., 1928, 47, 224T).—A description of a diaphragm by the use of which, for every spectrum of the substance under examination, six comparison spectra can be obtained, instead of two when using the ordinary three-aperture Hartmann form.

Apparatus for delivering gas at constant pressure. T. Gray (J.S.C.I., 1928, **47**, 187—188T).—An attachment to the ordinary laboratory aspirator bottle is described, which obviates the variation of pressure due to the changing level of the confining liquid and ensures delivery at a constant pressure during the whole period of discharge. With the addition of this device any gas-tight metal drum, such as is used for the transport of liquids, may be converted into a serviceable gas-holder.

Automatic time switch for prolonged heating etc. A. Guthrie (J.S.C.I., 1928, **47**, 202T).—The winder of an alarm clock is bolted to a gas tap. The turning of the winder when the alarm is released automatically cuts off the gas.

Densi-tensimeter. A. Smits (J.C.S., 1928, 2409—2410; cf. A., 1927, 819).—A number of improvements are described in an apparatus designed to measure vapour pressures and vapour densities simultaneously.

F. J. Wilkins.

Extraction of krypton and xenon from air and from gases dissolved in water. G. Claude (Compt. rend., 1928, **187**, 581—585; cf. Lepape, this vol., 970).—A description of modifications in plant for the fractionation of liquid air, in the form of an additional vaporiser, for obtaining krypton and xenon as by-products.

C. W. Gibby.

Nomographic conversion of percentages by weight into atomic percentages in ternary systems. O. Redlich (Z. anorg. Chem., 1928, **174**, 285—289).—A graphical method is described and illustrated.

H. F. Gillbe.

Geochemistry.

Effect of ozone on the temperature of the upper atmosphere. E. H. Gowan (Proc. Roy. Soc., 1928, A, **120**, 655—669).—From the abnormally high values obtained for the density of the atmosphere, calculated from observations of meteors, Lindemann and Dobson (*ibid.*, 1922, A, **102**, 411) concluded that the temperature above 60 km. is of the order of 300° Abs. Whipple (Nature, 1923, **111**, 187), from observations of the zones of audibility occurring at some distance round big explosions, found that near 60 km. a temperature of about 280° Abs. was to be expected. A theoretical consideration of the radiative equilibrium of the upper atmosphere, taking into account the effects, with selective absorption, of water vapour and ozone, leads to a region of high temperature in the neighbourhood of, and above, 60 km. The equation of equilibrium, considering only vertical radiation, for any layer of air in a non-convective region is $-Y_\lambda'+E \quad S_\lambda')d\lambda$, where $R_{\lambda T}$ is the radiation from any layer at temperature T, X_λ' and Y_λ' are the absorbed portions of the atmospheric radiations from above and below the layer, and E_λ' and S_λ' are the portions of the terrestrial and solar radiations absorbed in the layer. An analytical solution of this equation can be found when the coefficient of absorption does not vary with the wave-length. When selective absorption is used a graphical solution is possible, and has been obtained by successive approximation. The results, as regards both temperature and height of the warm region, agree well with those of indirect observations.

L. L. Bircumshaw.

Height of the ozone in the upper atmosphere. F. W. P. Gotz and G. M. B. Dobson (Proc. Roy. Soc., 1928, A, **120**, 251—259).—Measurements have been made by the spectrographic method of the thickness of the ozone layer at different times of the day at Arosa (Switzerland), and from this the height of the layer is calculated. The results are not conclusive, but the average height appears to be between 30 and 40 km. above sea-level. A table is given showing the height at various times of the year. Measurements have also been made during cyclones and anticyclones and the results are discussed.

J. L. Buchan.

Helium. VI. Helium content of terrestrial gases. F. Paneth, H. Gehlen, and K. Peters (Z. anorg. Chem., 1928, **175**, 383—401).—The percentages of helium in a number of gases occurring naturally in various parts of the world have been determined.

H. F. Gillbe.

Volcanic gases from Agnano. C. Olita (Z. Vulkanol., 1923–194, **7**, 155—161; Chem. Zentr., 1928, i, 2075).

Pozzuoli solfatara gases. E. Salvatore (Z. Vulkanol., 1923, **7**, 149—154; Chem. Zentr., 1928,

i, 2075).—The gases contain CO_2 99·19, H_2S 0·47, CH_4 0·0086, H_2 0·0682, N_2 and rare gases, 2·620, A+He 0·0021%. A. A. ELDRIDGE.

Determination of steam in the fumarole exhalations of Pozzuoli solfataras. E. SALVATORE (Z. Vulkanol., 1923—194, 7, 215—217; Chem. Zentr., 1928, i, 2075).—The average steam content was 91·03% for 9·37% CO_2. A. A. ELDRIDGE.

Physical and chemical conditions in San Francisco Bay, especially in relation to the tides. R. C. MILLER, W. D. RAMAGE, and E. L. LAZIER (Univ. Calif. Pub. Zool., 1928, **31**, 201—267).—Observations of salinity, temperature, turbidity, dissolved oxygen, dissolved hydrogen sulphide, and hydrogen-ion concentration are recorded.

CHEMICAL ABSTRACTS.

Petroleum and the filtering earths. P. G. NUTTING (J. Washington Acad. Sci., 1928, **18**, 409—414).—The filtering material is active only when there are free terminal hydroxyl radicals, which may combine with the alkyl radicals of certain hydrocarbons. Good results are obtained with silica, alumina, and ferric oxide gels from which most, but not all. of the water has been expelled. Materials such as greensand and serpentine with -OK and $-O_2Mg$ radicals are active after these basic radicals have been removed by acid treatment. Clays contain no hydroxyl that can be driven off leaving open linkings, and consequently they are not good filtering materials. The deposition of a sparingly soluble film of some silico-hydrocarbon on the mineral grains is discussed in connexion with the genesis of petroleum and asphalt. L. J. SPENCER.

Theory of the formation of petroleum. G. STADNIKOV and E. IVANOVSKI.—See B., 1928, 735.

Occurrence of hydrocarbons in volcanic rocks. J. FRIEDLANDER and E. SALVATORE (Z. Vulkanol., 1924—1925, **8**, 73—83; Chem. Zentr., 1928, i, 2074).—Extraction of 0—0·007% of hydrocarbons and 0·002—0·028% S is reported. A. A. ELDRIDGE.

Columbian glass meteorites. T. DORING and O. STUTZER (Zentr. Min. Geol., 1928, **A**, 35—41; Chem. Zentr., 1928, i, 1642—1643).—The meteorites have d^4 2·310, soften at 905°, swell considerably when more strongly heated, and contain SiO_2 76·37, TiO_2 0·11, Al_2O_3 12·59, Fe_2O_3 0·26, FeO 0·48, MnO 0·14, MgO 0·17, CaO 0·79, Na_2O 3·36, H_2O 0·97, SO_3 0·13, Sb_2O_3 0·07, P_2O_5 0·02%. The gas evolved on heating contained (HEINRICH) CO_2 27·1, CO 24·4, H_2 35·3, CH_4 2·2, O_2 1·1%. A. A. ELDRIDGE.

Origin and organisation of coal. E. C. JEFFREY (Mem. Amer. Acad. Arts Sci., 1924, **15**, 1—52).

CHEMICAL ABSTRACTS.

Changes in the oxidation of iron in magnetite. L. H. TWENHOFEL (Econ. Geol., 1927, **22**, 180—188).—The oxidation of magnetite and formation of hæmatite are functions of time and source of material, as well as of temperature. The additional oxygen atoms are irregularly spaced within the magnetite crystal structure. CHEMICAL ABSTRACTS.

Sagvandite, an eruptive rock containing magnesium. T. BARTH (Norsk geol. Tidsskr., 1926, **9**, 271—303; Chem. Zentr., 1928, i, 2074).

Members of the zoisite–epidote group poor in iron. A. ORLOV (Sitzungsber. Konigl. bohm. Ges. Wiss., 1926, II, No. 19, 42 pp.; Chem. Zentr., 1928, i, 2073).—The clinozoisites correspond with the formula $6SiO_2,3R_2O_3,4RO,H_2O$; *d* 3·349, the yellower portions being denser. The constants of Zillertal clinozoisite poor in iron are not regarded as limiting values in the clinozoisite–epidote group.

A. A. ELDRIDGE.

Hydrothermal alteration of certain silicate minerals. R. J. LEONARD (Econ. Geol., 1927, **22**, 18—43).—Alunite was produced at 20°, 65°, and 100° at 1 atm. and at 200° at 15 atm., but not at 350° at 1 atm., by the action of water, aluminium sulphate, and sulphuric acid, potassium sulphate, or sodium sulphate on microcline, albite, and bytownite. Zeolites were formed by the action of water and potassium or sodium carbonate at 200° and 15 atm. on the felspars; cryolite by the action of water on aluminium fluoride and sodium fluosilicate at 350° and 1 atm., at 400° and 8 atm., and at 575° and 10 atm. Leverrierite was probably formed from felspars by the action of water and aluminium chloride (with or without sodium or potassium chloride) at 350° and 1 atm. or by water and potassium carbonate, or water, potassium fluoride, and sodium fluosilicate at 575° and 10 atm. CHEMICAL ABSTRACTS.

Hydrothermal formation of iron ores. R. KLEMM (Zentr. Min. Geol., 1928, **A**, 90—94; Chem. Zentr., 1928, i, 1754).

Dumortierite. S. F. GLINKA (Min. Resources and Tech., Moscow, 1927, No. 3, 189—191; Chem. Zentr., 1928, i, 2072).

Pigment of emerald. A. FERSMANN (Compt. rend. Acad. Sci., U.S.S.R. [Russia], 1926, 24—25; Chem. Zentr., 1928, i, 2072).—Ural emeralds contained 0·11, 0·19% Cr_2O_3; vanadium was detected spectroscopically only in deeply-coloured specimens.

A. A. ELDRIDGE.

Pisekite. A. KREJCI (Časopis min. geol., 1923, No. 1, 2—5; Chem. Zentr., 1928, i, 2073).—The radioactive mineral pisekite (qualitative analysis recorded) has d^{18} 4·0346, H 5½—6. A. A. ELDRIDGE.

Slavikite. F. ULLRICH and R. JIRKOVSKY (Vestn. stát. ust. Ceskoslov., 1926, **2**, 345—351; Chem. Zentr., 1928, i, 2073).—The mineral, from Mt. Valachov near Skřivan, is trigonal, uniaxial negative, ε 1·506±0·002, ω 1·530±0·001; $d^{20.8}$ 1·905, and contains Fe_2O_3 20·08, Al_2O_3 4·29, CaO 0·01, Na_2O 1·63, K_2O 0·57, SO_3 34·06, H_2O (<110°) 3·10, (>110°) 35·66, insol., 0·52, corresponding with the formula $(Na,K)_2SO_4,Fe_{10}(OH)_6(SO_4)_{12},63H_2O$.

A. A. ELDRIDGE.

Liévrite (ilvaite) of the arsenic deposits at Dijmara, N. Caucasus. J. KUSNETZOV (Bull. Com. Geol., 1925, **44**, 721—731; Chem. Zentr., 1928, i, 2073).—Analysis gave: SiO_2 29·18, Fe_2O_3 18·67, Al_2O_3 0·46, FeO 33·32, MnO 2·26, CaO 14·11, MgO 0·26, H_2O 1·53%: d^{18} 4·000. Type I has $a:b:c$ 0·6711 : 1 : 0·4469; 0·6586 : 1 : 0·4414; type II has $a:b:c$ 0·6843 : 1 : 0·4538. A. A. ELDRIDGE.

Crystals of calcite from Voldelée. V. BILLIET (Natuurwetensch. Tijdschr., 1928, **10**, 158—159).—

Examination of calcite crystals from the marble quarries of Vodelee, between the Sambre and the Meuse, has disclosed crystals with a form 701 (Bravais 71$\bar{8}$6), not hitherto observed in Belgium.

S. I. LEVY.

The Whin sill and related dikes of the north of England. A. HOLMES and H. F. HARWOOD (Min. Mag., 1928, **21**, 493—542).—Several detailed analyses of these quartz-dolerites show that the sill and the dikes are practically identical in composition, indicating a genetic connexion between the two.

L. J. SPENCER.

Genesis of the jadeite of Burma. A. LACROIX (Compt. rend., 1928, **187**, 489—493).—The jadeite at Tawmaw, Upper Burma, occurs, as described by Bleeck (A., 1909, ii, 412), in the centre of a dike in serpentine, passing outwards into a jadeite-albite-rock (jadeitite) with some soda-amphibole, then into an amphibolite in which the amphibole is actinolite, and finally on the walls of the dike into a chloritic rock. The jadeite has been regarded as a dynamo-metamorphic product of a nepheline-syenite. The suggestion is now made that this is a case of desilicification of a granitic magma intruded into peridotite, but one in which the process has not proceeded so far as in the corundum-bearing rocks of South Africa.

L. J. SPENCER.

Japanese minerals containing rarer elements. VI. Beryl from Ishikawa, Iwaki Province. T. UEMURA (Japan. J. Chem., 1926, **2**, 117—121).—The beryl, analysed by a method previously adopted (A., 1926, 144), contained SiO_2 49·60, BeO 19·31, Fe_2O_3 0·11, Al_2O_3 24·09, CaO 0·79, MgO 0·14, ignition loss 2·81%, and the remainder alkali. Copaux's method (A., 1919, ii, 192) is not suitable for the analysis of Ishikawa beryl. A special molecular structure is suggested to account for this. The course of the analysis was followed spectroscopically. The green colour cannot be due to chromium, since no trace of the latter was observed.

M. S. BURR.

Clays. XII. Changes of certain clays into acidic ones through weathering. T. OKAZAWA (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 93—94; cf. this vol., 1110).—The so-called acidity of clays, supposed by the author to be the result of severe weathering, involves the production of aluminium salts and the corresponding acids when the clays are treated with solutions of neutral salts. The soluble free acid adsorbed by the clays is actually minute in quantity and ambiguous in nature. The behaviour of acid clays is analogous to that of the zeolites.

J. GRANT.

Rare earths in the stellar atmospheres. L. ROLLA and G. PICCARDI (Gazzetta, 1928, **58**, 521—532).—An account of the occurrence and distribution of the rare-earth elements in the atmospheres of the various types of stars.

O. J. WALKER.

Minerals. IV. H. COLLINS (Chem. News., 1928, **137**, 213—215).

Organic Chemistry.

[Cholesterol as parent of petroleum.] W. STEINKOPF (Ber., 1928, **61**, [*B*], 1639).—A reply to Zelinski (B., 1927, 865; this vol., 865).

H. WREN.

Thermal decomposition of ethane, ethylene, propane, and propylene. F. E. FREY and D. F. SMITH (Ind. Eng. Chem., 1928, **20**, 948—951).—The decomposition was carried out in silica vessels, which possess no appreciable catalytic activity. Decomposition of propane in the presence of a nickel catalyst at 200°, 350°, and 405° takes place: (1) $C_3H_8 \longrightarrow 2CH_4 + C$, (2) $C_3H_8 \longrightarrow C_3H_6 + H_2 \longrightarrow CH_4 + 2H_2 + C$, of which (1) takes place at all temperatures but (2) becomes important only at higher temperatures. Hydrogen has no effect on the reaction at 200°. A copper catalyst causes only slight decomposition of propane at 350° and 400°. Platinised (3%) and palladised (5%) asbestos at 568° have small but definite effects on the decomposition of propane, hydrogen, ethylene, ethane, and propylene being evolved and free carbon deposited. Silica has little catalytic effect at 575°, no carbon being formed, and the decomposition in unaffected by an increase in the surface area of the silica. Under these conditions the decomposition of propane may be explained thus: (1) $C_3H_8 \longrightarrow C_2H_4 + CH_4$, (2) $C_3H_8 \longrightarrow C_3H_6 + H_2$, (3) $2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$, (1) and (2) having considerable velocities of the same order of magnitude, whilst (3) is a much slower reaction. The only products formed by the decomposition of ethane under the same conditions are ethylene and hydrogen, the reaction being of the first order over a considerable pressure range. The velocity of hydrogenation of ethylene at 575° in silica vessels is greater than that of dehydrogenation (cf. Wartenberg, A., 1908, ii, 26), greater than that of propylene under the same conditions, and is more dependent on the concentration of hydrogen than on that of ethylene, which suggests that an appreciable part of the reaction takes place at the surface of the vessel. Both cases are complicated by the tendency to polymerisation. Polymerisation of ethylene at 575° yields a relatively large amount of propylene, together with methane, ethane, and higher hydrocarbons, whilst under the same conditions propylene yields butylene, methane, ethylene, and higher hydrocarbons. Polymerisation in the presence of hydrogen results in the formation of less unsaturated products.

J. W. BAKER.

Oxidation of *n*-hexane. M. BRUNNER (Helv. Chim. Acta, 1928, **11**, 881—897).—An extension of work already published (Brunner and Rideal, this vol., 731).

H. BURTON.

Allyl transformations and additive products of erythrene hydrocarbons. C. PRÉVOST (Ann. Chim., 1928, [x], **10**, 147—181).—Experimental details are given of work already published (this vol., 152, 613). Methylvinylcarbinol when boiled with 3·3% hydrochloric acid is converted into an equilibrium mixture

containing 30% of Δ^{β}-buten-α-ol, b. p. 119—120°, d_4^{21} 0·8500, n_D^{21} 1·4260, together with a trace of α-chloro-Δ^{β}-butene and the three possible ethers. By the action of phosphorus pentabromide, methylvinylcarbinol is converted into α-bromo-Δ^{β}-butene, which is not hydrolysed with aqueous potassium hydroxide, but is converted by boiling aqueous alkali carbonate into a mixture of methylvinylcarbinol (60%) and Δ^{β}-buten-α-ol (40%), and with alcoholic potassium hydroxide into a mixture of ethyl Δ^{β}-butenyl ether, b. p. 99—100°, d_4^{22} 0·7870, n_D^{22} 1·4050, and probably ethyl α-methyl-Δ^{β}-propenyl ether. Esterification of methylvinylcarbinol with acetic acid yields only the corresponding acetate, but trichloroacetic acid behaves like the hydrogen halides and converts either methylvinylcarbinol or the isomeric Δ^{β}-buten-α-ol into a mixture of 50—55% of α-methyl-Δ^{β}-propenyl trichloroacetate, b. p. 74—74·5°/12 mm., d_4^{22} 1·2990, n_D^{22} 1·4588, and 40—45% of Δ^{β}-butenyl trichloroacetate, b. p. 89—89·5°/12 mm., d_4^{22} 1·3130, n_D^{22} 1·4710, together with a mixture of the ethers $(CH_2\!:\!CH\cdot CHMe)_2O$ and $CH_2\!:\!CH\cdot CHMe\cdot O\cdot CH_2\cdot CH\!:\!CHMe$. Hydrolysis of either of the trichloroacetates yields exclusively the corresponding alcohol. Physical data given are revised values (cf. Charon, A., 1899, i, 848).

J. W. Baker.

Relative reactivities of *n*-butyl bromide and bromobenzene towards magnesium in ether. H. Gilman and E. A. Zoellner (J. Amer. Chem. Soc., 1928, **50**, 2520—2523).—Determinations of the amount of Grignard reagent formed under standard conditions (cf. A., 1923, ii, 272; 1926, 535) in periods of 45 and 90 sec. after mixing show that *n*-butyl bromide reacts more rapidly than bromobenzene with magnesium in ether.

H. E. F. Notton.

Action of metallic tin on methylene halides. K. A. Kozeschkov (Ber., 1928, **61**, [*B*], 1659—1663).—Methylene bromide, b. p. 97·5°/753 mm., d_4^{20} 2·4953, n_D^{20} 1·5420, is prepared in about 80% yield by the action of arsenious oxide dissolved in aqueous potassium hydroxide on bromoform. It is transformed by tin at 180—220° into tin methyl tribromide, m. p. 53°, and carbon: $3CH_2Br_2+2Sn= 2MeSnBr_3+C$. If excess of methylene bromide is employed, tin tetrabromide results. Analogously, methylene chloride affords tin methyl trichloride, m. p. 42—43°, whereas tin tetraiodide is the main product from methylene iodide.

H. Wren.

Rate of hydrolysis of esters of unsaturated alcohols. M. H. Palomaa and A. Juvala (Ber., 1928, **61**, [*B*], 1770—1776).—The velocity coefficients of acid (k_s) and alkaline (k_a) hydrolysis in aqueous solution at 25°±0·1° are recorded for the following esters of the general type $R\cdot CO_2\cdot[CH_2]_n\cdot CH\!:\!CH_2$. Allyl formate ($k_s$ 0·149); *Δγ-butenyl formate*, b. p. 112—113°, d^{20} 0·9267 (k_s 0·151); *Δδ-pentenyl formate*, b. p. 135—136°/777 mm., d^{20} 0·9124 (k_s 0·133); allyl acetate (k_s 0·00473, k_a 12·76); Δγ-butenyl acetate, b. p. 124—126°/753 mm. (k_s 0·00553, k_a 8·09); *Δδ-pentenyl acetate*, b. p. 144—146°/762 mm., d^{20} 0·9114 (k_s 0·00331, k_a 4·40).

H. Wren.

Synthesis of butane-βγ-diol, its nature and odour. S. Maruyama and T. Higasi (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 934—939).—Butane-βγ-diol, b. p. 183—184°, prepared from *n*-butyl alcohol through Δ^{β}-butene, its dibromide, and diacetate, is a syrupy, colourless, almost odourless liquid, and hence, contrary to Taira (Rep. Dept. Ind. Govt. Res. Inst., Formosa, No. 8), the odour of "shoyu" is not due to this compound.

J. W. Baker.

Semisaturated derivatives of erythrenic hydrocarbons. C. Prevost (Bull. Soc. chim., 1928, [iv], **43**, 996—1018).—Polar considerations of published and unpublished results on the semisaturated derivatives of erythrenic hydrocarbons lead to the conclusion that these derivatives exist in three forms, a γ- or 1 : 4-form and two stereoisomeric α-(or 1 : 2- or 3 : 4)-forms. There is no evidence of *cis–trans*-isomerism among the γ-derivatives, and the two glycols, b. p. 108°/12 mm. and 126°/12 mm., previously described (A., 1926, 818) are now regarded as Δ^{β}-pentene-δε-diol and *trans*-Δγ-pentene-βε-diol, respectively; the physical constants of the six erythrene glycols are thus in harmony with one another and also with erythrol. According to the mobility of the additive group the α- and γ-isomerides can be desmotropic (with pseudomerism as the limiting case) or mesomeric. In any case, they are tautomeric, giving generally in double decomposition reaction mixtures of the three isomeric forms of the new compound. Desmotropism has been observed in the case of the dibromo-derivatives, but equilibrium between the α-(1 : 2- or 3 : 4-) and γ-(1 : 4-) forms is only very slowly attained, and at low temperatures the phenomena approximate to pseudomerism, the γ-form predominating. When this form is solid and in the absence of a solvent the γ-form alone is present at equilibrium. The α-isomerides are stable only when they are themselves solid. At the ordinary temperature the diacetins, glycols, and divinyl derivatives are mesomeric, and the reaction diacetins $\rightleftharpoons$ glycols is normal, multipolar ions playing no part. The reactions bromo-derivatives acetins, glycols, or divinyls are always abnormal, but the anomaly can be masked in some cases by one mesomeride greatly preponderating in the product. In these reactions of double decomposition, qualitatively the three mesomerides behave similarly, but quantitatively each tends to give mainly the derivative corresponding with itself. Secondary reactions may lead to the formation of substituted erythrenes. If this loss of hydrogen bromide occurs on erythrenes containing methyl groups in the 1 : 4-positions erythrylic derivatives may be formed.

Hydrolysis of the αδ-dibromo-Δ^{β}-pentenes, b. p. 85—86°/11 mm., obtained by bromination of crude Δαγ-pentadiene (A., 1926, 496) at 80°, with 10% sodium carbonate affords 15% of glycol of b. p. 92°/12 mm., 15% of glycol of b. p. 108°/12 mm., and 70% of glycol of b. p. 126°/12 mm. With dibromopentene, b. p. 60—80°/12 mm., these fractions are obtained in 25%, 20%, and 55% yield, respectively. With boiling 50% sodium carbonate solution the yield of glycols is poor, but the proportions are unchanged. The glycol of b. p. 92°/12 mm. has been separated by distillation into two fractions, b. p. 88—90°/12 mm., d^{21} 1·0074, n^{21} 1·4572, and

b. p. 93—95°/12 mm., d^{21} 1·0103, n^{21} 1·4585, consisting essentially of the two racemic forms of Δ^{α}-*pentene-γδ-diol*. In addition to the glycols, the product obtained by hydrolysis contains a little Δ^{β}-pentenal, b. p. 127°, d^{21} 0·858, n^{21} 1·4385 (semicarbazone, m. p. 177·5°), a substance, *d* 1·268, probably a pentenol, and a little *erythryl bromide*, CH_2:CH·CH:CH·CH_2Br, b. p. 33—34°/16 mm., n^{21} 1·5205, d^{21} 1·335, which cannot be separated from the accompanying α-bromo-$\Delta^{\beta\delta}$-pentadiene. Erythryl bromide is prepared by the action of quinoline on αδ-dibromo-Δ^{β}-pentene; with bromine at 50° it affords *αβγδε-pentabromopentane*, m. p. 150°. R. Brightman.

Reactions relating to carbohydrates and polysaccharides. XV. The isomeric benzylideneglycerols. H. S. Hill, M. S. Whelen, and H. Hibbert (J. Amer. Chem. Soc., 1928, **50**, 2235—2242).—The work of Irvine, Macdonald, and Soutar (J.C.S., 1915, **107**, 337) indicated that the product of condensation of glycerol with benzaldehyde was αβ-benzylideneglycerol, but the possibility of formation of the αγ-derivative is suggested by the existence of a cyclic acetal of α-methylglucoside, which has an amylene-oxide structure. Condensation of benzaldehyde with glycerol by the method of Gerhardt (A., 1913, i, 47) or by heating with 40% sulphuric acid yielded products which were separable by crystallisation from light petroleum and benzene into *αγ-benzylideneglycerol*, m. p. 80·5° (*benzoate*, m. p. 103°), and *αβ-benzylideneglycerol*, b. p. 143—144°/2 mm. (*benzoate*, an oil), in the proportions of 1 : 7·5 and 1 : 3, respectively, in the two methods. The structure of these compounds was determined by Irvine's methylation–hydrolysis method. The αγ-derivative, with silver oxide and methyl iodide, yielded *αγ-benzylideneglyceryl β-methyl ether*, m. p. 52°, from which was obtained *glyceryl β-methyl ether*, b. p. 123°/13 mm., d_4^{17} 1·1306, n_D^{17} 1·4505. The products from the αβ-derivative were identical with those obtained by Irvine (*loc. cit.*). The two benzylideneglycerols were interconvertible, and an equilibrium mixture containing five parts of αβ- to one part of αγ-derivative was obtained when either isomeride was treated with a trace of dry hydrogen chloride and heated or kept for some time. R. K. Callow.

Dodecane-αμ-diol. Lespieau (Compt. rend., 1928, **187**, 605—607).—The action of magnesium on an ethereal solution of pentamethylene dibromide yields a mixture of magnesium compounds of the type $[(CH_2)_5]_n(MgBr)_2$, the proportion of each decreasing as *n* increases. From the products of the action of chloromethyl ether on these compounds are isolated: αμ-dimethoxyheptane, *methyl* n-*hexyl ether*, b. p. 124—125°, d^{19} 0·7897, n_D 1·4065; *αμ-dimethoxydodecane*, b. p. 156—156·5°/13 mm., m. p. 11·5°, d^{22} 0·8563, n_D 1·436. This last by the action of gaseous hydrogen bromide at 100° yields *αμ-dibromododecane*, m. p. 38·5—39°, converted by silver acetate and acetic acid into the *diacetate*, m. p. 36·5—37·5°, from which is obtained *dodecane-αμ-diol*, m. p. 80—81°. J. W. Baker.

Configuration of pentaerythritol. II. Optically active compounds of pentaerythritol and pyruvic acid. J. Böeseken and B. B. C. Felix (Ber., 1928, **61**, [*B*], 1855—1857; cf. this vol., 616).—The action of pentaerythritol on ethyl pyruvate in alcoholic solution in presence of hydrochloric acid gives the *compound*, $C[C_2H_4O_2{>}CMe{\cdot}CO_2Et]_2$, m. p. 46°, hydrolysed to the corresponding *acid*, $C_{11}H_{16}O_8$, m. p. 238°. The acid is resolved by means of its *monostrychnine* salt into the corresponding l- and d-*acids*, $[\alpha]_D$ −3·98° and +3·72° in acetone ($[\alpha]_D$ +6·87° in water). The acids rapidly become racemised in boiling, aqueous solution. The tetrahedral configuration of pentaerythritol appears therefore established, at any rate in alcoholic solution. The assumption of pyramidal molecules is not immediately necessary. H. Wren.

Identity of volemitol and α-sedoheptitol. F. B. La Forge and C. S. Hudson (J. Biol. Chem., 1928, **79**, 1—3).—The identity of volemitol and α-sedoheptitol (cf. La Forge, A., 1920, i, 595) is confirmed, the discrepancy in the m. p. of the benzylidene derivatives previously noted (A., 1917, i, 444) having been due to a mistaken reference. C. R. Harington.

Mechanism of the acetal reaction; explosive rearrangement of hydroxyethyl vinyl ether to ethylidene glycol. H. S. Hill and L. M. Pidgeon (J. Amer. Chem. Soc., 1928, **50**, 2718—2725).—The mechanism suggested for the formation of ethylidene ethylene ether from acetylene and ethylene glycol (A., 1924, i, 133) is supported by the observation that this ether is produced quantitatively, and with explosive rapidity from β-hydroxyethyl vinyl ether, in presence of a trace of acid. Similarly, acetal formation probably consists of (*a*) formation of a semi-acetal (cf. Adkins, this vol., 396), and (*b*) dehydration to a vinyl ether, which then undergoes inter- or intramolecular rearrangement. The application of this mechanism to sugar chemistry is discussed. β-Bromoethylidene ethylene ether (cf. A., 1923, i, 439), prepared by an improved method, yields with sodium in ether *β-hydroxyethyl vinyl ether*, b. p. 44—45°/10 mm., n_D^{17} 1·4564, the *benzoate*, b. p. 133°/9 mm., of which does not undergo rearrangement in presence of acid. H. E. F. Notton.

Vinyl derivatives: their relationship to sugars and polysaccharides. H. S. Hill (J. Amer. Chem. Soc., 1928, **50**, 2725—2731).—Bromoethylidene trimethylene ether (cf. A., 1923, i, 439) and sodium in ether give the *sodium* salt (I) of *γ-hydroxypropyl vinyl ether*, b. p. 64—65°/10 mm., which combines with bromine, and changes with violence in presence of a trace of hydrogen chloride into ethylidene trimethylene ether. This is also formed from the vinyl ether and 1 mol. of methyl alcohol in presence of acid, but with 3 mols. of alcohol the principal product is dimethylacetal (*a*). The sodium salt (I) and methyl iodide give *γ-methoxypropyl vinyl ether*, b. p. 75—76°/137 mm. In presence of a trace of hydrogen chloride this forms (*b*) with 1 mol. of methyl alcohol, mainly the mixed acetal, *α-methoxyethyl γ-methoxypropyl ether*, b. p. 153—155°; (*c*) with excess of alcohol, dimethylacetal; (*d*) with ethylene glycol, ethylidene ethylene ether and γ-methoxypropyl alcohol, and (*e*) with α-methylglucoside, ethylidene α-methylglucoside, but not the desired mixed acetal. Reaction (*b*) supports, by analogy, the suggestion (cf.

preceding abstract) that an unsaturated derivative (tetrahydroxy-Δ^{α}-hexene $\alpha\varepsilon$-oxide) is an intermediate in the formation of α-methylglucoside from dextrose; (*a*) and (*c*) show the lability of the alcohol residues in acetals, whilst (*d*) and (*e*) indicate a preference for the formation of cyclic derivatives rather than open-chain acetals. H. E. F. NOTTON.

Constitution of hexosediphosphoric acid. II. Dephosphorylated α- and β-methylhexosides. W. T. J. MORGAN and R. ROBISON (Biochem. J., 1928, **22**, 1270—1276).—By the action of the bone phosphatase on the α- and β-methylhexosidediphosphoric acids, α- and β-methylhexosides, $[\alpha]_{5461}$ +55° and −47°, have been obtained as non-reducing syrups. The properties of these compounds agree with those expected for α- and β-methyl-γ-fructosides. They have been converted into fully methylated derivatives from which tetramethyl-γ-fructose, $[\alpha]_{-461}$ +40°, has been obtained. It is suggested that hexosediphosphoric acid is γ-fructose-1 : 6-diphosphoric acid. S. S. ZILVA.

Nitroamides of methionic [methanedisulphonic] acid. H. J. BACKER (Rec. trav. chim., 1928, **47**, 942—949).—Phenyl methanedisulphonate (Schroeter, A., 1919, i, 516) reacts with methylamine in benzene solution at 140°, forming *methanedisulphonmethylamide*, $CH_2(SO_2{\cdot}NHMe)_2$, m. p. 172·5°, which is nitrated at 0° to *methanedisulphon-nitromethylamide*, $CH_2(SO_2{\cdot}NMe{\cdot}NO_2)_2$, m. p. 118·5° (decomp.), also obtained by the action of nitric acid at 70—75° on *methanedisulphonacetmethylamide*, m. p. 174—175·5°. This nitroamide is decomposed by aqueous alkali hydroxides to methylnitroamine and alkali methanedisulphonate. The following are prepared similarly: methanedisulphonethylamide, m. p. 144—145° (*acetyl* derivative, m. p. 78°; *nitro*-derivative, m. p. 61—61·5°); *methanedisulphonpropylamide*, m. p. 171·5° (*nitro*-derivative, m. p. 47—48°); *methanedisulphonbutylamide*, m. p. 181—181·5° (*nitro*-derivative, m. p. 41—41·5°); *methanedisulphonamylamide*, m. p. 179·5—180° (*nitro*-derivative, m. p. 21°), and *methanedisulphonpiperidide*, m. p. 117—117·5°. Methanedisulphonethylanilide is nitrated to the corresponding 2 : 4-*dinitroethylanilide*, m. p. 219°, and phenyl methanedisulphonate affords the p-*nitrophenyl* ester, m. p. 169°. H. BURTON.

Organic cyclic polysulphides. Condensation of ethylene mercaptan with di- and tri-chloroacetic acids. G. C. CHAKRAVARTI and J. M. SAHA (J. Indian Chem. Soc., 1928, **5**, 453—458).—When ethylene mercaptan is boiled with dichloroacetic acid there is formed a *pentamethylene tetrasulphide* (I), m. p. 96°; in presence of xylene three *trimethylene disulphides*, m. p. 192—194°, m. p. 83—84°, and an oil, respectively, are obtained. Potassium dichloroacetate and monopotassium ethylene mercaptan react in alcohol solution, giving an oily *acid* (II),

$C_2H_4{<}^{S}_{S}{>}CH{\cdot}CO_2H$ (*potassium* salt), whilst ethyl

dichloroacetate affords a mixture of the *ethyl* ester of (II) and a *compound*, $C_8H_{14}O_2S_4$. Trichloroacetic acid and ethylene mercaptan react in boiling xylene, forming (I) and polymerides of ethylene disulphide. H. BURTON.

Effect of structure of organic halides on their rate of reaction with inorganic halides. II. Effect of methylthiol group. New vesicant. W. R. KIRNER (J. Amer. Chem. Soc., 1928, **50**, 2446—2454).—The preparation of an anhydrous ethereal suspension of sodium methyl sulphide is detailed. This forms with chloromethyl acetate *methylthiolmethyl acetate*, b. p. 60—62°/20 mm., which gives on hydrolysis with methyl-alcoholic hydrogen chloride a *substance*, b. p. 70—71°/48 mm., and a sulphur-free product, but no hydroxydimethyl sulphide. Sodium methyl sulphide and ethylene chlorohydrin in boiling ether yield *methyl* β-*hydroxyethyl sulphide*, b. p. 80·5—81°/30 mm., d_{20}^{20} 1·0640, n_D^{20} 1·4867; *methyl* γ-*hydroxypropyl sulphide*, b. p. 105—105·5°/30 mm., d_{20}^{20} 1·0314, n_D^{20} 1·4832, is obtained similarly. These are respectively converted by thionyl chloride in chloroform into *methyl* β-*chloroethyl sulphide* (1·52), b. p. 44°/20 mm., d_{20}^{20} 1·1245, n_D^{20} 1·4902, which has a vesicant action similar to that of ββ′-dichloroethyl sulphide, and *methyl* γ-*chloropropyl sulphide* (2·52), b. p. 71·2°/29 mm., 1·0863, 1·4833, which is not a vesicant. The reactivities of the chlorine atoms in these derivatives (butyl chloride=1) given in parentheses are in accordance with results obtained in other series (cf. A., 1924, i, 273). They show no connexion with the vesicant effect (cf. Peters and Walker, A., 1923, i, 734), which appears in compounds of this type to be a specific property of β-chloroethyl derivatives. H. E. F. NOTTON.

Allyl derivatives. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1927, **15**, 418—422).—Allyl acetate, b. p. 103—105°, was obtained by boiling allyl alcohol with acetic anhydride and a few drops of concentrated sulphuric acid. Bromination of allyl formate in carbon disulphide yielded βγ-*dibromopropyl formate*, b. p. 221—223°. The acetate was prepared similarly. R. K. CALLOW.

Preparation of pentadecoic acid. S. LANDA (Chem. Listy, 1928, **22**, 361—362).—Good yields of pentadecoic acid are obtained by the oxidation of cetene, using hot 1% potassium permanganate solution. R. TRUSZKOWSKI.

Three-carbon system. XVIII. Influence of alkyl substituents on the αβ-βγ change in unsaturated acids: reduction of sorbic acid, and a new synthesis of pyroterebic acid. A. A. GOLDBERG and R. P. LINSTEAD (J.C.S., 1928, 2343—2360).—The equilibrium between the following pairs of αβ- and βγ-unsaturated acids in the presence of aqueous potassium hydroxide has been investigated; the figures in brackets give the proportion of αβ-isomeride in the equilibrium mixture. (i) Δ^{α}-Pentenoic acid and Δ^{β}-pentenoic acid [75·4%], (ii) Δ^{α}-hexenoic acid (*anilide*, m. p. 109—110°) and Δ^{β}-hexenoic acid (hydrosorbic acid) [about 77%], (iii) γ-methyl-Δ^{α}-pentenoic acid (Δ^{α}-*iso*hexenoic acid) (*acid chloride*, b. p. 67°/20 mm.; *anilide*, m. p. 119°) and γ-methyl-Δ^{α}-pentenoic acid (pyroterebic acid) (*acid chloride*, b. p. 60°/15 mm.; *anilide*, m. p. 106°) [5·6%], (iv) α-methyl-Δ^{α}-pentenoic acid (*acid chloride*, b. p. 63°/16 mm.; *amide*, m. p. 80°) and α-methyl-Δ^{β}-pentenoic acid (*acid chloride*, b. p. 47°/17 mm.; *amide*,

m. p. 74°; *anilide*, m. p. 76°) [80·7%], (v) *cyclo*pentylideneacetic acid and Δ^1-*cyclo*pentenylacetic acid [13·7%]. Rules governing the effect of alkyl substituents on the equilibrium are formulated. The mobilities of the acids $10(k_1+k_2)$ (Linstead, A., 1927, 1167) are (i) 7, (ii) 7, (iii) 4·5, (iv) 7, and (v) 22. The equilibrium value of (iii) is so far on the βγ-side that equilibration of the αβ-isomeride (Δ^{α}-*iso*hexenoic acid) with aqueous potassium hydroxide affords a convenient method for the preparation of pyroterebic acid. Abnormal results were obtained with "hydrosorbic acid" and these were shown to be due to the presence of about 50% of the γδ-isomeride simultaneously produced in its preparation by the reduction of sorbic acid by sodium amalgam (cf. Fittig and Baker, A., 1895, i, 206). A. I. VOGEL.

Synthesis of certain γ-ketonic acids closely allied to Balbiano's acid. II. Syntheses of αββ- and ααβ-trimethyl-lævulic acids, of the lactone of α′-hydroxy-ααβ-trimethylglutaric acid, and of γ-keto-αββ-trimethylpropane-αγ-dicarboxylic acid (Balbiano's acid). J. C. BARDHAN (J.C.S., 1928, 2604—2621; cf. this vol., 1243).—Trimethylsuccinic anhydride was converted by sodium ethoxide into the acid ester; the latter on treatment with thionyl chloride followed by zinc methyl iodide gave a mixture of two ketonic esters which was hydrolysed to the acids with methyl-alcoholic potassium hydroxide. These were separated by fractional crystallisation of the semicarbazones from methyl alcohol, when two pure *semicarbazones*, m. p. 155° and 174°, respectively, were obtained. The former yielded αββ-*trimethyl-lævulic acid*, m. p. 65—66° (*ethyl* ester, b. p. 110°/14 mm., d_4^{19} 0·981537, n_D 1·43638; trimethylsuccinic acid was obtained on oxidation with potassium hypobromite), whilst the latter gave ααβ-trimethyl-lævulic acid, m. p. 77—78°, with dilute hydrochloric acid. The structure of the ααβ-acid was established by the following rational synthesis: methyl ethyl ketone was condensed with ethyl α-bromo*iso*butyrate and zinc to *ethyl* β-*hydroxy*-ααβ-*trimethyl*-n-*valerate*, b. p. 92°/11 mm., which was dehydrated with phosphoric oxide to *ethyl* ααβ-*trimethyl*-Δ^{β}-*pentenoate* (I), b. p. 100—102°/45 mm., $d_4^{16\cdot8}$ 0·906942, $n_4^{16\cdot8}$ 1·43878 (acetaldehyde was isolated on ozonolysis). Hydrolysis of (I) with methyl-alcoholic alkali furnished the corresponding acid, b. p. 113°/10 mm., $d_4^{19\cdot4}$ 0·963434, $n_D^{18\cdot2}$ 1·45283 (*silver* salt; p-*toluidide*, m. p. 71°), which when treated with a slight excess of bromine at 0° gave an unstable dibromide, decomposing on distillation with the elimination of hydrogen bromide and the production of the *lactone* of γ-*hydroxy*-ααβ-*trimethyl*-Δ^{β}-*pentenoic acid*, b. p. 80°/13 mm. Hydrolysis of the lactone with methyl-alcoholic potassium hydroxide yielded ααβ-*trimethyl-lævulic acid*, m. p. 77—78° (*semicarbazone*, m. p. 173°; p-*nitrophenylhydrazone*, m. p. 207°; *piperonylidene* derivative, m. p. 115°), identical with the acid obtained from the less fusible semicarbazone. Methyl mesityl oxide (*semicarbazone*, m. p. 186°), prepared from trimethylacrylyl chloride and zinc methyl iodide, when condensed with potassium cyanide gave chiefly a nitrogenous *substance*, $C_9H_{15}O_3N$, m. p. 238° (decomp.), probably $\begin{array}{l}CMe_2\cdot CHMe\\ CO\text{———}NH\end{array}\!\!>CMe\cdot CO_2H$ (A), and a very small quantity of the *semicarbazone* of ααβ-trimethyl-lævulic acid, m. p. 175°, insufficient for conversion into the solid acid.

By the oxidation of αββ-trimethyl-lævulic acid with alkaline permanganate γ-keto-αββ-trimethylglutaric acid, m. p. 119° (quinoxaline derivative, m. p. 223—224°), was obtained; this yielded αββ-trimethylglutaric acid when heated with hydriodic acid and red phosphorus, trimethylsuccinic acid and carbon monoxide when heated alone, and was identical in all respects with the acid $C_8H_{12}O_5$ prepared by Balbiano from camphoric acid (A., 1894, i, 614). This establishes the keto-formula first suggested by Mahla and Tiemann (A., 1895, i, 678) and disproves the original oxide formula of Balbiano.

Attempts to prepare γ-keto-ααβ-trimethylpropane-αγ-dicarboxylic acid by the oxidation of ααβ-trimethyl-lævulic acid or of the *lactone* of α′-*hydroxy*-ααβ-*trimethylglutaric acid*, m. p. 110° (synthesised by the action of hydrocyanic acid on the semi-aldehyde of trimethylsuccinic acid followed by the hydrolysis of the resultant lactonic nitrile with concentrated hydrochloric acid), with alkaline permanganate gave only trimethylsuccinic acid. Condensation of ethyl chloroacetate with ethyl dimethylacetoacetate in the presence of sodium ethoxide gave the oxidic *ester*, $CO_2Et\cdot CMe_2\cdot CMe\cdot CH\cdot CO_2Et$, b. p. 162°/26 mm., from which no definite compound was isolated on hydrolysis and distillation. I. VOGEL.

Synthesis of glyceric acid-monophosphoric acid. C. NEUBERG, F. WEINMANN, and M. VOGT (Biochem. Z., 1928, **199**, 248—252).—Glyceric acid-monophosphoric acid was prepared by the action of 2 mols. (*i.e.*, an excess) of ethyl metaphosphate on glyceric acid; it was isolated as the normal *barium* salt in a yield of 17% of the theoretical. The *monobarium* salt ($C_3H_5O_7PBa$) was prepared from the normal salt by acidification with hydrobromic acid. By means of the *brucine* salt the acid was resolved into its optical antipodes. J. H. BIRKINSHAW.

Walden inversion. H. N. K. RØRDAM (J.C.S., 1928, 2447—2453; cf. Holmberg, A., 1926, 384; 1927, 1169).—It is assumed that the inversion takes place in two steps, (*a*) a spontaneous elimination of one group and (*b*) the addition of another group X, during which period the remainder of the molecule is capable of rotation. The application of the activity factor of Bronsted (A., 1922, ii, 699) to this conception leads to the equation $n=kc_xf_1f_x/f_{1,x}$, where n is the fraction of the reaction product retaining its original steric configuration, c_x the mean concentration of X at the beginning and at the end of the reaction, f_1, f_x, and $f_{1,x}$, respectively, are the activity coefficients of the oscillating molecule, of X, and of the compound resulting from the union of these two, whilst k is a constant. The equation is applied to the reaction between salts of *l*-bromosuccinic acid and alkali xanthates (Holmberg, *loc. cit.*) and also to the reaction between hydrosulphides and salts of *l*-bromosuccinic acid (Holmberg, Arkiv Kemi, Min., Geol., 1915, **6**, 1). Various assumptions are made as to the values of the

activity coefficients and of k and fair agreement is obtained between theory and experiment.

I. VOGEL.

Stereochemical studies. XVIII. Nitromalic acids. XIX. Diazotisation of aspartic acid and its ethyl ester. B. HOLMBERG (Ber., 1928, 61, [*B*], 1885—1892, 1893—1905).—XVIII. dl-*Nitromalic acid* [*nitro-oxysuccinic acid*], $CO_2H\cdot CH(O\cdot NO_2)\cdot CH_2\cdot CO_2H$, m. p. 132—133° (decomp.), is prepared by the action of sulphuric acid on a mixture of *dl*-malic acid and nitric acid (d 1·45) at 0°. Attempts to resolve it by *d*-phenylethylamine yielded only the corresponding *salt* ($+2H_2O$). l(—)-*Nitromalic acid*, m. p. 114—115° (decomp.), $[\alpha]_D$ —36·8°, —38·6°, —42·8°, —23·1° in alcohol, acetone, ethyl acetate, and water, respectively, is prepared similarly from *l*(—)-malic acid. The *sodium hydrogen*, $[\alpha]_D$ —26·7° in water, *di-sodium*, $[\alpha]_D$ —10·5° in water, *barium*, and *silver* salts are described. The ethyl ester has d_4^{20} 1·202, $[\alpha]_D^{20}$ —30·55°. Reduction of the acid by sodium amalgam or of the acid or ester by hydrogen sulphide affords almost homogeneous *l*-malic acid. The action of alkali hydroxide gives mainly fumaric acid. It could not be caused to react with sodium iodide in acetone or potassium xanthate in water. Racemisation under the influence of nitrates or formation of a lactone from normal nitromalates could not be established. Hydrolytic fission of *l*(—)-nitromalic acid does not proceed simply, since it is accompanied by auto-oxidation leading to carbon dioxide and unidentified products. The action of water appears to cause inversion and the production of *d*(+)-malic acid, whereas hydrolysis catalysed by hydrogen or copper ions gives *l*(—)-malic acid. Alkali bromosuccinates do not appear to react with nitrates, but the *l*(—)-acid, with the nitrate ion in presence of silver ions, affords *l*(—)-nitromalic acid; the interpretation of the change is uncertain with respect to the configuration of the acids.

XIX. The optical activity of the malic acid produced by diazotisation of (+)-aspartic acid varies greatly with the hydrogen-ion concentration of the solution. If this is sufficiently great, a change predominates which results in the formation of *l*(—)-malic acid, whereas with lower hydrogen-ion concentration the simultaneous occurrence of a reaction affording *d*(∓)- or *r*-malic acid is obvious. If the aspartic acid is added to a moderately concentrated solution containing an excess of nitrite, an unexpectedly strongly lævorotatory malic acid is produced which is attributed to the production of β-nitronitrosopropionic acid and a nitrous ester of *l*-malic acid. Addition of sodium nitrate to the solution causes the production of *l*(—)-nitromalic acid in amount too small to influence the optical results. The yields decrease with decreasing acidity of the mixture, but a parallel diminution of the lævorotation of the acid is not observed. Similar results are obtained by the addition of chlorides with respect to the (—)-chlorosuccinic acid produced, but experiments with sulphates afford no conclusive evidence of the participation of the sulphate ion. Diazotisation of ethyl *d*(+)-aspartate gives an inactive or a very feebly dextrorotatory malic acid, according to the concentration of mineral acid in the solution. In presence of the corresponding normal salts, the esters of the nitromalic, chloro- and bromo-succinic acids show the same qualitative behaviour, but the halogen esters are much more strongly active than the nitro-compound.

The production of substituted succinic acids by the diazotisation of aspartic acid definitely involves two antipodal reactions in addition to the production of inactive materials through diazosuccinic ester. Experiments with the latter ester do not give support to the hypothesis of its existence in stereoisomeric forms. It is difficult to determine the extent to which inactive products arise from the corresponding diazosuccinic acid from aspartic acid.

The mechanisms of the diazo-reactions and of the conversion of halogenosuccinic into aminosuccinic acids are discussed in detail. It is concluded that the (+)-halogenosuccinic acids are configuratively related to the (—)-hydroxy-acids and are therefore *l*-forms and that natural (+)-aspartic acid has the *lævo*-configuration. With regard to the latter, the author is in agreement with Freudenberg and Noe (A., 1926, 53), but differs from Freudenberg and Lux (this vol., 735) in respect of the halogenosuccinic acids.

H. WREN.

Bromination of tetraethyl dicarboxyglutaconate and the constitution of glutaconic acids. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 8, 200—207; cf. A., 1927, 1059).—Addition of two atoms of bromine to ethyl αγ-dicarbethoxyglutaconate occurs almost instantaneously and is immediately followed by elimination of 1 mol. of hydrogen bromide, the removal of which is completed by treatment with pyridine, the final product being ethyl α-bromo-αγ-dicarbethoxyglutaconate, $CBr(CO_2Et)_2\cdot CH{:}C(CO_2Et)_2$ (Faltis and Pirsch, A., 1927, 856). This is hydrolysed by boiling aqueous-alcoholic hydrochloric acid for 3—4 hrs. to yield *α-chloroglutaconic acid*, m. p. 155°, in accordance with the scheme $>CBr\cdot CH{:}C< \longrightarrow >CBr\cdot CH_2\cdot CCl< \longrightarrow >C{:}CH\cdot CCl<$. Addition of bromine to ethyl α-methyl-αγ-dicarbethoxyglutaconate is not complete, the equilibrium $C_{16}H_{24}O_8Br_2$ being established, since in this case elimination of hydrogen bromide is not possible. The isolated dibromo-compound eliminates bromine spontaneously to re-establish this equilibrium. Since the equivalence of the α- and γ-positions in glutaconic acid derivatives (Thorpe, J.C.S., 1905, 87, 1669) depends on reactions involving hydrolysis with concentrated hydrochloric acid, the author doubts the validity of this evidence and regards the postulated existence of a normal form as unnecessary, only one form of glutaconic acid being considered stable.

J. W. BAKER.

Constitution of aldehyde and ketone hydrogen sulphites. II. G. SCHROETER [with M. SULZBACHER] (Ber., 1928, 61, [*B*], 1616—1627; cf. A., 1926, 1226).—The failure of Raschig and Prahl (this vol., 273) to repeat the author's quantitative hydrolysis of phenyl propane-ββ-disulphonate to phenol, barium sulphite, and barium β-hydroxypropane-β-sulphonate is attributed to the use of barium hydroxide containing barium chloride, which greatly affects the analytical results. Treatment of the barium salt with the requisite amount of sulphuric

acid followed by neutralisation of the liberated acid with freshly-precipitated copper oxide readily yields homogeneous *copper* β-*hydroxypropane*-β-*sulphonate* (*anhydrous* and *trihydrate*). Raschig's purification of this compound by crystallisation from acetic acid is unfortunate, since it leads to *copper* β-*acetoxypropane*-β-*sulphonate*. The presence of the hydroxyl group in β-hydroxypropane-β-sulphonic acid is further established by the conversion of its sodium salt by an excess of phosphorus pentachloride into Δ^{α}-*propene*-β-*sulphonyl chloride*, b. p. 90—100°/17 mm., converted by methylaniline into Δ^{α}-*propene*-β-*sulphonmethylanilide*, m. p. 58—59°, regarded by Autenrieth as Δ^{α}-propene-α-sulphonmethylanilide. Gentle treatment of β-hydroxypropane-β-sulphonic acid or its sodium salt with 1 mol. of phosphorus pentachloride affords β-*hydroxypropane*-β-*sulphonyl chloride*, whence β-*hydroxypropane*-β-*sulphonethylanilide*, m. p. 44·5—45°. The difference between sodium β-hydroxypropane-β-sulphonate and "acetone sodium bisulphite" is therefore regarded as definitely established. Since the latter compound cannot be regarded as a sulphurous ester, its unitary formulation is no longer possible. It is therefore assumed that the known, labile, additive compounds of aldehydes and ketones with sulphur dioxide unite with water to more stable trimolecules $(R_2C{:}O),(SO_2),(H{\cdot}OH)$ which behave as monobasic acids, giving salts in which the character of the individual components is masked unless dissociation occurs, since their molecular valencies are mutually saturated.

Phenyl propane-ββ-disulphonate with 1 mol. of barium hydroxide gives unchanged material, barium propane-ββ-disulphonate, phenol, sulphurous acid, and β-hydroxypropane-β-sulphonic acid, which is partly transformed into the lactide. Hydrolysis of propane-ββ-disulphonethylanilide with 1 mol. of barium hydroxide affords mainly ethylaniline and *barium propane*-ββ-*disulphonate* $(+2H_2O)$; with an excess of the hydroxide, barium β-hydroxypropane-β-sulphonate is also formed in considerable amount. Similarly, butane-ββ-disulphonethylanilide with equivalent amount and excess of barium hydroxide yields respectively *barium butane*-ββ-*disulphonate trihydrate* almost exclusively or mixed with *barium* β-*hydroxybutane*-β-*sulphonate*. Analogously, *barium* Δ^{δ}-*pentene*-ββ-*disulphonate* $(+3H_2O)$ and *barium* β-*hydroxy*-Δ^{δ}-*pentene*-β-*sulphonate* $(+3H_2O)$ are derived from Δ^{δ}-pentene-ββ-disulphonethylanilide. H. WREN.

Constitution of hydrogen sulphite compounds of aldehydes and ketones. O. STELLING (Cellulosechem., 1928, 9, 100—102; cf. A., 1925, ii, 935).—The absorption band of formaldehyde and acetone hydrogen sulphite compounds is at 4992·0 X., that of the sulphonic acids at 4992·2, whilst that of the metal alkyl sulphites is at 4996·0 and the dialkyl sulphites at 4997·7X. Hence it is concluded that the hydrogen sulphite compounds have the constitution $R_1R_2C(OH){\cdot}SO_3Na$. A critical review of the literature is given. J. W. BAKER.

Aldehydes from acetylenic carbinols. III. Two dimethylhexenals. H. RUPE, A. WIRZ, and P. LOTTER (Helv. Chim. Acta, 1928, 11, 965—971).—The action of acetylene on the sodium derivative of methyl *iso*butyl ketone furnishes *methyl*iso*butylethinylcarbinol*, b. p. 85—87°/80 mm. (*silver derivative*), which when heated with 70% formic acid gives a mixture of 4 parts of γε-*dimethyl*-Δ^{γ}-*hexenal* (I), b. p. 94—96°/80 mm. (*semicarbazone*, m. p. 178—179°; *oxime*, m. p. 53—54°), and 1 part of γε-*dimethyl*-Δ^{β}-*hexenal* (II) (*methyl*iso*butylacraldehyde*), b. p. 102—112°/80 mm. (*semicarbazones*, m. p. about 125° and 147°). Oxidation of (I) with cold alkaline potassium permanganate gives *iso*butyric and acetic acids, whilst (II) furnishes methyl *iso*butyl ketone and a small amount of an acid, m. p. 88—89°. Reduction of a mixture of (I) and (II) with hydrogen in presence of water and a nickel catalyst gives βδ-*dimethylhexaldehyde*, b. p. 93—94°/80 mm., when regenerated from its *semicarbazone*, m. p. 121—122°. H. BURTON.

Auto-oxidation of citronellal. J. ZIMMERMANN (Rec. trav. chim., 1928, 47, 940—941).—When citronella oil or pure citronellal is treated with zinc and then allowed to remain for some time in presence of light and air, zinc formate is produced. The oxidation is almost completely inhibited if the citronellal contains a small amount of phenolphthalein and is stored in brown bottles. H. BURTON.

Action of diazomethane on ketones in presence of catalysts. H. MEERWEIN and W. BURNELEIT (Ber., 1928, 61, [B], 1840—1847).—The possibility of activating strictly homopolar compounds or atomic groups by complex formation is examined in the case of the carbonyl group. A solution of diazomethane in acetone scarcely undergoes decomposition at 0°. If 10—15% of water is added, nitrogen is freely evolved and the reaction continues as diazomethane is further added until about 80% of the equivalent amount has been used. The products of the action are *as*-dimethylethylene oxide (identified as *as*-dimethylethylene glycol), methyl ethyl ketone, probably diethyl ketone and methyl *n*-propyl ketone, and traces of *iso*butaldehyde probably produced secondarily. The change is probably: $Me_2C{:}O \longrightarrow Me_2C\genfrac{}{}{0pt}{}{<O-N}{\;\;CH_2{\cdot}N} \longrightarrow Me_2C\genfrac{}{}{0pt}{}{<O^-}{\;\;CH_2^+} \longrightarrow Me_2C\genfrac{}{}{0pt}{}{<O}{\;\;CH_2}$ and $Me{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.
The formation of higher ketones is due to an analogous reaction of diazomethane with methyl ethyl ketone. Water does not appear to be methylated. Its action cannot be attributed to hydrogen ions, since $0{\cdot}1N$-sodium hydroxide solution behaves analogously. Alcohols appear to behave similarly to but less energetically than water. Methyl alcohol is most active; with increase in mol. wt. and transition from primary to secondary and tertiary alcohols the activity decreases. The products from acetone are the same in alcoholic as in aqueous solution; methylation of the alcohols is scarcely appreciable. Lithium chloride (in $0{\cdot}1N$-solution) enhances the activity of acetone to about the same extent as 10% of water, but reaction ceases after about 70% of the theoretical amount of diazomethane has been introduced. The possible catalytic activity of acids cannot be preparatively tested, but comparison of the behaviour of diazomethane towards hydrochloric and oxalic acids dissolved in acetone and ether indicates that

enhancement of the activity of acetone can be thus induced. H. WREN.

Preparation of acetonecyanohydrin. K. N. WELCH and G. R. CLEMO (J.C.S., 1928, 2629).—Acetonecyanohydrin is obtained in good yield by treatment of a mixture of acetone and aqueous potassium cyanide with 30% sulphuric acid (by wt.) below 20°; it is isolated by extraction with ether and rapidly distilled under diminished pressure (b. p. 81°/15 mm.) (cf. Urich, Annalen, 1872, **164**, 255; Bucherer and Grolee, A., 1906, i, 405). I. VOGEL.

Thiocyanoacetone, its isomerides and polymerides. A. HANTZSCH (Ber., 1928, **61**, [*B*], 1776—1788; cf. this vol., 187).—Mainly a reply to Tcherniac (J.C.S., 1919, **115**, 1071; this vol., 530). The conversion of thiocyanoacetone into hydroxymethylthiazole is effected by ebullition for 30 min. with 2*N*-hydrochloric acid. The action of bases on thiocyanoacetone has been examined by the author and by Tcherniac under considerably different conditions owing to the presence or absence of water. In anhydrous ether, thiocyanoacetone is converted by ammonia with partial resinification into aminomethylthiazole which is always accompanied by methylthiazolone, formed by the water liberated during closure of the ring. On the other hand, the action of methylamine proceeds without formation of resin or thiazolone, and the unstable, intermediate *compound*, $COMe\cdot CH_2\cdot S\cdot C(NHMe){:}NH$, passes at the atmospheric temperature into methylaminomethylthiazole, m. p. 70°. Aminomethylthiazole exhibits tautomerism in forming two methyl derivatives, $\begin{matrix}S\cdot C(:NH)\\ | \\ CH{=}CMe\end{matrix}\!\!>\!NMe$ and $\begin{matrix}S\cdot C(:NMe)\\ | \\ CH{=}CMe\end{matrix}\!\!>\!NH$, which, according to Traumann, yield exclusively ammonia and methylamine, respectively, when acted on by concentrated hydrochloric acid. Repetition of this work, possibly under more drastic conditions, shows that each compound evolves a mixture of ammonia and methylamine. Tcherniac's observation that methylamine is obtained from methylthiazolone *N*-methyl ether cannot be construed as disproof of its structure or evidence of the constitution $\begin{matrix}S\cdot C(:NMe)\\ | \\ CH{=}CMe\end{matrix}\!\!>\!O$.

Tcherniac's so-called "β-methylrhodim" is bimolecular and therefore not an isomeride of thiocyanoacetone; it is regarded as bimolecular hydroxymethylthiazole. *iso*Methylrhodim is termolecular thiocyanoacetone in which polymerisation is due to the thiocyano-group and hence is to be regarded as *triacetonyl trithiocyanurate*,

$CH_2Ac\cdot S\cdot C\!\!<\!\begin{matrix}N\cdot C(S\cdot CH_2Ac)\\ N{:}C(S\cdot CH_2Ac)\end{matrix}\!\!>\!N$. Its ability to give a *diphenylhydrazone*, *di*-p-*tolylhydrazone*, *semicarbazone*, and *dioxime* is incompatible with Tcherniac's thiazolone formula, since compounds containing the $\cdot CO\cdot NH\cdot$ group do not show ketonic properties. The production of cyanuric acid from "*iso*methylrhodim" in alkaline solution and of trimethylsulphonium iodide and cyanuric acid by the action of alcoholic methyl iodide is direct evidence of the pre-existence of the cyanuric ring in the molecule. The conversion of *iso*methylrhodim into dithiazylamine is simply explained as follows: partial hydrolysis causes removal of one $CH_2Ac\cdot S\cdot$ group as acetonylmercaptan which condenses to Tcherniac's dimethylthiene, $C_6H_8S_2$. The residual cyanuric derivative passes into its tautomeric, ketonic form,

$CO\!\!<\!\begin{matrix}NH\cdot C(S\cdot CH_2Ac)\\ N{=}C(S\cdot CH_2Ac)\end{matrix}\!\!>\!N$ thereby giving the possibility of the production of the thiazole ring. Under further action of hydrochloric acid the cyanuric ring is ruptured with production of the carboxylic acid, $\begin{matrix}Me\cdot NH\\ \| \\ CH\quad S\end{matrix}\!\!>\!C{:}NH\cdot C({:}N\cdot CO_2H)\cdot S\cdot CH_2Ac$, which loses water and carbon dioxide to produce dithiazylamine, $NH\left(C\!\!<\!\begin{matrix}N\cdot CMe\\ \|\\ S{-}CH\end{matrix}\right)_2$ H. WREN.

Three-carbon system. XIX. Homomesitones. A. E. ABBOTT, G. A. R. KON, and R. D. SATCHELL (J.C.S., 1928, 2514—2524).—The four theoretically possible intermolecular condensation products from methyl ethyl ketone, $CH_2Me\cdot CMe{:}CH\cdot COEt$ (I), $CHMe{:}CMe\cdot CH_2\cdot COEt$ (II), $CH_2Me\cdot CMe{:}CMe\cdot COMe$ (III), $CHMe{:}CMe\cdot CHMe\cdot COMe$ (IV) have been synthesised and their mutual relationships elucidated. Alkaline condensing agents gave mixtures of I and II, whilst acid condensing agents gave mixtures of III and IV. Descude's method (A., 1903, i, 735) after slight modification gave III only. The structures of I, III, and IV were confirmed by synthesis. Ketones I and II when treated with sodium ethoxide formed an equilibrium mixture (mobility high; equilibrium reached in 24 hrs. at the ordinary temperature; 67·5% of αβ-compound) identical with the crude homomesitone obtained by the action of sodium ethoxide on methyl ethyl ketone. Similar treatment with III and IV gave half equilibration after a fortnight at the ordinary temperature; complete equilibration was reached only after 9 hrs. at the b. p. of the reagent (mobility low; 17% of αβ-compound). The mobility differences are attributed to the α-methyl group in III and IV which favours the βγ-phase (cf. Kon and Narayanan, A., 1927, 873; Goldberg and Linstead, this vol., 1214).

Methyl ethyl ketone and ethyl α-bromopropionate in the presence of zinc gave *ethyl* β-*hydroxy*-αβ-*dimethyl*-n-*valerate*, b. p. 89—90°/13 mm., $d_4^{19\cdot5}$ 0·96457, $n_D^{19\cdot5}$ 1·4319. The liquid acid obtained by alkaline hydrolysis on dehydration with acetic anhydride gave poor yields of αβ-*dimethyl*-Δ^{α}-*pentenoic acid*, b. p. 116°/18 mm., $d_4^{17\cdot5}$ 0·97497, $n_D^{17\cdot5}$ 1·45952, $[R_L]_D$ 36·06 (p-*toluidide*, m. p. 123°), the *chloride*, b. p. 66°/17 mm., of which reacted with zinc methyl iodide to give γδ-*dimethyl*-Δ^{γ}-*hexen*-β-*one* (III), b. p. 65°/20 mm., $d_4^{17\cdot4}$ 0·86856, $n_D^{17\cdot4}$ 1·45283, $[R_L]_D$ 39·23. Ethyl β-hydroxy-αβ-dimethyl-*n*-valerate was readily dehydrated by phosphoryl chloride in benzene, giving *ethyl* αβ-*dimethyl*- -*pentenoate*, b. p. 69°/13 mm., $d_4^{21\cdot1}$ 0·92379, $n_D^{21\cdot1}$ 1·43628, from which was prepared the *acid*, b. p. 116°/20 mm., $d_4^{19\cdot7}$ 0·97002, $n_D^{19\cdot7}$ 1·4498, $[R_L]_D$ 35·50 (p-*toluidide*, m. p. 56°), and the *acid chloride*, b. p. 52°/13 mm. The last-named compound with zinc (better magnesium) methyl iodide gave γδ-*dimethyl*-Δ^{δ}-*hexen*-β-*one* (IV), b. p. 48°/12 mm.,

154°/750 mm., d_4^{19} 0·85385, 1·43768, $[R_L]_D$ 38·74. Similarly, the chloride of β-methyl-β-ethylacrylic acid (Kon and Linstead, A., 1925, i, 506) and zinc ethyl iodide gave *ε-methyl-Δ^δ-hepten-γ-one* (I), b. p. 66°/18 mm., 53—54°/8 mm., $d_4^{21·5}$ 0·85516, $n_D^{21·5}$ 1·45073, $[R_L]_D$ 39·69.

*Ethyl β-keto-α-acetyl-αδ-dimethyl-Δ^δ-*n*-heptenoate*, $CHMe{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}CMe(CO_2Et){\cdot}COMe$, b. p. 158—168°/19 mm., obtained by condensation of β-methyl-Δ^{β}-pentenoyl chloride with ethyl sodiomethylaceto-acetate in ethereal solution gave on alkaline hydrolysis an equilibrium mixture of I and II from which II was isolated by treatment with aluminium amalgam, whereby I became converted into a bimolecular reduction product and *ε-methyl-Δ^ε-hepten-γ-one* (II), b. p. 63°/19 mm., $d_4^{21·2}$ 0·85244, $n_D^{21·2}$ 1·43668, $[R_L]_D$ 38·73 (*semicarbazone*, m. p. 134°). Ketones IV, III, and I each gave a pair of *semicarbazones*, m. p. 203—204° and 163°, 186° and 166—167°, and 162° and 158° (Blaise and Maire, A., 1909, i, 85), respectively, indicating their possible existence in *cis*- and *trans*-forms. R. J. W. LE FÈVRE.

Synthesis of acetylmethylcarbinol and its two homologues and their odour. T. HIGASI and S. MARAYAMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 940—947).—Acetylmethylcarbinol, prepared either by the reduction of diacetyl, or by hydrolysis of methyl α-bromoethyl ketone, or the corresponding acetate, has a faint agreeable odour, quite unlike that characteristic of Japanese saké and has no influence on the odour of these fermentation products. Its homologues have similar odours. J. W. BAKER.

Hantzsch and Werner's stereochemical hypothesis in comparison with experimental facts and the constitution of isomeric oximes. G. MINUNNI (Gazzetta, 1928, 58, 504—521).—The constitution of isomeric oximes is discussed in relation to results published within the last few years, these emphasising the author's view that Hantzsch and Werner's hypothesis of geometrical isomerism is not only unnecessary, but also incapable of explaining the existence of known isomeric oximes. This hypothesis is not in accord with the author's observation that the acetyl and benzoyl derivatives of α-aldoximes undergo ready transformation into nitriles. The author's view that isomerism of the oximes is structural in character (A., 1891, 1354) is supported by the existence of five isomeric dioximes of *p*-methoxybenzil (cf. Ponzio and Bernardi, A., 1924, i, 293; Meisenheimer, Lange, and Lamparter, A., 1925, i, 1073) and by the fact that mesityl oxide and its isocyclic analogue, methyl*cyclo*hexenone, each form two isomeric oximes. T. H. POPE.

Action of alkali and carbon disulphide on xylan. E. HEUSER and G. SCHORSCH (Cellulosechem., 1928, 9, 93—100).—Treatment of xylan with 4—14·5% sodium hydroxide solution and precipitation and washing the sodium *compound* three times with 20 c.c. of 96% alcohol in accordance with the technique of Karrer (A., 1921, i, 231) yields an alkali xylan containing the same proportion of sodium; the value closely approximates to that required by the compound $(C_5H_8O_4)_2,NaOH$, the alkali being determined either by titration or, for more trustworthy results, as sodium sulphate. Further washing with 96% alcohol causes a diminution in the sodium content, since the compound decomposes: $(C_5H_8O_2)_2,NaOH - (C_5H_8O_2)_2 + NaOH$. In the case of cellulose a compound containing the theoretical proportion of sodium is formed only with alkali concentrations between 15 and 30%; at lower concentrations the proportion of sodium in the product increases with increasing concentration of sodium hydroxide solution employed. Washing the alkali xylan with water causes a rapid decrease in the sodium content, whilst with varying concentrations of alcohol the loss of alkali is more rapid the more dilute is the alcohol, the sodium content tending to reach an equilibrium value. Washing with methyl alcohol or glycol gives results intermediate between those obtained with water and alcohol. A resinous product is obtained by the action of cold alcohol on xylan treated with 20% sodium hydroxide, or of alcohol at 70° on xylan treated with 12% sodium hydroxide solution. Similar treatment of xylan with sodium sulphide solution and washing until the filtrate is free from sulphur gives a product the sodium and sulphur content of which varies according to the concentration of alkali sulphide solution used. With potassium hydroxide the theoretical *compound* is obtained only with more concentrated alkali (8—12%), and then, like the sodium compound, the potassium content decreases if washed more than three times with alcohol. The lithium *compound* is more stable and requires ten washings to remove the excess of alkali, whilst the rubidium *compound* is stable only to four washings. Treatment of the unwashed alkali xylan (containing excess of alkali) with carbon disulphide yields a "xylan viscose," the viscosity of which, unlike that of cellulose viscose, decreases only slightly with time and is not coagulated after keeping for one month. A product free from combined sodium and sulphur compounds is obtained by neutralising the "viscose" with dilute acetic acid, precipitation and trituration of the product with alcohol, washing with ether, and drying over phosphoric oxide. The proportion of sulphur in the product so obtained varies slightly with the period of treatment with alkali and carbon disulphide, but is always much lower than that required by any of the possible cellulose xanthates, and, moreover, the proportion of sodium and sulphur present is less when xylan free from copper salts and ash is used. Hence the formation of the "xylan viscose" does not depend on xanthate formation, but involves merely a dissolution of sodium and sulphur compounds in the xylan. The action of alkali on xylan involves a chemical (hydrolysis) and not a physical degradation, since the proportion of xylan in the "viscose" compound determined as furfuraldehydephloroglucide is much less than that estimated from the carbon content determined by oxidation with potassium dichromate and sulphuric acid. Xylan regenerated from the "viscose" obtained by long keeping with alkali and carbon disulphide has a lower carbon and a higher hydrogen content than the original xylan. J. W. BAKER.

Colour tests for simple sugars. S. Y. WONG (Chinese J. Physiol., 1928, 2, 255—257).—By using

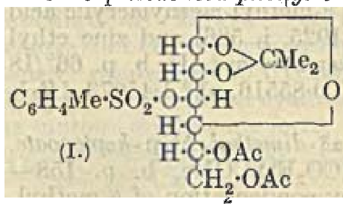
glacial acetic acid instead of water or alcohol as solvent for the reagents of Molisch, Selivanov, and Tollens, their specificity and keeping power are enhanced. With 3 c.c. of such a 0·3% solution and 3 drops of a 1% sugar solution in the case of: (*a*) α-naphthol, 1 c.c. of sulphuric acid gives a pink to purple ring, which on heating, if the sugar be lævulose, gives a deep violet colour, or rhamnose an orange-red readily distinguished from the cherry-red of xylose and the much weaker reddish-violet of arabinose, whilst dextrose and galactose give only a faintly coloured solution; (*b*) resorcinol and 0·5 c.c. of hydrochloric acid when heated with lævulose, sucrose, or inulin give a red colour almost immediately, but scarcely any colour with the others after 1 min.; (*c*) phloroglucinol and 0·5 c.c. of hydrochloric acid on boiling with pentoses, gum-arabic, or yeast-nucleic acid readily give a cherry-red colour, whilst rhamnose gives only a yellow colour; (*d*) orcinol and 1 c.c. of hydrochloric acid (containing 5 drops of 10% ferric chloride per 100 c.c.), on boiling, give with pentoses, gum-arabic, and yeast-nucleic acid, but not with rhamnose, a greenish-blue colour. L. C. BAKER.

Colour reactions of carbohydrates. L. EKKERT (Pharm. Zentr., 1928, **69**, 597—600).—Colour reactions of arabinose, xylose, rhamnose, dextrose, mannose, galactose, lævulose, sucrose, lactose, maltose, dextrin, glycogen, and soluble starch with resorcinol, α- and β-naphthol, morphine, codeine, phenacetin, and α-naphthylamine in presence of sulphuric acid are described. E. H. SHARPLES.

Rotatory dispersion of sugars. T. WAGNER-JAUREGG (Helv. Chim. Acta, 1928, **11**, 786—789).—Solutions of αβ-glucose, αβ-galactose, αβ-fructose, αβ-arabinose, α-methylglucoside, α-phenylglucoside, and β-pentamethylglucose in water, and β-pentaacetylglucose in chloroform, show simple dispersion, whilst β-pentamethylglucose in chloroform exhibits complex dispersion. H. BURTON.

Degradation of dextrose by oxidation. III. B. BLEYER and W. BRAUN (Biochem. Z., 1928, **199**, 186—194).—In the oxidation of dextrose with chloroamine in alkaline solution the end-products are acetic acid and carbon dioxide. The full acidity (or decrease in alkalinity) is produced before the oxidation is complete. The evidence points to pyruvic acid as the intermediate product; this is supposed to arise from the hydrolysis of gluconic acid, the first step in the oxidation. The other intermediate product should be methylglyoxal; however, an attempt to oxidise this in alkaline solution with chloroamine was not successful. It is suggested that the hydrolysis product is a more active labile form. J. H. BIRKINSHAW.

Acetone [*iso*propylidene] derivatives of sugars and their transformation products. XII. Displacement of the oxygen bridge during the action of hydrogen bromide–glacial acetic acid on acyl derivatives of monoacetoneglucose [glucose *iso*propylidene ether]. H. OHLE and H. ERLBACH (Ber., 1928, **61**, [*B*], 1870—1875; cf. A., 1926, 1126).—3-*p*-Toluenesulphonyl*iso*propylideneglucose is converted by acetic anhydride in the presence of pyridine into 3-p-*toluenesulphonyl*-5 : 6-*diacetyliso*propylidene-d-*glucose* (I), m. p. 85—86°, $[\alpha]_D^{20}$ −16·96° in chloroform; indications of the production of an isomeride, m. p. 78·5°, $[\alpha]_D^{20}$ −16·17° in chloroform, are obtained.


(I.)

Its constitution is deduced from its mode of production and from its alkaline hydrolysis to *iso*propylideneglucose. It is transformed by hydrogen bromide in glacial acetic acid into 1-*bromo*-3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-d-*glucose*, m. p. 140° after darkening at 115° and softening at 135°, $[\alpha]_D^{20}$ −198·9° in chloroform, converted by methyl alcohol and silver carbonate into 3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-β-*methylglucoside*, m. p. 128°, $[\alpha]_D$ −64·25° in chloroform, which differs from the analogous compound obtained by Freudenberg and Ivers from 3-*p*-toluenesulphonyldi*iso*propylideneglucose and by Ohle and Spencker from 3-*p*-toluenesulphonyl*iso*propylideneglucose. If too much acetone is used in the crystallisation of 1-bromo-3-*p*-toluenesulphonyl-2 : 5 : 6-triacetylglucose, the compound loses hydrogen bromide and forms 3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-α-*glucose*, m. p. 129·5°, $[\alpha]_D^{20}$ +62·97° to +40·65° in chloroform. 3-p-*Toluenesulphonyl*-2 : 4 : 6-*triacetylglucose* has m. p. 178·5—179°, $[\alpha]_D^{20}$ +40·11° to +51·48° in chloroform.

The applicability of hydrogen bromide and glacial acetic acid for the examination of the relative stability of the ring structure of a sugar and its derivatives is examined theoretically. H. WREN.

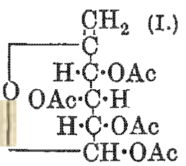
Acetone [*iso*propylidene] derivatives of sugars and their transformation products. XIII. Behaviour of completely acylated derivatives of monoacetoneglucose [glucose *iso*propylidene ether] towards hydrogen bromide–glacial acetic acid. K. OHLE, H. ERLBACH, and H. VOGL (Ber., 1928, **61**, [*B*], 1875—1885; cf. A., 1926, 1126).—The acyl derivative of *iso*propylideneglucose can be divided into two groups according to their behaviour towards hydrogen bromide–glacial acetic acid. 3-Benzoyl*iso*propylidene-, 3-benzoyldi*iso*propylidene-, 3-*p*-toluenesulphonyl-mono- and -di-*iso*propylidene-, 6-benzoyl*iso*propylidene-, 6-*p*-toluenesulphonyl-mono- and -*iso*di-*iso*propylidene-, 6-benzoyl-5-*p*-toluenesulphonyl*iso*propylidene-, 5 : 6-di-*p*-toluenesulphonyl*iso*propylidene-, triacetyl- and tribenzoyl-*iso*propylidene-glucose give characteristic colour reactions and compounds with firmly-combined bromine, whereas 3-*p*-toluenesulphonyl-5 : 6-dibenzoyl-, 3 : 5-di-*p*-toluenesulphonyl-6-benzoyl-, tri-*p*-toluenesulphonyl-, 5-*p*-toluenesulphonyl-3 : 6-anhydro-, and [3-*p*-toluenesulphonyl-5 : 6-diacetyl]-*iso*propylideneglucose do not exhibit this behaviour. Examination of the optical data of related derivatives of furoid glucose in the light of Hudson's rules shows that the principle of optical superposition is limited to compounds of similar constitution which exhibit only steric differences.

*iso*Propylideneglucose is converted with difficulty by *p*-toluenesulphonyl chloride in pyridine and chloroform at 36° into *tri*-p-*toluenesulphonyliso*-

propylidene-α-glucose, m. p. 95—96°, $[\alpha]^{19}$ −5·15° in chloroform, which is transformed by hydrogen bromide and glacial acetic acid into the unstable 1-*bromo*-3 : 5 : 6-*tri*-p-*toluenesulphonyl*-2-*acetyl*-d-*glucose*, m. p. 124—125°, $[\alpha]^{19}_{D}$ +124·5° in chloroform, conveniently isolated as the additive *product* with 1 mol. of benzene, m. p. 106·5—108° (decomp.), $[\alpha]^{20}_{D}$ +114·5° in chloroform. The latter compound is converted by methyl alcohol and silver carbonate into 3 : 5 : 6-*tri*-p-*toluenesulphonyl*-2-*acetyl*-β-*methylglucoside*, m. p. 129·5°, $[\alpha]^{20}$ −8·9° in chloroform. Successive treatment of tri-*p*-toluenesulphonyl*iso*propylideneglucose with hydrogen bromide and acetic acid and with acetone and silver carbonate affords 2-*acetyl*-3 : 5 : 6-*tri*-p-*toluenesulphonylglucose*, m. p. 117—118°, $[\alpha]^{20}_{D}$ +51·09° to +37·2° in chloroform. 3 : 5-Di-*p*-toluenesulphonyl-6-benzoyl*iso*propylideneglucose similarly affords 1-*bromo*-3 : 5-*di*-p-*toluenesulphonyl*-2-*acetyl*-6-*benzoyl*-d-*glucose*, m. p. 159—160°, $[\alpha]^{20}_{D}$ +156·6° in chloroform, 3 : 5-*di*-p-*toluenesulphonyl*-2-*acetyl*-6-*benzoyl*-β-*methylglucoside*, m. p. 105°, $[\alpha]^{20}_{D}$ −4·16°, and 3 : 5-*di*-p-*toluenesulphonyl*-2-*acetyl*-6-*benzoyl*-d-*glucose*, m. p. 139°, $[\alpha]^{20}_{D}$ +69·2° to +46·33° in chloroform. 3-*p*-Toluenesulphonyl-5 : 6-dibenzoyl*iso*propylideneglucose is transformed into a very unstable acetylated bromide which yields 3-p-*toluenesulphonyl*-2-*acetyl*-5 : 6-*dibenzoyl*-β-*methylglucoside*, m. p. 132·5°, $[\alpha]^{20}_{D}$ −74·3° in chloroform, and 3-p-*toluenesulphonyl*-2-*acetyl*-5 : 6-*dibenzoyl*-d-*glucose*, m. p. 122°, $[\alpha]^{20}_{D}$ +3·55° to −20·52° in chloroform.

H. WREN.

New unsaturated anhydroglucose. B. HELFERICH and E. HIMMEN (Ber., 1928, **61**, [*B*], 1825—1835).—Acetyldibromoglucose dissolved in acetic anhydride is converted by concentrated sulphuric acid into *α-tetra-acetyl*-d-*glucose*-6-*bromohydrin*, m. p. 172—173° (corr.) after softening at 171°, $[\alpha]^{25}$ +108·5° in ethyl acetate, $[\alpha]^{24}_{D}$ +110·6° in chloroform, transformed by sodium iodide in acetone at 100° into *α-tetra-acetyl*-d-*glucose*-6-*iodohydrin*, m. p. 182° (corr.), $[\alpha]_{D}$ +102·0° in chloroform. The latter compound is converted by technical silver fluoride (containing subfluoride and oxide) in presence of pyridine into the unsaturated anhydroglucose derivative (I), for which the name *α-tetra-acetyl*-d-*glucoseen* is proposed; it has m. p. 115—116° (corr.), $[\alpha]^{22}_{D}$ +110·9° in chloroform.


(I.)

β-Tetra-acetyl-*d*-glucose-6-iodohydrin similarly affords β-*tetra-acetyl*-d-*glucoseen*, m. p. 119° (corr.), $[\alpha]^{22}_{D}$ −35·0° in chloroform. 2 : 3 : 4-Triacetyl-α-methyl-*d*-glucoside is converted by *p*-toluenesulphonyl chloride in pyridine into the corresponding 6-p-*toluenesulphonate*, m. p. 77—78·5° (corr.), hydrolysed by Zemplen's method to *p*-toluenesulphonyl-*d*-methylglucoside and converted by sodium iodide in acetone at 130° into *triacetyl-α-methyl*-d-*glucoside*-6-*iodohydrin*, m. p. 150—151° (decomp.), $[\alpha]^{24}_{D}$ +116·3° in chloroform. From the latter compound *triacetyl-α-methyl*-d-*glucoseenide*, m. p. 100—101° (corr.) after softening at about 98°, $[\alpha]_{D}$ +123·8° in chloroform (also +0·5MeOH), is derived. Ozonisation of triacetyl-α-methyl-*d*-glucoseenide in glacial acetic acid followed by reduction of the ozonide and peroxide with zinc dust yields *triacetyl-α-methyl*-d-*xyluronic acid*, $C_{12}H_{16}O_9$, m. p. 83—84°, $[\alpha]^{18}_{D}$ +92·0° in chloroform. *Triacetyl-β-methyl*-d-*glucoseenide*, prepared from triacetyl-β-methyl-*d*-glucoside-6-iodohydrin, has m. p. 92—93° (corr.), $[\alpha]^{20}_{D}$ −34·8° in chloroform; silver fluoride in its preparation may be replaced by silver sulphate or, less advantageously, by silver acetate and pyridine by acetonitrile or methyl alcohol (which causes some production of the 6-methoxy-derivative). The compound readily absorbs 1 mol. of hydrogen in acetic acid in presence of spongy platinum. It instantaneously decolorises bromine, giving an unstable additive product, whereas the corresponding *dichloride*, $C_{13}H_{18}O_8Cl_2$, m. p. 129·5—132° (corr.), is readily isolated. Triacetyl-β-methyl-*d*-glucoseenide is hydrolysed by sodium methoxide to β-*methyl*-d-*glucoseenide*, $C_7H_{12}O_5$, m. p. 109—110° (corr.), $[\alpha]^{25}$ 115·5° in aqueous solution. The compound does not reduce Fehling's solution. It is very sensitive to acids and is easily re-acetylated to the original compound. Solutions of hydrolysed β-methyl-*d*-glucoseenide give with phloroglucinol and hydrochloric acid, orcinol, pyrogallol, aniline, and *m*-nitroaniline colorations very closely resembling those of certain components of wood or of lignin itself. Since unsaturated substances are present in wood, it is possible that glucoseen is related to the transition products between dextrose and lignin or the compounds from which lignin arises biologically.

H. WREN.

New *h*-fructose anhydride. H. H. SCHLUBACH and H. ELSNER (Naturwiss., 1928, **16**, 772).—From the syrup obtained by the action of acetone on lævulose (Irvine and Garrett, J.C.S., 1910, **97**, 1282) is isolated, in addition to 2 : 3-*iso*propylidenefructose, a 1 : 2-h-*fructose anhydride*, which by methylation is converted into 3 : 4 : 6-trimethyl-γ-fructose, identical with that obtained by Haworth and Learner (this vol., 510) from inulin, and a *di*-h-*fructose* which readily yields a *difructose anhydride*.

J. W. BAKER.

Halogenohydrins of gentiobiose and dextrose. B. HELFERICH and H. COLLATZ (Ber., 1928, **61**, [*B*], 1640—1646; cf. A., 1926, 386).—Acetodibromoglucose is converted by tetra-acetylglucose and silver oxide in the presence of chloroform into *hepta-acetylgentiobiose*-ζ′-*bromohydrin*, $C_{26}H_{35}O_{17}Br$, m. p. 240° (corr.), $[\alpha]^{17}_{D}$ +2·38° in chloroform, from which the hygroscopic *gentiobiose*-ζ′-*bromohydrin*, m. p. 125—130° (decomp.) after softening at about 100°, $[\alpha]^{18}_{D}$ −12·8° in water after addition of sodium borate, is obtained by hydrolysis with the requisite amount of sodium methoxide and removal of sodium as the sulphate. *Acetodibromogentiobiose*, from the ζ′-bromohydrin in chloroform and acetic acid saturated with hydrogen bromide, has m. p. about 193° (decomp.), $[\alpha]^{21}_{D}$ +109·5° in chloroform; it is converted by silver carbonate in moist acetone into *hexa-acetylgentiobiose*-ζ′-*bromohydrin*, $C_{24}H_{33}O_{16}Br$, m. p. 264° (corr.), $[\alpha]^{20}_{D}$ +40·97° in pyridine (final value; the substance is highly mutarotatory and appears initially lævorotatory).

β-Tetra-acetylglucose-6-bromohydrin (cf. Fischer, A., 1920, i, 529) is transformed by sodium iodide in acetone at 100° into β-*tetra-acetylglucose*-6-*iodohydrin*, m. p. 152° (corr.), $[\alpha]^{22}_{D}$ +9·34° in chloroform. The

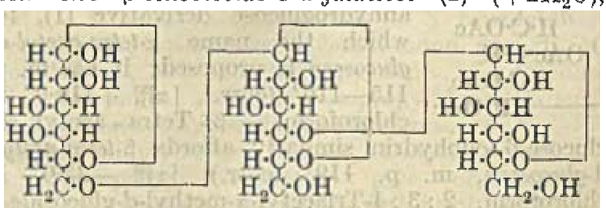
latter substance with hydrogen bromide in glacial acetic acid affords *triacetylglucose*-1-*bromo*-6-*iodohydrin*, m. p. 168—177° (decomp.) according to the rate of heating, $[\alpha]_D^{21}$ +178·9° in chloroform, converted by silver carbonate in moist acetone into β-*triacetylglucose*-6-*iodohydrin*, m. p. 159—160° (decomp.), $[\alpha]_D$ +32·23° to +81·25° in 6 days. *Acetyl*-1 : 6-*di-iodoglucose*, $C_{12}H_{18}O_7I_2$, decomp. about 150° after darkening at 130°, $[\alpha]_D^{21}$ +205·9° in chloroform, is obtained from β-tetra-acetylglucose-6-iodohydrin and hydrogen iodide in glacial acetic acid. H. Wren.

Mechanism of carbohydrate oxidation. X. Action of potassium hydroxide on mannose; comparison with that of dextrose and lævulose. W. L. Evans and D. C. O'Donnell (J. Amer. Chem. Soc., 1928, **50**, 2543—2556).—The action of aqueous potassium hydroxide on mannose at 25°, 50°, and 75° has been studied by the methods previously employed with dextrose, for which revised results are given, and lævulose (cf. this vol., 397, 741). The amounts of pyruvaldehyde, lactic, acetic, and formic acids obtained vary with the alkali concentration in the same general manner with each sugar, although at 25° and 50° the results differ quantitatively. At 75°, however, the proportions of lactic, acetic, and formic acids formed at a given alkalinity are independent of the hexose used. This supports the view that alkaline solutions of these sugars contain equilibrium mixtures which become identical in composition at 75°, but contain different proportions of the same components at lower temperatures. H. E. F. Notton.

Acetone [*iso*propylidene] sugars. XIII. Hydrolysis of certain disaccharides, glucosides, and *iso*propylidene sugars. K. Freudenberg, W. Dürr, and H. von Hochstetter [with H. vom Hove, W. Jacobi, A. Noë, and E. Gärtner] (Ber., 1928, **61**, [*B*], 1735—1743; cf. A., 1927, 230).—The inversion constants of glucosido-β-6-galactose, cellobiose, turanose, maltose, lactose, galactosido-β-6-galactose, melibiose, α- and β-methyl-, α- and β-phenyl-, β-benzyl-glucoside, α- and β-methylgalactoside, and 1 : 2-*iso*propylideneglucose by sulphuric acid at 70° have been determined polarimetrically. Among disaccharides, the two β-glucosides have the smallest and the β-galactosides the highest constants corresponding with the relationship of β-methylglucoside to β-methylgalactoside. Maltose and turanose are more rapidly hydrolysed than cellobiose and glucosido-β-6-galactose, whereas the order is inverted with α- and β-methylglucoside. *iso*Propylideneglucose is much more rapidly hydrolysed than the disaccharides or glucosides. Hydrolysis of the other *iso*propylidene sugars occurs so rapidly that it must be measured in a boiling aqueous, buffered solution followed by titrimetric determination of acetone in the distillate. *iso*Propylideneglucose is most stable. The constants of di*iso*propylidenegalactose are of the same order of magnitude, so that it is impossible to prepare mono*iso*propylidenegalactose by partial hydrolysis of the di-derivative. *iso*Propylidenerhamnose is hydrolysed about ten times as rapidly as *iso*propylideneglucose. With di*iso*propylidenemannose marked progression is observed in the values of the "constant," which is even more obvious with di*iso*propylideneglucose.

The dependence of the production of di*iso*propylideneglucose on the quality of the acetone employed is shown to be due to the high accelerating action of acetaldehyde and acetals. Removal of the εζ-acetone group of di*iso*propylideneglucose is best effected with acetic acid. The sodium derivative of *iso*propylideneglucose is transformed by benzyl chloride into γ-benzyl*iso*propylideneglucose. The benzyl ethers of the sugars appear very stable towards acid and alkali, but may be decomposed by hydrogenation in presence of platinum metals or of sodium amalgam. The crude di*iso*propylidenemethylmannoside of Freudenberg and Hixon (A., 1923, i, 1179) contains a crystalline component, m. p. 40—41°, $[\alpha]_D$ −42°, which appears to belong to the β-series. Levene and Meyer's product (A., 1924, i, 616) and the liquid component of Freudenberg's preparation are regarded as mixtures of the α- and β-forms. The unstable hepta-acetylchloromaltose (A., 1922, i, 524; 1925, i, 635) is a probable intermediate compound in the conversion of octa-acetylmaltose into the ordinary acetylchloromaltose. The following new compounds are described incidentally: γ-*benzyl*iso*propylideneglucose diacetate*, m. p. 119—119·5°, $[\alpha]_D$ −53° in *s*-tetrachloroethane; γ-*methyl*iso*propylideneglucose*, b. p. 173—175°/1 mm. (*dibenzoate*, m. p. 81—82°); iso*propylidenemannose triacetate*, m. p. 59°, $[\alpha]_D$ +49·9° in *s*-tetrachloroethane. H. Wren.

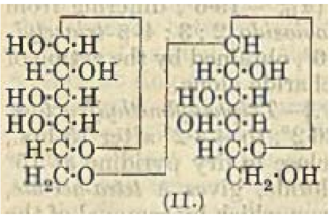
Acetone [*iso*propylidene] sugars. XIV. Syntheses of further di- and tri-saccharides from galactose, dextrose, and mannose. K. Freudenberg, A. Wolf, E. Knopf, and S. H. Zaheer (Ber., 1928, **61**, [*B*], 1743—1750; cf. A., 1927, 230).—The initial value $[\alpha]_D^{18}$ +1·6° (±0·5°) and final value $[\alpha]_D^{18}$ +13·9° (±0·5°) in water for β-galactosido-6-β-galactose are now recorded. Acetylbromocellobiose and di*iso*propylidenegalactose are converted by silver oxide in the presence of chloroform into *hepta-acetylcellobiosidodi*iso*propylidenegalactose*, m. p. 227°, $[\alpha]_D^{18}$ −47·1° in *s*-tetrachloroethane, hydrolysed by aqueous barium hydroxide to the syrupy *cellobiosidodi*iso*propylidenegalactose*, converted by 0·02*N*-sulphuric acid into β-*cellobiosido*-6-α-*galactose* (I) (+$2H_2O$),


(I.)

$[\alpha]_D^{18}$ +24·6° to +9·9° in water during 3 hrs. (calculated for anhydrous substance) [*osazone*, m. p. 207° (decomp.)].

Acetylbromolactose and di*iso*propylidenegalactose afford the non-crystalline *hepta-acetyl-lactosidodi*iso*propylidenegalactose*, converted successively into *lactosidodi*iso*propylidenegalactose*, m. p. 117°, $[\alpha]_D^{18}$ −39·8° in water, and β-*lactosido*-6-*galactose*, $[\alpha]_D^{18}$ +22·2° in water [osazone, m. p. 211° (decomp.)]. Di*iso*propylidenegalactose and acetylbromogalactose yield successively *tetra-acetylgalactosidodi*iso*propylidenegalactose*, m. p. 101—102°, $[\alpha]_D^{16}$ −44·7° in *s*-tetra-

chloroethane, non-crystalline *galactosidodiisopropylidenegalactose*, and β-*galactosido*-6-β-*galactose* (II), $[\alpha]_D$ +23·2° to +34·1° in water during 48 hrs. (*osazone*, m. p. 207° (decomp.)]. Chlorodi*iso*propylidenemannose and di*iso*propylidenegalactose afford *diisopropylidenemannosidodiisopropylidenegalactose*, b. p. 205—210°/1 mm., $[\alpha]_D$ −44·6° in *s*-tetrachloroethane, and thence 6-*mannosidogalactose*, $[\alpha]_D^{20}$ +144° to +134° in aqueous solution during 3 hrs. *Diisopropylidenemannosidodiisopropylidenemannose*, m. p. 180—181°, $[\alpha]_D^{18}$ +84° in *s*-tetrachloroethane, from chlorodi*iso*propylidenemannose and di*iso*propylidenemannose, is converted into the non-crystalline 1-*mannosidomannose*, $[\alpha]_D^{17}$ +53° in water. H. Wren.

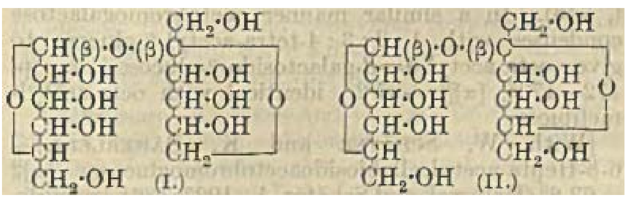


(II.)

Acetone [*iso*propylidene] sugars. XV. Syntheses of disaccharides. K. Freudenberg, H. Toepffer, and C. C. Andersen (Ber., 1928, **61**, [*B*], 1750—1760).—Acetyldibromoglucose is converted into triacetylglucose-ζ-bromohydrin (cf. Fischer and Zach, A., 1912, i, 239), which is hydrolysed by 5% hydrobromic acid to *glucose-ζ-bromohydrin*, m. p. 134° (decomp.), $[\alpha]_D^{16}$ +86·9° to +48·95° in water after 18 hrs. The latter compound is converted by acetone in the presence of concentrated sulphuric acid into a mixture of *diisopropylideneglucose-ζ-bromohydrin*, $C_{12}H_{19}O_5Br$, b. p. 146°/1—2 mm., $[\alpha]_D^{18}$ +42·0° in alcohol, and *isopropylideneglucose-ζ-bromohydrin*, m. p. 87°, $[\alpha]_D^{16}$ −13·1° in water. *Diacetylisopropylideneglucose-ζ-bromohydrin*, m. p. 115°, $[\alpha]^{20}$ −7·11° in *s*-tetrachloroethane, from the latter compound and acetic anhydride in pyridine, is converted by thallium acetate in a mixture of acetic anhydride and acetic acid into triacetyl*iso*propylideneglucose, m. p. 72°. The bromine atom of the di*iso*propylidene derivative could not be smoothly removed by silver acetate or toluenesulphonate, whereas sodium methoxide causes the production of *isopropylideneanhydroglucose*, $C_9H_{14}O_5$, m. p. 126°, $[\alpha]_D^{18}$ −27·1° in water, more conveniently prepared from *iso*propylideneglucose-ζ-bromohydrin and silver oxide in acetone. Acetobromoglucose and *iso*propylideneglucose-ζ-bromohydrin in chloroform are transformed by silver carbonate into *tetra-acetylglucosidomonoacetylmonoisopropylideneglucose-ζ-bromohydrin*, m. p. 161°, $[\alpha]_D^{17}$ −63·6° in *s*-tetrachloroethane, in which the bromine atom could not be replaced by the acetoxy-group. Di*iso*propylideneglucose-ζ-bromohydrin is transformed by sodium iodide in acetone at 100° into *diisopropylideneglucose-ζ-iodohydrin*, m. p. 58°, $[\alpha]_D^{18}$ +30·9° in alcohol, and, similarly, the above bromo-compound is converted into *tetra-acetylglucosidomonoacetylmonoisopropylideneglucose-ζ-iodohydrin*, m. p. 186°, $[\alpha]_D$ −80·8° in *s*-tetrachloroethane, from which *tetra-acetylglucosidoisopropylideneanhydroglucose*, m. p. 126°, is obtained by means of thallium acetate. Treatment of the α- and β-methylglucosides with zinc chloride and benzaldehyde gives benzylidene-α-methylglucoside, m. p. 161—162°, and benzylidene-β-methylglucoside, m. p. 205°. Methylation of these products affords dimethylbenzylidene-α-methylglucoside, m. p. 122—123° (cf. Irvine and Scott, J.C.S., 1913, **103**, 575), and *dimethylbenzylidene-β-methylglucoside*, m. p. 134°, $[\alpha]_D^{22}$ −61·0° in alcohol. 3-Methylglucose is converted by methyl-alcoholic hydrogen chloride into a syrupy mixture of its α- and β-methylglucosides, from which two *benzylidene-3-methyl(methylglucosides)*, m. p. 133°, $[\alpha]_D^{22}$ +49·1° in *s*-tetrachloroethane, and m. p. 164°, $[\alpha]_D^{22}$ −39·1° in *s*-tetrachloroethane, respectively, are derived. Further methylation affords two benzylidenedimethylmethylglucosides identical with the product of methylation of the benzylidene-α-methylglucoside, m. p. 161—162°, and with that of benzylidene-β-methylglucoside. It follows therefore that the 3-hydroxy-group is unsubstituted in the monobenzylidene derivatives of α- and β-methylglucoside. Benzylidene-α-methylglucoside is readily converted by hydrogen in the presence of spongy platinum into α-methylglucoside. A mixture of acetobromoglucose and benzylidene-α-methylglucoside is converted by silver carbonate in presence of chloroform into *tetra-acetylglucosidobenzylidene-α-methylglucoside*, m. p. 232°, $[\alpha]^{25}$ +47° in chloroform, converted by sodium methoxide into *glucosidobenzylidene-α-methylglucoside*, m. p. 245°, whence β-glucosido-2(or 3)-α-methylglucoside, m. p. 252° (decomp.), $[\alpha]_D^{20}$ +62·7° in water, is derived. H. Wren.

Sucrose *B*. A. Pictet and H. Vogel (Helv. Chim. Acta, 1928, **11**, 901—905).—When sucrose is crystallised from aqueous-acetone, -pyridine, -*iso*-propyl alcohol, -ethylene glycol, -glycerol, and -acetaldehyde the *A* form, m. p. 185°, is obtained. The *B* modification, m. p. 171°, is obtained only from aqueous methyl alcohol. The analytical composition, rotation, and octa-acetate of the *B* form are identical with those of the *A* modification, and the conversion of *B* into *A* appears to be instantaneous in water, but is only slow in alcohol. The differences in the two modifications appear to be purely physical (cf. Helderman, A., 1927, 1174). H. Burton.

Sucroses *C* and *D*. A. Pictet and H. Vogel (Helv. Chim. Acta, 1928, **11**, 905—909).—A chloroform solution of equal parts of β-tetra-acetylglucose and tetra-acetylfructose is treated during 14 hrs. with phosphoric anhydride, and the residual product after repeated dissolution in water gives a 15% yield of the *octa-acetate*, m. p. 113—114°, $[\alpha]_D$ −60·8° in chloroform, of *sucrose* C (I), m. p. 104°, $[\alpha]_D$ −24·6° in water. This new sugar is decomposed by warming with traces of alkali, this being the probable cause of its ability to reduce Fehling's and potassium permanganate solutions, but is more resistant to acids than sucrose *A*. Inversion by hot 10% hydrochloric acid gives ordinary invert-sugar.

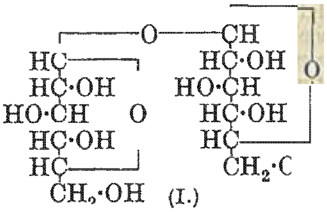


(I.) (II.)

When octa-acetylsucrose *A* is triturated with concentrated hydrochloric acid, neutralised with barium

carbonate, extracted with alcohol, and finally treated with silver carbonate, a mixture of tetra-acetylglucose and -fructose is obtained. When this is treated with phosphoric oxide in chloroform solution the *octa-acetate*, m. p. 125°, $[\alpha]_D$ +20·3° in chloroform, of *sucrose* D (II), m. p. 127°, $[\alpha]_D$ +19·0° in water, is obtained. This sugar is readily hydrolysed by acids giving ordinary invert-sugar, does not reduce Fehling's or potassium permanganate solution, and does not yield an osazone. H. BURTON.

New sugars of trehalose type. H. VOGEL and H. DEBOWSKA-KURNICKA (Helv. Chim. Acta, 1928, **11**, 910—915).—A solution of β-tetra-acetylglucose in pure toluene is heated for 2·5 hrs. with a small amount of zinc chloride, and then for a further 6 hrs. with phosphoric anhydride. Trituration of the resulting product with alcohol gives the *octa-acetate*, m. p. 68—70°, $[\alpha]_D$ +68·1° in chloroform, of αβ-*trehalose* (I), m. p. 85°, decomp. 97°, $[\alpha]_D$ +67·1° in water. This sugar is not a reducing agent, and when hydrolysed yields dextrose.



(I.)

Treatment of a chloroform solution of β-tetra-acetylgalactose with phosphoric oxide gives the *octa-acetate*, m. p. 82—83°, $[\alpha]_D$ +51·7° in chloroform, of a *galactobiose*, m. p. 122°, $[\alpha]$ +67·8° in water, which is hydrolysed to galactose.

Similar treatment of hepta-acetylmaltose affords the *tetradeca-acetyl* derivative, m. p. 105°, $[\alpha]_D$ +105·4° in chloroform, of a *maltotetrose*, $C_{24}H_{42}O_{21}$, m. p. 120—122°, $[\alpha]_D$ +113·5° in water, readily hydrolysed to dextrose. H. BURTON.

Sugar syntheses. VIII. Synthesis of vicianose, melibiose, and cellobiosidogentiobiose acetate, and a new tetra-acetylfructose. B. HELFERICH and H. BREDERECK (Annalen, 1928, **465**, 166—184; cf. Helferich and Rauch, A., 1927, 44, 859).—1 : 2 : 3 : 4-β-Tetra-acetylglucose is condensed with *l*-(+)-acetobromoarabinose (Gehrke and Aichner, A., 1927, 544) in chloroform in presence of silver oxide to give *hepta-acetyl*-6-β-l-*arabinosidoglucose*, m. p. 158—160°, $[\alpha]_D^{14}$ +7°, which by hydrolysis (cf. Helferich and Collatz, this vol., 1221) yields 6-β-*l*-arabinosidoglucose, m. p. 210°, $[\alpha]_D^{14}$ +56·6°, to +40·5°, identical with vicianose.

α-Acetobromo-*d*-galactose, when melted with phenol and quinoline, yields a mixture of α- and β-galactosides, from which is isolated *tetra-acetyl-α-phenol*-d-*galactoside*, m. p. 131—132°, $[\alpha]_D^{20}$ +175·5° (in chloroform), differing thus from the β-isomeride prepared from sodium phenoxide (Fischer and Armstrong, A., 1902, i, 746). In a similar manner acetobromogalactose condenses with 1 : 2 : 3 : 4-tetra-acetyl-β-glucose to give octa-acetyl-6-α-*d*-galactosido-β-glucose, m. p. 172—173°, $[\alpha]_D^{20}$ +97·2°, identical with octa-acetylmelibiose.

[With W. SCHAFER and K. BAUERLEIN.]—6-β-Hepta-acetylcellobiosidoacetobromoglucose, $[\alpha]_D^{19}$ +63·8° (Helferich and Schafer, A., 1927, 136; bromide, m. p. 209°, not 231°), condenses with 1 : 2 : 3 : 4-β-tetra-acetylglucose in chloroform in presence of silver oxide to form 6′-β-*cellobiosido*-β-*gentiobiose tetradeca-acetate*, m. p. 239—240°, $[\alpha]^{15}$ −19·6°, differing from the *hepta-acetyl*-6-β-*cellobiosido*-2 : 3 : 4-β-*triacetylglucose*, m. p. 233°, $[\alpha]_D^{15}$ −6°, obtained by the action of silver oxide on the trisaccharide alone.

[With T. MODROW.]—*Triphenylmethylfructose*, m. p. 160—165°, $[\alpha]_D^{15}$ −26·2°, to +4·2° after 75 hrs., obtained by treating lævulose in dry pyridine at 15° with triphenylmethyl chloride, gives a *tetra-acetate*, m. p. 146°, $[\alpha]^{20}$ +42·4°, from which by removal of the triphenylmethyl residue with hydrobromic and acetic acids at 5° there is obtained a new *tetra-acetylfructose*, m. p. 112°, $[\alpha]_D^{11}$ +51·0°. This yields α-penta-acetylfructose and thus contains the usual 2 : 6-oxygen bridge. It is extraordinarily unstable, even esterification with toluenesulphonyl chloride in pyridine leading only to decomposition products. It condenses, however, with acetobromoglucose to give an octa-acetyl-β-*d*-glucosidofructose, m. p. 80°, $[\alpha]_D^{20}$ +14·1°, probably identical with Pictet and Vogel's compound (this vol., 1224).

All the above m. p. are corrected. C. HOLLINS.

Synthesis of raffinose. H. VOGEL and A. PICTET (Helv. Chim. Acta, 1928, **11**, 898—900).—When a mixture of sucrose and galactose or sucrose and α-galactosan (A., 1922, i, 811) is heated at 160—165°/13—15 mm. for $1\frac{1}{4}$ hrs. and the resulting product extracted with methyl alcohol, about 1% of raffinose, m. p. (hydrated) 80—81°, $[\alpha]_D$ +104·9° in water, is obtained. This is hydrolysed by hot 10% acetic acid to melibiose and lævulose, and on acetylation gives an acetate, m. p. 98—100°, $[\alpha]_D$ +91·9° in alcohol (cf. Scheibler, A., 1887, 306). H. BURTON.

Methyl salicylate glucoside of *Gaultheria procumbens*, L., identical with monotropitin. M. BRIDEL and (MLLE.) S. GRILLON (Compt. rend., 1928, **187**, 609—611).—Contrary to the suggestion of Procter (1844), *Gaultheria procumbens*, L., does not contain methyl salicylate in the free state but combined in the form of a glucoside, m. p. 179·5°, α_D −57·91° (in water), containing 3·85% of water, which is isolated (yield, 4 g./kg. of fresh plant) and shown to be identical with monotropitin, isolated from *Monotropa hypopitys* (A., 1923, i, 1275). J. W. BAKER.

Ameliaroside, a new glucoside from *Amelanchier vulgaris*, Moench. M. BRIDEL, C. CHARAUX, and G. RABATÉ (J. Pharm. Chim., 1928, [viii], **8**, 345—357, and Bull. Soc. Chim. biol., 1928, **10**, 1111—1122).—A more detailed account of work already published (this vol., 992).

Röntgen diagram of native starch. S. VON NÁRAY-SZABÓ (Annalen, 1928, **465**, 299—304).—The Debye–Scherrer method of *X*-ray analysis has been applied to starch from different sources (cf. Herzog and Jancke, A., 1921, i, 308; Sponsler, A., 1923, i, 999; Ott, A., 1926, 460). A copper–potassium anticathode is used, and the starch is contained in a glass capillary. Starches may be divided into the potato group (from potato, *Curcuma angustifolia*, *Canna indica* and *C. edulis*, *Musa paradisiaca*, *Dioscoræa alata*, *Arracalia esculenta*, *Jatropha manihot*, and *Araucaria brasiliensis*) and the rice group (from rice, wheat, millet, *Maranta arundinacea*, *Ipomœa tjalappa*, *Arum esculentum*, and *Batatas edulis*). The former are

characterised by a strongly-marked ring 1 (not observed by Sponsler or by Ott, *loc. cit.*), from which the distance between planes of the crystal lattice is calculated as 16·0 Å.; there is a second strong interference at ring 5. In the rice group ring 1 is absent, and rings 5 and 8 are present.

The variations in strength of the rings from groups I and II cannot be due to contamination or deformation; the amount of amylopectin has no influence on the diagrams, and swelling by absorption of water has only normal effects. It is therefore suggested that the parameters of the unit cell (of which the volume is calculated to be $2{\cdot}524\times10^{-21}$ cm., *i.e.*, 16 $C_6H_{10}O_5$ groups) vary, through either physical or chemical differences between the different starches.

E. W. Wignall.

Starch. I. Potato starch. K. Hess, H. Friese, and F. A. Smith (Ber., 1928, **61**, [*B*], 1975—1982).—Potato starch, dried in air and thus containing 18% of moisture, is readily acetylated without suffering acetolysis if first swollen with pyridine and then treated with acetic anhydride and pyridine at 50—70° for 4 days, yielding thereby *starch triacetate.* Under similar conditions, starch which has been dehydrated over phosphoric oxide at 100°/1 mm. reacts only superficially if at all. Undried "amylose" and "amylopectin" are acetylated in a similar manner. The starch triacetate is a white, granular powder with a phosphoric acid content corresponding with that of the starch previous to acetylation. It is not dissolved by chloroform, acetone, glacial acetic acid, or other usual solvents. It is hydrolysed by methyl-alcoholic ammonia or sodium hydroxide to a carbohydrate which, like natural starch, does not reduce Fehling's solution. "*Amylopectin*" *triacetate* is identical in solubility with starch triacetate. The disruption of starch into amylose and amylopectin might be expected to find its counterpart in the division of starch triacetate by solvents into the more soluble amylose triacetate and less soluble amylopectin triacetate. This cannot, however, be effected and it is therefore probable that starch suffers partial hydrolysis when treated with water at 80°. When treated with water at 55°, 69% of the starch passes into solution, whilst, on raising the temperature to 80°, 31·8% of the residue is dissolved, making 80% in all. Microscopical examination of the most soluble portion shows it to retain the structure of the original material but to be composed of smaller particles so that water has merely removed the outer layers of carbohydrate. The final residue is, however, completely de-organised. It must therefore be assumed that, at most, that portion of the starch which is removed by water at 80° corresponds with a particular nucleus material of the starch granule and even this assumption is somewhat uncertain since the swelling temperature has been exceeded. The final residue is completely insoluble in water and may be designated "amylopectin" if the differentiation of starch into chemically different carbohydrates ultimately proves to be practicable. Amylopectin cannot be the "integument substance" of starch. The portion of the starch granules dissolved by water contains reducing components. Its non-homogeneity is further established by fractionation experiments with acetic anhydride and pyridine. Reducing fractions have a higher acetyl content than starch triacetate. With increasing reducing power the fractions exhibit diminishing rotation in chloroform and negatively increasing mutarotation of their hydrolytic products. Non-reducing carbohydrates which give a triacetate have the same specific rotation in alkali hydroxide as starch. The acetate, in contrast to those of starch and amylopectin, is soluble in chloroform ($[\alpha]_D^0$ $+169{\cdot}41°$). The final residue from the extraction of starch (corresponding with "amylopectin") has $[\alpha]_D^{20}$ $+153{\cdot}37°$ in *N*-sodium hydroxide and gives a triacetate; it possibly represents the purest form of starch yet isolated.

Apart from the solubility of the purest "amylose" fractions in organic media, there appear to be no reasonable grounds for supposing that amylose, amylopectin, and natural starch are chemically different substances.

H. Wren.

Starch. XXI. Constitution of glycogen. H. Pringsheim and G. Will (Ber., 1928, **61**, [*B*], 2011—2017).—Glycogen triacetate is rendered sufficiently soluble in chloroform by treatment during 20 min. with boiling naphthalene and is then heated with a solution of benzenesulphonic acid in chloroform whereby partial removal of the acetyl groups is effected; hydrolysis is completed by alcoholic potassium hydroxide or aqueous barium hydroxide, the ultimate product being *glycogesan*, which has the same optical activity and identical iodine coloration as glycogen. Cryoscopic examination of the product in water establishes its trisaccharide character, independent of details of its mode of preparation. In boiling water glycogesan passes into the colloidal state. Under the influence of pancreatic amylase, glycogesan is degraded to maltose, fission being approximately quantitative if yeast complement is added. The kinetics of fermentation are exactly parallel when glycogen or glycogesan is used as substrate, thus establishing the constitutional similarity of the polysaccharide with its structural element. Towards glycolysis the behaviour of glycogen and glycogesan is quantitatively identical. Re-acetylation of glycogesan affords a *triacetate*, identical in optical activity with glycogen triacetate. Determination of mol. wt. of glycogesan triacetate in glacial acetic acid gives the values of a triacetylhexosan at concentrations up to 0·3%; with more highly concentrated solutions association is observed.

H. Wren.

Inulin. VII. H. Pringsheim and J. Reilly (Ber., 1928, **61**, [*B*], 2018—2019).—Inulin acetate is converted by treatment with benzenesulphonic acid in boiling toluene and subsequently with alcoholic potassium hydroxide into inulan, identical with inulin in specific rotation and behaviour towards inulinase but having the mol. wt. of a disaccharide anhydride (cf. Pringsheim and Fellner, this vol., 742). H. Wren.

Cellulose. K. Hess and C. Trogus (Ber., 1928, **61**, [*B*], 1982—1996).—Attempts are made to establish relationships between the results of preparative chemical research and *X*-ray investigation in the sugar group. In the examination of the diagrams of cellulose it is not valid to assume that the compound is

composed of cellobiose residues. The production of cellobiose from cellulose and dextrose from cellobiose is governed by a completely different chemical mechanism. The fact that dextrose, under the condition of acetolysis, does not pass into cellobiose is not evidence that the latter exists preformed in cellulose. Attempts to interpret the X-ray diagrams of cellulose on the basis of a cellobiose unit are of very doubtful value. Observations on cellulose and its derivatives, molten and in solution, indicate that it does not contain glucosidic disaccharide linkings. The disentanglement of the structural factors of cellulose from its X-ray diagram is rendered difficult by lack of knowledge of the corresponding diagrams of carbohydrates of known structure. The following diagrams are reproduced in the original: hexa-acetylbiosans of Hess and Friese and of Bergmann and Knehe, acetates II and I, biosan of Hess and Friese, cellulose hydrate, hexamethylbiosan, trimethylcellulose, dextrose, mannose, cellobiose, lactose, βγζ-trimethylglucose, trimethylcellulose, "amorphous" cellulose, and amorphous cellulose after dissolution and re-precipitation from ammoniacal copper solution. The most striking feature of a comparison of the individual diagrams is the very close similarity between those of biosan, which is certainly a substance of low mol. wt. ($C_{12}H_{20}O_{10}$), and cellulose. It is therefore considered that the mass distribution of the atoms in the molecule of cellulose does not differ widely from that in biosan. The diagrams of dextrose, mannose, cellobiose, maltose, and lactose all show a maximal intensity the identity period of which differs within narrow limits in the individual cases. This intensity corresponds with net-plane distance of about 4·5 Å. The same intensity is observed in the case of cellulose hydrate and biosan which hence have a mass distribution in a hydropyran ring analogous to that in known sugars. The same general concordance is noted in the cases of βγζ-trimethylglucose, - triethylglucose, octamethylcellobiose, octaethylcellobiose, trimethylcellulose, trimethylbiosan, and penta-acetylglucose. The relatively indistinct interferences of cellulose and its derivatives may be attributed to an arrangement of masses of a glucosan-like complex held together by directed associative forces. The sharpening of the interference lines in the transition from cellulose to biosan depends on the transition from this "diffuse" force to exact oxygen bridges whereby the mass distribution remains approximately the same. The effect of substitution on mass distribution is exhaustively discussed. The noteworthy result is obtained that tristearylcellulose gives an X-ray diagram with only one marked ring corresponding with a hydropyran ring instead of the probable thread diagram.

Cellulose which has been cautiously nitrated (13·5% N) and then denitrated by ammonium sulphide gives only a moderately strong line and thus appears amorphous; when dissolved in ammoniacal copper solution and re-precipitated, it shows the X-ray diagram of cellulose hydrate.

It is concluded that a model with greater mass concentration explains more closely the present knowledge of cellulose than that deduced by Sponsler and Dore or by Meyer and Mark (cf. this vol., 621, 939). H. Wren.

New degradation of cellulose. I. H. Pringsheim, E. Kasten, and E. Schapiro (Ber., 1928, **61**, [*B*], 2019—2025).—If a 4% solution of cellulose acetate ("agfa") in chloroform is heated with 0·1% of anhydrous benzenesulphonic acid, the acetyl groups are partly removed and the particles become smaller. The process continues so far that the acetate loses its power of dissolving in chloroform and becomes soluble in water for the most part. After 3 or 6 days, 25—28% or 9% of acetyl is retained. If hydrolysis is completed with aqueous barium hydroxide and barium is quantitatively removed by sulphuric acid from the dilute, aqueous solution, the clear filtrate deposits a gelatinous precipitate A when evaporated in a vacuum. In ammoniacal copper solution the material has $[\alpha]_{Hg}$ $-1·7°$ to $-1·95°$ under conditions for which cellulose has $-2·6°$; its X-ray diagram is not distinguishable from that of cellulose hydrate. Addition of alcohol to the filtrate from A gives a preparation B, corresponding analytically with $C_6H_{10}O_5,H_2O$ or $C_6H_{10}O_5$ after intensive desiccation. It does not reduce Fehling's solution. In water, sodium hydroxide, or 95% pyridine it has $[\alpha]_D$ $+38°$. It is converted quantitatively into dextrose by boiling, dilute hydrochloric acid or by aqueous malt extracts. It is strongly associated in aqueous solution. It is converted by acetylation into a *triacetate*, $C_6H_7O_5Ac_3$, which, in 0·5% solution in glacial acetic acid, gives the mol. wt. required for a hexose anhydride acetate. In 1% solution it is associated. It is hydrolysed to the preparation B, $[\alpha]$ $+38°$.

Degradation by benzenesulphonic acid is not a specifically catalytic action, but is due to the acidity of the reagent; a similar effect is not produced by ethyl benzenesulphonate. H. Wren.

Action of highly concentrated nitric acid on cellulose. K. R. Andress (Z. physikal. Chem., 1928, **136**, 279—288).—By X-ray examination native cellulose may be referred to the monoclinic system with a unit having the constants $a = 8·35$ Å., $b = 10·28$ Å., $c = 7·96$ Å., $\beta = 78°$. The additive compound prepared by Knecht by the action of nitric acid (d 1·415) is formed with a distortion of the cellulose lattice, the new unit having the dimensions $a = 12·20$ Å., $b = 10·28$ Å., $c = 9·73$ Å., $\beta = 53° 7'$.
F. G. Tryhorn.

Cellulose formate. II. Formation of cellulose formate. Y. Ueda and K. Kato (J. Cellulose Inst. Tokyo, 1928, **4**, 203—205; cf. this vol., 399).—Cellulose formate is prepared from regenerated cellulose, 100% formic acid, and sulphuric acid. The formic acid content of the ester increases with the reaction period to a maximum and subsequently decreases. Similar variations occur with increasing proportions of sulphuric acid. In both cases the maximum figures are slightly below the theoretical for the triformate. A. G. Pollard.

Sulphuric esters from cellulose. E. Gebauer-Fulnegg, W. H. Stevens, and O. Dingler (Ber., 1928, **61**, [*B*], 2000—2003).—Carefully dried cotton wool or filter-paper is converted by chlorosulphonic acid in excess of pyridine at 100° into a homogeneous, gelatinous product which gives with water a transparent, colloidal solution. The cellulose derivatives

are precipitated (i) by alcohol with or without addition of ether, (ii) by alcohol and sodium chloride, (iii) by sodium hydroxide with or without alcohol, and (iv) by hydrochloric acid in presence of alcohol. Products, i, ii, and iii are white, very hygroscopic solids which have no reducing power and give optically inactive, colloidal solutions in water. Product i is a *pyridine* salt, whereas ii and iii are composed of a *sodium* salt of a cellulose hydrogen sulphate. Solutions of the freshly-prepared products, i, ii, and iii, give a precipitate with barium salts which dissolves in hydrochloric acid but is again formed by addition of a further quantity of barium salt. When isolated, the *barium* salt is insoluble in water or other media, very little affected by boiling alkali hydroxide, and only very slowly decomposed by boiling hydrochloric acid. Aqueous solutions of i, ii, and iii give sparingly soluble *precipitates* with lead, iron, calcium, and benzidine salts. Analyses of the barium salt gives the ratio C : S : Ba=6 : 2·78 : 1·48, but, after further treatment, a substance with the composition of a trisulphate is obtained.

Attempts to decide whether the sulphate is actually a derivative of cellulose are hindered by the impossibility of removing the sulphuric acid residues by acids or alkalis without considerable decomposition of the cellulose components; this can, however, be effected by methyl-alcoholic hydrogen chloride. H. Wren.

Structural matter of the leaves of white cabbage. H. Pringsheim, K. Weinreb, and E. Kasten (Ber., 1928, **61**, [*B*], 2025—2028).—The material is converted by 6—8% sodium hydroxide into a white, swollen mass which is treated further with chlorine dioxide and sodium hydroxide. The removal of those components which yield a furfuraldehyde–phloroglucinol precipitate is not completely effected by 18% sodium hydroxide. The remaining substance definitely contains only a small proportion of cellulose and represents a polysaccharide or mixture of polysaccharides extraordinarily resistant to hydrolytic agents. It is only slightly soluble in Schweizer's reagent. It is converted by treating the wet (but not dried) material with glacial acetic acid and acetic anhydride in the presence of a little sulphuric acid into a *triacetate*, $C_6H_7O_5Ac_3$, $[\alpha]_D^{20} > +1°$ in chloroform, from which the polysaccharide is regenerated. The substance now appears almost free from pentosans, since the differences given in the determination of furfuraldehydes by the phloroglucinol and barbituric acid methods indicate the production of hydroxymethylfurfuraldehyde, probably derived from decomposition products of the polysaccharide. The acetate is heated with a solution of benzenesulphonic acid and subsequently with 2% hydrochloric acid, thus giving a material which, in reducing power and optical activity, is not identical with any of the common hexoses; the temperature of decomposition of its osazone is identical with that of galactosazone.

H. Wren.

Lignin and cellulose. VII. Lignin. K. Freudenberg, M. Harder, and L. Markert (Ber., 1928, **61**, [*B*], 1760—1765).—The variation in the amounts of protocatechuic acid (20—30%) recorded as derivable by the action of molten potassium hydroxide on lignin is due to the difficulty of purifying the acid, particularly when oxalic acid is also present, and to the untrustworthiness of the colorimetric process. Experiments in which protocatechuic acid is determined colorimetrically in ferric chloride solution and gravimetrically after transformation into veratric acid indicate about 5% of this substance; if unavoidable losses are taken into consideration, it appears that about 9—10% of protocatechuic acid and traces of pyrocatechol are obtained from lignin. Since eugenol gives similar results, it remains possible that the actual content of pyrocatechol derivatives in lignin greatly exceeds 8%.

Use of "dimedon" in the determination of formaldehyde obtained by distillation of wood with 12% hydrochloric acid indicates not more than 1%, although the actual amount is estimated to be 2%. Comparison of the behaviour of triformalmannitol, piperonylic acid, narceine, and narcotine with that of lignin towards acidic hydrolysis indicates that the formaldehyde group in lignin is present as a methylenedioxy-group attached to the pyrocatechol nucleus. Appreciable quantities of formaldehyde are not present in wood except in the lignin component.

The lignin and cellulose in wood are readily separable from one another by repeated alternate treatment with hot 1% sulphuric acid and ammoniacal copper solution; even 0·1% sulphuric acid can be successfully used. Apparently the union between lignin and cellulose is resolved by removal of wood gum, pentosans, and hemicelluloses. This hypothesis is supported by the observation that wood thus treated and then methylated yields considerable amounts of methylcellulose to chloroform or acetic acid. The lignin preparations contain about 16% OMe.

H. Wren.

Beech wood. Acetylation of beech wood and hydrolysis of the acetylated product. H. Suida and H. Titsch (Ber., 1928, **61**, [*B*], 1599—1604; cf. Fuchs, this vol., 743, and following abstract).—Attempts are described to protect the active groups of wood in such a manner as not to disturb the union of the wood components and subsequently to hydrolyse the products without removal of the groups thus introduced. Powdered beech wood is extracted with alcohol and benzene (1 : 1) and degummed by 5% sodium hydroxide. Acetylation with boiling acetic anhydride followed by treatment with acetic anhydride and pyridine affords a product containing 37% OAc which does not react with aniline sulphate or phloroglucinol and hydrochloric acid. Hydrolysis is effected with boiling glacial acetic acid containing 0·25% of hydrogen chloride, whereby deacetylation is not completely avoided. The residue, which still contains a small proportion of lignin, consists mainly of partly acetylated cellulose containing 25·8% OAc. The lignin fraction, isolated by dilution of the filtrate from the acetylcellulose with water, contains 28·9% OAc and 14·1% OMe; the latter datum shows that it corresponds closely with primary lignin. H. Wren.

Methylation of beech wood and hydrolysis of the methylated product. A. von Wacek (Ber., 1928, **61**, [*B*], 1604—1609; cf. preceding abstract).—Repeated treatment of powdered beech wood, free

from resin and gum, with methyl sulphate yields a product containing 39—39·4% OMe which is unchanged by the customary solvents for methylcellulose and lignin. The product is hydrolysed with cold 17% hydrochloric acid and subsequently treated with boiling alcohol or, preferably, acetone. The lignin fraction precipitated from the acetone solution contains 26·5% OMe. The residue is repeatedly extracted with cold water and the extracts are heated, whereby a mixture of di- and tri-methylcellulose (mainly the latter) is precipitated. Treatment of the portion insoluble in cold water with chloroform allows a further separation of it into methylcelluloses and, probably, non-hydrolysed initial material. Even if it is assumed that cellulose is not uniformly united in wood, it follows that the linking of a part of it does not involve one or more of its three hydroxyl groups. H. WREN.

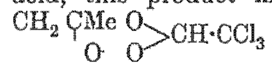
Formation of bases from carbonyl compounds. II. A. SKITA and F. KEIL [with E. BAESLER and L. BOENTE] (Ber., 1928, **61**, [*B*], 1682—1692; cf. this vol., 1120).—Ketones react generally with aliphatic amines and ammonia, even in aqueous suspension, giving intermediate *N*-substituted imines which are reduced to secondary amines in the presence of platinum. On the other hand, if nickel is used as catalyst, ketones and ammonia give substantially primary amines, which are also obtained from aldehydes. If, however, the conditions used for nickel are followed (temperature 90°) but the amount of platinum is greatly diminished, the production of primary amines becomes marked, but always subordinate to that of secondary amines. At the atmospheric temperature, secondary amines are produced exclusively. In confirmation, mixtures of acetone, methyl ethyl ketone, diethyl ketone, or *cyclo*hexanone with *cyclo*hexylamine do not form secondary amines in the presence of nickel, whereas they readily do so under the influence of platinum at 90° or at atmospheric temperature. Similarly, benzaldehyde and acetophenone in aqueous suspension are transformed into secondary bases in presence of platinum. Palladium appears to have an action intermediate between those of platinum and nickel. The production of tertiary bases from certain aldehydes occurs in accordance with the scheme: $\longrightarrow$

$$R{\cdot}CH_2{\cdot}NH{\cdot}CH_2R \underset{+H_2O}{\overset{+R\cdot CHO}{\rightleftharpoons}} [(R{\cdot}CH_2)_2NR{:}CH{\cdot}OH] \xrightarrow{+H_2} (R{\cdot}CH_2)_3N.$$

Reduction of diketones in the presence of primary amines affords amino-alcohols in very satisfactory yield; these compounds are also derived from hydroxyaldehydes and hydroxyketones in presence of bases. The method can be applied in the sugar group.

The following data appear new. N-*Phenyl*cyclo*hexylamine*, b. p. 146—148°/16 mm. (non-hygroscopic *hydrochloride*, m. p. 204—205°), apparently differing from the compound thus designated by Sabatier and Senderens (A., 1904, i, 305); N-iso*propyl*cyclo*hexylamine*, from acetone and *cyclo*hexylamine, b. p. 169—171° (*hydrochloride*, m. p. 204—205°; *picrate*, m. p. 142°); N-sec.-*butyl*cyclo*hexylamine*, from methyl ethyl ketone and *cyclo*hexylamine, b. p. 193° (*hydrochloride*, m. p. 211°; *picrate*, m. p. 118°); N-α-*ethyl*-n-*propyl*cyclo*hexylamine*, from diethyl ketone, b. p. 208—209° (*hydrochloride*, m. p. 178°; *picrate*, m. p. 124°); *di*-α-*ethyl*-n-*propylamine*, b. p. 172—174° (*hydrochloride*, m. p. 115—117°); benzyldiethylamine from benzaldehyde, acetaldehyde, and ethylamine, or benzylethylamine and acetaldehyde; β-cyclo*hexylaminopentan*-γ-*ol*, from acetylacetone and *cyclo*hexylamine, b. p. 123—125°/13 mm. (*hydrochloride*, m. p. 157—158°; *diacetyl* derivative, b. p. 183°/13 mm.); β-cyclo*hexylaminopropan*-α-*ol*, b. p. 116—117°/13 mm. (*hydrochloride*, m. p. 148—149°); N-cyclo*hexylarabinamine*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_{11}$, from arabinose and *cyclo*hexylamine, m. p. 135—137° (*hydrochloride*, m. p. 167°; N-cyclo*hexylmannamine hydrochloride*, m. p. 165—167°. H. WREN.

Action of anhydrous chloral on amino-alcohols and on hydroxy-amino-ethers containing a tertiary amino-group. E. FOURNEAU and (MLLE.) W. BRYDOWNA (Bull. Soc. chim., 1928, [iv], **43**, 1023—1027). — Methyldimethylaminomethylethylcarbinol reacts with anhydrous chloral with evolution of heat, giving a *semi-acetal*, which at 56—58°/10 mm., dissociates into chloral and the base, with formation of the acetal on cooling. With hydrogen chloride in ether it affords a *hydrochloride*, m. p. 128—130° (decomp.), decomposed by sodium hydroxide, giving chloroform. Benzoyl chloride in benzene gives a *benzoate hydrochloride*, m. p. 196—198° (decomp.), possessing powerful anæsthetic properties which are of no value on account of its strong acidic nature, and a little stovaine. Acetyl chloride in acetone gives the *hydrochloride* of the *acetate*, m. p. 193°, from which the *acetyl* derivative, b. p. 158—160°, is obtained on treatment with sodium carbonate, the dissociation of the acetal being thus prevented by acetylation of the hydroxy-group.

Since both ethyl and propyl γ-dimethylamino-β-hydroxy-β-methylpropionate with anhydrous chloral afford the same product, b. p. 140—142°/22 mm., m. p. 66—67° (hydrochloride, m. p. 180—186°), yielding on hydration in moist air γ-dimethylamino-β-hydroxy*iso*butyric acid, this product must have the structure  and not $NMe{\cdot}CH_2{\cdot}CMe(CO_2R){\cdot}O{\cdot}CH(OH){\cdot}CCl_3$ as originally suggested in the patent. It may thus be considered an ether or semi-acetal of chloral hydrate or a chloralide. R. BRIGHTMAN.

Structure of chitin. K. H. MEYER and H. MARK (Ber., 1928, **61**, [*B*], 1936—1939).—A review of the literature on chitin combined with examination of Gonell's *X*-ray diagrams of the compound leads the author to assume that the 1 : 5-rings are joined by 1 : 4-oxygen bridges and oriented at an angle of 180° round a screw axis; the main valency chains thus produced are linked with one another to micellæ. Eight acetylglucosamine anhydride residues appear present in the unit. Nothing quantitative is known with respect to the size of the micellæ in chitin, but the general similarity of the chitin and cellulose diagrams indicate that it is of the same order as in cellulose or silk. H. WREN.

Action of acetic anhydride and pyridine on amino-acids. P. A. LEVENE and R. E. STEIGER

(J. Biol. Chem., 1928, 79, 95—103).—Further study of the reaction previously observed (this vol., 61) leads to conclusions similar to those reached by Dakin and West (this vol., 874). C. R. HARINGTON.

Structure of silk fibroin. K. H. MEYER and H. MARK (Ber., 1928, 61, [B], 1932—1936; cf. Brill, A., 1924, i, 102).—The conception that the structural unit of fibroin is composed of one or two alanylglycyl residues as peptide or peptide anhydride is not compatible with the known properties of the known, open tetrapeptides. The assumption of four main-valency chains which connect the elementary bodies is in harmony with all experimental data. The identity period is identical with the length of a glycylalanyl residue. The length of the micelles and hence the mean length of the main-valency chain corresponds with a polypeptide containing at least twenty glycylalanyl residues. The distances of the main-valency chains from one another amount to 4·6 Å. in one direction and 5·2 Å. in the other, these values being observed frequently with molecules attached to one another by subsidiary valencies. The close attachment of the chains is attributed to the high associating power of the –CO·NH– group.

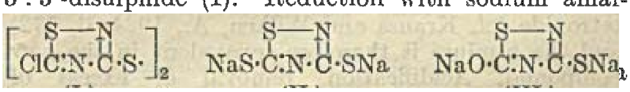
The diagrams of different silks indicate that the proportion of crystalline material is less than in the case of cellulose and is estimated to be about 40—60%. H. WREN.

Determination of carbamide. J. M. LUCK (J. Biol. Chem., 1928, 79, 211—219).—Carbamide is precipitated with xanthydrol; the precipitate is dissolved in dilute sulphuric acid, and the resulting yellow solution is warmed to 70—75° and titrated with potassium permanganate until colourless; 0·1 mg. of carbamide may be determined with an error of ±5%. C. R. HARINGTON.

Nitroaminoguanidine. R. PHILLIPS and J. F. WILLIAMS (J. Amer. Chem. Soc., 1928, 50, 2465—2470).—Hydrazine and nitroguanidine in dilute aqueous solution at 50—60° probably yield first an additive compound which then decomposes into nitrous oxide, aminocyanamide which is hydrolysed, and *nitroaminoguanidine*, $NO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}NH_2$, m. p. 190° with explosion. The nitrogen in this compound can be determined only by a special procedure. It reduces copper and silver solutions with formation of explosive metallic derivatives and quantitatively precipitates nickel as the *salt*, $NiO[NO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}NH_2]_2$, the blue solution of which in alkali hydroxide affords a delicate test for nickel. Nitroaminoguanidine gives characteristic colour tests and forms with aldehydes and ketones crystalline hydrazones which may be detonated. It is reduced by zinc dust and acetic acid to diaminoguanidine. H. E. F. NOTTON.

Ureides of bromovaleric acids. III. Influence of the position of the halogen atom in the acid on physiological properties. E. FOURNEAU and G. FLORENCE (Bull. Soc. chim., 1928, [iv], 43, 1027—1040).—Examination of the ureides of the bromo-*n*-valeric acids and of bromo-α-methylbutyric acids has confirmed the conclusions reached from earlier work (this vol., 401) that the α-bromine atom is not a condition of hypnotic action, ureides containing β- and γ-bromine atoms being also active. Branching of the chain produces a marked increase in the solubility in water and in the partition coefficient, and in this series of compounds the partition coefficient and the hypnotic action are closely parallel. The following data are recorded (percentage figures indicate solubility in water, and ordinary figures partition coefficients): α-bromo-*n*-valerureide, 0·83%, 0·44; *β-bromo-*n*-valerureide*, m. p. 184°, 0·78%, 0·35; *γ-bromo-*n*-valerureide*, m. p. 160—161°, 0·97%, 0·29; α-bromo-α-methylbutyrureide, 5·3%, 1·99; *β-bromo-α-methylbutyrureide*, m. p. 125—126°, 3·2%, 1·7; *α-bromomethyl-*n*-butyrureide*, m. p. 108°, 4·01%, 0·84; *γ-bromo-α-methylbutyrureide* (yield, 30%), m. p. 147·5°, 1·05%, 0·90. Attempts to obtain the ureide of δ-bromo-*n*-valeric acid, m. p. 39—40°, from the chloride in the usual way were unsuccessful. γ-Bromo-α-methylbutyryl chloride, b. p. 128°/18 mm., is obtained in good yield by the action of phosphorus trichloride or pentachloride on the methylbutyrolactone. R. BRIGHTMAN.

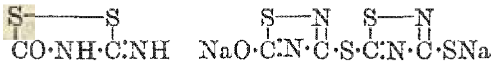
Tetrathiocyanogen dichloride and thiodiazoles obtainable therefrom. E. SODERBACK (Annalen, 1928, 465, 184—210; cf. A., 1920, i, 219).—The "thiocyanogen monohydrochloride," m. p. 60—70°, previously described is shown by analysis and mol. wt. determinations to be tetrathiocyanogen dichloride, its preparation from thiocyanogen and hydrogen chloride in absolute ether being represented by the equation $3(SCN)_2+2HCl=(SCN)_4Cl_2+2HSCN$. It forms with metallic mercury a *compound*, $C_4N_4Cl_2S_4Hg$, m. p. 168—169°, from which the dichloride is regenerated by the action of bromine or iodine. This behaviour distinguishes it from aliphatic and aromatic disulphides, but is analogous to the reaction of diantipyryl disulphide and the disulphides from 5-thiol-3-phenyl-1 : 2 : 4-thiodiazole and 5-thiol-2-thioketo-3-phenyl-1 : 3 : 4-thiodiazoline with metallic mercury, and suggests a heterocyclic disulphide structure. By the action of hydrogen bromide in benzene the dichloride is converted, with liberation of bromine, into thiocyanogen dihydrobromide, which is entirely analogous to the dihydrochloride (*loc. cit.*) and is therefore 3 : 3-dibromo-5-imino-1 : 2 : 4-dithioazolidine. The dichloride hence contains S–C–N groupings and must be 5-chloro-1 : 2 : 4-thiodiazolyl 3 : 3′-disulphide (I). Reduction with sodium amal-



(I.) (II.) (III.)

gam gives the sodium salt of the 3-thiol, "*sodium chlorodithiocyanate*," much more readily obtained by the action of sodium sulphide on the mercury compound; a white *polythiocyanogen*, decomp. above 300°, is obtained as a by-product in the preparation of sodium chlorodithiocyanate, or by decomposition of the latter at 15° in acetone solution. The *lead*, *cuprous*, and *silver* salts are described, but the free thiol is obtained only in solution. Sodium chlorodithiocyanate is converted by hot sodium sulphide solution into sodium perthiocyanate (II), which is obtained crystalline from hot acetone. Sodium hydroxide similarly yields "*sodium hydroxydithio-*

cyanate" (III), m. p. 108° ($+4H_2O$; *lead* salt described), which is easily hydrolysed in aqueous solution to thiocarbamide, sulphur, and sodium carbonate. Acidification of the ice-cooled aqueous solution of sodium hydroxydithiocyanate gives "thiocyanogen hydrate" (3-imino-1 : 2 : 4-dithioazolidone; IV) by isomerisation of the hydroxydithiocyanic acid transiently formed. By the action of iodine on

(IV.)  (V.)

sodium hydroxydithiocyanate the corresponding *disulphide*, "sodium dihydroxydithiocyanate," $C_4O_2N_4S_4Na_2,5H_2O$, is obtained, which on acidification gives the free acid, 5 : 5'-*dihydroxy*-3 : 3'-*di*-1 : 2 : 4-*thiodiazolyl disulphide*, decomp. 160°. The acid and its sodium salt react with metallic mercury to give 5-hydroxy-3-mercurithiol-1 : 2 : 4-thiodiazole and its sodium salt, respectively.

In the preparation of sodium hydroxydithiocyanate there is also produced "*sodium hydroxytetrathiocyanate*" [disodium salt of 5-hydroxy-3'-thioldi-1 : 2 : 4-thiodiazolyl sulphide (V)], the aqueous solution of which gels even at 0·02 molar concentration. The "*acid*" is precipitated on acidification. The sodium salt reacts with iodine to give a *disulphide* containing four thiodiazole residues. C. HOLLINS.

Determination of cyanides and basic cyanides of mercury. A. IONESCO-MATIU and (MLLE.) A. CARALE (J. Pharm. Chim., 1928, [viii], **8**, 258—263).—Mercuric cyanide and basic mercuric cyanide, $Hg(CN)_2,HgO$, can be accurately determined by transforming the mercury into the sulphate, adding sodium nitroprusside, and titrating the mixture with sodium chloride solution until the turbidity just disappears (cf. Votocek, A., 1923, ii, 184).

E. H. SHARPLES.

Cyanogen compounds of the platinum metals. IV. Cyano-oxo-salts of osmium. F. KRAUSS and G. SCHRADER (J. pr. Chem., 1928, [ii], **120**, 36—40).—Addition of excess of potassium cyanide to an aqueous solution of osmium tetroxide furnished an orange-red solution containing the complex salt $K_2[OsO_2(CN)_4]$, which could not be isolated in a pure state. The amount of iodine liberated on treatment of the solution with concentrated hydrochloric acid and potassium iodide was half that liberated by osmium tetroxide (cf. Krauss and Wilken, A., 1924, ii, 772) and the osmium is therefore sexavalent in the new compound. Acidification, removal of excess of hydrogen cyanide, and addition of copper sulphate or silver nitrate yielded, respectively, precipitates of the *compounds* $Cu[OsO_2(CN)_4]$, grey, and $Ag_2[OsO_2(CN)_4]$, yellow. Digestion of these with ammonia yielded the *compounds* $[Cu(NH_3)_4][OsO_2(CN)_4]$, black, and $[Ag_2(NH_3)_4][OsO_2(CN)_4]$, dark reddish-brown, respectively, which lost ammonia slowly in air.

R. K. CALLOW.

Organic compounds of arsenic. XIV. Tenacity of hydrocarbon residue to arsenic. W. STEINKOPF, H. DUDEK, and S. SCHMIDT (Ber., 1928, **61**, [*B*], 1911—1918; cf. A., 1922, i, 994, and previous abstracts).—Methyldichloroarsine is converted by magnesium *iso*amyl chloride in ether into *methyldi*-iso*amylarsine*, b. p. 95—99°/11 mm., transformed by chlorine in light petroleum into the corresponding *dichloride*, which decomposes at 186—210° into methyl*iso*amylchloroarsine, b. p. 68—72°/11 mm., *di*iso*amylchloroarsine*, b. p. 114—122°/11 mm., methyl chloride, and *iso*amyl chloride; the methyl and *iso*amyl groups are therefore attached to arsenic with almost equal firmness. Arsenic trichloride and magnesium *cyclo*hexyl chloride in ether afford *tri*cyclo*hexylarsine*, b. p. 208—215°/11 mm., solidif. pt. 41—40°. The corresponding *dichloride* decomposes at 200°/vacuum into *di*cyclo*hexylchloroarsine*, b. p. 168—171°/10 mm., from which the *oxide*, $[As(C_6H_{11})_2]_2O$, is obtained by means of aqueous sodium carbonate. The monochloride is converted successively into the corresponding *trichloride*, decomp. 80—90°, and cyclo*hexyldichloroarsine*, b. p. 122—125°/15 mm. Di*cyclo*hexylphenylarsine (cf. Roberts, Turner, and Bury, A., 1926, 852), obtained in 93% yield from phenyldichloroarsine and magnesium *cyclo*hexyl chloride, is transformed into the *trichloride*, m. p. 167° (decomp.), and cyclo*hexylphenylchloroarsine*, b. p. 183—184°/15 mm., from which the *oxide*, $C_6H_{11}\cdot AsPh.O$, is derived. Phenyl*cyclo*hexylmethylarsine and cyanogen bromide in ether give a solid *bromocyanide* which decomposes when heated into cyclo*hexylphenylcyanoarsine*, b. p. 156·5°/about 2 mm., also derived from *cyclo*hexylphenylchloroarsine and potassium cyanide. The bromocyanide is converted by moisture into the *hydroxybromide*, $C_6H_{11}\cdot AsMePh(OH)\cdot Br$, characterised as the *picrate*, $C_6H_{11}\cdot AsMePh(OH)\cdot O\cdot C_6H_2(NO_2)_3$, m. p. 132·5—133°. n-*Propyldi-iodoarsine*, b. p. 136—137°/11 mm., is prepared in 55% yield by the action of sulphur dioxide on an aqueous solution of magnesium propylarsinate, potassium iodide, and concentrated hydrochloric acid. n-*Propylarsine oxide*, b. p. 142—145°/1 mm., is described. The di-iodide and propyl bromide afford *di*-n-*propyliodoarsine*, b. p. 103·5—106°/12·5 mm., converted by magnesium *cyclo*hexyl chloride into cyclo*hexyldi*-n-*propylarsine*, b. p. 126·5—129·5°/12 mm. The latter compound yields a solid *bromocyanide* which is decomposed by heat into propyl bromide and cyclo*hexyl*-n-*propylcyanoarsine*, b. p. 108·5—110°/1 mm. The action of moisture on the bromocyanide affords the corresponding *hydroxybromide*, $C_{12}H_{26}OBrAs$, m. p. 64—67°, converted into the *picrate*, $C_{18}H_{28}O_8N_3S$, m. p. 110—111°. *cyclo*Hexyldipropylarsine is converted by chlorine in light petroleum into the corresponding *dichloride*, m. p. about 40°, which decomposes at 200° into *n*-propyl chloride and cyclo*hexyl*-n-*propylchloroarsine*, b. p. 131—132°/16 mm. The *cyclo*hexyl group is therefore more firmly united to arsenic than the methyl or *n*-propyl groups and less firmly than the phenyl radical. H. WREN.

β-Chlorosubstituted compounds of arsenic. V. V. NEKRASSOV and A. S. NEKRASSOV (Ber., 1928, **61**, [*B*], 1816—1821).—β-Chloroethyldichloroarsine, b. p. 89—90°/12 mm., d^{15} 1·573, is prepared in very modest yield by passing a current of dry ethylene through a mixture of arsenic trichloride and aluminium chloride at 0°. Preferably, ethylene chloro-

hydrin is converted by sodium arsenite into β-hydroxyethylarsinic acid, $OH\cdot CH_2\cdot CH_2\cdot AsO_3H_2$, which is reduced by sulphur dioxide to the corresponding *oxide*, $OH\cdot CH_2\cdot CH_2\cdot AsO$, a colourless, viscous liquid which could not be distilled without decomposition; it does not evolve ethylene when treated with cold alkali hydroxide and is re-converted by hydrogen peroxide into the syrupy arsinic acid. Hydrogen chloride converts the oxide into the corresponding dichloride without affecting the hydroxyl group, whereas phosphorus trichloride in chloroform converts it into β-chloroethyldichloroarsine in moderately good yield. Aqueous alkali hydroxides immediately decompose β-chloroethyldichloroarsine into ethylene chloride and arsenite. Since this behaviour is shared by β-chlorovinylarsines, the explanation of the reaction put forward by Lewis and Stiegler (A., 1925, i, 1470) can scarcely be maintained, since it fails to cover both cases. Oxidising agents convert β-chloroethyldichloroarsine into β-*chloroethylarsinic acid*, m. p. 133°, which is monobasic towards methyl-orange but dibasic in presence of phenolphthalein.

H. Wren.

β-Substituted alkylarsinic acids and their derivatives. S. M. Scherlin and G. Epstein (Ber., 1928, **61**, [*B*], 1821—1825).—Ethylene chlorohydrin is converted by sodium arsenite into β-hydroxyethylarsinic acid, which is reduced to the corresponding oxide and thence converted by hydrogen chloride into β-hydroxyethyldichloroarsine; isolation of the products in the homogeneous state could not be effected. Treatment of the dichloro-compound with 95—96% acetic acid and hydrogen chloride affords β-*acetoxyethyldichloroarsine*, $OAc\cdot CH_2\cdot CH_2\cdot AsCl_2$, b. p. 120—121°/9—10 mm., d_4^{20} 1·6766, which evolves ethylene when boiled with water or alkali hydroxide. β-Hydroxyethyldichloroarsine is transformed by phosphorus pentachloride or, preferably, by a small excess of phosphoryl chloride into β-*chloroethyldichloroarsine*, b. p. 90·8°/12·5 mm., d_{20}^{20} 1·8401, oxidised by hydrogen peroxide to β-*chloroethylarsinic acid*, m. p. 134°. Carbonyl chloride transforms β-hydroxyethyldichloroarsine into a *compound* with a pronounced odour of ethyl chloroformate, which loses carbon dioxide and gives β-chloroethyldichloroarsine when distilled under diminished pressure.

H. Wren.

Trypanocidal action and chemical constitution. VIII. Derivatives of β-aminoethyl- and γ-aminopropyl-arsinic acids. G. A. C. Gough and H. King (J.C.S., 1928, 2426—2447).—A series of amphoteric acids, $R_1R_2N\cdot[CH_2]_n\cdot AsO_3H_2$, where R_1 and R_2 are hydrogen, aliphatic, or alicyclic radicals, have been synthesised by the action of the appropriate amines on the chloro-acids, $Cl\cdot[CH_2]_n\cdot AsO_3H_2$. The reaction proceeds normally when $n=3$, but when $n=2$, unless alkalinity be avoided when exhaustive substitution of the amine takes place, the arsinic acid decomposes with the formation of ethylene and the corresponding arsenate and hydrochloride of the base. Of all the compounds described only triethylamine-ββ′β″-triarsinic acid and γ-piperidinopropylarsinic acid were found to have any curative action when tested on experimental trypanosomiasis in mice.

β-Hydroxyethylarsinic acid (*calcium* salt) on dissolution in hydrochloric acid and treatment with sulphur dioxide in the presence of hydrogen iodide followed by thionyl chloride in petroleum was converted into β-chloroethyldichloroarsine, b. p. 92—93°/32 mm., which on oxidation with chlorine water gave β-*chloroethylarsinic acid*, m. p. 134—135°. Similarly γ-*hydroxypropylarsinic acid* (*calcium* salt) (from trimethylene chlorohydrin and sodium arsenite) gave γ-*chloropropyldichloroarsine*, b. p. 120—122°/16 mm., and γ-*chloropropylarsinic acid*, m. p. 146—148° (*barium* and *calcium* salts). From the reaction between γ-hydroxypropylarsinic acid and sulphur dioxide in hydrochloric acid solution, the *di-ester* of γ-*hydroxypropyldichloroarsine* and γ-*hydroxypropylarsinous acid*, b. p. 35°/0·16 mm., was isolated. β-Chloroethylarsinic acid gave with carbamide in aqueous solution *triethylamine*-ββ′ -*triarsinic acid*, m. p. 184—185° (*calcium*, *barium*, and *magnesium* salts); with methylamine, *methyldiethylamine*-ββ′-*diarsinic acid*, m. p. 192—194°; with dimethylamine, *dimethyldiethylammonium chloride*-ββ′-*diarsinic acid*, m. p. 178°, and β-*dimethylaminoethylarsinic acid hydrochloride*, m. p. 138—145°; with trimethylamine, β-*dimethylaminoethylarsinic acid methochloride*, m. p. 187—188° (decomp.); with piperidine, β-*piperidinoethylarsinic acid hydrochloride*, m. p. 155—157° (β-*piperidinoethyl-dichloroarsine hydrochloride*, m. p. 126—127°; -*di-iodoarsine hydriodide*, m. p. 158—159°); with piperazine hydrate, NN′-*piperazinodi*-ββ′-*ethylarsinic acid dihydrochloride*. *Methyl*-β-*chloroethyldiethylammonium iodide*, m. p. 219—220°, was obtained from β-chloroethyldiethylamine (*chloroaurate*, m. p. 68—71°) and methyl iodide and was converted into the *chloride* (*chloroaurate*, m. p. 202—204°) with silver chloride. A small yield of methylarsinic acid was obtained from the reaction between methyl *p*-toluenesulphonate and sodium arsenite. From the interaction between *p*-toluenesulphonyl chloride and β-diethylaminoethanol *tetraethylpiperazinium di*-p-*toluenesulphonate*, m. p. 300—301° (decomp.) (*di-iodide*; *dichloroaurate*), was isolated, whilst with trimethylene glycol the chief products were *trimethyleneglycol di*-p-*toluenesulphonate*, m. p. 93—94°, and *propane*-αγ-*dipyridinium di*-p-*toluenesulphonate*, m. p. 118—120° (*dichloride*; *dichloroaurate*; *dipicrate*, m. p. 176°; *tetramercurichloride*). γ-Chloropropylarsinic acid gave with ammonia, γ-*aminopropylarsinic acid*, m. p. 212—214° (decomp.); with dimethylamine, γ-*dimethylaminopropylarsinic acid hydrochloride*, m. p. 108—110°; with trimethylamine, γ-*dimethylaminopropylarsinic acid methochloride*, m. p. 174—176°; with *n*-propylamine, γ-n-*propylaminopropylarsinic acid*, m. p. 222—224° (*hydrochloride*, m. p. 210—212°; m-*nitrobenzoyl* derivative, m. p. 132—134°; γ-n-*propylaminopropyldichloroarsine hydrochloride*, m. p. 195—196°); with *n*-hexylamine, γ-n-*hexylaminopropylarsinic acid hydrochloride*, m. p. 221—223° (m-*nitrobenzoyl* derivative, m. p. 118—120°; with ethyl chloroformate, γ-*carbethoxy*-n-*hexylaminopropylarsinic acid*, m. p. 58—60°; *phenylcarbamyl* derivative, m. p. 118—124°; γ-n-*hexylaminopropyldichloroarsine hydrochloride*, m. p. 190—192°); with *l*-α-phenylethylamine, l-α-*phenylethylaminopropyldichloroarsine hydrochloride*, m. p. 194—196°;

with piperidine, *γ-piperidinopropylarsinic acid hydrochloride*, m. p. 162—164° (*γ-piperidinopropyldichloroarsine hydrochloride*, m. p. 194—196°; *γ-4-hydroxy-2 : 2 : 6-trimethylpiperidinopropylarsinic acid*, m. p. 162°, with vinyl diacetonealkamine); with 2 : 2 : 6-*trimethylpiperidine* (prepared by reduction of 4-bromo-2 : 2 : 6-trimethylpiperidine hydrochloride with zinc and acetic acid), b. p. 138—139° (*hydrochloride*, m. p. 236—237°; *chloroaurate*, m. p. 127—129°; *picrate*, m. p. 195—196°), *γ-2 : 2 : 6-trimethylpiperidinopropylarsinic acid*, m. p. 150—160°; with piperazine hydrate, *γ-piperazinopropylarsinic acid dihydrochloride* (*benzoyl* derivative, m. p. 204—206°); with ethyl nipecotinate, *γ-3-carbethoxypiperidinopropylarsinic acid*. A. I. VOGEL.

Auto-oxidation of Grignard's magnesium compounds. J. MEISENHEIMER and W. SCHLICHENMAIER (Ber., 1928, **61** [*B*], 2029—2043).—The determination of the content of solutions of magnesium aryl or alkyl halides by addition of water followed by titration of magnesium oxide and magnesium halide with nitric acid and silver nitrate (cf. this vol., 624) gives inaccurate results when solutions of the iodides are greatly diluted with ether before decomposition. The incidence of "etherolysis," $MeMgI+Et_2O=MeMg{\cdot}OEt+EtI$, is excluded by the absence of formation of considerable amounts of alkyl iodide and the phenomenon is traced to auto-oxidation. Experiments with magnesium methyl iodide show that dilution in absence of oxygen has no effect on the analytical results. Even in the diluted solutions, methyl iodide is exclusively produced (recognised as tetramethylammonium iodide); the absence of ethyl iodide proves that the ether is not oxidised. With increasing dilution the ratio $OH' : I'$ at first increases rapidly, but ultimately attains a limiting value which does not exceed 2 : 1. The net reaction may therefore be expressed: $3MeMgI+3O=MeI+MgO+2MeO{\cdot}MgI$. Solutions of magnesium methyl iodide in amyl ether behave similarly to those in ethyl ether, the greatest observed displacement being $OH' : I'$—1·92 : 1 with 10 vols. of the ether. Magnesium ethyl iodide behaves similarly.

Auto-oxidation of solutions of magnesium phenyl iodide affords iodobenzene, phenol, phenylmethylcarbinol, and benzene. The effect of dilution is less marked than with alkyl iodides, the highest observed value for the ratio $OH' : I'$ being 1·67 : 1, which corresponds with the reaction $4PhMgI+3O+Et{\cdot}O{\cdot}Et=PhI+MgO+CHPhMe{\cdot}O{\cdot}MgI+C_6H_6+EtO{\cdot}MgI+PhO{\cdot}MgI$. Direct measurement of the absorption of oxygen by solutions of magnesium alkyl halides indicates that the ratio Grignard compound : oxygen=1 : 0·95. With magnesium phenyl iodide the corresponding observed ratio is 1 : 0·66, but, in view of the results with the alkyl compounds, the true ratio is regarded as 1 : 0·75. Magnesium alkyl and aryl bromides are less sensitive to atmospheric oxidation, but the ratio $OH' : I'$ increases with dilution. Measurement of the oxygen consumed by magnesium phenyl bromide gives the ratio mols. of Grignard compound : atoms of oxygen=1 : 0·69. The production of diaryls during the auto-oxidation of aromatic Grignard compounds is considered doubtful.

The primary reaction between magnesium methyl iodide and oxygen is considered to be the formation of a complex $[MeMgI \cdots 3O \cdots MeMgI{\cdot}Et_2O]$ which subsequently decomposes according to (*a*) a unimolecular reaction in which the two iodine atoms are replaced by oxygen, giving iodine, which reacts immediately with unchanged magnesium methyl iodide, and the complex $[MeMg \cdots 3O \cdots MgMe,Et_2O]$, giving MgO and $Mg(OMe)_2$, and (*b*) a bimolecular change in which the complex oxidises 1 mol. of MeMgI to $MeO{\cdot}MgI$; in the residue $[MeMgI \cdots 2O \cdots MeMgI,Et_2O]$, the oxidation potential is so diminished that expulsion of the iodine atoms does not occur and the methyl groups become oxidised to methoxy-residues. In concentrated solutions (*a*) and (*b*) are concurrent, whereas at greater dilutions (*b*) disappears. Under all conditions (*b*) preponderates with bromides on account of the greater affinity of bromine for magnesium. Similar views may be developed for the auto-oxidation of magnesium aryl halides, the essential difference lying in the oxidation of the ether, which is not explained.

The gradual decomposition of magnesium methyl iodide at 75° (*loc. cit.*) is not a thermal action but is due to insufficient exclusion of air. H. WREN.

Monomagnesium derivative of acetylene. V. GRIGNARD, L. LAPAYRE, and T. FAKI (Compt. rend., 1928, **187**, 517—520).—The magnesium acetylenyl bromide obtained by the action of acetylene on magnesium phenyl bromide (Oddo, A., 1904, i, 862; 1908, i, 748; Zalkind and Rosenfeld, A., 1924, i, 1291) affords with carbon dioxide 15% of propiolic acid and with *n*-butyl bromide at 80—90°, 29% of true hexinene and nearly as much dibutylacetylene. When the magnesium phenyl bromide is prepared with excess of magnesium and ether yields of 39% of true hexinene and 30% of *s*-decinene can be obtained. If the acetylene is passed in under pressure (0·5 atm.) the product on treatment with carbon dioxide affords 28% of propiolic acid and 13% of acetylenedicarboxylic acid. Gentle heating and special agitation (cf. A., 1913, ii, 1046) similarly give a product yielding 62% of propiolic acid and only 10% of the acetylenedicarboxylic acid. Further evidence that the product is an equilibrium mixture of the mono- and di-magnesium acetylenyl derivatives, in proportions depending on the temperature and pressure, is afforded by experiments with magnesium ethyl bromide. Excess of acetylene under normal pressure gives a solution containing 95% of the dimagnesium derivative. When the ether is partly replaced by benzene, and acetylene is passed in at 65° and 0·5 atm., after 4 hrs. the solution contains 80—81% of monomagnesium derivative, and with benzyl bromide affords 70% of γ-phenyl-Δ^{α}-propinene, b. p. 71—73°/17 mm., n_D^{23} 1·53481, d_4^{23} 0·931, 8% of dibenzylacetylene, m. p. 80°, and 12% of acetylene (by hydrolysis). In ether at 45° the absorption is more rapid, and after 50 min. the solution contains 70% of monomagnesium derivative, and after 4 hrs. 85%. With carbon dioxide, 78% of propiolic acid, 8% of acetylenedicarboxylic acid, and 5% of acetylene are obtained. At —10° absorption is theoretical in

45 min. and with allyl bromide the product gives in 75% yield *allylacetylene*, b. p. 41—42°, n_D^{20} 1·3653, d_{20}^{20} 0·777, and a small fraction, b. p. 120—125°, probably *γ-allylallylacetylene* (*γ-allyl-Δ^α-penten-Δ^δ-inene*), b. p. 29°/17 mm. The absence of *s*-diallylacetylene is attributed to the acidic nature of the central $\cdot CH_2\cdot$ group of allylacetylene, which probably decomposes the dimagnesium acetylenyl derivative, giving $CH_2{:}CH\cdot CH(MgBr)\cdot C{:}CH$. *n*-Butyl bromide similarly affords butylacetylene, b. p. 71—72°, d^{17} 0·720, n_D^{10} 1·402, in 72% yield. Allylacetylene, *γ*-allylallylacetylene, and *γγ-diallylallylacetylene*, b. p. 49°/17 mm., have been obtained by Lespieau (private communication) by the action of allyl halides on monosodium acetylide in liquid ammonia.

R. Brightman.

Action of acetylene on aryl-hydrocarbons in presence of a mercury catalyst. II. J. A. Reilly and J. A. Nieuwland (J. Amer. Chem. Soc., 1928, **50**, 2564—2566; cf. A., 1924, i, 156).—*αα-Diarylethanes* containing the following aryl radicals have been prepared: n-*propylphenyl-*, b. p. 192—194°/42 mm.; iso*propylphenyl-*, b. p. 240—245°/15 mm.; n-*butylphenyl-*, b. p. 244—248°/37 mm.; tert.*-butylphenyl-*, m. p. 94°, b. p. 212—214°/16 mm.; *α-methyl-*n*-propylphenyl-*, b. p. 250—252°/11 mm.; *α-ethylpropylphenyl-*, b. p. 234—236°/29 mm., and *α-methyl*iso*butylphenyl-*, b. p. 225—228°/13 mm. Di- and tri-phenylmethane, diphenyl, dibenzyl, and naphthalene fail to react, but tetrahydronaphthalene gives *αα-di-*ar*-tetrahydronaphthylethane*, b. p. 261—263°/16 mm., and a trace of a cyclic product. The yields of diarylethanes decrease with increasing mol. wt. and, among isomeric compounds, with increasing length of side-chain.

H. E. F. Notton.

Ring strain and radical formation. II. G. Wittig and F. von Lupin (Ber., 1928, **61**, [*B*], 1627—1634; cf. this vol., 642).—Unsuccessful attempts to prepare 1 : 1 : 2 : 2-tetraphenyl-*cyclo*butane and -*cyclo*butene are recorded.

Treatment of ααδδ-tetraphenylbutane-αδ-diol with boiling acetic and hydrochloric acids, or saturation of its solution in acetic acid with hydrogen bromide, affords *ααδδ-tetraphenyl-Δ^{αγ}-butadiene*, m. p. 201°, also obtained from the glycol and thionyl chloride in chloroform. The hydrocarbon is converted by the successive action of chlorine in carbon tetrachloride and methyl alcohol into *βγ-dichloro-αδ-dimethoxy-ααδδ-tetraphenylbutane*, m. p. 183° (decomp.), which is reduced by sodium in amyl alcohol to ααδδ-tetraphenylbutane, converted by heat into *β-chloro-ααδδ-tetraphenyl-Δ^{αγ}-butadiene*, m. p. 246—247°, and oxidised by chromic acid to 3 : 4*-dichloro-*2 : 2 : 5 : 5*-tetraphenyltetrahydrofuran*, m. p. 280—281°; 3*-chloro-*2 : 2 : 5 : 5*-tetraphenyl-*2 : 5*-dihydrofuran*, from the last compound, sodium, and amyl alcohol, has m. p. 168—169°. ααδδ-Tetraphenylbutadiene is converted by sodium–potassium alloy in the presence of ether into the strongly coloured *dipotassium* derivative which, with alcohol and carbon dioxide, respectively, affords *ααδδ-tetraphenyl-Δ^β-butene*, m. p. 132—133°, and *ααδδ-tetraphenyl-Δ^β-butene-αδ-dicarboxylic acid*, m. p. 260—261°. In ethereal suspension, the metallic derivative is immediately decolorised by iodine, methylene iodide, tetramethylethylene dibromide, benzoyl chloride, oxygen, and sulphur, but in all cases only more or less pure ααδδ-tetraphenylbutadiene is obtained after addition of water.

as-Diphenylethylene gives a potassium derivative when shaken with sodium–potassium alloy in presence of ether, which is converted by alcohol into ααδδ-tetraphenylbutane; treatment of the metallic compound with iodine, methylene iodide, or tetramethylethylene bromide unexpectedly affords *as*-diphenylethylene; with dry oxygen the potassium derivative yields the *compound*, $CH_2<\substack{CPh_2—O\\ CH\cdot CPh_2}>O$, m. p. (indef.) 171—180°. as*-Didiphenylylethylene*, m. p. 204—205·5°, prepared by the action of magnesium methyl iodide on didiphenylyl ketone and dehydration of the product by glacial acetic acid, similarly yields a *potassium* derivative converted by alcohol into *ααδδ-tetradiphenylylbutane*, m. p. 234—235°; attempts to prepare 1 : 1 : 4 : 4-tetradiphenylyl*cyclo*butane were unsuccessful.

H. Wren.

Oxidation in the benzene series by gaseous oxygen. IV. Mechanism of slow oxidation of saturated hydrocarbons. H. N. Stephens (J. Amer. Chem. Soc., 1928, **50**, 2523—2529).—Oxidation of xylene at 102—104° in presence of acetic anhydride gives no xylyl acetate, but much more tolualdehyde than is obtained from xylene alone, on account of the removal of traces of water. Xylyl acetate does not yield tolualdehyde under these conditions. Similarly, ethylbenzene and acetic anhydride give an increased yield of acetophenone but no α-phenylethyl acetate. In parallel oxidations at 122—124° more acetophenone is formed from ethylbenzene in 11 days than from phenylmethylcarbinol. These and other facts (cf. A., 1926, 1028; 1927, 48; this vol., 285) indicate that alcohols are not intermediates in the formation of aldehydes and ketones in the oxidation of hydrocarbons. All the known facts are explained by assuming that the following series of reactions occurs: (*a*) reversible formation of a molecular aggregate from 1 mol. of hydrocarbon and 1 mol. of oxygen, (*b*) reversible decomposition of the aggregate into 1 mol. of water and an unsaturated residue, and (*c*) irreversible transformation of the unsaturated residue into an aldehyde or a ketone. The second stage accounts for the inhibitory action of water and also for the absence of inhibition in the oxidation of the *iso*propyl group, since in this case methyl alcohol is eliminated in (*b*). Oxidation to alcohols under exceptional conditions is explained by the formation of termolecular aggregates.

H. E. F. Notton.

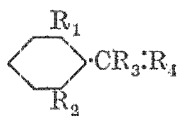
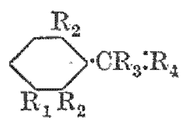
Alternating reactive positions in the nucleus of *tert.*-butylbenzene. J. B. Shoesmith and A. Mackie (J.C.S., 1928, 2334—2340).—Malherbe (A., 1919, i, 261) and the present authors were unable to confirm Senkowski's observation (A., 1890, 1296) that both *ortho-* (b. p. 247—248°/738 mm.; acetyl derivative of amino-compound, m. p. 159°) and *para-tert.*-butylbenzenes are produced by direct nitration. By the further nitration of *p*-nitro-*tert.*-butylbenzene to 2 : 4-dinitro-*tert.*-butylbenzene, reduction of the latter with ammonium hydrogen sulphide in alcohol to 2*-nitro-*4*-amino-*tert.*-butylbenzene*, m. p. 55°, and

elimination of the amino-group *o*-nitro-*tert.*-butylbenzene, b. p. 114—115°/10 mm. or 250·5°/765 mm., was obtained; reduction with iron and hydrochloric acid gave *o*-amino-*tert.*-butylbenzene (acetyl derivative, m. p. 161°). This, together with the observation that only *o*- and *p*-iodo-*tert.*-butylbenzenes react with hydrogen iodide in glacial acetic acid, the *meta*-compound being unaffected, are examples of the alternations of the reactive positions in the nucleus of *tert.*-butylbenzene. *p*-Nitro-*tert.*-butylbenzene with bromine and finely-divided iron at 90° is converted into o-*bromo*-p-*nitro*-tert.-*butylbenzene*, m. p. 94·5°, which with iron and hydrochloric acid gives 2-*bromo*-4-*amino*-tert.-*butylbenzene*, b. p. 153—155°/11 mm. [*hydrochloride*, m. p. 235° (decomp.); *acetyl* derivative, m. p. 142—143°]; o-*bromo*-tert.-*butylbenzene*, b. p. 96—98°/12 mm., was obtained from the last-named by elimination of the amino-group. Both o-*iodo*- (prepared from the corresponding amino-compound) and o-*bromo*-tert.-*butylbenzene* react with magnesium and carbon dioxide to give o-tert.-*butylbenzoic acid*, m. p. 68·5° (cf. Tschitschibabin, Elgasine, and Lengold, this vol., 404). A. I. VOGEL.

Micro-identification of isomerides and homologues in mixtures. I. Three isomeric xylenes. M. MAGITA (Bull. Chem. Soc. Japan, 1928, 8, 191—199)—2 : 4 : 6-Trinitro-*m*-xylene in alcoholic solution gives an instant intense bluish-green coloration (changing to dull yellow on keeping) on addition of a drop of potassium hydroxide solution, whilst 2 : 3 : 5-trinitro-*p*-xylene slowly develops an orange colour, the solution becoming turbid on keeping and a reddish-brown deposit is formed. In acetone solution the colours produced are respectively dark green and reddish-brown, both appearing instantaneously, but the trinitro-*m*-xylene is almost insoluble in hot acetone, whilst the trinitro-*p*-xylene is freely soluble. These colour reactions may, therefore, be used to detect the presence of *m*- and *p*-xylenes in mixtures if compounds such as trinitro-ψ-cumene, 2 : 4-di- and 2 : 4 : 6-tri-nitrotoluenes which give similar colour reactions are first removed by extraction with ether, alcohol, or acetone, in which the trinitroxylenes are only sparingly soluble. Identification of the three isomeric xylenes has been attempted by the polarisation-microscope method (Ernich, "Lehrbuch der Mikrochemie," 2nd Ed., 1926, 21). For this purpose the tetrabromo-compounds are unsuitable, but *m*- and *p*-xylenes may be distinguished by examination of their trinitro-compounds, 2 : 4 : 6-trinitro-*m*-xylene in α-bromonaphthalene having $n_1<N<n_2$ (n_1, n_2, and N representing the refractive indices for the faster and shorter rays in the crystal, and that of the medium, respectively) and positive elongation, and 2 : 3 : 5-trinitro-*p*-xylene having $n_1>N$ and negative elongation. Similar examination of sodium *o*- and *m*-xylene-4-sulphonates and *p*-xylene-2-sulphonate enables the last to be distinguished from *o*- and *m*-compounds by its refractive indices in cedar oil ($n_1>N$), but the *o*- and *m*-compounds can be distinguished only by their crystalline form, prismatic and rhombic plates, respectively, the value of n_1 for the former being lower than that of the cedar oil. Application of these methods to a sample of commercial xylene shows the absence of any appreciable quantity of the *o*-compound. Contrary to the principle of the technical separation of *p*-xylene, this hydrocarbon is readily absorbed by concentrated sulphuric acid. J. W. BAKER.

Introduction of the benzyl group into the benzene nucleus by means of sulphonic esters. Z. FOLDI (Ber., 1928, 61, [*B*], 1609—1616; cf. A., 1927, 453).—The introduction of the benzyl group into the benzene nucleus of hydrocarbons, phenols, phenolic ethers, carboxylic esters, and aldehydes is readily effected when a considerable excess of them is heated with benzyl benzenesulphonate in the absence of solvent, usually at 110—140°. The yields of monosubstituted derivatives are somewhat restricted by the pronounced tendency towards the production of di-derivatives and by the formation of *cyclo*paraffins from the eliminated benzylidene group. The change is considered to consist in the primary decomposition of the sulphonate into benzenesulphonic acid and benzylidene, followed by union of the latter with the benzenoid compound, giving an intermediate dicyclic *cyclo*propane which passes into the benzyl derivative. Benzene yields diphenylmethane (80%) and a mixture of *o*- and *p*-dibenzoylbenzenes. Toluene affords 85% of phenyl-*p*-tolylmethane (3 : 4′-dinitro-4-methyldiphenylmethane, m. p. 142—143°) and dibenzyltoluenes. Diphenylmethane gives a small yield of *o*-dibenzylbenzene, m. p. 77—79°, but the reaction is complicated by the production of much *cyclo*paraffin. Nitrobenzene and benzyl benzenesulphonate give a very dark product from which (?) 3 : 5-*dinitrodiphenylmethane*, m. p. 183—185°, is isolated in small amount (due to the presence of dinitrobenzene in the nitrobenzene used). Phenol yields *p*-benzylphenol, m. p. 83°, o-*benzylphenol*, b. p. 303—307°, and a small amount of benzyl phenyl ether, b. p. 284—286°. Anisole affords p-*benzylanisole*, b. p. 288—295°, in 77% yield. A benzylated benzaldehyde could not be obtained. Methyl salicylate is converted into *methyl* 6-*hydroxy*-3-*benzylbenzoate*, m. p. 79—80°, b. p. 134—138°/1 mm., and probably, methyl 2-hydroxy-3-benzylbenzoate. Tiglic acid does not appear to unite with the benzylidene group. Ethyl cinnamate is transformed into a mixture of the α-benzylcinnamate and (?) $\alpha\beta$-dibenzylcinnamate. H. WREN.

Possible isomerism of analogues of resolvable diphenyl compounds. J. F. HYDE and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 2499—2506).—If the forces preventing free rotation in the resolvable diphenyl compounds are entirely mechanical in nature, derivatives of types I and II might exist in

(I.)   (II.)

enantiomorphic forms providing R_4 is sufficiently large to interfere with the *o*-substituents. Attempts to resolve derivatives of these types (R_4 being oxygen) have been unsuccessful. Bromomesitylene, benzoyl

chloride, and aluminium chloride in carbon disulphide yield 2-*bromo*-4-*benzoylmesitylene*, m. p. 48—49°, the ketonic group of which does not react with zinc and ethyl bromoacetate, or magnesium phenyl bromide. 2-*Bromo*-4-p-*nitrobenzoylmesitylene*, m. p. 154—155°, prepared similarly, is hydrogenated (platinum) in alcohol to 2-*bromo*-4-p-*aminobenzoylmesitylene*, m. p. 138° (*hydrochloride*), an *azo*-derivative, m. p. 203—205°, being formed as a by-product in ethyl acetate. The d-*camphorsulphonate*, m. p. 175—200° (decomp.), of this amine has $[\alpha]_D$ +13·7°, changing in several hours to +7·1°, in chloroform. This is probably not due to stereoisomeric change (cf. Pope and Read, J.C.S., 1914, **105**, 800), since aniline *d*-camphorsulphonate shows a still greater variation ($[\alpha]_D$ +33·3° to $[\alpha]_D$ +6·6° in chloroform). 2-*Bromo*-4-mm'-*dinitrobenzoylmesitylene*, m. p. 160—161·5°, is hydrogenated to 2-*bromo*-4-mm'-*diaminobenzoylmesitylene*, m. p. 168—169°, which yields a d-*camphorsulphonate*, m. p. 216—218°, $[\alpha]_D$ +21·2° or 20·2° in chloroform, decreasing on keeping. Fractionation of these camphorsulphonates gave no indications of resolution and the regenerated amines were inactive. Attempts to obtain an optically active acid from the *brucine* salt, m. p. 90—95° (decomp.), $[\alpha]_D$ −21·3° or 19·9° in chloroform, of *iso*propyl 2-nitro-6-carboxybenzoate, or from *brucine* 3-*nitro*-2-(2'-*hydroxy*-p-*toluoyl*)*benzoate*, m. p. 160—165° (decomp.), $[\alpha]_D$ +18·3°, were unsuccessful. The anomalous rotation of the latter salt and that of quinine 4 : 4'-dinitrodiphenate (Kuhn and Albrecht, A., 1927, 876) is probably not due to asymmetric transformation, but to effects such as those observed by Hilditch (J.C.S., 1911, **99**, 224). H. E. F. NOTTON.

Hydrogenation of fluorene under pressure in the presence of nickel or osmium with addition of cerium and thorium. V. S. SADIKOV and A. K. MICHAILOV (Ber., 1928, **61**, [*B*], 1792—1796).—Hydrogenation of fluorene in the presence of osmium at 300° and 165 atm. original pressure proceeds much more rapidly than in the presence of nickel (cf. Ipatiev, A., 1909, i, 466) and gives a small proportion of dodecahydrofluorene in addition to decahydrofluorene, which is the sole product when nickel is used. Addition of cerium dioxide to the osmium catalyst causes an extraordinary enhancement of its activity, the yield of dodecahydrofluorene attaining about 93% at 300° with a maximal pressure of 153 atm. With thorium dioxide in place of cerium dioxide a still greater activation is observed, and dodecahydrofluorene is the sole product. With nickel oxide hydrogenation proceeds slowly and yields decahydrofluorene and unchanged fluorene; addition of cerium dioxide enormously increases the activity and causes almost exclusive production of dodecahydrofluorene. Thorium dioxide, on the other hand, greatly diminishes the activity of the nickel oxide catalyst. H. WREN.

α-Chloronaphthalene. II. Nitration. P. FERRERO and C. CAFLISCH (Helv. Chim. Acta, 1928, **11**, 795—812).—Mononitration of α-chloronaphthalene with nitric (*d* 1·4; 1·01 mols.) and sulphuric acids (2 mols.) gives a mixture of 1-chloro-4-, -5-, and -8-nitronaphthalenes. The proportion of the 1 : 5-derivative diminishes with rise of the reaction temperature (at 0—5°, 18·5%; at 95°, nil), whilst the 1 : 4-derivative increases (47%; 63·5%). The amount of the 1 : 8-compound is approximately constant (about 36·5%). A detailed study of numerous methods of nitration has been carried out and the results show that the isomerides can be obtained in varying amounts: 1 : 4-, 34·4—63·5%; 1 : 5-, 0—21·5%; 1 : 8-, 30·6—65·2%.

Determination of the amounts of the above isomerides in a mixture is not possible by physical methods. The following method was used. Treatment of the mixture with a 10% solution of ammonia in ethylene glycol at 150—160° removes the 1 : 4-isomeride as the corresponding amine. Sulphonation of the residue with sulphuric acid monohydrate at 95° for 3 hrs. effects the removal of the major part of the 8-nitro-derivative, the 5-nitro-compound being unaffected. H. BURTON.

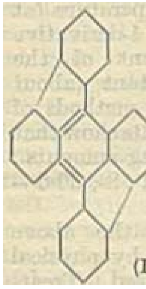
Chlorodecalin [chlorodecahydronaphthalene]. P. FERRERO and M. FEHLMANN (Helv. Chim. Acta, 1928, **11**, 763—776).—A modified Gysin apparatus (A., 1926, 389) is described for chlorinating decahydronaphthalene in an atomised state. The maximum yield of 2-chlorodecahydronaphthalene (about 40%) is obtained in presence of 0·5% of iodine and by repeated and rapid passage of the hydrocarbon through the chlorinating chamber. 2-Chlorodecahydronaphthalene is converted by fusion with potassium hydroxide at 150—160° into decahydro-β-naphthol, but does not give recognisable products when heated with amines. Condensation of 2-phenyldecahydronaphthalene, b. p. 163—164°/13 mm., d^{14} 0·9799, n^{12} 1·5419 (2-*p*-tolyl derivative, b. p. 178—180°/12 mm.), with phthalic anhydride in presence of aluminium chloride and carbon disulphide gives a small amount of 2 : 3'-β-*decahydronaphthylbenzoylbenzoic acid*, m. p. 184—186°; with *p*-chlorophenol, quinol, or benzoic acid and chlorodecahydronaphthalene, or with benzoyl- and chlorobenzoylbenzoic acids and decahydronaphthalene, no recognisable products were obtained.

Chlorination of benzene by the above process gives a mixture of polyhalogenated benzenes, whilst naphthalene in carbon tetrachloride solution gives under favourable conditions a 65% yield of α-chloronaphthalene. H. BURTON.

Attempt to prepare *p*-diphenylene. A. C. SIRCAR and J. N. MAJUMDAR (J. Indian Chem. Soc., 1928, **5**, 417—418; cf. A., 1927, 50).—When 4 : 4'-di-iododiphenyl is heated with copper powder at 300—310° for 15 hrs. in a sealed tube, *tetraphenylene*, $C_{24}H_{16}$, m. p. 304—305°, is formed. If the reaction is carried out at 280—300° for 5—6 hrs. in presence of a small quantity of water diphenyl is obtained. H. BURTON.

Constitution and synthesis of rubicene. W. SCHLENK and M. KARPLAS (Ber., 1928, **61**, [*B*], 1675—1680).—9 : 10-Diphenylanthracene, m. p. 240°, is obtained by the action of calcium hydride on boiling benzophenone, the product, $CHPh_2{\cdot}O{\cdot}Ca{\cdot}O{\cdot}CHPh_2$, being probably formed intermediately. Phenyl

diphenylyl ketone under similar conditions at 300° affords 9 : 10-didiphenylylanthracene (I), m. p. considerably above 300°, identical with rubicene obtained by the distillation of diphenic acid with alkali hydroxide (cf. Pummerer, A., 1912, i, 182). The hydrocarbon is prepared synthetically by converting anthraquinone by means of magnesium *p*-diphenyl iodide into 9 : 10-*dihydroxy*-9 : 10-*didiphenylyldihydroanthracene*, m. p. 29°, which is reduced by boiling formic acid. Boiling fluorenone and calcium hydride also yield rubicene. The reaction does not, however, appear generally applicable, since anthracene derivatives are not obtained from Michler's ketone or 4 : 4′-dimethoxybenzophenone. Acetophenone and calcium hydride afford 1 : 3 : 5-triphenylbenzene, m. p. 171—172°, and a *substance*, $C_{24}H_{20}O$, m. p 165—165·5°


(I.)

H. WREN.

Arylamine salts of the naphthalenesulphonic acids. V. Acetylation of Peri, Laurent, and Bronner acids and the arylamine salts of their acetyl derivatives. R. B. FORSTER, T. H. HANSON, and R. WATSON (J.S.C.I., 1928, 47, 155—157T).—Peri acid (α-naphthylamine-8-sulphonic acid), Laurent acid (α-naphthylamine-5-sulphonic acid), and Bronner acid (β-naphthylamine-6-sulphonic acid) behave in the same manner towards arylamines as naphthionic acid. They do not form arylamine salts unless the amino-group is acetylated first, showing that the inhibiting action of the amino-group on arylamine salt formation is independent of the relative positions of the sulphonic groups.

All these acids are acetylated readily by acetic anhydride in the presence of pyridine. The free acetamidosulphonic acids are easily hydrolysed, especially in the presence of dilute mineral acid; the sodium and potassium salts are quite stable and may be purified by recrystallisation from water. The pure naphthylaminesulphonic acids may be obtained by hydrolysing the alkali salts of the pure acetyl derivatives with dilute hydrochloric acid. The acetyl derivatives readily yield arylamine salts, most of which are well-defined crystalline substances with definite m. p. They are easily hydrolysed by either alkali hydroxide or mineral acid, but may be purified by recrystallisation from dilute acetic acid.

1-Acetamidonaphthalene-8-sulphonic acid forms arylamine *salts*, with m. p. as follows: aniline, 273°; *o*-toluidine, 198°; *p*-toluidine, 207°; ψ-cumidine, 257°; α-naphthylamine, 242°; benzidine, 287° (decomp.); tolidine, 267° (decomp.); dianisidine; *p*-chloroaniline; *p*-nitro-*o*-toluidine, 277° (decomp.).

1-Acetamidonaphthalene-5-sulphonic acid gives *salts* with m. p. as follows: aniline, 344° (decomp.); *o*-toluidine, 259°; *p*-toluidine, 255°; α-naphthylamine, indef.; β-naphthylamine, 280°; benzidine, 322° (decomp.); tolidine, 307° (decomp.); dianisidine, 328° (decomp.); ψ-cumidine, *p*-chloroaniline, and *p*-nitro-*o*-toluidine, no m. p.

2-Acetamidonaphthalene-6-sulphonic acid forms *salts* with m. p. as follows: aniline, 256°; *o*-toluidine, 262°; *p*-toluidine, 243°; ψ-cumidine, 277°; α-naphthylamine, 258°; β-naphthylamine, 262°; benzidine, 246°; tolidine, 315° (decomp.); *p*-chloroaniline, 275°; *p*-nitro-*o*-toluidine, 287° (decomp.); *o*-anisidine, 230°; *o*-phenetidine, 225°; *m*-bromoaniline, 249°; *p*-bromoaniline, 267° (decomp.).

Arylamine salts of the naphthalenesulphonic acids. VI. Salts of Koch acid, "H" acid, and chromotropic acid. R. B. FORSTER and D. H. MOSBY (J.S.C.I., 1928, 47, 157—159T).—Koch acid (α-naphthylamine-3 : 6 : 8-trisulphonic acid) forms salts with arylamines, containing 1 mol. of Koch acid to 2 mols. of monoamine or 1 mol. of a diamine. The third sulphonic acid group forms an inner salt with the amino-group. In "H" acid (1-amino-8-naphthol-3 : 6-disulphonic acid) only one of the sulphonic acid groups takes part in arylamine salt formation. The salts with diamines, therefore, consist of 2 mols. of "H" acid and 1 mol. of the diamine, and those with monoamines of 1 mol. of "H acid and 1 mol. of the monoamine. In chromotropic acid (1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid), which contains no basic group, both sulphonic acid groups are free to take part in arylamine salt formation.

The majority of the arylamine salts of Koch acid and chromotropic acid are extremely soluble in water and to a smaller extent in alcohol. Those of "H" acid are only sparingly soluble in either water or alcohol. It is pointed out that the capability of a sulphonic acid group to take part in arylamine salt formation depends on the stability of its sodium salt in dilute mineral acid solution.

The *salts* of Koch acid described have the following m. p.: aniline, 312°; *o*-toluidine, 304°; *p*-toluidine, 292°; *m*-xylidine, 284°; *o*-anisidine, 290°; *p*-anisidine, 287°; α-naphthylamine, 312°; β-naphthylamine, 322° (all decomp.); benzidine, decomp. 348°; tolidine, decomp. 345°; dianisidine, decomp. 339°.

The corresponding *salts* of "H" acid all decompose without melting between 320° and 345° (*p*-nitro-*o*-toluidine *salt*, 286°). The *salts* of chromotropic acid have the following m. p. (decomp.): aniline, 300°; *o*-toluidine, 290°; *p*-toluidine, 308°; *m*-xylidine, 307°; α-naphthylamine, 311°; β-naphthylamine, 293°; benzidine, decomp. 312°.

Nitration of substituted tertiary aromatic amines. G. R. CLEMO and J. M. SMITH (J.C.S., 1928, 2414—2422).—*p*-Chloro- and *p*-bromo-dimethylaniline when nitrated in concentrated sulphuric acid give a good yield of almost pure *m*-nitro-derivative (purity improved by the presence of carbamide), but when nitrated in dilute sulphuric acid yield the pure *o*-nitro-compound; the latter reaction is inhibited in the presence of carbamide. It is found that the change-over from *o*- to *m*-nitration is not a gradual process, but occurs between the sulphuric acid concentrations of 86% and 90%. *p*-Methyldimethylaniline, tetramethylbenzidine, *pp*′-tetramethyldiaminodiphenylmethane, and p-*dimethylaminobenzyl alcohol* (see this vol., 1239) are nitrated in the *m*-position in concentrated sulphuric acid, but readily yield *o*-nitro-derivatives with dilute sulphuric acid in the presence of carbamide. Further nitration and the ultimate effect of fuming nitric acid on *p*-bromo-

dimethylaniline are recorded. The following are described: 4-chloro-2-nitrodimethylaniline, m. p. 56°, converted by iron and hydrochloric acid into 4-*chloro-2-aminodimethylaniline*, b. p. 158°/22 mm. (*acetyl* derivative, m. p. 90°); 4-chloro-3-nitrodimethylaniline, m. p. 79°; 4-*chloro-3-aminodimethylaniline*, m. p. 54° (*acetyl* derivative, m. p. 97°); 4-bromo-2-nitrodimethylaniline, m. p. 64° (lit. 72°); 4-*bromo-2-aminodimethylaniline*, b. p. 165°/23 mm. (*acetyl* derivative, m. p. 111°); 4-*bromo-3-nitrodimethylaniline*, m. p. 93·5°; 3 : 3'-dinitro-4 : 4'-tetramethyldiaminodiphenylmethane, m. p. 121°; 3 : 3'-dinitrotetramethylbenzidine, m. p. 188°. Nitration of 4-bromo-2-nitrodimethylaniline with dilute nitric acid yields 4-*bromo-2 : 6-dinitrodimethylaniline*, m. p. 118°, together with 4-*bromo-2 : 6-dinitrophenylmethylnitrosoamine*, m. p. 124° (preferably prepared by direct dinitration of 4-bromodimethylaniline in dilute sulphuric acid), converted by alcoholic hydrogen chloride into 4-*bromo-2 : 6-dinitromethylaniline*, m. p. 104—105°, and by fuming nitric acid into 4-bromo-2 : 6-dinitrophenylmethylnitroamine, m. p. 113—114° (lit. 110°); treatment with fuming nitric acid for a longer period yields 2 : 4 : 6-trinitrophenylmethylnitroamine (tetryl), m. p. 127°. 4-Bromodimethylaniline when nitrated in concentrated sulphuric acid at 40° yields 4-bromo-3 : 6-dinitrodimethylaniline, m. p. 107° (lit. 108°), and with fuming nitric acid 4-bromo-2 : 3 : 6-trinitrophenylmethylnitroamine, m. p. 158° (lit. 165°).

C. W. Shoppee.

Nitro-derivatives of dibenzylaniline. R. D. Desai (J. Indian Chem. Soc., 1928, 5, 425—431).—Nitration of dibenzylaniline with nitric and acetic acids at 5° gives mainly *p*-nitrodibenzylaniline together with a small amount of the *o*-nitro-derivative. If an excess of nitric acid is used some 2 : 6-*dinitrodibenzylaniline*, m. p. 107°, accompanies the 2 : 4-dinitro-derivative, m. p. 103—104° (cf. Pinnow and Wiskott, A., 1899, i, 500). These dinitro-compounds are decomposed by heating with acetic anhydride and concentrated hydrochloric acid to the corresponding dinitroanilines. Reduction of *p*-nitrodibenzylaniline with zinc dust and hydrochloric acid in alcohol solution gives *p*-aminodibenzylaniline, m. p. 89—90° (*acetyl* derivative, m. p. 137—138°; *benzoyl* derivative, m. p. 166°), which condenses normally with benzaldehyde to give the corresponding *benzylidene* derivative, m. p. 166—167° [*hydrochloride*; *dibromide*, m. p. 220—225° (decomp.)], and not the substituted amino-carbinol (cf. Matzudaira, A., 1887, 812). *m*-Nitroaniline condenses with benzyl chloride in presence of sodium acetate and a trace of iodine at 125—130° to give m-*nitrodibenzylaniline*, m. p. 73—74° (*hydrochloride*, m. p. 140—142°), reduced to m-*aminodibenzylaniline* (*acetyl* derivative, m. p. 143—144°; *benzoyl* derivative, m. p. 171—172°), which affords a *benzylidene* derivative, m. p. 156—158° [*hydrochloride*, m. p. 195° (decomp.); *dibromide*, m. p. 196—198° (decomp.)]. *p*-Aminobenzylaniline (*acetyl* derivative, m. p. 141—142°; *benzoyl* derivative, m. p. 182—183°) yields a *benzylidene* derivative, m. p. 92—93° [*hydrochloride*, m. p. 170—172°; *dibromide*, m. p. 210° (decomp.) after sintering at 200°]. *o*-Aminodibenzylaniline (*acetyl* derivative, m. p. 121—122°; *benzoyl* derivative, m. p. 155—156°) is described.

H. Burton.

Action of sulphur monochloride on diphenylamine, and the preparation of trithiodiphenylamine and of other diphenylamine derivatives from diphenylamine. E. I. Orlov (Ukraine Chem. J., 1928, 3, 171—175).—Sulphur monochloride reacts at the ordinary temperature with diphenylamine to yield a precipitate of trithiodiphenylamine, $S_3{<}^{C_6H_4}_{C_6H_4}{>}NH$, whilst dithiodiphenylamine remains in solution. The former product, when nitrated, yields *di*-(p-*hydroxy*-o-*nitrophenyl*)*amine*, which is reduced to the corresponding amino-compound. The nitro-derivative forms a tetrammine salt with ammonia, which dyes wool a red colour.

R. Truszkowski.

Manufacture of 2 : 3- and 2 : 5-dichloroaceto-*p*-toluidides and -*p*-toluidines. I. G. Farbenind. A.-G.—See B., 1928, 704.

Ring formation. II. Constitution of monophthalylbenzidine. III. Condensation of benzidine with dibasic acid anhydrides. A. C. Sircar and P. R. Sen-Gupta (J. Indian Chem. Soc., 1928, 5, 397—399, 401—404).—II. When monophthalylbenzidine is treated with benzaldehyde, salicylaldehyde, or *m*-nitrobenzaldehyde in boiling nitrobenzene the corresponding benzylidene, m. p. above 300°, salicylidene, m. p. 297°, or m-*nitrobenzylidene*, m. p. 280°, derivative is obtained (cf. Le Fèvre and Turner, A., 1926, 1131). Diazotisation and treatment with β-naphthol affords 4'-*phthalimidodiphenylylazo*-β-*naphthol*, m. p. 273—275°. The presence of a free amino-group is thus definitely established.

III. Dibasic acid anhydrides condense with benzidine to form monosubstituted derivatives of the type $R{:}C_2O_2{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$. *Naphthalylbenzidine*, m. p. above 300° (*benzylidene*, m. p. 297°, *salicylidene*, m. p. 283°, and m-*nitrobenzylidene*, m. p. 299°, derivatives), *camphorylbenzidine*, m. p. 190°, and *quinolinylbenzidine*, m. p. above 300°, are described. Tolidine and quinolinic anhydride afford 4'-*aminoditolylylquinolinamic acid*, m. p. 231°, whilst benzidine and diphenic anhydride give 4'-*aminodiphenylyldiphenamic acid*, m. p. 199°. *Dinaphthalylbenzidine*, m. p. above 300°, is described.

H. Burton.

Action of diazo-salts on aromatic sulphonamides. II. Mechanism of the reaction and constitution of the diazosulphonamides. A. Key and P. K. Dutt (J.C.S., 1928, 2035—2040).—The reaction $R{\cdot}SO_2{\cdot}NH_2+R'{\cdot}N_2X \longrightarrow R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR'$ (I)$\longrightarrow R{\cdot}SO_2H+R'{\cdot}N_3$ readily takes place in presence of alkali even at low temperatures (*ibid.*, 1921, **119**, 2088). Investigation of the mechanism (where R= *p*-tolyl, R'=Ph) shows that this is not a case of true migration of the hydrogen atom from the nitrogen to the oxygen, followed by fission into the two final products, since when the pure, dry diazosulphonamide is heated alone or in a non-ionising solvent at a temperature above its decomposition point, conversion into the azoimide fails to take place. An electronic interpretation is therefore offered. It is suggested that the hydrogen in the

diazosulphonamide (I) is incipiently ionised because of the strong electron attraction actuated by the neighbouring positive charges. The proton is removed as water and the complex ion $R\cdot SO_2\cdot N\cdot N\dot{:}NR'$ (II) then undergoes further change due to the proximity of the positively-charged sulphur; the latter appropriates the two electrons between the sulphur and the nitrogen and fission into the sulphinate ion $R\cdot SO_2'$ and $R'\cdot N_3$ then takes place. The diazosulphonamide reacts with acid hydrolytic agents, forming only $R\cdot SO_2\cdot NH_2$ and $R'\cdot OH$, but no $R'\cdot NH_2$. In this case, ionisation to II again takes place and the two lone pairs of electrons in the nitrogen atom then appropriate two hydrogen ions, completing the system $R\cdot SO_2\cdot NH_2$ and leaving a positive ion $R'\cdot N\dot{:}N$ which is responsible for the formation of the phenol. When the diazosulphonamide is methylated in the cold, only one monomethyl derivative is formed. This substance yields, on reduction, $R\cdot SO_2\cdot NH_2$, ammonia, $R'\cdot NHMe$, $R'\cdot NMe\cdot NH_2$, and $R'\cdot NMe\cdot N\dot{:}N\cdot NMeR'$, and must therefore have the constitution $R\cdot SO_2N\dot{:}N\cdot NMeR'$ (III). In this case, velocity of methylation is much greater than that of the reaction yielding the azoimide, and it is accordingly the substance $R\cdot SO_2\cdot NH\cdot N\dot{:}NR'$ and not the ion which reacts. The $R\cdot SO_2\cdot NH\cdot N\dot{:}NMe\cdot R'X$ first formed is converted by elimination of HX into III. The isomeric methyl derivative $R\cdot SO_2\cdot NMe\cdot N\dot{:}NR'$, prepared from $R\cdot SO_2\cdot NHMe$ and $R'\cdot N_2Cl$, yields, on reduction, $R'\cdot NH_2$ and $R'\cdot NH\cdot NH_2$. M. CLARK.

Azo dyes from acetoacetanilides. H. E. FIERZ-DAVID and E. ZIEGLER (Helv. Chim. Acta, 1928, **11**, 776—786).—Acetoacetanilides are prepared from ethyl acetoacetate and anilines in presence of xylene and a small amount of pyridine. When these are treated with diazotised sulphanilic acid or other anilines, azo dyes of the form $SO_3H\cdot C_6H_4\cdot N\dot{:}N\cdot CHAc\cdot CO\cdot NHAr$ are obtained, which when reduced with stannous chloride and hydrochloric acid regenerate the aniline (or its reduction product) and yield 2 : 5-dimethyldihydropyrazine-3 : 6-dicarboxydianilides. The following are described : dianilide, m. p. 218° (decomp.); *di-o-toluidide*, m. p. 236—237°; *di-p-toluidide*, m. p. 227—228°; *di-m-xylidide*, m. p. 190°; *di-o-anisidide*, m. p. 231°; *di-o-chloroanilide*, m. p. 197°, and *di-2 : 5-dichloroanilide*, m. p. 215°.

Reduction of the "Hansa yellow" dyes G, GA, 3G, 5G, 10G, and R, and identification of the substituted anilines and dihydropyrazines obtained indicate that these dyes are prepared from the following diazotised anilines and acetoacetanilides : G and GA, 3-nitro-*p*-toluidine and acetoacetanilide; 3G, 4-chloro-*o*-nitroaniline and acetoacetanilide; 5G, *o*-nitroaniline and acetoacetanilide; 10G, 4-chloro-*o*-nitroaniline and acetoacet-*o*-chloroanilide; R, 2 : 5-dichloroaniline and 1-phenyl-3-methyl-5-pyrazolone. H. BURTON.

Superheating of phenyl ββ-dimethylacrylate. S. SKRAUP (Ber., 1928, **61**, [*B*], 1665—1666).—The production of *o*-ββ-dimethylacroylphenol by superheating phenyl ββ-dimethylacrylate is confirmed (cf. Skraup and Beng, A., 1927, 560). The inability of von Auwers (this vol., 407) to repeat this observation is probably due to insufficient regard to the very narrow limits of temperature within which the change occurs. H. WREN.

Additive compounds of phenols and ammonia. III. System phenol–ammonia. E. BRINER and O. AGATHON (Helv. Chim. Acta, 1928, **11**, 922—925; cf. A., 1926, 1241; 1927, 1181).—This system has now been studied by the manometric method. The results are not as conclusive as in previous systems examined by this method, since no flat portion is obtained on the curve of pressure against volume of ammonia introduced. This is attributed to a liquefaction of the phenol which occurs when brought in contact with ammonia. Support, however, is obtained for the view, advanced previously, that a compound $PhOH,NH_3$ is formed. R. N. KERR.

Additive compounds of phenols and ammonia. IV. Ammoniation of naphthols, dihydroxybenzenes, hydroxybenzoic acids, hydroxyanthraquinones, dihydroxyanthraquinones, and *o*-nitrophenol; heats of ammoniation. E. BRINER and A. MORF (Helv. Chim. Acta, 1928, **11**, 926—944; cf. preceding abstract).—The manometric method of investigation has been extended to the systems of the above compounds with ammonia. Satisfactory curves have been obtained in all cases except with salicylic acid, which, like phenol, liquefies in contact with ammonia. The dissociation pressures of the ammoniates formed have been measured and their heats of formation from the original substance and ammonia have been calculated from the dissociation pressures at two different temperatures; these are signified by Q expressed per g.-mol. Proof of the formation of the following has been obtained: *α-naphthol monoammoniate*; *β-naphthol semiammoniate*, $C_{10}H_7\cdot OH,0\cdot 5NH_3$, crystalline, $Q=5$ kg.-cal.; *β-naphthol monoammoniate*, $Q=9$ kg.-cal. The three dihydroxybenzenes form monoammoniates very readily and also diammoniates, the stabilities of which increase from *o*- to *p*-; *pyrocatechol monoammoniate*, needles, $Q=13$ kg.-cal.; *pyrocatechol diammoniate*, unstable, $Q=18$ kg.-cal.; *quinol diammoniate*, crystalline. The three hydroxybenzoic acids form *monoammoniates* very readily; the *m*- and *p*-acids form *diammoniates* at low pressures, but the *o*- requires a pressure of 2 atm. at 20°; the heats of formation of the diammoniates are *o*-, 5 kg.-cal.; *m*-, 7·5 kg.-cal.; *p*-, 8·5 kg.-cal. The mono- and di-hydroxyanthraquinones form very stable monoammoniates: *α-hydroxyanthraquinone monoammoniate*, deep red; *β-hydroxyanthraquinone monoammoniate*, yellowish-red; *alizarin monoammoniate*, violet, $Q=5$ kg.-cal.; *quinizarin monoammoniate*, violet; *hystazarin monoammoniate*, deep red. The dissociation pressures of the mono- and tri-ammoniates of *o*-nitrophenol, already described, have been determined at several temperatures; the heats of formation are respectively 17·6 and 33·6 kg.-cal. R. N. KERR.

Chloro-*o*-xylenols. II. 3-Chloro-*o*-4-xylenol, the dichloro-*o*-4-xylenols, and 4 : 5-dichloro-*o*-3-xylenol. L. E. HINKEL, E. E. AYLING, and L. C. BEVAN (J.C.S., 1928, 2529—2533; cf. *ibid.*, 1923, **123**, 2968).—Syntheses of five of the eight remaining

chloro-*o*-xylenols are described. 3-Benzeneazo-*o*-4-xylenol was reduced to 3-*amino*-o-4-*xylenol*, m. p. 126°, from which 3-*chloro*-o-4-*xylenol*, m. p. 27° (*benzoyl* derivative, m. p. 87°), was obtained. Nitration of 5-chloro-*o*-4-xylenol gave 5-*chloro*-3-*nitro*-o-4-*xylenol*, m. p. 127·5°, which was reduced to 5-*chloro*-3-*amino*-o-4-*xylenol*, m. p. 175°. Attempts to replace the amino-group by chlorine in the last compound led to a mixture of chloroxylenols from which only 3 : 5-*dichloro*-o-4-*xylenol*, m. p. 52° (*benzoyl* derivative, m. p. 89°) (also obtained from 3 : 5-dichloro-*o*-4-xylidine), was isolated. Benzenediazonium chloride coupled with 6-chloro-*o*-4-xylenol to give 6-*chloro*-5-*benzeneazo*-o-4-*xylenol*, m. p. 143°, which yielded on reduction 6-*chloro*-5-*amino*-o-4-*xylenol*, m. p. 144·5°. Attempts to displace NH_2 by Cl led to elimination of nitrogen and the regeneration of 6-chloro-*o*-4-xylenol. 3 : 5-*Dichloro*-o-3-*xylenol*, m. p. 90° (*benzoyl* derivative, m. p. 133°), 3 : 6-*dichloro*-o-4-*xylenol*, m. p. 84° (*benzoyl* derivative, m. p. 124°), and 5 : 6-dichloro-*o*-4-xylenol (cf. Hinkel, A., 1924, i, 1204) were prepared from the corresponding dichloroxylidines (this vol., 995). R. J. W. LE FEVRE.

Synthesis of 1-phenanthrol. J. B. SHOESMITH and A. GUTHRIE (J.C.S., 1928, 2332—2334).—α-*Naphthylparaconic acid*, m. p. 169° (decomp.), prepared from α-naphthaldehyde (p-*nitrophenylhydrazone*, m. p. 233—235°), is converted by heating at 340° (metal bath temp.) into 1-*phenanthrol*, m. p. 156° (*picrate*, m. p. 182°), which on methylation yields 1-methoxyphenanthrene, m. p. 105°, identical with that obtained by Pschorr, Wolfes, and Buckow (A., 1900, i, 232). C. W. SHOPPEE.

Catalytic condensation of acetylene with phenols. II. Resorcinol. S. A. FLOOD and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1928, **50**, 2566—2573).—2 : 4-*Dihydroxystyrene* (I) (+MeOH), decomp. above 250°, the intermediate product in the formation of 3 : 6-dihydroxy-9-methylxanthen (II) from resorcinol and acetylene in presence of a mercury catalyst (cf. A., 1924, i, 282), may be isolated from methyl-alcoholic solutions. Excess of acetylene causes resinification, and a similar resin is formed from acetal and resorcinol in presence of acid. The styrene I forms an insoluble *polymeride* when kept. It is reduced by tin and hydrochloric acid to ethylresorcinol, and its *diacetate*, m. p. 285—286°, is identical with the so-called acetalresorcinol diacetate of Causse (A., 1887, 40). With resorcinol in alcohol I gives the xanthen II. Resorcinol monomethyl ether gives amorphous products with acetylene, but the dimethyl ether gives 2 : 4-*dimethoxystyrene*, b. p. 235° (decomp.), which is oxidised by permanganate to 2 : 4-dimethoxybenzoic acid. The products I and II are also formed consecutively from acetaldehyde and resorcinol in methyl alcohol in presence of acid (cf. Mohlau and Koch, A., 1895, i, 46). H. E. F. NOTTON.

Reductive fission of dieugenyl ethylene ether. A. S. PFAU (Helv. Chim. Acta, 1928, **11**, 877—881).—Reduction of dieugenyl ethylene ether, m. p. 88—89° (lit. 85°; 1 part), with sodium (2 parts) and alcohol gives *m*-propylanisole (I), dihydroeugenyl β-hydroxyethyl ether, b. p. 170°/10 mm., m. p. 50·5°, *iso*eugenyl β-hydroxyethyl ether (II), m. p. 92—92·5°, and bisdihydroeugenyl ethylene ether (III), m. p. 104—104·5° (lit. 101°). When reduction is effected with 1 part of sodium the products are di-*iso*eugenyl ethylene ether, m. p. 118—119°, (I), (II), (III), and unchanged material. The first stage of the reduction is the isomerisation of the allyl to the propenyl group. H. BURTON.

Naphthylene-1 : 8-disulphide. W. B. PRICE and S. SMILES (J.C.S., 1928, 2372—2374).—A continuation of previous work on the formation of sulphur ring systems (cf. this vol., 647, 769), which is now extended to five- and six-membered dithiorings involving the *peri*-system of naphthalene. 1-*Sulphinonaphthalene*-8-*sulphonic acid* is obtained by treatment of naphthalene-1 : 8-diazosulphonic acid with sulphurous acid and copper powder. Reduction of its *sodium* salt with sulphurous acid and dilute hydriodic acid yields 1 : 1′-*dithiodinaphthalene*-8 : 8′-*disulphonic acid*, from the di-sulphonyl chloride of which 1 : 1′-*dithiodinaphthalene*-8 : 8′-*disulphinic acid*, m. p. 144°, is obtained by reduction with sodium sulphite. Further reduction with zinc dust and alcoholic hydrochloric acid yields 1 : 8-*dithiolnaphthalene*, m. p. 113—114°, characterised by the *dimethylthiol*, m. p. 84°, and by a crystalline brownish-purple *nickel* derivative, $C_{10}H_6S_2Ni$. The dithiol is readily oxidised in air or with mild oxidising agents to *naphthylene*-1 : 8-*disulphide*, m. p. 116°, without the simultaneous formation of complex polysulphides, and condenses with benzaldehyde in the presence of hydrogen chloride to yield 2-*phenyl*-peri-*naphtha*-1 : 3-*dithian*, m. p. 116°. C. W. SHOPPEE.

Iodine values of some sterols by Dam's method. A. M. COPPING (Biochem. J., 1928, **22**, 1142—1144).—Certain sterols and their derivatives yield abnormal values by the pyridine–sulphate–dibromide method (cf. Dam, A., 1925, ii, 444; i, 856). Ergosterol shows a high value. The presence of a ketonic group in the molecule, as in cholestenone, causes low values to be obtained. Structural differences within the molecule of the type represented by *allo*cholesterol do not cause variations in the iodine values of sterols of the same empirical formula. Except in the case of ergosterol the duration of the reaction does not greatly affect the iodine value. S. S. ZILVA.

Reduction of *p*-dimethylaminobenzaldehyde and preparation of *p*-dimethylaminobenzyl alcohol. G. R. CLEMO and J. M. SMITH (J.C.S., 1928, 2423—2426).—p-*Dimethylaminobenzyl alcohol* is obtained in 20% yield by reduction of the corresponding aldehyde with sodium amalgam in alcoholic solution as an oil, b. p. 123°/1 mm. [*benzoate*, m. p. 91°; m-*nitrobenzoate*, m. p. 76°; *methiodide*, m. p. 232° (decomp.); *chloroplatinate*, +2EtOH, m. p. 100° (decomp.); a picrate could not be prepared]; the substance described by Braun and Kruber (A., 1912, i, 968) as *p*-dimethylaminobenzyl alcohol picrate is probably dimethyl-*p*-toluidine picrate. Together with the alcohol is obtained a mixture of stereoisomeric s-*bis*-(p-*dimethylaminophenyl*)*ethylene glycols*, m. p. 113° [*dimethiodide* +EtOH, m. p. 97° (decomp.)] and m. p. 178° [*monomethiodide*, m. p. 232° (decomp.)], from which hydroxylic derivatives could not

be prepared (cf. Rousset, A., 1895, i, 176). The alcohol could not be obtained from the aldehyde by treatment with potassium hydroxide (cf. Rousset, *loc. cit.*), and electrolytic reduction of the aldehyde yields a mixture of the alcohol, dimethyl-*p*-toluidine, 4 : 4-tetramethyldiaminodiphenylmethane, and the glycol, m. p. 178° (cf. Schepss, A., 1913, i, 1154).

C. W. SHOPPEE.

Dependence of rotatory power on chemical constitution. XXXII. Resolution of phenylbenzylcarbinol. W. GERRARD and J. KENYON (J.C.S., 1928, 2564—2567).—To examine the effect of introducing two aromatic nuclei into the molecule of an aliphatic secondary alcohol the *d*- and *l*-forms of phenylbenzylcarbinol (Levene, A., 1925, i, 1375) were prepared by crystallising *quinine phenylbenzylcarbinyl phthalate* [*d*A,*l*B salt, m. p. 205° (decomp.)] and *cinchonine phenylbenzylcarbinyl phthalate* [*l*A,*d*B salt, m. p. 110°, $[\alpha]_{5461}^{25}$ +82·3° (in ethyl alcohol)], followed by acidification, giving the d- and l-*phenylbenzylcarbinyl hydrogen phthalates*, both m. p. 131°, $[\alpha]^{25}$ +32·75°, $[\alpha]_{5461}^{25}$ +38·75°, and $[\alpha]_{5461}^{25}$ −38·80°, respectively (all in ethyl alcohol). Boiling with aqueous sodium hydroxide liberated d- and l-*phenylbenzylcarbinols*, both m. p. 67°, the specific rotatory powers of which, in both the homogeneous state at different temperatures and in various solvents together with the specific rotatory powers of l-*phenylbenzylcarbinyl acetate*, b. p. 182°/15 mm., in the homogeneous state at different temperatures and of *d*-phenylbenzylcarbinyl hydrogen phthalate in various solvents are recorded. The rotatory power of the carbinol at 20° is the highest yet recorded for a secondary alcohol. The homogeneous *d*-carbinol has $[\alpha]_{4358}$ +16·7° at 125° and +120·2° at 20°.

R. J. W. LE FÈVRE.

Mobility of symmetrical triad (prototropic) systems. III. Three-carbon prototropy in an αγ-diphenylallyl ether. C. W. SHOPPEE (J.C.S., 1928, 2567—2571).—The assignation of one of two possible mechanisms (Burton and Ingold, this vol., 634; Ingold, Shoppee, and Thorpe, A., 1926, 939) for the change OH·CHR′·CH:CHR″ ⟶ R′·CO·CH_2·CH_2R″ was attempted by examining an ether of type OR·CR′:CH·CH_2R″, in which pinacolic electron displacement is precluded. αγ-Diphenylallyl alcohol (from cinnamaldehyde and magnesium phenyl bromide) gave, by treatment with hydrogen bromide in glacial acetic acid, *bis-αγ-diphenylallyl ether*, m. p. 98—99°, ozonolysis of which led to benzaldehyde and benzoic acid, whilst bromination gave *bis-βγ-dibromo-αγ-diphenylpropyl ether*. Boiling sodium ethoxide solution caused isomerisation to *bis-αγ-diphenylpropenyl ether*, the constitution of which followed from bromination in chloroform, giving *bis-β-bromo-αγ-diphenylpropenyl ether* [(CH_2Ph·CHBr·CBrPh)$_2$O ⟶ (CH_2Ph·CBr:CPh)$_2$O+2HBr], and ozonolysis in acetic acid, yielding phenylacetaldehyde (isolated as semicarbazone) and benzoic acid. This occurrence of simple three-carbon prototropy (not involved in a pentad keto–enol complex) favours the second mechanism of Burton and Ingold (*loc. cit.*).

Phenyl β-phenylethyl ketone semicarbazone has m. p. 144°.

R. J. W. LE FÈVRE.

Infra-red absorption spectra of organic compounds of sulphur. I. Aryl mercaptans and sulphides. F. K. BELL (Ber., 1928, **61**, [*B*], 1918—1923; cf. A., 1927, 1052).—The infra-red absorption spectra of benzyl mercaptan, thiophenol, thio-*p*-cresol, dibenzyl, and diphenyl sulphide have been investigated between 1·0 and 12·0 μ. The occurrence of a well-marked absorption band at 3·9 μ with the mercaptans which is not present with the sulphides allows a further extension of the author's method for the qualitative discrimination of these two classes of compounds (*loc. cit.*). The relative intensity of the 3·9 μ band is greatest for purely aryl mercaptans and least for the strictly aliphatic compounds. With arylalkyl and alkylaryl mercaptans the intensity is approximately the same and intermediate between that of the aryl and alkyl compounds.

H. WREN.

Existence of optically active carbonium salts. P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1928, **11**, 842—847).—Phenyl-*o*-tolyldiphenylylmethyl chloride (I) reacts with α-methylglucoside in presence of pyridine, yielding the *phenyl-*o*-tolyldiphenylylmethyl α-methylglucoside ether*, +0·5H_2O, m. p. 121°, which after one crystallisation from aqueous methyl alcohol has $[\alpha]_D$ +49·19° in methyl alcohol, and after three crystallisations +55·8°. Decomposition of the ether with hydrogen chloride gives I, whilst with 0·2% alcoholic hydrochloric acid the *ethyl ether* of *phenyl-*o*-tolyldiphenylylcarbinol*, m. p. 144° after sintering at 142°, is obtained. Both these compounds are optically inactive. From *d*-camphylcarbinol and I the *phenyl-*o*-tolyldiphenylylmethyl* d-*camphylcarbinol ether* is obtained. This ether has m. p. 134°, $[\alpha]_D$ +28·86° in benzene, after one crystallisation from alcohol, and m. p. 148° (sinters at 145°), $[\alpha]_D$ +13·92°, after four crystallisations. It is decomposed by hydrogen chloride, yielding I. The results indicate that in the ethers the carbinol radical exists in an optically active form, but the carbonium salts are very rapidly racemised.

H. BURTON.

Oil-soluble bismuth salts; hexahydrobenzoate and camphocarbonate. M. PICON (J. Pharm. Chim., 1928, [viii], **8**, 206—211; cf. this vol., 288).—Bismuth hexahydrobenzoate and camphocarbonate are prepared from bismuth oxide and the corresponding acids. *Bismuth hexahydrobenzoate*, Bi($C_7H_{11}O_2$)$_3$, amorphous, pale yellow, is soluble in organic solvents not containing oxygen, but, with the exception of oils, it is decomposed by solvents containing oxygen in the molecule with the formation of the *basic hexahydrobenzoate*, C_6H_{11}·CO_2BiO. The basic salt is also formed on treatment of the benzene solution of the neutral salt with water, but water alone has no action on the neutral salt, which is insoluble. *Bismuth camphocarbonate*, Bi($C_{11}H_{15}O_3$)$_3$, is soluble without decomposition in all the usual organic solvents; it is insoluble in water and its solution in benzene is not attacked by water. Both salts are soluble in oils, forming solutions which yield stable emulsions with water.

E. H. SHARPLES.

Syntheses with diazomethane. F. ARNDT, B. EISTERT, and J. AMENDE (Ber., 1928, **61**, [*B*], 1949—1953; cf. Arndt and others, this vol., 739 and previous abstracts; Nierenstein, this vol., 739).—The amount of

chloroacetophenone produced by the action of diazomethane on benzoyl chloride is determined by adding the product, after removal of ether, to a saturated solution of *o*-nitrophenylhydrazine in ether, whereby the chloro- but not the diazo-acetophenone is precipitated as the sparingly soluble *o*-nitrophenylhydrazone, m. p. 149°. From 5 g. of benzoyl chloride, 0·5 g. or 0·6 g. of chloroacetophenone is derived by the action of 2 mols. or 1 mol. of diazomethane. If ammonia is passed into the solution and the ammonium chloride removed before vaporisation of the ether, the amount of chloroacetophenone falls to 0·17 g. The bulk of the chloro-ketone is therefore produced from the diazo-ketone and free hydrogen chloride during removal of the ether. The authors accordingly share the views of Bradley and Robinson (this vol., 894) with regard to the mechanism of the action.

The authors conclude that the course of the action of diazomethane on aldehydes is governed generally by the nature of the aldehyde, although experimental conditions may have an important influence with certain definite aldehydes (cf. Mosettig, this vol., 887).

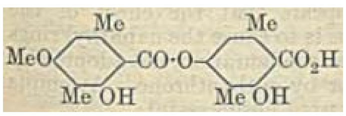
Acknowledgment is made that the isomerisation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid is not specifically a photochemical change and that *o*-nitrophenylacetone (*o*-nitrobenzyl methyl ketone) has been obtained previously by Neber (A., 1925, i, 1073).

H. WREN.

Iminodicarboxylic and nitrilotricarboxylic acids. G. STADNIKOV and N. TITOV (Ber., 1928, **61**, [*B*], 1788—1789; cf. A., 1912, i, 116).—Nitrilodi-α-propionicphenylacetic acid, $(CO_2H·CHMe)_2{:}N·CHPh·CO_2H$, m. p. 201° (decomp.), is converted by fuming hydrochloric acid at 160° into phenylglycine acid in almost quantitative yield. The same product is obtained analogously from anhydronitritodi*iso*butyricphenylacetic acid, $C_{16}H_{19}O_5N$, m. p. 187° (decomp.). Under these conditions the intermediate iminodiacetic acids are, therefore, also unstable. H. WREN.

Conversion of cyanonaphthalenesulphonic acids, and products of the conversion. I. G. FARBENIND. A.-G.—See B., 1928, 780.

Constituents of lichens. II. Constitution of barbatic acid. A. S. PFAU (Helv. Chim. Acta, 1928, **11**, 864—876; cf. Stenhouse and Groves, Annalen, 1880, **203**, 285; Hesse, A., 1903, i, 702).—Steam-distillation of the alcoholic extract from 35 kg. of the lichen *Evernia prunastri*, L. Ach., gives 2·5 g. of rhizonic acid (now shown to be 2-hydroxy-4-methoxy-3 : 6-dimethylbenzoic acid), m. p. 233—235° [*methyl* ester (I), m. p. 95°; *ethyl* ester (II), m. p. 82°], obtained also by the hydrolysis of barbatic acid (annexed formula), m. p. 191°, with barium hydroxide solution. The prolonged action of hot alcohol on barbatic acid affords II. Methylation of methyl β-orcinolcarboxylate (cf. A., 1926, 836) yields I together with *methyl* 2 : 4-*dimethoxy*-3 : 6-*dimethylbenzoate*, b. p. 161—163°/10 mm. (free *acid*, m. p. 104·5°). Treatment of a mixture of β-orcinol and formanilide with phosphorus oxychloride in absolute



ether and decomposition of the resulting product with sodium hydroxide solution gives 2 : 4-*dihydroxy*-3 : 6-*dimethylbenzaldehyde*, m. p 163—164° [*oxime*, m. p. 224—225°; *semicarbazone*, m. p. 285° (decomp.)], methylated to 2-*hydroxy*-4-*methoxy*-3 : 6-*dimethylbenzaldehyde* (III), m. p. 136° (cf. Sonn, A., 1917, i, 143) (*oxime*, m. p. 188—189°).

When rhizonic acid is heated with copper powder at 200° β-orcinol monomethyl ether, b. p. 135—138°/10 mm., m. p. 67·5—68° (lit. 118—121°), is obtained. The action of formanilide and phosphorus oxychloride on this ether is to give III. Treatment of the *O*-acetyl derivative of III with zinc and ethyl bromoacetate in presence of benzene and subsequent hydrolysis of the product with alcoholic potassium hydroxide gives 5 : 8-*dimethylumbelliferone methyl ether*, m. p. 128—129°, thus demonstrating that in III the hydroxyl and aldehyde groups are in the *o*-position (cf. Sonn, *loc. cit.*).

The *iso*rhizonic acid from the lichen *Ramalina dilacerata*, Hoffm. (Nakao, J. Pharm. Soc. Japan, 1923, No. 496), and the rhizonic acids from *Evernia prunastri* and *Usnea ceratina* (Hesse, *loc. cit.*) are identical.

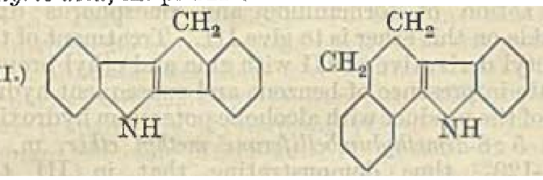
[With A. OFNER.]—β-Orcinol monomethyl ether undergoes the Gattermann reaction using zinc cyanide, yielding a mixture of 94% of III and 6% of 4-*hydroxy*-2-*methoxy*-3 : 6-*dimethylbenzaldehyde*, m. p. 150—150·5°, whilst orcinol monomethyl ether gives evernaldehyde (26%), m. p. 64°, and *iso*evernaldehyde (74%), m. p. 194—195° (lit. 188°). H. BURTON.

Thiophthalic acids. I. G. C. CHAKRAVARTI (J. Indian Chem. Soc., 1928, **5**, 405—410; cf. A., 1927, 970).—When phthalyl chloride is treated with alcoholic potassium hydrosulphide at −5 to 10° a mixture of 2 : 2′-*dicarboxydibenzoyl disulphide* (I), m. p. 242° (*potassium* and *lead* salts), monothiophthalic acid (II), m. p. 198° (decomp.; *sodium* and *lead* salts), *diphthalyl disulphide*, m. p. above 320°, and thiophthalic anhydride, m. p. 114°, is obtained. It is assumed that the primary product of the reaction is dithiophthalic acid, which, by loss of hydrogen sulphide, gives thiophthalic anhydride, and by atmospheric oxidation, diphthalyl disulphide. By the action of water it gives monothiophthalic acid, which oxidises with great readiness to (I). Hydrolysis of ditolyl dithiophthalate with alcoholic potassium hydrosulphide at 120° in a sealed tube gives I, also formed by oxidation of II when its ethereal solution is evaporated.

H. BURTON.

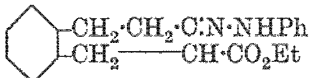
Conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus. III. A. F. TITLEY (J.C.S., 1928, 2571—2583).—Attempts are described to effect ring closure by the Dieckmann reaction between the *o*-, *m*-, and *p*-positions in esters of general formula $CO_2R·C_6H_4·[CH_2]_n·CO_2R$ and $C_6H_4([CH_2]_n·CO_2R)_2$. Thus *ethyl* β-o-*carbethoxyphenylpropionate*, b. p. 182—183°/14 mm. (from *o*-aldehydobenzoic acid and malonic acid by way of *o*-carboxycinnamic acid, by sodium amalgam reduction and esterification of the product) reacted with sodium under toluene at 100° to form successively ethyl sodio-1-hydrindone-2-carboxylate (I) and ethyl 1-hydrindone-2-carboxylate

(cf. Mitchell and Thorpe, J.C.S., 1910, **97**, 2273). The phenylhydrazone of the last ester was converted by hydrochloric acid into 2 : 3-*indeno*-(1 : 2)-*indole* (II), m. p. 251° (cf. Armit and Robinson, *ibid.*, 1922, **121**, 838). Methylation (methyl iodide) of I gave ethyl 2-methyl-1-hydrindone-2-carboxylate, which did not form a phenylhydrazone or a semicarbazide. Hydrolysis gave, besides 2-methyl-1-hydrindone (Mitchell and Thorpe, *loc. cit.*), β-o-*carboxyphenyl*iso-*butyric acid*, m. p. 141°.

(II.)  (III.)

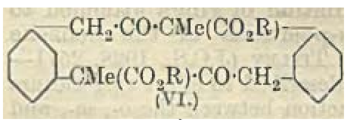
Ethyl γ-o-*carbethoxyphenyl*-n-*butyrate*, b. p. 188—189°/14 mm., with sodium gave ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (IV), m. p. 33° (Hückel and Goth, A., 1924, i, 1196, give 34°), converted by treatment with phenylhydrazine hydrochloride and hydrochloric acid into 1 : 2-*indolo*-(2 : 3)-3 : 4-*dihydronaphthalene* (III), m. p. 161°. By the methyl iodide methylation of the sodio-derivative of IV, *ethyl* 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene-2-carboxylate*, b. p. 183—184°/18 mm., was obtained, acid hydrolysis of which led to 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 143°/20 mm., whilst alkaline hydrolysis gave a mixture of this ketone with γ-o-*carboxyphenyl*-α-*methylbutyric acid*, m. p. 173°.

Ethyl o-*phenylenedipropionate*, b. p. 200—202°/12 mm., and sodium gave low yields of the *phenylhydrazone* of *ethyl* 3-*ketophenheptamethylene-2-carboxylate* (V), m. p. 198° (decomp.).



(V.)

No ring compounds were obtained by the action of sodium at 100° on *methyl* m-*phenylenediacetate*, b. p. 185—187°/15 mm., *ethyl* m-*phenylenediacetate*, b. p. 188—189°/12 mm., *methyl* p-*phenylenediacetate*, b. p. 189—190°/15 mm., or *ethyl* p-*phenylenediacetate*, m. p. 59° (all prepared by hydrolysis of corresponding nitriles by methyl- or ethyl-alcoholic hydrogen chloride), the only isolable products being: (from the second) a *compound*, $C_{12}H_{12}O_3$, m. p. 30—40°; (from the fourth) a *compound*, isolated as the *phenylhydrazone*, $C_{18}H_{18}O_2N_2$, m. p. 194—195° (with previous softening at 190°); from the first, a *compound* (possibly VI), $C_{24}H_{24}O_6$, b. p. 217—222°/1



(VI.)

alkalir an alkali·oluble *su-stance*, $C_{22}H_{18}O_5$, .p. 345—346° (sintering at 340°), and also a fraction yielding by hydrolysis *m*-phenylenediacetic acid and *phenylene*-1-*acetic*-3-α-*propionic acid*, m. p. 132°, and from the third a *substance*, $C_{24}H_{24}O_6$, b. p. 225—228°/1 mm., together with (after hydrolysis) *p*-phenylenediacetic acid and *phenylene*-1-*acetic*-4-α-*propionic acid*, m. p. 189°.

The *methyl* ester, b. p. 184—185°/15 mm., of m-*carboxyphenylpropionic acid*, m. p. 177° (from *iso*phthalaldehydic acid and malonic acid through *m*-carboxycinnamic acid by sodium-amalgam reduction), by treatment with sodium etc. led only to β-m-*carboxyphenyl*iso*butyric acid*, m. p. 137—138° (corr.), synthesised by the following sequence: *m*-toluoyl chloride to ω-*chloro*-m-*toluoyl chloride*, b. p. 149—150°/20 mm. (direct chlorination), to *ethyl* ω-*chloro*-m-*toluate*, b. p. 168—169°/25 mm., to *ethyl* m-*carbethoxybenzylmethylmalonate*, b. p. 234°/24 mm., to the corresponding *acid*, m. p. 182—183° (decomp.), to β-*m*-carboxyphenyl*iso*butyric acid (*methyl* ester, b. p. 182°/18 mm.) identical with the compound above.

p-Carboxyphenylpropionic acid was prepared by two methods: (1) *p*-toluoyl chloride gave on bromination ω-bromo-*p*-toluoyl chloride, ω-*bromo*-p-*toluoyl bromide*, b. p. 170—171°/20 mm., m. p. 56°, and ωω-dibromo-*p*-toluoyl chloride and bromide (which gave with alcohol *ethyl* ωω-*dibromo*-p-*toluate*, m. p. 103°). The second of these gave *ethyl* ω-*bromo*-p-*toluate*, b. p. 165°/18 mm., m. p. 35—36°, which, by condensation with ethyl chloromalonate, gave *ethyl chloro*-p-*carbethoxybenzylmalonate*, b. p. 235°/20 mm., m. p. 54—55°, leading, by reduction with zinc dust and acetic acid, to *ethyl* p-*carbethoxybenzylmalonate*, b. p. 218—219°/15 mm. Hydrolysis gave p-*carboxybenzylmalonic acid*, m. p. 186—188°, which, on heating, gave *p*-carboxyphenylpropionic acid; (2) *p*-carboxycinnamic acid, m. p. 358° (decomp.) (*ethyl* ester, m. p. 52°), from terephthalaldehydic and malonic acids, gave on reduction with sodium amalgam *p*-carboxyphenylpropionic acid, m. p. 294° (lit. 280°) (*methyl* ester, m. p. 33°). *Ethyl* m-*phenylenedipropionate*, b. p. 197—198°/15 mm., and *ethyl* p-*phenylenedipropionate*, m. p. 67°, were prepared by the method of Kipping (J.C.S., 1888, **53**, 21).

R. J. W. Le Fevre.

Stereochemistry of aromatic compounds. VII. Inclination of rings in α-dinaphthyls. R. Kuhn and O. Albrecht (Annalen, 1928, **465**, 282—287).—1 : 1′-Dinaphthyl-2 : 2′-dicarboxylic acid, new m. p. 268·5—270° (corr.), obtained from 1-chloro-2-naphthoyl chloride by way of methyl 1-chloro-2-naphthoate (cf. Kalb, A., 1914, i, 850), has been resolved by way of its *quinine* salt, m. p. about 202° (decomp.), $[\alpha]_D^{22}$ +230·4° (in chloroform), which is separated by crystallisation from ether into the *salt*, m. p. 197·5—198°, $[\alpha]_D^{24}$ +301·6° (in chloroform), of l-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylic acid*, m. p. 177° (uncorr.) after becoming transparent at 145°, $[\alpha]_D^{22}$ −101·6°, and the impure *salt*, m. p. about 230°, $[\alpha]_D^{22.5}$ +15·4°, of d-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylic acid*, m. p. 239—248° (uncorr.) after sintering at about 185°, $[\alpha]_D^{22}$ +46° (in 0·1*N*-sodium hydroxide solution). The last when treated with sulphuric acid gave anthanthrone (Kalb, *loc. cit.*) with no apparent optical rotation. It thus appears that the effect of the 2 : 2′-dicarboxyl groups is to cause the naphthyl rings to assume a multiplanar configuration, not adopted by α-dinaphthyl itself, nor by anthanthrone. Attempts to racemise the *l*-acid were unsuccessful.

E. W. Wignall.

Addition reactions of unsaturated α-ketonic acids. II. M. Reimer and M. Howard (J. Amer. Chem. Soc., 1928, **50**, 2506—2512).—o-*Methoxybenzylidenepyruvic acid* (*o*-methoxystyrylglyoxylic acid) (I), orange-red, m. p. 131° (*ethyl* ester, b. p.

223°/15 mm.), has been prepared for comparison with the *p*-methoxy-derivative (A., 1926, 1139), from *o*-methoxybenzaldehyde and pyruvic acid in 10% sodium hydroxide at 0°. The acid and its *methyl* ester, m. p. 48°, are rapidly altered in sunlight. The former gives in chloroform an impure *dibromide*, m. p. 90° (decomp.), which decomposes in boiling benzene into β-*bromo*-o-*methoxystyrylglyoxylic acid*, m. p. 173°. This may also be obtained by direct bromination of the acid I or of its methyl ester; it is oxidised by alkaline hydrogen peroxide to α-bromo-*o*-methoxycinnamic acid and converted by diazomethane into its *methyl* ester, m. p. 88—89°. With 2 mols. of bromine the acid I yields impure 5-*bromo-2-methoxystyrylglyoxylic acid dibromide*, m. p. 95—100°, which decomposes in boiling 40% acetic acid into colourless β : 5-*dibromo-2-methoxystyrylglyoxylic acid*, m. p. 210° (*methyl* ester, m. p. 131°). An isomeric yellow β : 5-*dibromo-acid* (pale yellow *methyl* ester, m. p. 143°), which passes into the colourless form at 145—150°, is obtained by hydrolysing the *methyl* ester, m. p. 103—106°, of the dibromide with potassium methoxide. The series of colour changes (tabulated for 21 acids) given by the styrylglyoxylic acids with cold concentrated sulphuric acid is dependent on the presence of the ketonic group and differs sharply with the nature and position of other substituents. Thus, successive introduction of (*a*) *o*- and *p*-methoxyl, (*b*) bromine into the side-chain, and (*c*) bromine into the ring, changes the yellow to brown colour given by styrylglyoxylic acid to (*a*) *o*-, red; *p*-, orange; (*b*) orange to reddish-violet, and (*c*) green to blue. Increase in the number of substituents has, therefore, the same effect on the colour reaction as increase in the number of conjugated linkings (cf. Kuhn and Winterstein, this vol., 281). H. E. F. NOTTON.

Action of sodium benzyl cyanide with cinnamic ester. II. S. AVERY (J. Amer. Chem. Soc., 1928, **50**, 2512—2519).—γ-Cyano-βγ-diphenylbutyric acid is converted by methyl alcohol and hydrogen chloride into its *methyl* ester, m. p. 106·5° (all m. p. corr.), which is also formed from phenylacetonitrile and methyl or ethyl cinnamate in presence of sodium methoxide (cf. A., 1908, i, 343, 796). It is hydrolysed by alcoholic potassium hydroxide to *γ-carbamyl- -diphenylbutyric acid*, m. p. 200—205° (decomp.), and by hydrochloric acid at 150° to αβ-diphenylglutaric acid, m. p. 225—228°, the methyl ester, m. p. 143·0°, of which is identical and not stereoisomeric (cf. Meerwein and Dott, A., 1919, i, 21) with that prepared by Borsche's method (A., 1910, i, 35). The product obtained by Erlenmeyer (A., 1900, i, 493) from 1 mol. of phenylacetonitrile and 2 mols. of ethyl cinnamate may also be prepared from ethyl γ-cyano-βγ-diphenylbutyrate, ethyl cinnamate, and sodium ethoxide, or from *ethyl γ-cyano-βγδ-triphenylpimelate*, m. p. 102·5°, and sodium ethoxide, and is therefore *ethyl* 5-*cyano-2-keto-4 : 5 : 6-triphenylhexahydrobenzoate*, m. p. 208—209°. The corresponding *methyl* ester, m. p. 242—244°, an impure specimen of which was previously regarded as γ-cyano-βγδ-triphenylpimelic anhydride, is prepared similarly from methyl cinnamate or from *methyl γ-cyano-βγδ-triphenylpimelate*, m. p. 108·2°. H. E. F. NOTTON.

Syntheses of certain γ-ketonic acids allied to Balbiano's acid. I. Syntheses of α-methyl-*cyclo*pentane-1 : 1-diacetic acid; the lactone of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid, and 1-acetyl*cyclo*pentane-1-acetic acid. J. C. BARDHAN (J.C.S., 1928, 2591—2604).—Unsuccessful attempts to synthesise α-methyl-γ-keto*cyclo*pentane-1 : 1-diacetic acid (*cyclo*pentane analogue of Balbiano's acid) are described. The *anhydride*, b. p. 193°/24 mm., m. p. 48° [giving a β-*naphthylamic acid*, $C_{10}H_7 \cdot NH \cdot CO \cdot CHMe \cdot C(\dot{:}C_4H_8) \cdot CH_2 \cdot CO_2H$(?), m. p. 133—134°, which when heated passed into the β-*naphthylimide*, m. p. 179°], of *α-methyl*cyclo*pentane-1 : 1-diacetic acid*, m. p. 90—91° (*silver* salt; *imide*, m. p. 123—124°) (prepared, along with small quantities of a *substance*, $C_{13}H_{16}O_4N_2$, m. p. 223—224°, by acid hydrolysis of the N-*methyl-ω-imide* of *αα'-dicyano-α-methyl*cyclo*pentane-1 : 1-diacetic acid*, m. p. 136—137°, obtained by methyl iodide–sodium ethoxide methylation of the condensation product from *cyclo*pentanone, ethyl cyanoacetate, and alcoholic ammonia), gave on bromination in a sealed tube *α-bromo-α-methyl*cyclo*pentane-1 : 1-diacetic anhydride*, m. p. 95°, which by alkaline hydrolysis yielded the *lactone* of *α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid*, m. p. 140° (*silver*, *lead*, and *barium* salts; *ethyl* ester, b. p. 197°/30 mm.). The last acid was synthesised as follows: the *anhydride*, b. p. 154°/20 mm., m. p. 30° (*anilic acid*, m. p. 167—167·5°; *anil*, m. p. 127—128°), of *cyclo*pentane-1-acetic-1-carboxylic acid (Lapworth and McRae, J.C.S., 1922, **121**, 2754) was converted successively into the corresponding *monomethyl* ester, m. p. 80—81°, and *monomethyl* ester *chloride*, b. p. 132°/16 mm. (p-*toluidide*, m. p. 111°), which, by interaction with zinc methyl iodide followed by alkaline hydrolysis of the product (I) gave 1-*acetyl*cyclo*pentane-1-acetic acid* (II), m. p. 83—84° (*semicarbazone*, m. p. 197°; *oxime*, m. p. 124—125°; *methyl* ester, b. p. 131°/18 mm.; *methyl* ester *semicarbazone*, m. p. 152—153°). The constitution of II was proved by its reduction by sodium and ethyl alcohol, giving the *lactone*, b. p. 132°/15 mm., $d_4^{15·8}$ 1·057645, $n_D^{15·8}$ 1·4742, $[R_L]_D$ 40·9, of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid, which, when heated with potassium cyanide under pressure, yielded, after acid hydrolysis of the resulting product, α-methyl*cyclo*pentane-1 : 1-diacetic acid.

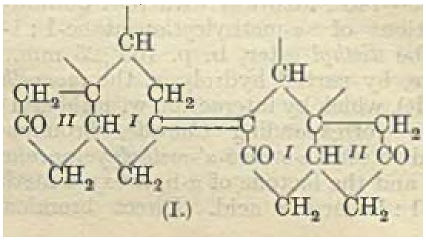
The product I on oxidation with alkaline permanganate gave α-keto*cyclo*pentane-1 : 1-diacetic acid (Lanfear and Thorpe, J.C.S., 1923, **123**, 1688), which with *o*-phenylenediamine formed the quinoxaline of α-keto*cyclo*pentane-1 : 1-diacetic acid, m. p. 221° (lit., 222°). II reacted with hydrocyanic acid, giving 1-*α-cyano-α-hydroxyethyl*cyclo*pentane-1-acetic acid*, which by acid hydrolysis gave a lactonic acid, m. p. 139—140°, identical with that obtained in the bromination of α-methyl*cyclo*pentane-1 : 1-diacetic acid. The *diethyl* ester, b. p. 165°/25 mm., of this acid gave, by partial hydrolysis, the *monoethyl* ester (*silver* salt), which by interaction with thionyl chloride gave the corresponding *chloride*, bromination of which led to *ethyl α-bromo-α'-methyl*cyclo*pentane-1 : 1-diacetate* and the lactone of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid. Direct bromination of

the *N*-methyl-ω-imide of αγ-dicyano-α-methyl*cyclo*pentane-1 : 1-diacetic acid readily yielded the *methylimide* of *α-bromo-αγ-dicyano-γ-methyl*cyclo*pentane-1 : 1-diacetic acid*, m. p. 180° (decomp.), which lost bromine on acid hydrolysis, giving only α-methyl*cyclo*pentane-1 : 1-diacetic acid. The Blaise reaction applied to α-methyl*cyclo*pentylideneacetic acid (from *cyclo*pentanone, ethyl α-bromopropionate, and magnesium) (*acid chloride*, b. p. 123°/30 mm.) gave *α-methyl*cyclo*pentylideneacetone* [two stereoisomeric(?) *semicarbazones*, m. p. 189° and 169°, from which were regenerated *ketones* with b. p. 108°/27 mm., 109°/25 mm., 0·960808, $d_4^{20 \cdot 3}$ 0·958084, $n_D^{19 \cdot 2}$ 1·49642, $n_D^{20 \cdot 3}$ 1·49528, $[R_L]_D$ 41·986, 42·025, respectively].

*α-Methyl-Δ¹-*cyclo*pentenylacetic acid*, b. p. 108—110°/30 mm., $d_4^{17 \cdot 7}$ 0·96668, $n_D^{17 \cdot 7}$ 1·4583, $[R_L]_D$ 47·45 (obtained by dehydration of the corresponding ester with phosphorus oxychloride), gave by hydrolysis the *acid*, b. p. 150°/28 mm., $d_4^{19 \cdot 7}$ 1·050988, $n_D^{18 \cdot 5}$ 1·4792, $[R_L]_D$ 37·79 (cf. Wallach and Martius, A., 1909, i, 383). The *acid chloride*, b. p. 86—88°/20 mm., gave with zinc methyl iodide *α-methyl-Δ¹-*cyclo*pentenylacetone*, b. p. 82°/17 mm., d_4^{20} 0·921922, n_D^{20} 1·4632, $[R_L]_D$ 41·24 (*semicarbazone*, m. p. 144°). R. J. W. Le Fevre.

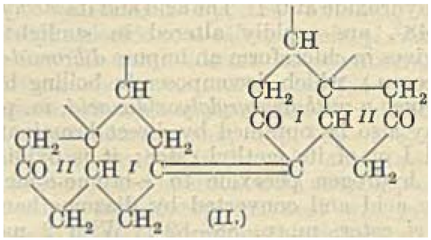
Molecular configurations of polynuclear aromatic compounds. VIII. 6 : 6′-Dimethoxydiphenic acid. J. Kenner and H. A. Turner (J.C.S., 1928, 2340—2343).—2-Nitro-*m*-cresol, prepared by the method of Gibson (*ibid.*, 1923, **123**, 1273; cf. Hodgson and Beard, A., 1925, i, 540), when methylated and oxidised yields 2-nitro-3-methoxybenzoic acid, which is converted by reduction and diazotisation into *2-iodo-3-methoxybenzoic acid*, m. p. 150—151°. The *methyl* ester, m. p. 57°, is converted by copper powder at 205—210° into *methyl 6 : 6′-dimethoxydiphenate*, m. p. 137—138°, from which *6 : 6′-dimethoxydiphenic acid*, m. p. 288—290° (decomp.), is obtained (*brucine hydrogen* salt, m. p. 268°). Resolution of the acid is accomplished through the quinine salts; *quinine* l-*6 : 6′-dimethoxydiphenate*, m. p. 172—173°, $[\alpha]_D$ +126°, yields the free l-*acid*, m. p. 294—295°, $[\alpha]_D$ −115°. *Quinine* d-*6 : 6′-dimethoxydiphenate* was obtained as a powder which shrank and decomposed about 60°, and had $[\alpha]_D$ −68°. An incomplete resolution was obtained by using quinidine. C. W. Shoppee.

Bile acids. XIV. Condensation of dehydrocholic acid with itself and with aromatic aldehydes. W. Borsche and E. Feske (Z. physiol. Chem., 1928, **178**, 148—155).—When dehydrocholic acid is heated in a sealed tube at 250° for 3—4 hrs., heated in a stream of carbon dioxide at 300° for 2 hrs., or treated with hydrogen chloride in acetic acid and kept for several days, an *acid*, $C_{48}H_{66}O_9$, m. p. 309—310°, is obtained to which the constitution I or II is assigned.



(I.)

This is analogous to the acid $C_{48}H_{70}O_7$ described by Shimizu (A., 1923, i, 40), which may be prepared under the same conditions from dehydrodeoxycholic acid.



(II.)

The acid $C_{48}H_{66}O_9$ yields a *dimethyl* ester, m. p. 265°, on treatment with diazomethane, and a *pentoxime*, m. p. 229° (sintering at 210°). Reduction with hydrogen and an active platinum catalyst yields a substance, considered to be *pentahydroxydicholanic acid*, of the composition $C_{48}H_{78}O_9,H_2O$ or $2C_{48}H_{78}O_9,AcOH$, m. p. 245—246° after sintering at 220°.

A mixture of benzaldehyde and dehydrocholic acid when heated in a sealed tube at 250—255° or treated with hydrogen chloride in acetic acid for a week at the ordinary temperature yielded *β-dibenzylidenedehydrocholic acid*, m. p. 219—220°, which becomes deep yellow in daylight. This would appear to have the same constitution as that assigned to (α-)dibenzylidenedehydrocholic acid, obtained by condensation in presence of sodium hydroxide (A., 1924, i, 1200), since bilianic acid, in which the ring I, containing the reactive methylene groups, is broken, does not condense with aldehydes under any conditions tried. Attempts to convert the α- into the β-form were, however, unsuccessful. *Di*-p-*chlorobenzylidenedehydrocholic acid*, m. p. 249°, was also prepared. R. K. Callow.

Isomerisation of di*cyclo*hexylacetaldehyde to a ketone. E. Venus-Danilova (Ber., 1928, **61**, [*B*], 1954—1966).—The action of magnesium *cyclo*hexyl bromide on ethyl ethoxyacetate affords a mixture of ethyl *cyclo*hexylacetate, *α-hydroxy-β-ethoxy-α-*cyclo*hexylethane*, b. p. 108°/23 mm. (oxidised to *cyclo*hexanecarboxylic acid and isomerised by sulphuric or oxalic acid to *cyclo*hexylacetaldehyde), di*cyclo*hexyl, and *α-hydroxy-β-ethoxy-αα-di*cyclo*hexylethane*, m. p. 53°. The last substance is converted by crystalline oxalic acid at 112—118° into *di*cyclo*hexylacetaldehyde*, b. p. 153—153·5°/11 mm., d_4^{20} 0·9621, which reacts only sluggishly with magenta and sulphurous acid, ammoniacal silver oxide, or sodium hydrogen sulphite, but readily yields a *semicarbazone*, m. p. 184—184·5°, and an *oxime*, m. p. 108—109°. The aldehyde is oxidised to *di*cyclo*hexylacetic acid*, m. p. 134—135° (*ammonium*, anhydrous and monohydrated *calcium* and *silver* salts), converted into the corresponding *chloride* and thence into the *anilide*, m. p. 203°, and *amide*, m. p. 188—189°.

The action of magnesium on a mixture of the iodohydrin of *cyclo*hexylcarbinol and hexahydrobenzaldehyde gives *cyclo*hexylcarbinol, *αβ-di*cyclo*hexylethane*, b. p. 136°/15 mm., and *αβ-di*cyclo*hexylethyl alcohol*, b. p. 162—164°/14 mm., m. p. 64—65°. The last-named compound is oxidised by potassium dichromate and sulphuric acid to *αβ-di*cyclo*hexyl-*

ethanone (*dodecahydrodeoxybenzoin*), b. p. 172—173°/26 mm., d_4^{20} 0·9511 (*semicarbazone*, m. p. 190—191°; *oxime*, m. p. 112—113°), which is converted by alcoholic potassium hydroxide into *cyclo*hexane and *cyclo*hexylacetic acid.

Di*cyclo*hexylacetaldehyde is isomerised to αβ-di*cyclo*hexylethanone when heated with dilute sulphuric acid or alcoholic mercuric chloride, by cold, concentrated sulphuric acid, or by decomposition of its semicarbazone with sufficiently concentrated sulphuric acid. H. WREN.

Conditions determining thermodynamic stability of cyanohydrins of carbonyl compounds. I. Effects of (*a*) substitution in aromatic aldehydes and (*b*) ring formation. A. LAPWORTH and R. H. F. MANSKE (J.C.S., 1928, 2533—2549).—The equilibrium constants ($K=C_{R,CO}\times C_{HCN}/C_{OH\cdot CR_2\cdot CN}$) for the dissociation of a number of aldehyde and ketone cyanohydrins have been determined in 96% alcohol at 20°±0·5°. The values of the free energy of dissociation ($\Delta F=1{\cdot}99\times 293\log_e K$) are relative measures of the depressant effects of substituents on the affinity of the aldehyde for hydrogen cyanide, and for nuclear-substituted benzaldehydes are as follows: *o*-substituents: OH>H>OMe>Cl>NO_2; *m*-substituents: Me>OH, H>OMe>NO_2>Cl; *p*-substituents: NMe_2>OH>OMe>NO_2>Me>Cl>H. The factors influencing the ionisation constants of benzoic acids (Flürscheim, J.C.S., 1909, **95**, 726) are found similarly to affect the dissociation constants of benzaldehydecyanohydrins, although the "electropolar" factor has relatively less importance in the *p*-substituted cyanohydrins and the "quantitative" factor little effect in the *meta*-series. The position of OH in the *ortho*-series is attributed to chelation between the hydroxyl and carbonyl group (Sidgwick and Callow, A., 1924, i, 506; 1925, i, 630), which would operate to reduce the stability of the cyanohydrin, and that of NO_2 in the *para*-series to the stabilising influence of a "Thiele" alternation of single and double linkings. Ring formation from a chain containing a carbonyl group leads sometimes to a large increase and sometimes to a large decrease in the dissociation constants of the derived cyanohydrins.

The bearing of the results on electronic theories is discussed and the suggestion made that the additive capacity of carbonyl and ethylenic carbon does not increase continuously with electron restraint, but reaches a maximum and then declines. R. J. W. LE FÈVRE.

Syntheses in the amino-acid group. I. Condensation of aldoximes with esters of β-ketonic acids. G. MINUNNI and S. D'URSO (Gazzetta, 1928, **58**, 485—504; cf. A., 1925, i, 1175).—In presence of zinc chloride at 120—125° or of crystallised phosphoric acid at 110—115°, benzaldoxime and ethyl acetoacetate condense to form *α-benzylideneaminocrotono-β-lactone*, $O<\substack{CMe\\CO}>C\cdot N{:}CHPh$, m. p. 146·5—147·5°, which, when either heated at 85—90° and then treated with potassium hydroxide or treated with hydroxylamine or its hydrochloride, yields a *compound*, m. p. 150—151°, to be studied further; when heated with phenylhydrazine in suspension in 50% alcohol, the β-lactone yields benzaldehyde-phenylhydrazone quantitatively and a compound which could not be obtained pure enough for analysis. The above condensation occurs in stages and yields first ethyl α-benzylideneaminoacetoacetate, $CO_2Et\cdot CHAc\cdot N{:}CHPh$, this undergoing conversion into its enolic form and losing a molecule of alcohol with formation of the β-lactone.

4 L

[With G. TERRANOVA.]—Similar condensation takes place, in presence of phosphoric acid, between benzaldoxime and ethyl benzoylacetate, giving *α-benzylideneaminocinnamo-β-lactone*, $O<\substack{CPh\\CO}>C\cdot N{:}CHPh$, m. p. 194—195°, which when heated with 1% potassium hydroxide solution yields benzaldehyde and a *compound*, m. p. 191—193°; with phenylhydrazine, the β-lactone gives the *compound* $C_{22}H_{19}O_2N_3$, decomposing at 140°. In presence of zinc chloride, however, benzaldoxime and ethyl benzoylacetate give a *compound*, C_7H_7ON, m. p. 132·5—133·5°, which, together with another *compound*, m. p. 226—227°, is formed also when zinc chloride acts on benzaldoxime alone. T. H. POPE.

Synthesis of aldehydes by means of iron pentacarbonyl. H. WOLF (Ber., 1928, **61**, [*B*], 1765—1766).—A modification of the Gattermann synthesis is described in which carbon monoxide is replaced by iron pentacarbonyl. A mixture of 17·5 g. of iron pentacarbonyl (=12 g. of carbon monoxide), 30 g. of toluene, and 45 g. of aluminium chloride saturated during 3 hrs. with hydrogen chloride at 40—45° yields 13—16 g. of *p*-tolualdehyde. H. WREN.

By-products of the Gattermann aldehyde reaction. F. BELL and T. A. HENRY (J.C.S., 1928, 2215—2227).—When the Gattermann aldehyde reaction, as modified by Adams and Montgomery (A., 1924, i, 860), is applied to alkylphenols, two secondary reactions occur: (*a*) a reversible Friedel–Crafts reaction, whereby the alkyl group is partly transferred to the solvent used; thus, in the case of thymol, with benzene as solvent, small quantities of *iso*propylbenzene and *m*-cresolaldehyde are formed; (*b*) condensation of the cyanohydrin of the phenolaldehyde with unchanged phenol to give, for example, in the case of thymol, dithymylacetonitrile.

Investigation of the conditions of formation of such diarylacetonitriles by reaction of cyanohydrins with the corresponding phenol in presence of hydrogen cyanide shows that, under the conditions finally selected (when an alcoholic solution of equimolecular quantities of the aldehyde and phenol was treated with hydrogen cyanide and the mixture heated to the b. p. after addition of zinc chloride), the aldehyde-cyanohydrins may (1) be too stable to undergo condensation, (2) condense with the elimination of hydrogen cyanide to produce eventually triarylmethanes, or (3) condense with elimination of water to form diarylacetonitriles. These different types of behaviour are conditioned by the nature and orientation of the substituents in the aldehydes used. The sole example of class (1) is *o*-nitrobenzaldehyde. Class (2) includes benzaldehyde itself, *o*- or *p*-chloro-, *m*- or

p-nitro-, and *m*-hydroxybenzaldehyde. Class (3) is represented by thymolaldehyde, carvacrolaldehyde, *o*-cresolaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde, and protocatechualdehyde. The following are described: *semicarbazones*, m. p. 198° and 226°, of 2- and 4-aldehydo-3-methyl-6-*iso*propylphenol; *semicarbazone*, m. p. 275°, of 4-hydroxy-3-aldehydo-5-methyl-2-*iso*propylphenyldicarvacrylmethane (?); *semicarbazones*, m. p. 180° and 224°, of 2- and 4-aldehydo-6-methyl-3-*iso*propylphenol; *semicarbazones*, m. p. 216° and 248° (decomp.), of 4- and 6-aldehydo-2-methylphenol; *trithymylmethane*, m. p. 280° (*triacetyl* derivative, m. p. 186°); *tricarvacrylmethane*, m. p. 275° (*triacetyl* derivative, m. p. 185°); *dithymylacetonitrile*, m. p. 205° (*diacetyl* derivative, m. p. 174°); *dithymylacetamide*, m. p. 243° (decomp.); *dicarvacrylacetonitrile*, m. p. 240° (*diacetyl* derivative, m. p. 196°); *thymylcarvacrylacetonitrile*, m. p. 227° (*diacetyl* derivative, m. p. 145°); *tolylthymylacetonitrile*, m. p. 153°; *tolylthymylacetamide*, m. p. 211°; *tolylthymylacetic acid*, m. p. 188°; *acetyltolylacetylthymylacetonitrile*, m. p. 131°; o- and p-*hydroxyphenylthymylacetonitrile*, m. p. 142° and 144°; *anisylthymylacetonitrile*, m. p. 106°; *pyrocatechylthymylacetonitrile*, m. p. 147—149°; m-*hydroxyphenyldithymylmethane*, m. p. 165°; m- and p-*nitrophenyldithymylmethane*, m. p. 171° and 145°; o- and p-*chlorophenyldithymylmethane*, m. p. 138° and 156°.

M. CLARK.

Bromine substitution products of vanillin and some derivatives. L. C. RAIFORD and W. C. STOESSER (J. Amer. Chem. Soc., 1928, **50**, 2556—2563).—In continuation of previous work (A., 1927, 564, 768) it is shown that one *o*-substituent has no noticeable effect on the reactivity of the aldehyde group in vanillin derivatives, whilst two *o*-substituents cause less than the expected diminution in reactivity. In agreement with the results of Brady and Dunn (J.C.S., 1915, **107**, 1859), the (? *anti*-)oximes of bromovanillins could not be isomerised by means of hydrogen chloride or by Goldschmidt's method. 6-Bromovanillinoxime yields an *acetate*, m. p. 149—151°. 6-Bromo-4-acetoxy-3-methoxybenzaldehyde forms an *oxime*, m. p. 150—152°, the *acetate*, m. p. 153—154°, of which is converted by acetic anhydride into 6-*bromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 148—149°. This is hydrolysed by potassium hydroxide to 6-*bromovanillic acid*, m. p. 190—191°. The nitration product of acetylvanillin contains 80% of 2-nitrovanillin (cf. Pschorr, A., 1900, i, 178) and about 5% of (?) 6-*nitrovanillin*, m. p. 212°. 5-Bromoacetylvanillin is successively converted into 5-*bromo*-2-*nitroacetylvanillin*, m. p. 128°; 5-*bromo*-2-*nitrovanillin*, m. p. 150—151°; 5-*bromo*-2-*aminovanillin*, m. p. 139—140°, and 2 : 5-*dibromovanillin*, m. p. 189°, from which an *acetate*, m. p. 68—70°; p-*nitrophenylhydrazone*, m. p. 249° (also $+C_5H_5N$); *semicarbazone*, m. p. 233—234°; *oxime*, m. p. 154—155° (*acetate*, m. p. 184—185°, and its *acetyl* derivative, m. p. 137—139°), and also 2 : 5-*dibromo*-4-*acetoxy*-3-*methoxybenzylidene diacetate*, m. p. 157—158°; *bis*-2 : 5-*dibromovanillylidenebenzidine*, m. p. above 350°; 2 : 5-*dibromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 89—90°, and 2 : 5-*dibromovanillic acid*, m. p. 179—180°, have been prepared. 6-Bromoacetylvanillin is converted into 6-*bromo*-2-*nitrovanillin*, m. p. 168—170°; 6-*bromo*-2-*aminovanillin*, m. p. 217—218°, shrinking from 210°, and 2 : 6-*dibromovanillin*, m. p. 155—156° (*oxime*, m. p. 144—145°; p-*bromophenylhydrazone*, m. p. 168—170°; *semicarbazone*, m. p. 216—217°), which gives with benzidine *bis*-2 : 6-*dibromovanillylidenebenzidine*, m. p. 238—239°, and with bromine in glacial acetic acid containing sodium acetate, 2 : 5 : 6-*tribromovanillin*, m. p. 177—178° (*oxime*, m. p. 192°; p-*bromophenylhydrazone*, m. p. 169—170°; *semicarbazone*, m. p. 222—223°). *Bis*-2 : 5 : 6-*tribromovanillylidenebenzidine* has m. p. above 330°.

H. E. F. NOTTON.

Auto-oxidation of organic compounds. VI. Thiobenzophenone. H. STAUDINGER and H. FREUDENBERGER (Ber., 1928, **61**, [*B*], 1836—1839; cf. this vol., 1010).—Auto-oxidation of thiobenzophenone gives benzophenone, a colourless *trisulphide* (probably $CPh_2{<}{\overset{S}{S\cdot S}}{>}CPh_2$), decomp. about 124°, and little sulphur dioxide. Reaction cannot occur according to the scheme $4CPh_2{:}S+2O_2=2CPh_2{:}O+SO_2+(CPh_2)_2S_3$, since it is accompanied by a slight gain in weight. It is therefore probable that the primary products are benzophenone and sulphur; the latter substance in the nascent condition causes formation of the trisulphide, is partly polymerised to amorphous sulphur, and only to a small extent oxidised. The best yields of the trisulphide are obtained when auto-oxidation of solid or dissolved thiobenzophenone occurs very slowly at a low temperature. At 120°, the trisulphide cannot be formed; under these conditions the products of auto-oxidation are benzophenone, crystalline sulphur, and a little sulphur dioxide. The auto-oxidation of thiobenzophenone is remarkable, since the oxygen reacts primarily with the carbon instead of the sulphur atom.

H. WREN.

Nitration and bromination of 4-methylbenzophenone. W. BLAKEY and H. A. SCARBOROUGH (J.C.S., 1928, 2489—2496).—The effect of a methyl group in the 4-position on substitution in the benzophenone series has been investigated; the methyl group is found to exert a marked directive influence. The first substituent enters the *o*-position to the methyl group (3-position) and this is unaffected by the presence of one or two nitro-groups, or by a chlorine atom. The second substituent enters the 3′-position and further substitution in this (the phenyl) nucleus is apparently inhibited by a substituent in the 3-position of the tolyl nucleus. The third entering substituent occupies the 5-position whatever the nature of the substituents previously introduced. The results are compared with those obtained for 4-methoxybenzophenone (A., 1927, 27).

Progressive nitration of 4-methylbenzophenone (Meyer, A., 1908, i, 25) yields: 3-*nitro*-4-*methylbenzophenone*, m. p. 129° (cf. Zincke and Plascuda, A., 1875, i, 69), its constitution being established by synthesis from 3-nitro-*p*-toluoyl chloride and benzene in the presence of aluminium chloride, reduced by tin and hydrochloric acid to 3-*amino*-4-*methylbenzophenone*, m. p. 109° (*hydrobromide*, m. p. 130°; *acetyl* derivative, m. p. 108°); 3 : 3′-*dinitro*-4-*methylbenzophenone*,

m. p. 135° (described by Limpricht and Lenz as the 2 : 3′-dinitro-compound, m. p. 125°); and 3 : 3′ : 5-*trinitro*-4-*methylbenzophenone*, m. p. 173°. The last-named compound was synthesised as follows: 3 : 5-dinitro-*p*-toluoyl chloride and benzene in the presence of aluminium chloride gave 3 : 5-*dinitro*-4-*methylbenzophenone*, m. p. 109° (yielding 5-*nitro*-3-*amino*-4-*methylbenzophenone*, m. p. 157°, by reduction with hydrogen sulphide and alcoholic ammonia), which on nitration yielded the 3 : 3′ : 5-trinitro-compound.

Nitration of 4′-nitro-4-methylbenzophenone yields 3 : 4′-dinitro-4-methylbenzophenone, m. p. 130° (cf. Limpricht and Lenz), reduced by hydrogen sulphide and alcoholic ammonia to 3-*nitro*-4′-*amino*-4-*methylbenzophenone*, m. p. 164°, deaminated to 3-nitro-4-methylbenzophenone (above); further nitration in concentrated sulphuric acid yields 3 : 4′ : 5-*trinitro*-4-*methylbenzophenone*, m. p. 160° (which does not react with piperidine, but gives an ill-defined *compound* with *p*-nitrosodimethylaniline), reduced by hydrogen sulphide and alcoholic ammonia to 3-*nitro*-4′ : 5-*diamino*-4-*methylbenzophenone*, m. p. 202°, deaminated to 3-nitro-4-methylbenzophenone (above); nitration with fuming nitric acid at 80° yields 3 : 3′ : 4′ : 5-*tetranitro*-4-*methylbenzophenone*, m. p. 187°, which reacts with piperidine, sodium methoxide, and alcoholic ammonia, giving indefinite brown compounds.

Bromination of 4-methylbenzophenone with excess of dry bromine in sunlight yields 3-*bromo*-4-*methylbenzophenone*, m. p. 107°, synthesised from 3-bromo-*p*-toluoyl chloride and benzene in the presence of aluminium chloride, and from 3-amino-4-methylbenzophenone (above) by the Sandmeyer reaction; under the same conditions 3′-nitro-4-methylbenzophenone yields 3-*bromo*-3′-*nitro*-4-*methylbenzophenone*, m. p. 124°, reduced by stannous chloride and alcoholic hydrochloric acid to 3-*bromo*-3′-*amino*-4-*methylbenzophenone*, m. p. 94°, deaminated to 3-bromo-4-methylbenzophenone (above). Bromination of 3′ : 5′-*dinitro*-4-*methylbenzophenone*, m. p. 134°, prepared by condensation of 3 : 5-dinitrobenzoyl chloride with toluene and aluminium chloride, yields 3-*bromo*-3′ : 5′-*dinitro*-4-*methylbenzophenone*, m. p. 173°. Similarly, 3-*bromo*-4′-*nitro*-4-*methylbenzophenone*, m. p. 119°, reduced by stannous chloride and alcoholic hydrochloric acid to 3-*bromo*-4′-*amino*-4-*methylbenzophenone*, m. p. 162°, deaminated to 3-bromo-4-methylbenzophenone, is obtained from 4′-nitro-4-methylbenzophenone.

4′-Chloro-4-methylbenzophenone, on nitration, gives an almost quantitative yield of 4′-*chloro*-3-*nitro*-4-*methylbenzophenone*, m. p. 98°, also obtained by condensing *p*-chlorobenzoyl chloride with toluene and aluminium chloride and nitrating the product (m. p. 128°), and by the Sandmeyer reaction from 3-nitro-4′-amino-4-methylbenzophenone, and from 3-nitro-*p*-toluoyl chloride with chlorobenzene and aluminium chloride; on reduction it is converted into -*chloro*-3-*amino*-4-*methylbenzophenone*, m. p. 142°. Further nitration in sulphuric acid yields 4′-*chloro*-3 : 3′-*dinitro*-4-*methylbenzophenone*, m. p. 131°, also obtained by nitrating -*chloro*-3′-*nitro*-4-*methylbenzophenone*, m. p. 121°, prepared by condensing 4-chloro-3-nitrobenzoyl chloride with toluene in the presence of aluminium chloride, together with 4′-*chloro*-3 : 3′ : 5-*trinitro*-4-*methylbenzophenone*, m. p. 182°, also prepared by nitration of 4′-*chloro*-3 : 5-*dinitro*-4-*methylbenzophenone*, m. p. 118°, which was synthesised from 3 : 5-dinitro-*p*-toluoyl chloride with chlorobenzene and aluminium chloride. Bromination of 4′-chloro-4-methylbenzophenone gives a quantitative yield of 4′-*chloro*-3-*bromo*-4-*methylbenzophenone*, m. p. 122°, also obtained from 4′-chloro-3-amino-4-methylbenzophenone (above) by the Sandmeyer reaction. C. W. SHOPPEE.

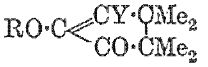
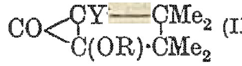
Intermolecular condensation of styryl ketones. II. Styryl nonyl ketone and the formation of dimerides. I. M. HEILBRON and F. IRVING (J.C.S., 1928, 2323—2326).—Methyl nonyl ketone condenses with aromatic aldehydes in the presence of cold, dilute alkali or piperidine to yield mono- and di-meric styryl nonyl ketones. The production of the latter is favoured with *p*-substituted aldehydes and by higher temperature and alkali concentration. Styryl nonyl ketone has m. p. 44° (cf. Carette, A., 1901, i, 127; Thoms, Ber. Deut. pharm. Ges., 1901, **11**, 3) and its dimeride yields an *oxime*, m. p. 125—126°. By cold alkaline condensation of methyl nonyl ketone with the appropriate aldehyde the following styryl nonyl ketones are obtained: 3 : 4-*dimethoxy*-, m. p. 61°; 4-iso*propyl*-, m. p. 40°; 2-*hydroxy*-, m. p. 79°; 4-*chloro*-, m. p. 62—63°; 3-*chloro*-, m. p. 57°; 2-*chlorostyryl nonyl ketone* was not isolated, but was characterised by its *semicarbazone*, m. p. 123—124°. With more concentrated alkali or under reflux are obtained: *bis*-(4-*methoxy*-), m. p. 120°; *bis*-(3 : 4-*dimethoxy*-), m. p. 135°; *bis*-(3 : 4-*methylenedioxy*-), m. p. 128°; *bis*-(4-*chloro*-), m. p. 126—127°; *bis*-(4-*methyl*-), m. p. 134—135°, and *bis*-(4-iso*propyl-styryl nonyl ketone*), m. p. 150°. Scholtz and Meyer (A., 1910, i, 561) erroneously describe the last two compounds as the corresponding monomerides. C. W. SHOPPEE.

Resolution of benzoin. I. V. HOPPER and F. J. WILSON (J.C.S., 1928, 2483—2489).—l-δ-(α-*Phenylethyl*)*semicarbazide hydrochloride*, m. p. 188°, $[\alpha]^{12\cdot 2}$ —66·06°, has been prepared in 79% yield from *l*-α-phenylethylamine and acetonesemicarbazone, and together with the *d*-isomeride (*ibid.*, 1922, **121**, 869) has been used to effect a resolution of benzoin. Preliminary work with *r*-δ-(α-phenylethyl)semicarbazide hydrochloride in pyridine solution yielded three of the four possible racemic *benzoin*-δ-(α-*phenylethyl*)-*semicarbazones* (α-*modification*, m. p. 174°; β-*modification*, m. p. 154°; γ-*modification*, m. p. 137°), all yielding benzoin on hydrolysis; in alcoholic solution only the α- and β-isomerides were obtained. For comparison (see below) *d*-benzoin was prepared from *d*-mandelic acid by Wren's method (*ibid.*, 1909, **95**, 1583) using quartz vessels and solvents which had been previously distilled in quartz apparatus; the product had m. p. 133—134°, $[\alpha]_D^{11}$ +118·5°, and its pyridine solution was not racemised by keeping for a week in quartz. d-*Benzoin*-d-δ-(α-*phenylethyl*)*semicarbazone* was prepared in pyridine solution and had m. p. 181—182°, $[\alpha]_D^{14}$ —140·7°.

r-Benzoin, condensed with *d*-δ-(α-phenylethyl)-semicarbazide hydrochloride, yielded as the sole crystalline product d-*benzoin*-d-δ-(α-*phenylethyl*)*semicarbazone*, m. p. 181—182°, $[\alpha]_D^{14}$ —141·5°, identical

with the synthetic product, giving on hydrolysis with oxalic acid *d*-benzoin, m. p. 133—134°, $[\alpha]^{11}$ +118·3°. From the non-crystalline condensation product *benzil-di*-d-δ-(*α-phenylethyl*)*semicarbazone*, m. p. 223°, $[\alpha]^{11}_{D}$ +178·2°, was isolated and yielded benzil on hydrolysis with concentrated hydrochloric acid. *r*-Benzoin and *l*-δ-(α-phenylethyl)semicarbazide hydrochloride similarly yielded l-*benzoin*-l-δ-(*α-phenylethyl*)*semicarbazone*, m. p. 181—182°, $[\alpha]^{14}_{D}$ +140·9°, as the sole crystalline product, converted by hydrolysis with oxalic acid into *l*-benzoin, m. p. 133—134°, $[\alpha]^{11}_{D}$ —118·5° C. W. SHOPPEE.

Possibility of ring–chain valency tautomerism, and of a type of mobile hydrogen tautomerism analogous to the Wagner–Meerwein rearrangement. IV. Substitution reactions of some cyclic derivatives of phorone. C. W. SHOPPEE (J.C.S., 1928, 2360—2365).—Numerous observations previously made (this vol., 414) indicate that the 5-carbon nuclei (I), (II), possess remarkable stability,

(I.)   (II.)

and exhibit a tendency to conservation of type such as is encountered in semi-aromatic and aromatic systems. The action of substituting agents has now been studied to determine the conditions under which the nuclear type is preserved. Treatment with bromine in chloroform of the acetoxy- [I, R=Ac, Y=H], methoxy- [I, R=Me, Y=H] and *p*-bromobenzyloxy- [I, R=C_7H_6Br, Y=H] derivatives yields bromohydroxyphorone with elimination of the substituent R; the mechanism of the reaction is discussed. Quinolinium bromide also causes elimination of the acyl group from the acetyl compound, but not of the *p*-bromobenzyloxy-group, simple nuclear substitution taking place instead. A similar result is achieved in the case of the acetyl compound by brominating with quinolinium bromide in the presence of quinoline. If the nuclear type is destroyed by reduction, bromination leads to its regeneration.

Various acyl and alkyl derivatives examined show little tendency to couple with diazonium salts, but hydroxyphorone (I and II; R—Y=H) readily does so, the position of coupling being the carbon atom bearing Y. The following are new: 2 : 5-*dibromo*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*, m. p. 93°; 4-2′ : 4′ : 6′-*tribromobenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*, m. p. indefinite; 4-p-*carbethoxybenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*, m. p. 160° (decomp.), yielding by reduction and hydrolysis 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. Bromination of 5-methoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone with bromine in chloroform yields bromohydroxyphorone, but in another experiment an unstable intermediate *dibromide*, $C_9H_{14}OBr_2$, m. p. 99—100°, was isolated.

C. W. SHOPPEE.

Acylation and alkylation of aromatic compounds in presence of stannic chloride. G. STADNIKOV and A. BARYSCHEVA (Ber., 1928, **61**, [*B*], 1996—1999).—In contrast with its behaviour towards benzyl chloride, benzene does not react with acetyl or benzoyl chloride in the presence of stannic chloride; under similar conditions, ethyl benzoate does not react with benzyl, benzoyl, or acetyl chloride. *o*-Tolyl methyl ether and acetyl chloride in cold benzene in the presence of stannic chloride afford 4-methoxy-3-methylacetophenone, b. p. 171—172°/39 mm., d_4^{18} 1·0812, n_D^{1} 1·5538 (*semicarbazone*, m. p. 206—207°; oxime, m. p. 101—101·5°), in 84% yield; 4-methoxy-3-methylbenzophenone, m. p. 79—80°, is similarly prepared. 4-Methoxy-2-methylacetophenone, b. p. 163—164°/33 mm., d_4^{17} 1·0803, n_D^{17} 1·5527 (oxime, m. p. 80·5—81·5°; *semicarbazone*, m. p. 179—180°), and a *methoxymethylbenzophenone*, b. p. 219—221°/23 mm., m. p. 172°, are derived from *m*-tolyl methyl ether. *p*-Tolyl methyl ether gives 2-methoxy-5-methylacetophenone, b. p. 143—146°/21 mm., 260—261°/739 mm., d_4^{17} 1·0636, n_D^{17} 1·5375 (*semicarbazone*, m. p. 176—177°; oxime, m. p. 88·5—89·5°), and a *methoxymethylbenzophenone*, b. p. 210—211°/20 mm., m. p. 37—38°.

m-Tolyl methyl ether and benzyl chloride afford a *methoxymethyldiphenylmethane*, b. p. 181—187°/20 mm., d_4^{18} 1·0466, and *methoxymethyldibenzylbenzene*, m. p. 75—76°. H. WREN.

Hydroxy-carbonyl compounds. IX. Constitution of cotoin and *iso*cotoin. *iso*Hydrocotoin. P. KARRER and N. LICHTENSTEIN (Helv. Chim. Acta, 1928, **11**, 789—795).—*p*-Toluenesulphonylation of cotoin (2 : 6-dihydroxy-4-methoxybenzophenone) gives 2-*hydroxy*-4-*methoxy*-6-p-*toluenesulphonyloxybenzophenone*, m. p. 138° (2 : 6-*di*-p-*toluenesulphonyl* derivative, m. p. 144°), which when methylated yields the p-*toluenesulphonyl* derivative, m. p. 112°, of hydrocotoin (2-hydroxy-4 : 6-dimethoxybenzophenone). *iso*Cotoin (2 : 4-dihydroxy-6-methoxybenzophenone) furnishes the 4-p-*toluenesulphonyl* derivative, m. p. 109°, together with the 2 : 4-*di*-p-*toluenesulphonyl* derivative, m. p. 137°. Partial hydrolysis of this last compound affords the 2-p-*toluenesulphonyl* derivative, m. p. 146°, of *iso*cotoin.

Phloroglucinol dimethyl ether condensed with benzonitrile in presence of zinc chloride yields a mixture of hydrocotoin and iso*hydrocotoin* (4-*hydroxy*-2 : 6-*dimethoxybenzophenone*), m. p. 177°.

H. BURTON.

Optical investigation of quinones and free radicals. S. GOLDSCHMIDT and F. GRAEF (Ber., 1928, **61**, [*B*], 1858—1869).—The red form of *o*-benzoquinone can be converted into the colourless modification as often as desired if its ethereal solution is rapidly cooled to —80°. This observation, considered in conjunction with the marked differences in colour exhibited by solutions of *o*-benzoquinone and *o*-naphthaquinone in chloroform, ether, and light petroleum, suggests equilibria between polymeric or tautomeric forms of the type $C_6H_4{<}{}^{O—O}_{O—O}{>}C_6H_4$, $C_6H_4{<}{}^{O-\,-}_{O-\,-}$, $C_6H_4{<}{}^{O}_{O}$, $C_6H_4{<}{}^{O}_{O}$. Since solutions of *o*-benzoquinone obey Beer's law, they cannot contain equilibrium mixtures of poly- and mono-meric forms. The absorption spectrum of *p*-benzoquinone differs widely from that of the *o*-compound, which resembles closely those of homo-*o*-benzoquinone and *o*-naphthaquinone. Observations of the absorption spectra of *o*-quinones in various solvents show them to have

little in common with the corresponding quinols, thus differing completely in behaviour from the true aroxyls (see later). Nevertheless, the marked influence of the solvent indicates the existence of an equilibrium, aroxyl quinone and this hypothesis is supported by the conversion of *o*-benzoquinone by triphenylmethyl into a colourless, non-crystalline ether, $C_6H_4(O{\cdot}CPh_3)_2$, from which triphenylmethyl is quantitatively separated as the peroxide by exposure to air.

The ultra-violet spectra of αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazine and αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazyl do not show differences greater than those of *o*-benzoquinone in two different media. In the visible spectrum, the radical gives a very high, flat band, this appearing to be characteristic of the transition from ter- to bi-valent nitrogen.

The spectrum of 9-chloro-10-hydroxyphenanthrene is very closely similar to that of phenanthrene, the hydroxy-group having unexpectedly little influence. In the spectrum of the corresponding peroxide only the two bands in the far ultra-violet remain unchanged, whilst a band appears between 3300 and 3600 Å. The linkings in the *meso*-nucleus appear therefore to have suffered considerable change. Solutions containing an equilibrium mixture of peroxide and chlorophenanthroxyl do not obey Beer's law, thus affording spectroscopic evidence of radical dissociation. The curve of chlorophenanthroxyl cannot be followed far into the ultra-violet on account of the presence of pyridine (added to induce equilibrium), but its concurrence with the curve of the peroxide permits the conclusion that the change in absorption is restricted to the visible part of the spectrum in which a band appears of similar breadth and intensity as in the case of αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazyl. On the other hand, the changes in comparison with 9-chloro-10-hydroxyphenanthrene also occur in part of the ultra-violet and are probably due to the *meso*-benzene nucleus.

The production of a *compound*, $C_{14}H_{18}O_4NCl$, m. p. 195°, from *p*-benzoquinone and 9-chloro-10-phenanthroxyl in chloroform and pyridine is recorded.

H. WREN.

Action of potassium ferricyanide on sodioformanilide in alkaline solution. Preparation of quinones and imides. E. I. ORLOV (Ukraine Chem. J., 1928, **3**, 161—169).—Sodioformanilide is oxidised by potassium ferricyanide to yield a mixture of products, amongst which 2-amino-5-hydroxy- and 2-amino-3-hydroxy-*p*-benzoquinone are identified. The tarry reaction product is partly soluble in dilute hydrochloric acid, the hydrochlorides $NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}NH_2,2HCl$ and $C_6H_4{:}NH,HCl$ being isolated from the extract. The first product of the reaction of oxidation is probably 2-amino-*p*-benzoquinone, which then reacts as follows:

$$2C_6H_3O_2{\cdot}NH_2 + H_2O = C_6H_2O_2(OH){\cdot}NH_2 + C_6H_4O_2 + NH_3.$$

R. TRUSZKOWSKI.

Subsidiary valency linking of nitro- and quinonoid groups. E. HERTEL and H. KURTH (Ber., 1928, **61**, [*B*], 1650—1653).—The power of 2 : 7-dinitroanthraquinone to form additive compounds with aromatic hydrocarbons has usually been ascribed to the presence of the two nitro-groups. Examination of the phase diagrams of 1 : 8-dinitronaphthalene and stilbene, 1 : 5-dinitronaphthalene and stilbene, or 3 : 3'-dinitrodiphenylmethane and naphthalene fails to disclose the production of additive compounds and attempts to isolate such products from 1 : 8- or 1 : 5-dinitronaphthalene, 3 : 3'-dinitrodiphenylmethane, and 2 : 7-dinitrofluorene and various aromatic hydrocarbons and their derivatives give only negative results. It is therefore concluded that a common residual field is not possessed by two nitro-groups present in different nuclei. The grouping, 3-nitro-carbonyl-3'-nitro-, does not induce the formation of additive compounds as evidenced by 3 : 3'-dinitrobenzophenone and naphthalene or 2 : 7-dinitrofluorenone and stilbene. The production of molecular compounds from Fritzsch's reagent is attributed to the carbonyl group strengthened by the neighbourhood of negative substituents. Thus the colour of the additive compounds of naphthalene, fluorene, acenaphthene, and anthracene with 1 : 2 : 3 : 5 : 6 : 7 : 8-heptachloro- is deeper than those with 2 : 7-dichloro-anthraquinone, but less pronounced than those with 1-nitroanthraquinone. The compounds exist only in the molten mixtures, but the introduction of two nitro-groups in different benzenoid nuclei of anthraquinone increases the quinonoid residual affinity to such an extent that additive compounds with hydrocarbons are crystalline. The behaviour of phenanthraquinone is similar to that of anthraquinone. 2 : 7-Dibromophenanthraquinone gives deeply-coloured molten mixtures with aromatic hydrocarbons but not crystalline compounds, whereas 2 : 7-dinitrophenanthraquinone affords additive *compounds* with acenaphthene (1 : 1), m. p. 255°, fluorene, (1 : 2), m. p. 270°, and anthracene (1 : 2), m. p. 250°. Additive *compounds*, m. p. 165° and 148°, respectively, are produced from 4 : 5-dinitrophenanthraquinone and acenaphthene (1 : 1) and from 2 : 6 : 7-trinitrofluorenone and stilbene (1 : 1).

H. WREN.

Production of benzanthrone derivatives [from 4-amino-3-hydroxy-1-*p*-amino-*o*-carboxyphenylnaphthalene]. I. B. ANDERSON, R. F. THOMSON, J. THOMAS, and SCOTTISH DYES LTD.—See B., 1928, 740.

Constitution of active principle of *Chita*. I. A. C. ROY and S. DUTT (J. Indian Chem. Soc., 1928, **5**, 419—424).—*Plumbagin* (I), $C_{18}H_{15}O_5$, m. p. 77—78°, is obtained from the air-dried roots ("chita") of *Plumbago rosea* or *P. zeylanica* in a maximum yield of about 1% by extraction with light petroleum. It contains one hydroxyl group, since it affords *monoacetyl*, m. p. 138°, *monobenzoyl*, m. p. 147°, and *monocarbethoxy*-, m. p. 109°, derivatives. It is suggested that I is a *p*-quinone, since it yields a *dioxime*, m. p. 220°, but only a *monophenylhydrazone*, m. p. 198°, and a *monosemicarbazone*, m. p. above 280°. This view is supported by the formation of a colourless leuco-compound from I by reduction with zinc dust and acetic acid. When I is oxidised with cold aqueous potassium permanganate, cinnamic acid and traces of benzoic and acetic acids are obtained, whilst zinc dust distillation furnishes naphthalene and β-methylnaphthalene. *Tetranitroplumbagin*, m. p. 172°, is

formed by the action of fuming nitric acid, and the action of bromine is to yield *plumbagin dibromide*, m. p. 122°. H. BURTON.

Colouring matters of fungi. VI. Constitution of atromentin. F. KÖGL and H. BECKER [with A. DETZEL and (FRL.) G. DE VOSS] (Annalen, 1928, **465**, 211—242).—The fungus extract, atromentin (A., 1925, i, 50, 1439), was regarded as having the formula $C_{20}H_{14}O_7$ and as being a derivative of 2 : 5-diphenylbenzoquinone containing a 3 : 2′ $OH\cdot CH_2\cdot C(OH)<$ bridge linking. The analogy between atromentin and polyporic acid, which has been shown (A., 1926, 407) to be 3 : 6-dihydroxy-2 : 5-diphenylbenzoquinone, has, however, suggested a re-investigation of the former substance, which is now found to have the formula $C_{18}H_{12}O_6$. The structure now favoured is that of 3 : 6 : 4′ : 4″-*tetrahydroxy-2 : 5-diphenylbenzoquinone* (I). The "penta-acetyl derivative," m. p. 242°, is found to be a *tetra-acetylatromentin*, and "hepta-acetyl-leucoatromentin," m. p. 236°, to be the *hexa-acetyl* compound. Reduction of tetra-acetylatromentin by zinc and acetic acid yields 3 : 6 : 4′ : 4″-*tetra-acetyl-leucoatromentin*, m. p. 248°.

Oxidation of atromentin, *e.g.*, by alkaline hydrogen peroxide, normally yields *p*-hydroxybenzoic acid. In hot acetic acid solution, however, a small quantity of hydrochloric acid, and hydrogen peroxide to furnish 4 atoms of oxygen, cause the separation of the *lactone*, m. p. 346° (decomp.), of *atromentic acid*, $C_{18}H_{12}O_7,H_2O$, m. p. 332° (decomp.). The action of acetic anhydride and sulphuric acid on either of these gives the *diacetyl* derivative, m. p. 271°, of the lactone; the last on keeping in ethyl alcohol furnishes *ethyl atromentate*, m. p. 346°.

Diazomethane converts atromentic acid into its *trimethyl ether*, m. p. 170°; the lactone dissolved in methyl alcohol and treated with diazomethane yields the fully methylated product, *methyl atromentate trimethyl ether*, m. p. 167° (depressed by admixture with the preceding compound). Chromic acid oxidises the trimethyl ether to anisic acid and *methyl* p-*methoxyphenylglyoxylate*, m. p. 54°, which is also obtained from leucoatromentin hexamethyl ether (see below), is reduced by hydriodic acid to *p*-hydroxyphenylacetic acid, and is synthesised by permanganate oxidation of *p*-methoxyacetophenone.

Hot 50% potassium hydroxide solution converts atromentic acid into *p*-hydroxyphenylacetic acid; this can be explained on the assumption that it is a pp′-*dihydroxypulvinic acid*,

$$HO\cdot C_6H_4\cdot C\overset{\overset{CO\text{———}O}{|\qquad\quad|}}{:}C(OH)\cdot C{:}C(CO_2H)\cdot C_6H_4\cdot OH$$

and that the above lactone, m. p. 346°, is the corresponding dilactone. The latter reacts with alcohol to give a lactone ester (cf. Piutti and Mazza, A., 1927, 1072). Since no other aromatic degradation product is obtained, it is established that the phenyl groups of atromentin carry only *p*-hydroxy-groups; the old bridged formula is thus excluded.

It is not possible to methylate atromentin completely in one stage. Tetra-acetylatromentin dissolved in methyl-alcoholic potassium hydroxide, and acidified, yields an *atromentin monomethyl ether*, m. p. 239°, easily hydrolysed, and thus containing a 3-methoxyl group. This furnishes a *triacetyl* derivative, m. p. 202°, and, by use of sodium hyposulphite, *penta-acetyl-leucoatromentin monomethyl ether*, m. p. 196°. Atromentin dimethyl ether is easily hydrolysed, supporting the 3 : 6-structure; with acetic anhydride and sulphuric acid it gives orange pp′-*diacetylatromentin* 3 : 6-*dimethyl ether*, m. p. 212°, oxidised by chromic acid to *p*-acetoxybenzoic acid (no anisic acid). Penta-acetyl-leucoatromentin dimethyl ether is renamed 1 : 4 : 4′ : 4″-*tetra-acetyl-leucoatromentin* 3 : 6-*dimethyl ether*, m. p. 263—264°.

Complete methylation of atromentin is effected by the action of diazomethane on leucoatromentin, or by that of methyl sulphate on atromentin dimethyl ether in methyl-alcoholic potassium hydroxide; *atromentin tetramethyl ether* has m. p. 199°. If the dimethyl ether is suspended in ethyl alcohol during methylation, *atromentin trimethyl* 3-*ethyl ether*, m. p. 186°, is obtained, readily converted by methyl-alcoholic potassium hydroxide into the tetramethyl ether, which is, however, slowly decomposed itself by this reagent, giving *atromentin* 3 : 4′ : 4″-*trimethyl ether*, m. p. 167°. This last is hydrolysed by sodium hydroxide to the 4′ : 4″-*dimethyl ether*, m. p. 290°.

Leucoatromentin hexamethyl ether, m. p. 238°, is obtained by the action of methyl sulphate on leucoatromentin in presence of methyl-alcoholic potassium hydroxide, and similarly from the tetramethyl or trimethyl ethyl ethers, or from the former of these by the action of diazomethane.

All these methylated products agree with the formulation $C_{18}H_{12}O_6$ for atromentin, which cannot be considered to have been degraded in any way during methylation.

A degradation process is, on the other hand, effected by means of aqueous alkali. The action of the latter on dihydroxydialkylbenzoquinones was studied by Fichter (A., 1908, i, 658), who obtained mixtures of stereoisomeric succinic acids, $CH_2R\cdot CH(CO_2H)\cdot CHR\cdot CO_2H$, assumed to be derived from lactonic acids. Stahlschmidt (A., 1879, 382) had not obtained such results with polyporic acid, which, he stated, yielded two acids, $C_9H_9O_2$, m. p. 163°, and $C_{10}H_9O$, m. p. 156°. This work has now been repeated and both products have been found to be impure. The action of boiling 10—15% aqueous potassium hydroxide on polyporic acid actually gives rise to three products: (*a*) the known α-benzylcinnamic acid, m. p. 158°; (*b*) a new isomeric *α-benzylcinnamic acid*, m. p. 100·5°, which, like (*a*), on reduction gives dibenzylacetic acid; and (*c*), phenylbenzylsuccinic acid (Avery, A., 1908, i, 343). The results of Fichter are thus supported by analogy, oxalic acid being lost instead of carbon dioxide during the reaction, which yields a benzylcinnamic acid instead of a succinic acid.

The action of alkali on atromentin (*pp*′-dihydroxypolyporic acid) follows a similar course. The product, m. p. 202°, obtained when steam is passed through a solution of atromentin in 30% alkali is now found to be $C_{18}H_4O_7,3H_2O$, and to be *α-keto-β-*p-*hydroxyphenyl-γ-*p′-*hydroxybenzylbutyrolactone-γ-carboxylic acid*. The acids of m. p. 183° and 164°, to which the formula $C_{11}H_{10}O_3$ was assigned, are now found to be $C_{16}H_{14}O_4$. Since the former of these is methylated by diazomethane to 4-*methoxy-α-*(p-*methoxybenzyl*)*cinnamic*

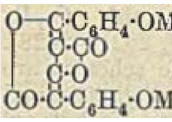
acid, m. p. 161° (synthesised by condensation of *p*-methoxy-β-phenylpropionic acid with anisaldehyde, in presence of acetic anhydride at 160—170°), it must be 4-*hydroxy*-α-(p-*hydroxybenzyl*)*cinnamic acid*. Since the two acids yield the same acetyl derivative, the acid of m. p. 164° may be an *allo*-form.

E. W. WIGNALL.

Colouring matters of fungi. VII. Synthesis of atromentin. Atromentic acid. F. KOGL [with H. BECKER, G. DE VOSS, and E. WIRTH] (Annalen, 1928, **465**, 243—258).—Atromentin (see preceding abstract) is synthesised by condensing methyl *p*-methoxyphenylacetate with methyl oxalate by the action of sodium in ether. This yields directly 3 : 6-*dihydroxy*-2 : 5-*bis*-(p-*methoxyphenyl*)*benzoquinone* (*atromentin* 4′ : 4″-*dimethyl ether*), m. p. 285° (uncorr.), from which the tetramethyl ether is also prepared, and, by the use of hydriodic acid, atromentin itself.

A second synthesis is effected by heating 2 : 5-bis-(*p*-hydroxyphenyl)benzoquinone with methyl alcohol and zinc chloride at 160°; atromentin 3 : 6-dimethyl ether is thus obtained, and is identified as the diacetyl derivative. Free atromentin is obtained by heating with saturated sodium carbonate solution. The yield is not good, but is better than that in the first described method.

Completely methylated atromentic acid is synthesised as follows. Ethyl oxalate is condensed with *p*-methoxyphenylacetonitrile under the influence of sodium, furnishing pp′-*dimethoxydiphenylketipinodinitrile*, m. p. 260°. When heated in alcohol and sulphuric acid, pp′-*dimethoxypulvinolactone* (I), m. p. 268·5° (which has not been demethylated), is obtained. This is dissolved in methyl-alcoholic potassium hydroxide, and on acidification gives rise to the lactone ester, pp′-*dimethoxyvulpinic acid*, m. p. 174·5°, of which the *methyl ether*, m. p. 168°,



(I.)

$$OMe\cdot C_6H_4\cdot C{<}\begin{matrix}C(OMe)\\CO{-}{-}O\end{matrix}{>}C{:}C(CO_2Me)\cdot C_6H_4\cdot OMe,$$ is

identical with methyl atromentate trimethyl ether (see preceding abstract).

In attempts to hydrolyse this ester to the corresponding acid by means of methyl-alcoholic potassium hydroxide with either synthetic or analytic material, the yellow solution acquired an intense violet colour, and on acidification a yellow compound, $C_{20}H_{18}O_5$, m. p. 147° (after sintering at 135°), separated. This is regarded as 3-*hydroxy*-4-*methoxy*-2 : 5-*bis*-(p-*methoxyphenyl*)cyclo*penta*-2 : 4-*dien*-1-*one*. Similarly, vulpinic acid methyl ether, prepared from silver vulpinate and methyl iodide, gives with methyl-alcoholic potassium hydroxide a violet solution from which acidification yields the corresponding diphenyl compound, $CO{<}\begin{matrix}CPh{:}C\cdot OMe\\CPh{:}C\cdot OH\end{matrix}$ m. p. 94—95°, identical with "oxalyldibenzyl ketone monomethyl ether" (Claisen, A., 1895, i, 373), together with a large quantity of an oily *substance* (the keto-form ?). This last also appears when the substance is prepared from the silver salt of oxalyldibenzyl ketone.

Claisen describes (*loc. cit.*) an inversion of the "oxalyldibenzyl ketone," which when heated above its m. p. is converted into "*iso*oxalyldibenzyl ketone" (pulvinone), $CO\cdot O\cdot C{:}CHPh$. The new reaction can be considered as a reversal of this; in fact, pulvinone methyl ether, m. p. 104—105° (obtained by Claisen as an oil), when treated with methyl-alcoholic potassium hydroxide gives rise to the above described diphenyl compound, m. p. 94—95°.

Atromentic acid forms red crystals containing 1 mol. of water, lost at 100° to give yellow crystals which very rapidly absorb water, becoming red, loss and re-adsorption of water occurring without loss of transparency.

E. W. WIGNALL.

Gitoxin. A. WINDAUS, K. WESTPHAL, and G. STEIN (Ber., 1928, **61**, [*B*], 1847—1855).—All previously described derivatives of gitoxin have been again prepared and subjected to a series of independent analyses. To gitoxin the formula $C_{41}H_{64}O_{14}$ is ascribed and its identity with "bigitalinum crystallisatum" of Cloetta (A., 1926, 755) is established; the m. p. of the compound depends greatly on the manner of heating. Gitoxigenin has the formula $C_{23}H_{34}O_5$; analyses of its acyl derivatives are unsuitable for the deduction of composition, since they are usually mixtures, although, under definite conditions, a *diacetyl* compound, $C_{23}H_{32}O_3Ac_2$, m. p. 249—250°, is isolated. Treatment of gitoxigenin with alcoholic hydrogen chloride gives dianhydrogitoxigenin, $C_{23}H_{30}O_3$, a trebly unsaturated monohydroxylactone identical with digitaligenin from *Digitalinum verum*. Hydrogenation of gitoxigenin (cf. Cloetta, *loc. cit.*) appears to yield two isomeric dihydrogitoxigenins, $C_{23}H_{36}O_5$, m. p. 212° and 241°, $[\alpha]_D$ −48·74° in methyl alcohol, each of which is converted by hydrogen chloride in alcohol into *dianhydrodihydrogitoxigenin*, $C_{23}H_{32}O_3$, m. p. 166°. The latter compound is very readily hydrogenated in the presence of platinum-black into *tetrahydrodianhydrodihydrogitoxigenin*, a mixture of isomerides from which a product, $C_{23}H_{36}O_3$, m. p. 214°, $[\alpha]_D^{20}$ +75·7° in alcohol, is isolated. Oxidation of the product with chromic acid mixture affords *tetrahydrodianhydrogitoxigenone*, $C_{23}H_{34}O_3$, m. p. 207°, $[\alpha]_D^{20}$ +85·9° in chloroform, doubtless identical with the hexahydrodigitaligenone of Bandte (A., 1923, i, 1107). Reduction of this ketone by Clemmensen's method yields the *lactone*, $C_{23}H_{36}O_2$, m. p. 173°, $[\alpha]_D^{18}$ +71° in chloroform (Bandte, *loc. cit.*, gives formula, $C_{24}H_{38}O_2$). Oxidation of the ketone with chromic acid in excess gives a dicarboxylic *acid*, $C_{23}H_{34}O_6$, m. p. 282°, $[\alpha]_D^{20}$ +100° in glacial acetic acid (*dimethyl* ester, m. p. 163°, $[\alpha]_D^{20}$ +82·3° in chloroform); the ketone thus probably contains a cyclic $-CO\cdot CH_2-$ group. The hexahydrodigitaligenin, m. p. 186—187°, of Bandte (*loc. cit.*) and of Windaus and Schwarte (A., 1925, i, 1295) is not homogeneous; from it the tetrahydrodianhydrodihydrogitoxigenin (see above) is isolated as the most sparingly soluble component. The acetyl derivative, m. p. 156°, and propionyl compound, m. p. 163—164°, are regarded as probably mixtures of stereoisomerides. Oxidation of "hexahydrodigitaligenin" by chromic acid affords a mixture of ketones from which tetrahydrodianhydrogitoxigenone is isolated with some difficulty. The portions of lower m. p., when oxidised with chromic acid, give an isomeric dicarboxylic acid, $C_{23}H_{34}O_6$ (see above), m. p.

278°, $[\alpha]_D^{18}$ +71° in glacial acetic acid (*dimethyl* ester, m. p. 171—172°, $[\alpha]_D^{22}$ +40° in chloroform). Distillation of the acid, $C_{23}H_{34}O_6$, in a high vacuum gives the *ketone*, $C_{22}H_{32}O_3$, m. p. 206° (*oxime*, m. p. 248°).

H. WREN.

Colouring matter of paprika. III. Catalytic hydrogenation. L. ZECHMEISTER and L. VON CHOLNOKY [with (FRL.) V. VRABELY] (Annalen, 1928, **465**, 288—299).—The method of isolation of capsanthin (cf. A., 1927, 669) is improved, and the new formula $C_{34}H_{48}O_3$ is obtained. The strongly unsaturated character of the substance, suspected from its ready resinification, is confirmed by catalytic hydrogenation. In alcohol or, better, acetic acid, reduction in presence of platinum introduces 9 mols. of hydrogen. A colorimetric survey of the reaction shows that 6 mols. of hydrogen are first introduced, removing all the colour, which during hydrogenation is constantly less than would be expected calculated on the assumption that there are nine conjugated ethylenic linkings present.

The product, perhydrocapsanthin, is a liquid (perhaps a mixture of stereoisomerides), with $[\alpha]_D^{20}$ −23·3° to −24·7°, possibly too low a value owing to racemisation (a preparation kept for 2 hrs. at 80° had $[\alpha]_D^{3}$ −15·3°).

The paprika pigment must be considered to belong to the class of natural "polyene" pigments; the lævorotation of its hydrogenated product is compared with the similar property of perhydroxanthophyll. It is assumed that the deepening of colour of paprika during ripening is due to dehydrogenation of the parent substance; attempts to influence this by injection were unsuccessful.

E. W. WIGNALL.

Xanthophyll. I. Catalytic hydrogenation. L. ZECHMEISTER and P. TUZSON (Ber., 1928, **61**, [*B*], 2003—2009).—Xanthophyll, $C_{40}H_{56}O_{21}$, m. p. 172° (corr.), is hydrogenated in ethyl or propyl alcohol, ether, chloroform, or glacial acetic acid in the presence of an unusually large amount of spongy platinum to non-crystalline *perhydroxanthophyll*, $C_{40}H_{78}O_2$, $[\alpha]_D^{20}$ −9·2° in ether, −9·8° in benzene. The hydrogenation graph of xanthophyll is very similar to that of carotin, showing a rectilinear progress until 8 mols. of hydrogen have been absorbed and the solution has become colourless. Xanthophyll therefore probably contains eight conjugated double linkings which rapidly become hydrogenated and three sluggish double linkings which are not responsible for the colour. It is possible that carotin contains two alkyl and xanthophyll two alkoxy-groups in corresponding positions in the molecule.

H. WREN.

Caoutchouc. K. H. MEYER and H. MARK (Ber., 1928, **61**, [*B*], 1939—1949; cf. Katz, A., 1925, ii, 667).—Examination of the *X*-ray diagrams of stretched caoutchouc show that two superposed isoprene residues almost exactly fill the space of an identity period if the methylene groups vicinal to the double linking are in the *cis*-position to one another and the two residues are placed at an angle of 180° to one another. The screw axis and the linkings are continued through the complete crystallite along the fibre axis. The distances of the individual chains from one another coincide with those observed in crystalline fatty acids. The neighbouring main-valency chains are inclined at different angles to the α-axis in the unit substance. It is estimated that 75—150 isoprene residues are involved in the structural molecule of caoutchouc. If the tension on stretched caoutchouc is released, the interferences disappear, but are immediately observed again when the material is again placed under tension. Direct determinations of the osmotic pressure of solutions of caoutchouc in benzene and chlorobenzene indicate that the size of the micelles is much greater than has been assumed previously and that the micelles unite with considerable proportions of the solvent; in 3—5% solutions the solvent is almost completely united to the micelles.

X-Ray examination shows that vulcanisation which does not effect the reversible extension does not alter the inner arrangement of the micelles. The forces of association which the micelles exert towards one another are strengthened in some manner during vulcanisation. Analogy is drawn between the action of sulphur chloride on ethylene and caoutchouc, which leads to the union of two double linkings by a sulphur bridge. The action of the chloride occurs immediately at the surface of the micelles and leads to the formation of sulphur bridges from double linkings present in the same and in neighbouring micelles. A strong union of the micelles at various points is thus established. Vulcanisation with large amounts of sulphur or sulphur chloride destroys the extensibility probably because the many sulphur bridges on and in the micelles stabilise the whole mass.

H. WREN.

Attempts to synthesise norpinic acid. G. R. CLEMO and K. N. WELCH (J.C.S., 1928, 2621—2628).—The following unsuccessful synthetic schemes are described: the condensation of dimethylketen and maleic or fumaric esters, of α-bromo*iso*butyryl bromide with ethyl sodioethanetetracarboxylate, of ethyl disodio*iso*propylidenemalonate with methylene iodide (giving ethyl *iso*propylidene malonate and methylenedimalonate; cf. Ingold and Powell, *ibid.*, 1921, **119**, 1976), of acetyl chloride or *iso*propyl bromide and ethyl sodiodicarbethoxyglutaconate, of magnesium methyl iodide and either α-acetyl-, α-bromo-α-acetyl-, or α-methyl-α-acetyl-glutaric esters.

Ethyl α-acetylglutarate gave with benzenediazonium chloride under the conditions of a Japp–Klingemann reaction *α-carboxypentane-γδ-dione-γ-phenylhydrazone*, NHPh·N:CAc·$[CH_2]_2$·CO_2H, m. p. 178° (*sodium* salt), whilst with phenylhydrazine it gave *ethyl 1-phenyl-3-methyl-5-pyrazolone-4-β-propionate*,

CO——CH·$[CH_2]_2$·CO_2Et
NPh·N:CMe

b 215°/3 mm. *Ethyl α-bromo-α-acetylglutarate* has b. p. 162—165°/14 mm. Ethyl α-acetylglutarate reacts with boiling aniline, giving diphenylcarbamide, and with gaseous ammonia, giving *ethyl α-(α′-aminoethylidene)glutarate*, NH_2·CMe:C(CO_2Et)·CH_2·CH_2·CO_2Et, m. p. 37°. Improved methods for the preparation of acetone cyanohydrin and *iso*propylidenemalonic esters have been worked out.

R. J. W. LE FÈVRE.

Ultra-violet absorption curves of terpene alcohols in relation to constitution. J. SAVARD (Compt. rend., 1928, **187**, 540—542).—The maxima

at 2260—2380 Å. in the absorption curves of butylpulegol, butyl*iso*pulegol, dihydrocarvacrol, α-, β-, and γ-terpineol, and 4-terpineol are attributed to the presence of the double linking, and the regular ascension of the curve from an unlocated maximum in the extreme ultra-violet is similarly attributed to the presence of the hydroxyl group. The position of the double linking is relatively unimportant, the position of the maximum in the absorption curve of γ-terpineol being shifted about 60 Å. towards the red as compared with β-terpineol, by the side-chain displacement $\colon CH \cdot CMe \colon CH_2 \longrightarrow \colon C \colon CMe_2$. The same change in the case of butylpulegol and butyl*iso*pulegol produces a displacement of about 80 Å. The shift of the hydroxyl group from a nuclear position (4-terpineol) to the side-chain (α-terpineol) has practically no effect on the position of the maximum (2309—2283 Å.) but produces a considerable decrease in the extinction coefficient. Substitution by the butyl group has little effect, the band being displaced from 2404 Å. (γ-terpineol) to 2325 Å. (butylpulegol), whilst β-terpineol and butyl*iso*pulegol (and also dihydrocarvacrol) show the same maximum at 2222 Å. When the position of the double linking is varied in alcohols not possessing the common menthene nucleus, the absorption intensity produced by the ethylenic linking depends on the number of carbon atoms separating the two functional groups in the molecule. The mutual induction of the two functional groups thus appears to be dependent on the nature and position of both groups.

R. BRIGHTMAN.

Influence of solvents on the rotation of optically active compounds. XXV. Bornyl benzene- and naphthalene-sulphonates in various solvents. T. S. PATTERSON and I. M. MCALPINE (J.C.S., 1928, 2472—2474).—Rotations in ethyl alcohol, benzene, pyridine, ethylene dibromide, quinoline, and nitrobenzene for mercury yellow, green, and violet light (λ=5790, 5461, and 4358) are recorded for bornyl benzenesulphonate, naphthalene-α-, and -β-sulphonate. The rotations vary considerably in the different solvents and the data lie on a characteristic diagram, the lines of which practically pass through the point of origin, in consequence of which the dispersion coefficients calculated in the ordinary way are almost constant.

M. CLARK.

Decomposition of bornyl benzene- and naphthalene-sulphonates by heat. Products of hydrolysis of bornyl and menthyl benzene- and naphthalene-sulphonates. Influence of solvents on the temperature of decomposition of these bornyl and menthyl sulphonates. T. S. PATTERSON and I. M. MCALPINE (J.C.S., 1928, 2464—2472; cf. A., 1927, 364).—Bornyl esters of benzene-, naphthalene-α- and -β-sulphonic acids, when directly distilled under reduced pressure, yield a small quantity of camphene, and a considerable quantity of dibornylene and a more complex gelatinous material which could be neither purified nor identified, as well as the corresponding sulphonic acid. When the esters are heated in sealed tubes at 80—90° for 2—3 hrs., and afterwards distilled, the products are dihydrocamphene (?), dibornylene, a gelatinous mass of high b. p., and the sulphonic acid. When the esters are heated to boiling in toluene solution, dibornylene and the sulphonic acid are obtained. The menthyl and bornyl esters of benzene- and the naphthalene-sulphonic acids do not hydrolyse to yield menthol and borneol, but decompose in somewhat the same way as when heated alone, yielding respectively menthene and camphene in small quantity. The rate at which these esters decompose in solution, investigated for toluene, nitrobenzene, ethylene dibromide, pyridine, and a series of alcohols, depends quite markedly on the nature of the solvent, and in the alcohols the velocity increases rapidly as the mol. wt. diminishes. Tables are given illustrating this behaviour. The following are described: l-*bornyl benzenesulphonate*, m. p. 52°, $[\alpha]_{5461}^{17}$ −22·40° in benzene, −22·00° in alcohol; d-*bornyl benzenesulphonate*; l-*bornyl naphthalene-β-sulphonate*, m. p. 76°, $[\alpha]_{5461}^{17}$ −16·50° in benzene, −16·00° in alcohol; d-*bornyl naphthalene-β-sulphonate*; l-*bornyl naphthalene-α-sulphonate*, m. p. 90°, $[\alpha]_{5461}^{17.5}$ −23·20° in benzene, −26·4° in alcohol.

M. CLARK.

Hyssop oil from the Crimea. B. RUTOVSKI and I. VINOGRADOVA.—See B., 1928, 768.

Constituents of Indian essential oils. XXV. *l*-α- and *l*-β-Curcumenes. B. S. RAO and J. L. SIMONSEN (J.C.S., 1928, 2496—2505).—Two crystalline derivatives, a nitrosate and a trihydrochloride, have been prepared from *l*-curcumene (cf. B., 1926, 1028). Fractional distillation of the oil remaining after separation of the trihydrochloride yields a sesquiterpene monohydrochloride, the parent hydrocarbon of which gives the crystalline nitrosate in a yield exceeding that obtained with the original terpene, whilst treatment with hydrochloric acid gives no trihydrochloride. *l*-Curcumene is therefore a mixture of two hydrocarbons, *l*-α-curcumene, which yields the crystalline nitrosate and liquid monohydrochloride, and *l*-β-curcumene, which yields the crystalline trihydrochloride.

Treatment of *l*-α-curcumene nitrosate, m. p. 100—101° (recrystallised after 3 weeks, m. p. 110°), with alcoholic potassium hydroxide solution yields l-*oximino-α-curcumene*, $C_{15}H_{22}\colon N \cdot OH$ (I), b. p. 182—185°/7 mm., d_{30}^{30} 0·9817, n_D^{30} 1·5134, $[\alpha]_D^{30}$ −27·2° (*benzoyl* derivative, m. p. 84—85°). Compound (I) forms a *monohydrochloride* apparently by addition of hydrogen chloride to one of the ethylenic linkings, since the product is not decomposed by alkali. Reduction of (I) with sodium in ethyl-alcoholic solution yields l-*dihydro-α-curcumenylamine*, $C_{15}H_{25} \cdot NH_2$ (II), b. p. 151—152°/17 mm., d_{30}^{30} 0·9026, n_D^{30} 1·4983, $[\alpha]_D^{30}$ −22·2° [*hydrogen oxalate* (+H_2O), m. p. 143—144°; *acetyl* derivative, m. p. 109—110°], one of the ethylenic linkings having been reduced as well as the oximino-group. This compound possesses only general toxic action. Methylation of (II) with methyl iodide in presence of alkali yields l-*dihydro-α-curcumenyltrimethylammonium iodide*, $C_{15}H_{25} \cdot NMe_3I$, m. p. 163—164°. Distillation of the corresponding hydroxide, crystalline but hygroscopic, gives a mixture of l-*dimethyldihydro-α-curcumenylamine*, b. p. 130—140°/15 mm., d^{30} 0·8824, n_D^{30} 1·4913, $[\alpha]_D^{30}$ −23·0°, and pure l-α-*curcumene*, b. p. 128—130°/7 mm., d^{30} 0·8633, n_D^{30} 1·4944, $[\alpha]_D^{30}$ −22·9° (*monohydro-*

chloride, b. p. 150—155°/8 mm.). *l*-α-Curcumene is very stable. It is not reduced by sodium in ethyl or amyl alcohol, is unattacked by dilute sulphuric acid, and only slowly oxidised by alkaline permanganate. It is not isomerised by heating at 380° in an inert atmosphere. It is not dehydrogenated with formation of a naphthalene derivative when heated at 270° with sulphur or selenium. When dissolved in chloroform it absorbs 1 mol. of bromine. The presence of three ethylenic linkings in the molecule is established by oxidation with perbenzoic acid (cf. Nametkin, A., 1926, 420). Catalytic reduction of *l*-α-curcumene in presence of platinum oxide yields *hexahydro-α-curcumene*, $C_{15}H_{30}$, b. p. about 128°/7 mm., d_{30}^{30} 0·8283, 1·4592, $[\alpha]^{30}$ +0°. l-α-*Curcumenenitrolbenzylamine* has m. p. 102—104°.

Treatment of *l*-β-curcumene trihydrochloride with anhydrous sodium acetate in acetic acid solution yields pure l-β-*curcumene*, b. p. 128—130°/6 mm., d_{30}^{30} 0·8810, n_D^{30} 1·4940, $[\alpha]_D^{30}$ −27·9°, a monocyclic terpene containing three ethylenic linkings, indicated by titration with bromine as well as by formation of the trihydrochloride. Catalytic reduction gives l-*hexahydro*-β-*curcumene*, b. p. about 128°/7 mm., d_{30}^{30} 0·8283, n_D^{30} 1·4552, $[\alpha]_D^{30}$ +6·3°. *l*-β-Curcumene is very unstable and is readily isomerised. It is converted by treatment with 10% sulphuric acid into a dicyclic *terpene* (?), b. p. 115—117°/7 mm., d_{30}^{30} 0·8932, n_D^{30} 1·4936, $[\alpha]_D^{30}$ −11·9. It is not reduced by sodium in amyl alcohol, but undergoes isomerisation and no longer yields the trihydrochloride. It is also isomerised by heating in an inert atmosphere at 380° under pressure. Dehydrogenation with either sulphur or selenium yielded no recognisable products.

M. CLARK.

Aromadendrene. I. L. H. BRIGGS and W. F. SHORT (J.C.S., 1928, 2524—2529).—Careful fractionation of the sesquiterpene fraction from the oil of *Eucalyptus nova-angelica* (Baker and Smith, "A Research on the Eucalypts," Sydney, 1920, pp. 46, 417) yields only aromadendrene, $C_{15}H_{24}$, a single tricyclic sesquiterpene (cf. Smith ,*op. cit.*, p. 417; Semmler, "Die Ätherischen Oele," 1906, II, 530) which exhibits an exaltation of approximately one unit in its molecular refractive power. Exhaustive hydrogenation of aromadendrene, either by the method of Skita or by that of Paal, gives *dihydroaromadendrene*, $C_{15}H_{26}$, b. p. 121—122°/10 mm., d_4^{17} 0·9014, n_D^{17} 1·4871, which also shows an exaltation of one unit in molecular refractive power. The exaltation exhibited by the sesquiterpene is therefore due to structural peculiarity and not to contamination with dicyclic sesquiterpenes. From its likeness in this respect to α-gurjunene and copaene (Semmler, A., 1914, i, 704; 1915, i, 427) it is probable that aromadendrene may contain either a *cyclo*propane ring conjugated with a double linking together with a *cyclo*butane ring, or, less probably, two *cyclo*propane rings. Dehydrogenation of aromadendrene with sulphur yields a deep blue oil, b. p. 122—165°/12 mm., from which no naphthalene hydrocarbon could be obtained, although a small quantity of a black picrate (azulene picrate ?), m. p. 114—116°, was isolated. The presence of the group C·C(:CH$_2$)·C in aromadendrene is clearly indicated by ozonisation in acetic acid solution, which gives *aromadendrone*, $C_{14}H_{22}O$, m. p. 80—81° [*oxime*, m. p. 103°, yielding no nitrile when digested with acetic anhydride; *semicarbazone*, m. p. 189·5—190·5° (decomp.)]. Aromadendrone did not yield an enol-acetate when boiled with acetic anhydride and sodium acetate. The carbonyl group is therefore either in the side-chain or attached to two quaternary carbon atoms in the nucleus.

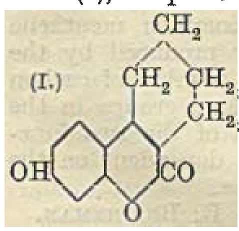
M. CLARK.

Essential oil of "Hiba" wood. Essential oil of Hiba leaves. S. UCHIDA.—See B., 1928, 768.

Essential oil of leaves of "Hinoki." S. UCHIDA.—See B., 1928, 768.

Essential oil of leaves of "Sawara." S. UCHIDA.—See B., 1928, 768.

Heterocyclic compounds. III. Interaction of *cyclo*hexanone-2-carboxylates with phenols. H. K. SEN and U. BASU (J. Indian Chem. Soc., 1928, 5, 467—476).—Ethyl *cyclo*hexanone-2-carboxylate condenses with resorcinol in presence of concentrated sulphuric acid (cf. Dieckmann, A., 1901, i, 539), forming 8-hydroxy-1 : 2 : 3 : 4-tetrahydrobenzcoumarin (I), m. p. 201—202° (*acetyl* derivative, m. p. 186—187°; *benzoyl* derivative, m. p. 157°; *methyl ether*, m. p. 121—122°). Condensation with phosphorus pentoxide gave tarry products. Similarly, 2-cyano-*cyclo*hexanone and resorcinol give a *compound*, m. p. 290°, which when hydrolysed with potassium hydroxide solution affords I.



Boiling potassium hydroxide solution has little effect on I, whilst potassium hydroxide fusion gives benzoic acid and a *compound*, $C_{13}H_8O_3$, m. p. 230° (*benzoyl* derivative, m. p. 195°), probably a dehydrogenated coumarin. Similarly, the above ester and *m*-cresol and α-naphthol give 8-*methyl*-1 : 2 : 3 : 4-*tetrahydrobenzcoumarin*, m. p. 119°, and 1 : 2 : 3 : 4-*tetrahydrobenznaphthacoumarin*, m. p. 190° (*nitro*-derivative, m. p. 244°), respectively.

Ethyl 5-methyl*cyclo*hexanone-2-carboxylate condenses with phloroglucinol, orcinol, and pyrogallol, yielding 8 : 10-*dihydroxy*-, m. p. 264—266°, 8-*hydroxy*-10-*methyl*-, m. p. 249°, and 7 : 8-*dihydroxy*-, m. p. 231°, -1 : 2 : 3 : 4-*tetrahydro*-2-*methylbenzcoumarin*, respectively.

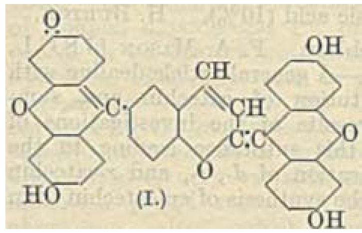
H. BURTON.

Derivatives of 2-phenyl-6-methyl-4-pyrone. Non-resolution of 2-phenyl-6-methyl-4-pyrone *d*-α-bromocamphor-π-sulphonate. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1928, 2307—2312).—Attempts to resolve into its diastereoisomerides the *d*-α-bromocamphor-π-sulphonate of 2-phenyl-6-methyl-4-pyrone were unsuccessful (cf. Levy, Holmyard, and Ruhemann, Proc. C.S., 1913, 29, 159). This non-resolution provides negative evidence in support of Hantzsch's co-ordination formulation of the salts of the 4-pyrones (A., 1920, i, 72). The following are described: 2-phenyl-6-methyl-4-pyrone (*hydrochloride*, m. p. 165°; *perchlorate*, m. p. 145—147°; *sulphate*, m. p. 168—169°; *methylmethosulphate*, m. p. 140—143°; *methiodide*, decomp. 105°, unstable); silver *d*-α-bromocamphor-π-sulphonate (+H_2O). 2-*Phenyl*-6-*piperonylidenemethyl*-4-*pyrone* (I) (*per*-

chlorate, decomp. 143°) has m. p. 194°. The intense orange colour of the d-α-*bromocamphor-π-sulphonate*, m. p. 205—206°, makes stereochemical investigation of this salt impossible. Treatment of I with bromine in chloroform solution gives a *compound* (*dibromo*-derivative ?), m. p. 155—157°, decomposing on recrystallisation from acetone with loss of hydrobromic acid and formation of the *monobromo*-derivative, decomp. 222°. M. CLARK.

Alkali sulphonates of coumarin and nitrocoumarin. R. N. SEN and D. CHAKRAVARTI (J. Indian Chem. Soc., 1928, **5**, 433—437).—Sulphonation of coumarin with fuming sulphuric acid at water-bath temperature (cf. Perkin, J.C.S., 1873, **24**, 37) gives coumarin-6-sulphonic acid (*sodium* salt; *acid chloride*, m. p. 115°; *acid amide*, m. p. 186°; *anilide*, m. p. 132°), oxidised by alkaline potassium permanganate to 5-sulphosalicylic acid. When sulphonation is carried out at 150° coumarin-3 : 6-disulphonic acid (*sodium* salt; *dichloride*, m. p. 170—173°; *diamide*, m. p. above 240°; *dianilide*) is obtained, which is oxidised to 5-sulphosalicylic acid also. 6-Nitrocoumarin affords 6-*nitrocoumarin-3-sulphonic acid* (*sodium* salt; *chloride*, m. p. 205°; *amide*, m. p. above 260°; *anilide*, m. p. 130°), oxidised to 5-nitrosalicylic acid. H. BURTON.

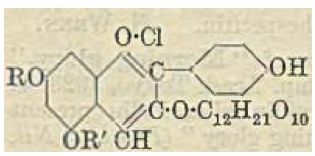
6-Aldehydocoumarin and derived dyes. R. SEN and D. CHAKRAVARTI (J. Amer. Chem. Soc., 1928, **50**, 2428—2436).—6-Aldehydocoumarin (*phenylhydrazone*, m. p. 205—207°) (Stoermer and Oetker, A., 1904, i, 244) is conveniently obtained in approximately 20% yield, together with a resinous product which contains a *substance*, m. p. 174—175° (decomp.), from coumarin by the Reimer–Tiemann method. It undergoes the benzoin reaction, giving *coumaroin*, $C_{20}H_{12}O_6$, m. p. 178—180°, and condenses with acetone and acetophenone in presence of alkali to *dicoumarylideneacetone* (αε-di-6-coumaryl-$\Delta^{\alpha\delta}$-pentadien-γ-one), m. p. 159°, and *coumarylideneacetophenone* (γ-phenyl-α-6-coumaryl-Δ^{α}-propen-γ-one), m. p. above 250°. The following azomethine dyes, $(C_9H_5O_2\cdot CH{:}N)_nR$, are formed by condensing the aldehyde with the appropriate amine in alcoholic hydrochloric or acetic acid: 6-*coumarylidene*-p-*toluidine*, yellow, m. p. 145—147°; *coumarylidene*-β-*naphthylamine*, pale yellow, m. p. 173°; *coumarylidene*-p-*nitroaniline*, yellow, m. p. above 250°; *coumarylideneaminoazobenzene*, reddish-yellow, m. p. 169°; *dicoumarylidene*-p-*phenylenediamine*, brown, m. p. above 250°; *dicoumarylidene*-m-*phenylenediamine*, brown, m. p. above 250°; *dicoumarylidene*-o-*phenylenediamine*, yellow, m. p. above 250°; *coumarylidenebenzidine*, yellow, m. p. above 250°; *tricoumarylidenerosaniline*, reddish-violet, m. p. 142°; *dicoumarylidenesafranine*, reddish-violet, and *coumarylidenechrysoidine*, orange, m. p. 210—212°. The aldehyde condenses with dimethylaniline in presence of hydrochloric acid at 100° to *tetramethyldiaminodiphenylcoumarylmethane*, m. p. 220°, which is oxidised by lead dioxide to the bluish-green *tetramethyldiaminodiphenylcoumarylcarbinol* (*hydrochloride*). Dyes containing two xanthen nuclei are formed from the aldehyde and 4 mols. of a phenol in presence of sulphuric acid at 120—130°, both the 6-aldehydo- and the 2-keto-groups being attacked (cf. Krishna, J.C.S., 1921, **119**, 1420; Sen and Sarkar, A., 1925, i, 812). Thus, resorcinol yields the red *product* (I) (*tripotassium* salt; *hexabromo*-derivative), quinol a reddish-violet *isomeride* (*tetrapotassium* salt; *tetrabromo*-derivative), β-naphthol a colourless *product*, $C_{50}H_{30}O_4$, α-naphthol an isomeric *product*, and gallic acid a polygenetic *dye*, $C_{38}H_{20}O_{19}$. Under similar conditions, however, the aldehyde combines with only 2 mols. of *m*-diethylaminophenol, forming bluish-violet 3 : 6-*bisdiethylamino*-9-*hydroxy*-9 : 6′-*coumarylxanthen*. The colours produced by these dyes on silk and wool are tabulated and it is shown that the coumaryl dyes are more bluish than the corresponding phenyl derivatives. H. E. F. NOTTON.



(I.)

Constitution of delphinin. K. KONDU (Helv. Chim. Acta, 1928, **11**, 919—921).—Methylation of delphinin chloride obtained from the flowers of *Delphinium consolida*, L. (Willstätter and Mieg, A., 1915, i, 284), with methyl sulphate and sodium hydroxide solution and subsequent treatment with 2% methyl-alcoholic hydrogen chloride gives a light red *chloride*, $C_{41}H_{34}O_{16}Cl(OMe)_5$, which when hydrolysed with aqueous-alcoholic sodium hydroxide affords anisic acid and a methylated *delphinidin chloride*, $C_{15}H_8O_4Cl(OMe)_3$. H. BURTON.

Plant colouring matters. VIII. Constitution of monardæin. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1928, **11**, 837—842).—Methylation of monardæin chloride (A., 1927, 252) with methyl sulphate and sodium hydroxide, followed by hydrolysis of the product with alcoholic potassium hydroxide solution, and subsequent acidification with hydrochloric acid gives *p*-methoxycinnamic acid and *monardin dimethyl ether chloride*, red needles. Hydrolysis of this with 20% hydrochloric acid affords *pelargonidin dimethyl ether*. The annexed structure is assigned to monardæin chloride (R and R′=either H or $OH\cdot C_6H_4\cdot CH{:}CH\cdot CO$). H. BURTON.



Plant colouring matters. IX. Yellow colouring matter from red rose. Organic acids from several flowers. P. KARRER and K. SCHWARZ (Helv. Chim. Acta, 1928, **11**, 916—919).—The petals of *Rosæ rubræ* are digested with sulphuric acid to hydrolyse the colouring matter glucoside, and after removal of water with anhydrous sodium sulphate the mixture is extracted with ether. There are obtained a colourless hydrocarbon and quercetin. When pentaacetylquercetin is treated with ozone, protocatechuic and diacetylprotocatechuic acids are obtained.

The flowers of the red peony, red pink, red rose, dark mallow, blue larkspur, violet poppy, and salmon-coloured dahlia (Tsingtau) all contain acetic (1—2%) and formic acids (0·1—0·2%). Several of the flowers

contain varying quantities of citric acid (0·7—7%); the poppy contains caffeic acid (2%), the dahlia a tannin, and the peony a tannic acid (10%). H. BURTON.

The catechin problem. F. A. MASON (J.S.C.I., 1928, **47**, 269—276T).—A general article dealing with the chemical constitution of catechin and summarising the chief results of the investigations of K. Freudenberg on this substance leading to the isolation and identification of *d*-, *l*-, and *r*-catechin and *epi*catechin and the synthesis of *epi*catechin from cyanidin.

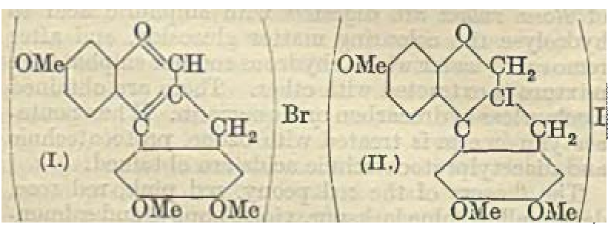
The catechin problem. M. NIERENSTEIN (Chem. Age, 1928, **19**, 291).—A criticism of Mason's article on the subject (preceding abstract). The constitution of cyanidin is regarded as being *sub judice*. E. E. TURNER.

The catechin problem. R. ROBINSON (Chem. Age, 1928, **19**, 337).—A reply to Nierenstein (preceding abstract). It is pointed out that in view of the two recorded syntheses (Willstatter; Robinson) of cyanidin, the constitution of the latter substance is satisfactorily established. E. E. TURNER.

Flavanone glucosides. III. Reduction of flavone and flavanone derivatives. T. ASAHINA and M. INUBUSE (Ber., 1928, **61**, [*B*], 1646—1650; cf. this vol., 1020).—Apigenin, suspended in water, is converted by reduction with sodium amalgam followed by treatment of the filtered solution with hydrochloric acid into apigenidin chloride, $C_{15}H_{11}O_4Cl$, m. p. not below 300°, which does not appear completely identical with the synthetic product of Pratt and Robinson (A., 1925, i, 825). The chloride is analytically and spectroscopically identical with the compound derived similarly from naringenin. Sakuranetin is reduced to the *chloride*, $C_{15}H_{10}O_3Cl{\cdot}OMe$, m. p. 236—237° (decomp.) (also *monohydrate*), whilst the analogous *substance*, $C_{15}H_{10}O_4Cl{\cdot}OMe$, m. p. 231—232° (decomp.) (also *dihydrate*), is derived from hesperitin. H. WREN.

Anthocyanin pigments of "Morning glory." II. T. KATAOKA (Proc. Imp. Acad. Tokyo, 1928, **4**, 389—392).—The anthocyanidin pharbitidin present in the red flower of "Morning glory" (*Pharbitis Nil*, Chois.) (A., 1926, 1150) is identical with pelargonidin. Fission of the anthocyanidin into *p*-hydroxybenzoic acid is effected by a much lower concentration of alkali if hydrogen peroxide is also added. J. W. BAKER.

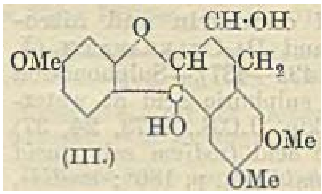
Brazilin and hæmatoxylin. VIII. Reduction of trimethylbrazilone and tetramethylhæmatoxylone. P. PFEIFFER, O. ANGERN, E. HAACK, and J. WILLEMS (Ber., 1928, **61**, [*B*], 1923—1932; cf. this vol., 426, 647).—The action of bromine in benzene



(I.) (II.)

on trimethylanhydrobrazilin leads through a non-isolable, red intermediate phase to the *pyrylium bromide* (I), gradual decomp. above 170°, whereas iodine affords the *di-iodide* (II), m. p. 175° (decomp.), converted by aqueous silver nitrate into the *iodo-nitrate* which rapidly loses hydrogen iodide and passes into a pyrylium salt.

Reduction of trimethylbrazilone in glacial acetic acid by hydrogen in the presence of spongy platinum at the atmospheric temperature yields a dihydroxy-*compound* (probably III), m. p. 151—152° (also *mono-hydrate*; mono-*p*-nitrobenzoyl derivative, m. p. 103—105°), regarded as identical (in spite of recorded difference in m. p.) with the product obtained by Perkin, Ray, and Robinson (this vol., 895) by reduction of trimethylbrazilone with aluminium amalgam in acetic acid.



(III.)

The compound is also obtained in good yield by treatment of trimethylbrazilone with magnesium in a mixture of benzene and glacial acetic acid; two *by-products*, m. p. 267° and 285°, respectively, are isolated. The compound cannot be re-converted by oxidation into trimethylbrazilone, a carboxylic acid, m. p. 225°, being obtained. Reduction of trimethylbrazilone by sodium amalgam in presence of alcohol and glacial acetic acid gives a monohydroxy-*compound*, $C_{16}H_{10}O(OMe)_3{\cdot}OH$, m. p. 133—134° (*acetyl* derivative, m. p. 123—124°), isomeric with trimethylbrazilin. Tetramethylhæmatoxylone is converted by catalytic reduction in presence of spongy platinum into a dihydroxy-*compound*, $C_{16}H_8O(OMe)_4(OH)_2$, m. p. 185—188°, which is completely analogous to the corresponding compound of the brazilin series; the *monoacetyl* derivative, m. p. 150—152°, and *mono-*p*-nitrobenzoyl* compound, m. p. 177—178°, are described. Tetramethylhæmatoxylone is not obtained from it by oxidation. The dihydroxy-compound is also obtained by reduction of tetramethylhæmatoxylone by magnesium in glacial acetic acid and benzene; two *by-products*, $C_{20}H_{22}O_7$, m. p. 283° (decomp.), and an *isomeride*, $C_{16}H_9O(OMe)_4{\cdot}OH$, of tetramethylhæmatoxylin, m. p. 188—192°, are characterised. H. WREN.

Pyrrolidine derivatives. F. B. LAFORGE (J. Amer. Chem. Soc., 1928, **50**, 2471—2477).—Ethyl sodioacetoacetate and β-*p*-tolyloxyethyl bromide (Weddige, A., 1881, 1136) yield *ethyl* β-p-*tolyloxyethylacetoacetate*, b. p. 202—204°/16 mm. This is hydrolysed by alcoholic sodium hydroxide to *methyl* γ-p-*tolyloxypropyl ketone*, b. p. 165—175°/16 mm. (*semicarbazone*, m. p. 158°), and a little γ-p-*tolyloxybutyric acid*, m. p. 84—85°. *Methyl* γ-p-*tolyloxypropyl ketoxime*, m. p. 54°, is reduced by sodium amalgam and acetic acid in alcohol to δ-*amino*-α-p-*tolyloxypentane*, b. p. 280—283°/760 mm. (*carbonate*), the *hydrochloride* of which is converted by 45% hydrochloric acid at 100° into 2-methylpyrrolidine (Fenner and Tafel, A., 1898, i, 446). α-Phenyl-*n*-butyl bromide, from phenylpropylcarbinol and hydrogen bromide, yields with methylamine α-*methylamino*-α-*phenylbutane*, b. p. 117—118°/33 mm., which could not be converted into a pyrrolidine derivative by bromination and removal of hydrogen bromide. The product (? αδ-dibromo-α-phenyl-

butane) obtained by saturating phenylallylcarbinol with hydrogen bromide in sunlight gives with alcoholic methylamine an unsaturated *amine*, $C_{11}H_{15}N$, b. p. 209—216 /770 mm., instead of the expected pyrrolidine. γ-Benzoylpropyl bromide and methylamine yield benzoyl*cyclo*propane (cf. Perkin, J.C.S., 1885, **47**, 836) and *2-phenyl-*1*-methylpyrroline*, b. p. 136—139°/34 mm., which could not be reduced to a pyrrolidine derivative. Ethyl sodiobenzoylacetate and β-*p*-tolyloxyethyl bromide yield *ethyl* β-p-*tolyloxyethylbenzoylacetate*, b. p. 240—250°/8 mm., from which *phenyl* γ-p-*tolyloxypropyl ketone*, b. p. 250—260°/8 mm., m. p. 63°; its *ketoxime*, m. p. 75°; δ-*amino*-α-p-*tolyloxy*-δ-*phenylbutane hydrochloride* and *nitrate*; δ-*chloro*-α-*amino*-α-*phenylbutane hydrochloride*, m. p. 200—205° (decomp.), and 2-*phenylpyrrolidine*, b. p. 236—238°/757 mm., are successively prepared.

2-Phenylpyrrolidine and methyl iodide in methyl alcohol yield 2-*phenyl*-1-*methylpyrrolidine*, b. p. 225—227°/760 mm. In spite of their structural relationship to nicotine, the above pyrrolidines and 2 : 5-dimethylpyrrolidine have only a slight insecticidal action.

H. E. F. Notton.

Products of the hydrogenation of quinoline under pressure in the presence of osmium and cerium. V. S. Sadikov and A. K. Michailov (Ber., 1928, **61**, [*B*], 1801—1806).—The presence of 1% of osmium dioxide in the cerium oxide–asbestos catalyst causes a more intense hydrogenation of quinoline beyond the tetrahydro-stage which is reached with cerium dioxide alone, thus causing a diminution in the amount of substances of high b. p. On the other hand, the use of the combined catalyst (20 or 1% of cerium dioxide with 1 or 20% of osmium dioxide) induces the production of compounds of low b. p. by further change from decahydroquinoline. From the products of high b. p. a base, b. p. 275—290°/15 mm. (*dihydrochloride*; *ferrocyanide*), is isolated which, on the basis of analyses and ability to give an additive product with methyl iodide, is regarded as 7-*methyldi*-1 : 2 : 3 : 4 : 7 : 8-*hexahydro*-1 : 1′-*quinolyl*. The substance, 1 : 2′-*methyl*-3′-*ethylpiperidino*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroquinoline* (*dihydrochloride*, m. p. 276°), is derived from the fractions of lower b. p.

From the products of the interrupted hydrogenation of quinoline the following compounds are isolated: from the fraction of b. p. 150—175°, the *hydrochlorides*, $C_{10}H_{20}N_2$,HCl, m. p. 226°, and $C_9H_{17}N$,HCl, m. p. 156°, probably derived respectively from 2-amino-3-methyldecahydroquinoline and 2-methyl-3-ethylpiperidine; from the fraction of b. p. 175—190°, a *hydrochloride*, $C_{19}H_{35}N_3$,2HCl, m. p. 172° probably derived from 2-amino-3-methyldidecahydro-1 : 1′-quinolyl, a base, $C_{14}H_{26}N_2$, possibly 1-piperidinodecahydroquinoline, and a *ferrocyanide*, $C_{14}H_{27}N,H_4FeC_6N_6$, probably a salt of 1-methyl-2 : 3-diethyldecahydroquinoline. Treatment of the fractions of b. p. 175—190° and 190—200° in alcohol with carbon dioxide or distillation in a current of carbon dioxide yields the *compounds* $C_{18}H_{36}O_2N_2$ and $C_{27}H_{55}O_2N_3$, respectively.

H. Wren.

Catalytic hydrogenation. Interrupted hydrogenation of quinoline under pressure in the presence of osmium and cerium. V. S. Sadikov and A. K. Michailov (Ber., 1928, **61**, [*B*], 1797—1800).—Quinoline and the catalyst (asbestos with 20% of osmium dioxide and 1% of cerium dioxide) are placed in an Ipatiev autoclave under 100 atm. of hydrogen. The apparatus is placed in an electric furnace pre-heated to 320—340° and the times required for the incidence of maximum pressure and subsequently the fall in pressure are observed. The first period is very variable and is followed by an induction period succeeded by one of oscillatory absorption, after which the catalyst becomes exhausted. If, however, the apparatus is cooled to the atmospheric pressure, hydrogenation of the quinoline again proceeds. It appears therefore that the permanent maintenance of high optimal temperatures is not necessary for the hydrogenation of the majority of cyclic compounds and that the high temperature only excites a process which subsequently occurs independently of temperature. Prolonged exposure to a high temperature tends to impair the activity of the catalyst.

H. Wren.

Fission of hydrocarbostyril and its derivatives to *o*-aminophenyl-propionic and -butyric acids. F. Mayer, H. Philipps, F. W. Ruppert, and A. T. Schmitt (Ber., 1928, **61**, [*B*], 1966—1975).—2-Keto-1 : 2 : 3 : 4-tetrahydroquinoline suffers fission of the ring when heated with aqueous barium hydroxide at about 150°, giving the barium salts of *o*-aminophenylpropionic and -butyric acids. Excess of barium hydroxide is exactly removed by carbon dioxide and the barium salts are transformed into the corresponding sodium salts. As exemplified by β-*o*-aminophenylpropionic acid, the free acids readily pass into the cyclic forms. The *sodium* salts of the following acids have been isolated: β-*o*-aminophenyl- (benzoyl derivative, m. p. 155—158°); β-3-chloro-2-aminophenyl-; β-5-chloro-2-aminophenyl- (*benzoyl* derivative, m. p. 189—192°); β-3 : 5-dichloro-2-aminophenyl-; β-3-methyl-2-aminophenyl-; β-5-methyl-2-aminophenyl- (*benzoyl* derivative, m. p. 170—172°); 3 : 6-diaminophenyl-1 : 2-$\beta\beta'$-di- (*benzoyl* derivative, m. p. 274°); β-5-methoxy-2-aminophenyl- (*benzoyl* derivative, m. p. 183—184°) -propionic acid: β-2-aminophenyl-; β-5-chloro-2-aminophenyl-; β-3-chloro-2-aminophenyl-; β-3 : 5-dichloro-2-aminophenyl-*n*-butyric acid. *Sodium* β-o-*methylaminophenylpropionate* from 2-keto-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline is converted by methyl sulphate into *methyl* β-o-*dimethylaminophenylpropionate*, b. p. 140°/20 mm., transformed by hydrochloric acid into β-o-*dimethylaminophenylpropionic acid hydrochloride*, m. p. 183—184°, from which *N*-methylhydrocarbostyril is obtained by sodium acetate. *Methyl* β-o-*methylethylaminophenylpropionate*, b. p. 145°/20 mm., is converted by hydrochloric acid into β-o-*methylethylaminophenylpropionic acid hydrochloride*, m. p. 130—133°, from which the free *acid*, b. p. 190°/20 mm., is obtained in almost homogeneous form. *Methyl* β-o-*phenylmethylaminophenylpropionate*, b. p. 200°/15 mm., is hydrolysed to *N*-phenylhydrocarbostyril.

The sodium salts of the aminophenyl-propionic or -butyric acids are mixed with sodium nitrite and water and added to dilute hydrochloric acid. The

diazo-solution is added to aqueous copper sulphate and sodium chloride. The free acids are converted by thionyl chloride into their chlorides and thence into indanones. The following substances are thus obtained: β-2-chlorophenylpropionic acid, m. p. 97°, its *chloride*, b. p. 155—158°/20 mm., and *4-chloro-1-keto-2 : 3-dihydroindene*, m. p. 92°; *β-2-bromophenylpropionic acid*, m. p. 98°, its *chloride*, b. p. 160—165°/18 mm., and 4-bromo-1-keto-2 : 3-dihydroindene, m. p. 98—99°; *β-2 : 3-dichlorophenylpropionic acid*, m. p. 114°, its *chloride*, b. p. 178—182°/28 mm., and *4 : 5-dichloro-1-keto-2 : 3-dihydroindene*, m. p. 88°; *β-2 : 5-dichlorophenylpropionic acid*, m. p. 118°, its *chloride*, b. p. 154—158°/18 mm., and *4 : 7-dichloro-1-keto-2 : 3-dihydroindene*, m. p. 124°; *β-2 : 3 : 5-trichlorophenylpropionic acid*, m. p. 113°, its *chloride*, b. p. 201—203°/12 mm., and *4 : 5 : 7-trichloro-1-keto-2 : 3-dihydroindene*, m. p. 114°; *β-2-chloro-3-methylphenylpropionic acid*, m. p. 118°, its *chloride*, b. p. 140—146°/18 mm., and *4-chloro-1-keto-5-methyl 2 : 3-dihydroindene*, m. p. 82°; *β-2-chloro-5-methylphenylpropionic acid*, m. p. 93°, its *chloride*, b. p. 160—168°/18 mm., and *4-chloro-1-keto-7-methyl-2 : 3-dihydroindene*, b. p. 168—173°/18 mm.; *β-2-chloro-5-methoxyphenylpropionic acid*, b. p. 200°/15 mm., m. p. 72—73°, its *chloride*, and *4-chloro-7-hydroxy-1-keto-2 : 3-dihydroindene*, m. p. 122°; *β-2-chlorophenyl-*n*-butyric acid*, b. p. 150°/13 mm., m. p. 60°, its *chloride*, b. p. 140°/20 mm., and *4-chloro-1-keto-3-methyl-2 : 3-dihydroindene*, m. p. 55°; *β-2 : 5-dichlorophenyl-*n*-butyric acid*, b. p. 180°/15 mm., m. p. 71°, its *chloride*, b. p. 160°/15 mm., and *4 : 7-dichloro-1-keto-3-methyl-2 : 3-dihydroindene*, m. p. 103°; *β-5-chloro-2-bromophenyl-*n*-butyric acid*, b. p. 200°/15 mm., m. p. 87°; *β-2 : 3-dichlorophenyl-*n*-butyric acid*, m. p. 115°, its *chloride*, b. p. 180°/15 mm., and *4 : 5-dichloro-1-keto-3-methyl-2 : 3-dihydroindene*, b. p. 170°/15 mm., m. p. 44°; *β-2 : 3 : 5-trichlorophenyl-*n*-butyric acid*, b. p. 190°/15 mm., m. p. 115—116°, its *chloride*, b. p. 160°/15 mm., and *4 : 5 : 7-trichloro-1-keto-3-methyl-2 : 3-dihydroindene*, m. p. 88—89°.

β-2-Cyanophenylpropionic acid, m. p. 136°, is hydrolysed to β-2-carboxyphenylpropionic acid, m. p. 165—166°. Similarly, *β-5-chloro-2-cyanophenyl-*n*-butyric acid*, b. p. 160°/15 mm., m. p. 120°, yields *β-5-chloro-2-carboxyphenyl-*n*-butyric acid*, m. p. 185°. Sodium β-2-aminophenylpropionate is converted into 1-chromanone, m. p. 25°, and sodium β-5-chloro-2-aminophenyl-*n*-butyrate into *6-chloro-4-methyl-1-chromanone*, b. p. 145—150°/15 mm., m. p. 66°; the latter compound is transformed by bromine at 250° into 6-chloro-4-methylcoumarin, m. p. 186°. Suitable treatment of sodium β-2-aminophenylpropionate yields β-phenylpropionic acid, m. p. 49°, *β-phenylpropionic-2-sulphinic acid* (as *sodium* salt), and *β-2-thiolphenylpropionic acid*, m. p. 118°. *6-Chloro-4-methylthiohydrocoumarin*, m. p. 56°, and *β-5-chloro-2-thiolphenyl-*n*-butyric acid*, m. p. 81—82°, are described.

H. Wren.

Decahydroquinoline derivatives. IV. Hofmann degradation of 2-methyloctahydroindole. S. Fujise (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 91—98).—Reduction of 2-methylindole in glacial acetic acid at 40—45° with hydrogen and platinum-black yields cis-*2-methyloctahydroindole*, b. p. 187·5—188°, d_4^{25} 0·9103, n_D^{25} 1·47432 [*hydrobromide*, m. p. 148—149°; *chloroaurate*, m. p. 118°; methiodide, m. p. 233—234° (decomp.); picrate, m. p. 178—179° (decomp.); benzenesulphonyl derivative, m. p. 125°; von Braun and Bayer, A., 1925, i, 428, give 296°, 192—193°, and 120—121°, respectively, for the last three derivatives, their specimen probably being contaminated with *o*-propyl*cyclo*hexylamine or with the *trans*-compound]. This by exhaustive methylation yields o-*dimethylaminopropenylcyclohexane*, b. p. 211—213°, d_4^{25} 0·8670, n_D^{25} 1·47196 [methiodide, m. p. 212° (decomp.); picrate, m. p. 146° (decomp.); von Braun, Bayer, and Blessing, A., 1924, i, 545, give, for the unidentified base, 187—188° and 129—130°, respectively], in accordance with the scheme $C_6H_{10}<\begin{matrix}CH_2\text{——}\\NMe_2(OH)\end{matrix}>CHMe \longrightarrow C_6H_{10}<\begin{matrix}CH{:}CHMe\\NMe_2\end{matrix}$ since it is converted by further catalytic reduction into *cis*-2-dimethylamino-*n*-propyl*cyclo*hexane, b. p. 214°, d_4^{20} 0·8602, n_D^{20} 1·46386, identical with the product obtained by the exhaustive methylation of *cis*-decahydroquinoline (this vol., 1022).

J. W. Baker.

Stereoisomerism in polycyclic systems. V. W. H. Perkin, jun., and S. G. P. Plant (J.C.S., 1928, 2583—2590; cf. this vol., 72, 527).—The simultaneous formation of relatively large quantities of both *cis*- and *trans*-modifications of 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole and 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline during reduction of 2 : 3 : 4 : 5-tetrahydroheptindole and 7 : 8 : 9 : 10-tetrahydroheptaquinoline respectively might be anticipated from consideration of the strains existing in the multiplanar configurations of these reduction products. The results are not in accordance with expectation. *2 : 3 : 4 : 5-Tetrahydroheptindole*, m. p. 144° (*picrate*, m. p. 142°), is obtained by Fischer's indole synthesis from suberonephenylhydrazone. When this compound is reduced with tin and hydrochloric acid in aqueous alcohol, the product consists almost entirely of a single form (presumably the *cis*, which is likely to be the less strained) of *2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole* (I), m. p. 77° [*picrate*, m. p. 176° (decomp.); *hydrochloride*; *10-acetyl* derivative, m. p. 87°; *10-benzoyl* derivative, m. p. 116°]. Not more than 5% of any stereoisomeride is present. When *7-bromo-2 : 3 : 4 : 5-tetrahydroheptindole*, m. p. 129—130°, prepared from *suberone-*p*-bromophenylhydrazone*, m. p. 57°, is similarly reduced, it undergoes partial debromination. Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline with tin and hydrochloric acid in aqueous-alcoholic solution yields a product consisting almost entirely of one of the possible forms of *5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline* (II), b. p. 203°/24 mm. (*picrate*, m. p. 96°; *5-benzoyl* derivative, m. p. 145°). The same substance is obtained as sole product when *11-keto-5 : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline*, m. p. 344—345°, obtained by condensation of anthranilic acid and suberone, is reduced with sodium amalgam.

The relative amounts of octahydroacridine-*A* and octahydroacridine-*B* formed by reducing tetra-

hydroacridine with tin and aqueous-alcoholic hydrochloric acid (Perkin and Sedgwick, A., 1925, i, 63) are now found to be in the ratio of approximately 1 to 4. The reduction of tetrahydroacridone with tin and aqueous-alcoholic hydrochloric acid yields a small quantity of one of the two possible forms of *hexahydroacridone*, m. p. 180° (*oxime*, m. p. 215—216°).

M. CLARK.

Derivatives of tetrahydrocarbazole. VII. Reactions of 3-methyltetrahydrocarbazole, 6-chlorotetrahydrocarbazole, and their acyl derivatives. S. G. P. PLANT and R. J. ROSSER (J.C.S., 1928, 2454—2464).—Like 9-benzoyltetrahydrocarbazole (*ibid.*, 1923, **123**, 676), the 9-benzoyl derivatives of 3-methyl- and 6-chloro-tetrahydrocarbazole react with nitric acid producing, in each case, the direct nitration product, together with a substance formed by addition of OH and NO_2 at the double linking; 9-carbethoxy-6-chlorotetrahydrocarbazole behaves in like fashion. Like 9-acetyltetrahydrocarbazole, the 9-acetyl derivatives undergo addition of OH and OH at the double linking; 9-carbethoxy-3-methyltetrahydrocarbazole behaves similarly. The *phenylhydrazone*, o- and p-*nitrophenylhydrazones*, m. p. 59° and 128·5°, of 4-methyl*cyclo*hexanone are converted by the Fischer indole synthesis into 3-*methyltetrahydrocarbazole*, m. p. 109—110°, and its 8- and 6-*nitro*-derivatives, m. p. 188° and 165—166°, respectively. The m-*nitrophenylhydrazone*, m. p. 80—81°, yields a mixture of 5(or 7)- and 7(or 5)-*nitro*-3-*methyltetrahydrocarbazoles*, m. p. 188° and 175°. Nitration of the 3-methyl-carbazole in sulphuric acid solution yields the 6-nitro-derivative as sole product. Nitration of the 9-*acetyl* derivative, m. p. 108·5°, in acetic acid solution, yields a mixture of 5(or 7)-*nitro*-9-*acetyl*-3-*methyltetrahydrocarbazole*, m. p. 134°, and 10 : 11-*dihydroxy*-9-*acetyl*-3-*methylhexahydrocarbazole*, m. p. 189—190°. Treatment of the last-named compound with acetic anhydride yields 6-*acetyl*-3-*methyl*-ψ-*indoxyl*spirocyclo*pentane*, m. p. 93·5°. 3-*Methyl*-ψ-*indoxyl*spirocyclo*pentane*, has m. p. 114·5°. Nitration of 9-*benzoyl*-3-*methyltetrahydrocarbazole*, m. p. 99° (prepared by successive treatment with magnesium methyl iodide and benzoyl chloride), in acetic acid solution yields a mixture of the 5(or 7)-*nitro*-9-*benzoyl* derivative, m. p. 142·5°, and 11-*nitro*-10-*hydroxy*-9-*benzoyl*-3-*methylhexahydrocarbazole*, m. p. 123° (decomp.). Nitration of 9-*carbethoxy*-3-*methyltetrahydrocarbazole*, m. p. 66—67°, under similar conditions yields a mixture of the 5(or 7)-*nitro*-9-*carbethoxy*-derivative, m. p. 104°, and *ethyl* 10 : 11-*dihydroxy*-3-*methylhexahydrocarbazole*-9-*carboxylate*, m. p. 135°.

Nitration of 6-chlorotetrahydrocarbazole in concentrated sulphuric acid solution yields the 5(or 7)-*nitro*-derivative (I), m. p. 183·5°. 4-*Chloro*-3-*nitrophenylhydrazine*, m. p. 109°, from 4-chloro-3-nitroaniline, reacts with *cyclo*hexanone, giving cyclo*hexanone* 4-*chloro*-3-*nitrophenylhydrazone*, m. p. 106—107°. The last-named compound is converted by the Fischer indole synthesis into a mixture of I and 6-*chloro*-7(or 5)-*nitro*-6-*tetrahydrocarbazole*, m. p. 162°. Similar reactions, starting with 4-chloro-o-nitroaniline, yield 4-*chloro*-2-*nitrophenylhydrazine*, m. p. 134°, cyclo*hexanone*-4-*chloro*-2-*nitrophenylhydrazone*, m. p. 101°, and 6-*chloro*-8-*nitrotetrahydrocarbazole*, m. p. 213°. Nitration of 6-*chloro*-9-*acetyltetrahydrocarbazole*, m. p. 136°, in hot acetic acid solution yields the 5(or 7)-*nitro*-derivative, m. p. 184·5—185·5°, and 6-*chloro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m. p. 222°. Similar nitration of 6-*chloro*-9-*benzoyltetrahydrocarbazole*, m. p. 122—123°, yields the 5(or 7)-*nitro*-derivative, m. p. 148°, and 6-*chloro*-11-*nitro*-10-*hydroxy*-9-*benzoylhexahydrocarbazole*, m. p. 147° (decomp.). Nitration of 6-*chloro*-9-*carbethoxytetrahydrocarbazole*, m. p. 111—112°, in hot acetic acid solution yields the 5(or 7)-*nitro*-derivative, m. p. 126°; when fuming nitric acid is used, the product is *ethyl* 6-*chloro*-11-*nitro*-10-*hydroxyhexahydrocarbazole*-9-*carboxylate*, m. p. 136—137°. When an alcoholic solution of the last-named compound is boiled for 1 hr., conversion into *ethyl* 6-*chloro*-10 : 11-*dihydroxyhexahydrocarbazole*-9-*carboxylate*, m. p. 132°, takes place.

When 3-methyltetrahydrocarbazole is reduced with tin and hydrochloric acid in aqueous alcohol, two stereoisomeric modifications of 3-*methylhexahydrocarbazole* (A), m. p. 58·5°, and (B), m. p. 128°, are obtained. The (A) modification (9-*acetyl* derivative, m. p. 101°; 9-*benzoyl* derivative, m. p. 81·5°; *picrate*, m. p. 115—116°) is the sole product of electrolytic reduction.

M. CLARK.

***ms*-Acridine derivatives.** K. LEHMSTEDT and E. WIRTH (Ber., 1928, **61**, [B], 2044—2049).—Acridine is converted by a boiling aqueous solution of sodium sulphite and hydrogen sulphite into colourless *sodium* 9 : 10-*dihydroacridine*-9-*sulphonate*, slowly oxidised by air when moist or when its solution is evaporated to the sparingly soluble red sulphite, converted by alkali hydroxide into the colourless salt and acridine. The colourless salt is converted into acridine by alkali hydroxide, thus permitting a ready separation of acridine from other bases. It is transformed by potassium cyanide in boiling alcoholic suspension into 9-*cyano*-9 : 10-*dihydroacridine*, m. p. 146° (*hydrochloride*; *picrate*, m. p. 222°), in which the cyano-group is replaced by the hydroxy-group by hydrolysing agents. Protracted boiling of an alcoholic solution of 9-cyano-9 : 10-dihydroacridine leads to the production of 9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*diacridyl*, m. p. 214° with decomposition into acridine and 9 : 10-dihydroacridine. Dehydrogenation of 9-cyano-9 : 10-dihydroacridine affords 9-*cyanoacridine*, m. p. 186° (*hydrochloride*; *picrate*, m. p. 229°), converted by 90% sulphuric acid at 100° into acridine-9-carboxylamide, m. p. 263—264°, and by the successive action of sulphuric acid and sodium nitrite into *acridine*-9-*carboxylic acid*, decomp. 289—290°. 9-Cyanoacridine and alcoholic ammonium sulphide yield *acridine*-9-*thiocarboxylamide*, m. p. 240°.

H. WREN.

Chloroform-soluble metal pyridine cyanates. T. L. DAVIS and A. V. LOGAN (J. Amer. Chem. Soc., 1928, **50**, 2493—2499).—Blue *hexapyridinecupric*, blue *hexapyridinenickelous*, pink *hexapyridinecobaltous*, and *hexapyridinecadmium cyanates* are extracted by chloroform from aqueous solutions of their components. They are stable in presence of pyridine vapour, but decompose on exposure to the air into dipyridinecupric (cf. Werner, J.C.S., 1923, **123**, 2577), pale blue *tetrapyridinenickelous*, blue *dipyridinecobaltous*, and *dipyridinecadmium cyanates*, respectively. *Dipyridine*-

zinc cyanate is stable in air, but *monopyridinesilver cyanate* loses pyridine. Both absorb pyridine vapour with deliquescence. Chloroform solutions of hexapyridinecobaltous and hexapyridinecupric cyanates show approximately 6·5 times the b. p. elevation calculated for the undissociated compounds. The colour of the former solution is that of the dipyridine derivative, but it changes towards that of the hexapyridine salt when pyridine is added or the temperature is lowered. H. E. F. NOTTON.

2-Acetamidopyridine. E. PLAZEK and E. SUCHARDA (Ber., 1928, **61**, [*B*], 1813—1816).—The action of nitric acid (*d* 1·5) on 2-acetamidopyridine in glacial acetic acid and acetic anhydride yields *2-acetamidopyridine nitrate*, m. p. 190°. Acetylation of the amino-group of 2-aminopyridine destroys completely its ability to facilitate the entry of the nitro-group. The nitrate is unaffected by boiling, fuming nitric acid or by a boiling mixture of nitric acid and acetic anhydride. It is converted by concentrated sulphuric acid into a mixture of 3- and 5-nitro-2-aminopyridines; since 2-nitroaminopyridine is an intermediate product of the reaction, it follows that nitration is preceded by hydrolysis of the acetamido-group. 2-Acetamidopyridine is converted by bromine into *ʋ-bromo-2-acetamidopyridine*, m. p. 175°, identified by hydrolysis to 5-bromo-2-aminopyridine, m. p. 137°. H. WREN.

Derivatives of pyridine. F. B. LAFORGE (J. Amer. Chem. Soc., 1928, **50**, 2477—2483).—Cyanopyridine (cf. Camps, A., 1902, i, 823) and magnesium methyl iodide followed by sulphuric acid yield 3-pyridyl methyl ketone (Engler, A., 1891, 1505), the oxime of which is reduced by zinc dust and acetic acid to *α-3-pyridylethylamine*, b. p. 219—221°/765 mm. (*picrate*, m. p. 186—187°). This gives with ethyl iodide *α-3-pyridyldiethylamine*, b. p. 223—226°/773 mm. *3-Pyridyl propyl ketone*, b. p. 240—248° (*semicarbazone*, m. p. 169—170°), yields a hydrazone, m. p. 129—130° (cf. Engler, *loc. cit.*), which is converted by concentrated hydrochloric acid into *2-β-pyridyl-3-ethylindole*, m. p. 158° (yellow *hydrochloride*), and by zinc dust and acetic acid into *α-3-pyridylbutylamine*, b. p. 247—251°. *Methyl-α-3-pyridylbutylamine* has b. p. 244—247°. The new pyridylalkylamines have only a slight insecticidal action, but nicotyrin, dihydro*meta*nicotine, and especially *meta*nicotine have a toxicity approaching that of nicotine. H. E. F. NOTTON.

2-, 3-, and 4-Benzylpyridines. F. B. LAFORGE (J. Amer. Chem. Soc., 1928, **50**, 2484—2487).—2- and 4-Benzylpyridines are conveniently isolated from the mixture obtained by Tschitschibabin's method (A., 1901, i, 484) by oxidation with permanganate to the benzoylpyridines, which are easily separated by crystallisation of the picrates, and reduced by Clemmensen's method. 3-Benzoylpyridine, from 3-cyanopyridine and magnesium phenyl bromide, is converted by reduction of the oxime into *α-3-pyridylbenzylamine*, b. p. 329—331°/760 mm. This yields, with nitrous acid, *α-3-pyridylbenzyl alcohol*, which is reduced by hydriodic acid to 3-benzylpyridine (*picrate*, m. p. 119°) (cf. A., 1903, i, 853). H. E. F. NOTTON.

Diphenylpyridylmethane dyes. E. PLAZEK and E. SUCHARDA (Ber., 1928, **61**, [*B*], 1811—1813; cf. A., 1924, i, 881).—*Tetramethyltriaminodiphenylpyridylmethane*, m. p. 163—165° (also $+0·5C_6H_6$), is obtained by the action of aqueous sulphuric acid on Michler's hydrol and 2-aminopyridine. It is not oxidised by manganese dioxide or lead peroxide to the corresponding dye below 100°. H. WREN.

Modification of the Skraup synthesis of quinoline. B. E. COHN and R. G. GUSTAVSON (J. Amer. Chem. Soc., 1928, **50**, 2709—2711).—Addition of acetic acid causes the reaction to proceed smoothly, without diminishing the yield. Thus, 38 g. of aniline, 24 g. of nitrobenzene, 100 g. of glycerol, 60 c.c. of acetic acid (80%), and 54 c.c. of sulphuric acid, gently refluxed for 16 hrs., yield 33 g. of quinoline H. E. F. NOTTON.

Complex salts of amphoteric hydroxyquinoline derivatives. E. HERTEL and H. KLEU (Ber., 1928, **61**, [*B*], 1653—1654).—Addition of copper sulphate to a solution of 5 : 7-dibromo-8-hydroxyquinoline gives an amorphous precipitate which becomes crystalline when heated. This *copper* salt and that derived similarly from 5 : 7-dichloro-8-hydroxyquinoline dissolve in halogen acids, giving intensely coloured *salts*, $(CuCl_4)\colon(H\cdot\cdot NC_9H_4Cl_2\cdot OH)_2,2H_2O$; $(CuCl_4)\colon(H\cdot\cdot NC_9H_4Br_2\cdot OH),2H_2O$; $(CuBr_4)\colon(H\cdot\cdot NC_9H_4Cl_2\cdot OH)_2,2H_2O$; $(CuBr_4)\colon(H\cdot\cdot NC_9H_4Br_2\cdot OH)_2,2H_2O$; $(CuI_4)\colon(H\cdot\cdot NC_9H_4Br_2\cdot OH)_2,2H_2O$. The chlorides and iodides at 90° lose 2 mols. of water and 4 mols. of halogen acid, giving the copper salts, $Cu(O\cdot C_9H_4NX_2)_2$, whereas the bromides exhibit greater thermostability. H. WREN.

Preparation of 2-phenylquinoline-4-carboxylic acid [atophan]. F. CHEMNITIUS.—See B., 1928, 767.

Pyrazolones. Action of thiosemicarbazide and semicarbazide on ketonic esters. II. S. C. DE and N. C. DUTT (J. Indian Chem. Soc., 1928, **5**, 459—465).—Ethyl benzoylacetate reacts with thiosemicarbazide, yielding *3-phenylpyrazolone-1-thiocarbamide*, m. p. 161° (4 : 4-*dibromo*-derivative, loses bromine at 130°; 4-iso*nitroso*-derivative, m. p. 174°), and with 4-phenyl-, 4-*p*-tolyl-, and 4-ethyl-thiosemicarbazides, forming *3-phenylpyrazolone-1-thiocarbophenylamide*, m. p. 127°, *-p-tolylamide*, m. p. 106°, and *-ethylamide*, m. p. 136°, respectively. *3-Phenylpyrazolone-1-carbamide*, m. p. 179° (4 : 4-*dibromo*-derivative, m. p. 144°; 4-iso*nitroso*-derivative, m. p. 204°), is obtained similarly from semicarbazide.

Ethyl diacetosuccinate and semicarbazide give 4 : 4′-*bis-3-methylpyrazolone-1-carbamide*, m. p. 128° (*-1-thiocarbamide*, m. p. 197°; *-1-thiocarbophenylamide*, m. p. 191°; *-1-thiocarbo-p-tolylamide*, m. p. 201—202°; *-1-thiocarboethylamide*, m. p. 191°), which when heated above its m. p. decomposes into 4 : 4′-bis-3-methylpyrazolone, m. p. 290° after darkening at 250°.

Ethyl acetoacetate and 4-phenylthiosemicarbazide give 3-methylpyrazolone-1-thiocarbophenylamide, m. p. 117°. The corresponding *p*-tolylamide and ethylamide have m. p. 121° and 84°, respectively. H. BURTON.

Constitution of "compral." P. PFEIFFER and R. SEYDEL (Z. physiol. Chem., 1928, **178**, 81—96). Compral is an additive compound of pyramidone and

voluntal, $CCl_3 \cdot CH_2 \cdot O \cdot CO \cdot NH_2$ (1 : 1, m. p. about 76°). Investigation of the m.-p. curves of related compounds led to the conclusion that the acid amide group, and not the dimethylamino-group of pyramidone was the cause of the formation of additive compounds, whilst the hydrogen atoms of the amino-group in voluntal were indispensable, and the replacement of the chlorine by hydrogen greatly weakened the tendency to form additive compounds. Compral is assigned the constitution :

$$\mathrm{NMe}\!\!<\!\!\begin{array}{l}\mathrm{CMe{:}\overset{|}{C}{\cdot}NMe_2}\\ \mathrm{NPh{\cdot}C{:}O \cdots H_2N{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CCl_3}\end{array}$$

The m.-p. curves of the following pairs of substances were examined: acetamidoantipyrine–voluntal (*compound*, 1 : 1); antipyrine–voluntal (*compound*, 1 : 1); sarcosine anhydride–voluntal (*compound*, 1 : 2, m. p. 73°); pyramidone–*N*-phenylvoluntal; acetamidoantipyrine–*N*-phenylvoluntal; antipyrine–*N*-phenylvoluntal (*compound*, 1 : 1, m. p. 70°); sarcosine anhydride–*N*-phenylvoluntal (*compound*, 1 : 2, m. p. 121°); antipyrine–*N*-phenyl-*N*-methylvoluntal; pyramidone–*N*-phenyl-*N*-methylvoluntal; sarcosine anhydride–*N*-phenyl-*N*-methylvoluntal; antipyrine–urethane; sarcosine anhydride–urethane (*compound*, 1 : 2, m. p. 70°); and sarcosine anhydride–*N*-phenylurethane (*compound*, 1 : 2, m. p. 95—97°). R. K. CALLOW.

Constitution of hypnal and trigemin. P. PFEIFFER and R. SEYDEL (Z. physiol. Chem., 1928, **178**, 97—108).—Hypnal and bihypnal were shown by Tsakalotos (A., 1913, i, 521) to be additive compounds of antipyrine and chloral hydrate in the proportions 1 : 1 and 1 : 2, respectively. This was confirmed by examination of the m.-p. curves, and the existence of additive *compounds* of pyramidone and butylchloral hydrate (1 : 1, m. p. 84°) (trigemin, cf. G.P. 150799) and of antipyrine and butylchloral hydrate (1 : 1, m. p. 72°) was also shown. The investigation of the m.-p. curves of related compounds showed that additive *compounds* were formed by sarcosine anhydride and chloral hydrate (1 : 1, m. p. 92—95°; 1 : 2, m. p. 83—86·5°). On the other hand, antipyrine, pyramidone, or sarcosine anhydride formed no additive compounds with cholesterol or mannitol, suggesting that the existence of two hydroxyl groups on the same carbon atom is the cause of formation of additive compounds by chloral hydrate. The loose combination of the components in hypnal is shown by the ease with which each reacts separately with appropriate reagents. To it is assigned the constitution :

$$\begin{array}{l}\mathrm{\overset{}{C}Me{=}CH}\\ \mathrm{NMe{\cdot}NPh}\end{array}\!\!>\!\mathrm{C{:}O}\!<\!\!\begin{array}{l}\mathrm{HO}\\ \mathrm{HO}\end{array}\!\!>\!\mathrm{CH{\cdot}CCl_3},$$

whilst anhydrohypnal, which is formed from hypnal by loss of water, is a "normal valency compound":

$$\mathrm{NMe}\!\!<\!\!\begin{array}{l}\mathrm{CMe{:}C{\cdot}CH(OH){\cdot}CCl_3}\\ \mathrm{NPh{\cdot}CO}\end{array}$$

(cf. Krey, Diss., Jena, 1892). R. K. CALLOW.

Hydrogenation of glyoxaline ring. E. WASER and A. GRATSOS (Helv. Chim. Acta, 1928, **11**, 944—964).—Hydrogenation of lophine (2 : 4 : 5-triphenylglyoxaline) with hydrogen in presence of acetic acid and platinum-black gives 2 : 4 : 5-*tri*cyclo*hexyl*-4 : 5-*dihydroglyoxaline* (I), m. p. 211—213° (corr.) [*acetate* (II), m. p. 162—163° (corr.); *hydrochloride*, $+0{\cdot}5H_2O$, m. p. 268—270°; *hydrobromide* (III), m. p. 290—292°; *chloroplatinate*, $+6H_2O$, m. p. 251—252°; *styphnate*, m. p. 201—202°; *nitroso*-derivative, m. p. 175° (decomp.)], which on oxidation with chromic and acetic acids furnishes a small amount of *cyclo*hexanecarboxylamide. The action of hot nitric acid (d 1·4) on II is to give adipic acid, a *dinitro*-derivative, m. p. 249·5—251°, of I, and a red oil, whilst the action of ozone has afforded in one experiment a *substance*, $C_{12}H_{19}O_2N$ or $C_{12}H_{21}O_2N$, m. p. 192·5—193·5°, and in another case a *compound*, $C_{21}H_{31}ON_2$, m. p. 266·5—267°, together with oily products. Bromine (1 mol.) is decolorised by I in cold carbon tetrachloride solution, but after removal of the solvent the product is III. With 3 mols. of bromine a *dibromide hydrobromide*, $C_{21}H_{37}N_2Br_3$, m. p. 162°, is obtained, which is decomposed by treatment with petrol, or by heating at 220° into III. Excess of bromine converts amarine (2 : 4 : 5-triphenyl-4 : 5-dihydroglyoxaline) into a *dibromide hydrobromide*, m. p. 122° (decomp.), which when decomposed with petrol gives amarine hydrobromide, but when heated at 220° or treated with alcoholic potassium hydroxide it eliminates 2 mols. of hydrogen bromide, yielding lophine hydrobromide and lophine, respectively. When lophine is treated with a 4% solution of bromine in chloroform the product, m. p. about 78°, is a substitution derivative; with a 2% solution lophine hydrobromide is obtained.

Hydrogenation of amarine gives a mixture of I and 2 : 4 : 5-*tri*cyclo*hexyltetrahydroglyoxaline*, m. p. 171—172° (corr.) [*hydrochloride*, decomp. 302° after sintering at 292°; *hydrobromide*, m. p. 296° (decomp.); *acetate*, m. p. 152—153°; *chloroplatinate*, $+4H_2O$, m. p. 216·5—217°; *styphnate*, m. p. 168·5—169·5°; *nitroso*-derivative].

It was not possible to hydrogenate glyoxaline, 2 : 4 : 5-trimethylglyoxaline, 2-methyl-4 : 5-dihydroglyoxaline, histidine, or benziminazole. H. BURTON.

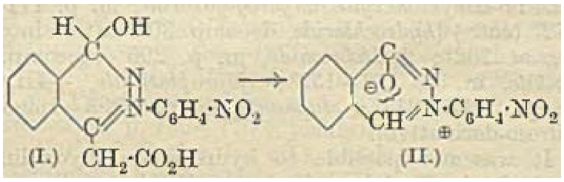
Absorption of ultra-violet light by α-amino-acids, polypeptides, 2 : 5-diketopiperazines, and betaines. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1928, **178**, 156—163).—The absorption spectra in the ultra-violet were measured of most carefully purified samples of glycylglycine, glycine anhydride, *dl*-leucylglycine, *dl*-leucylglycine anhydride, glycyl-*dl*-leucine, *dl*-leucylglycylglycine, betaine, betaine hydrochloride, hordenine, and hordenine hydrochloride. The spectrographic method was applied to determine whether perfectly pure cysteine was spontaneously transformed into cystine. The purest specimen of cysteine obtained, either free or as hydrochloride, still gave evidence of this transformation on keeping the solutions. R. K. CALLOW.

Diketones. I. Reaction between 4-phenylsemicarbazide and acetylacetone. A. S. WHEELER and R. D. NORTON (J. Amer. Chem. Soc., 1928, **50**, 2488—2490).—In aqueous alcohol a *product*, m. p. 255—257°, and 1-*phenylcarbamyl*-3 : 5-*dimethylpyrazole*, m. p. 69° to an opaque liquid which clears at 200°, are formed in proportions varying with the

conditions. The latter is identified by its conversion by boiling alcohol into 3 : 5-dimethylpyrazole and phenylurethane, by boiling water into carbon dioxide, carbanilide, and dimethylpyrazole, and by bromine into *4-bromo-1-phenylcarbamyl-3 : 5-dimethylpyrazole*, m. p. 100—101°, which with boiling water yields 4-bromo-3 : 5-dimethylpyrazole, m. p. 123° (cf. Morgan and Ackerman, J.C.S., 1923, **123**, 1316). H. E. F. NOTTON.

Preparation of 2 : 2′-dipyridyl. F. HEIN and W. RETTER (Ber., 1928, **61**, [*B*], 1790—1791).—2 : 2′-Dipyridyl is obtained in 52% yield by heating pyridine with sublimed ferric chloride in a sealed tube for about 35 hrs. at 300°. The product is dissolved in water and the solution is successively extracted with ether and distilled with steam after neutralisation with sodium hydrogen carbonate, whereby pyridine is removed. The residual solution is rendered strongly alkaline and again distilled with steam, thus giving 2 : 2′-dipyridyl, which is decolorised with charcoal and crystallised from aqueous alcohol. H. WREN.

New reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. II. Constitution of nitro- and amino-phenylphthalazones. F. M. ROWE and E. LEVIN (J.C.S., 1928, 2550—2555).—The soluble product obtained by boiling an aqueous-sulphuric acid solution of 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (I) is shown to be *4′-nitro-3-phenylphthalaz-1-one* (II), m. p. 333°, reduction of which gave *4′-amino-*



(I.) (II.)

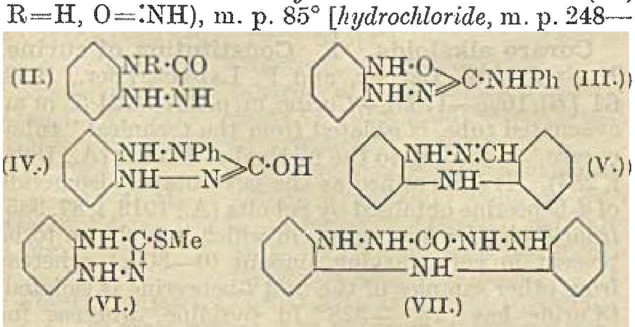
3-phenylphthalaz-1-one, m. p. 259° (previously described as 4′-amino-3-phenylphthalaz-4-one, A., 1926, 625). Attempts to deaminate the last compound were unsuccessful. The compound described by Seekles (A., 1924, i, 642) as a nitrophenylphthalazone is found to be the *lactone*, m. p. 254° (previous darkening at 228°), of *o-carboxybenzaldehyde-p-nitrophenylhydrazone*, decomp. 21·8° (resolidifying at 249°), but when boiled in nitrobenzene solution this passed into *4′-nitro-3-phenylphthalaz-4-one*, m. p. 258°, not identical with II. Reduction with sodium sulphide gave *4′-amino-3-phenylphthalaz-4-one*, m. p. 184° (*hydrochloride*; *acetyl* derivative, m. p. 233°), whilst zinc dust and hydrochloric acid gave 4′-amino-*N*-phenylphthalimidine. The amphoteric nature of 4′-nitro-3-phenylphthalaz-1-one is best explained by II; thus it forms well-crystallised *salts*, and a *picrate*, m. p. 218°. Treatment with methyl sulphate in nitrobenzene solution led to an aqueous solution of the *methosulphate*, which was isolated (by addition of sodium carbonate) as a *substance*, m. p. 138—141° and 173—175° after crystallisation from ethyl and methyl alcohols respectively (*hydrochloride*). These when heated formed *4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine* (neutral), m. p. 199°, demethylation of which gave *1 : 4-diketo-3-(4′-nitrophenyl)tetrahydrophthalazine*, m. p. 307°. R. J. W. LE FÈVRE.

Reaction of diazosulphonates derived from β-naphthol-1-sulphonic acid. III. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from *m*-nitroaniline. F. M. ROWE, M. A. HIMMAT, and E. LEVIN (J.C.S., 1928, 2556—2563; cf. preceding abstract).—Conversion of 3′-nitrobenzene-2-naphthol-1-diazosulphonate through *sodium 3′-nitrobenzeneazo-β-naphthaquinone-1-sulphonate* into *sodium hydrogen 3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid-1-sulphonate* does not proceed so readily as in the case of the 4′-nitro-isomeride. On boiling the product with concentrated hydrochloric acid *1-hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid*, m. p. 234° (*methyl* ester, m. p. 184°; *ethyl* ester, m. p. 195°; *anilide*, m. p. 239°), is obtained. Reduction with stannous chloride and hydrochloric acid (alkaline reduction gives an indefinite product: compounds in the 3′-nitro-series are more sensitive to alkalis than their 4′-nitro-isomerides) gives *1-hydroxy-3-(3′-aminophenyl)tetrahydrophthalazine-4-acetic acid*, m. p. 252° (*acetyl* derivative, m. p. 167°), which when boiled with aqueous sulphuric acid gives *3′-amino-3-phenylphthalaz-1-one*, m. p. 210° (*hydrochloride*; *acetyl* derivative, m. p. 204°), from which ammonia can be eliminated by treatment with zinc dust and hydrochloric acid, giving *3′-amino-N-phenylphthalimidine*, m. p. 175° (*acetyl* derivative, m. p. 204°; *zinc double chloride*), which, in turn, readily (relatively to the corresponding 4′-amine) gives *3-hydroxy-N-phenylphthalimidine*, m. p. 268° (*methyl ether*, m. p. 122°; *ethyl ether*, m. p. 115°), by diazotisation. By boiling 1-hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid with sulphuric acid, *3′-nitro-3-phenylphthalaz-1-one*, m. p. 324° (well-crystallised *salts*; *picrate*, m. p. 234°), is obtained, reduction of which by sodium sulphide or zinc dust and hydrochloric acid gives 3′-amino-3-phenylphthalaz-1-one or 3′-amino-*N*-phenylphthalimidine, respectively. Treatment with methyl sulphate in boiling nitrobenzene (cf. 4′-nitro-analogue, preceding abstract) gives a *substance*, m. p. 114—117° or 116—120° after crystallisation from methyl or ethyl alcohol, respectively, which, when heated, gives *4-keto-1-methoxy-3-(3′-nitrophenyl)-3 : 4-dihydrophthalazine*, m. p. 182°, accompanied (especially if heating be rapid) by a complex *substance*, m. p. 289°. Hydrobromic acid reacts with the above methoxy-compound, giving *1 : 4-diketo-3-(3′-nitrophenyl)tetrahydrophthalazine*, m. p. 280°. Phthalaldehydic acid and *m*-nitrophenylhydrazine condense in boiling alcoholic solutions, giving the *lactone*, m. p. 240° (becoming colourless at 200°), of *o*-carboxybenzaldehyde-*m*-nitrophenylhydrazone; from this, by boiling its solution in nitrobenzene, *3′-nitro-3-phenylphthalaz-4-one* (neutral and inactive), m. p. 240°, is obtained, from which, by alkaline hyposulphite reduction, *3′-amino-3-phenylphthalaz-4-one*, m. p. 156° (*hydrochloride*), can be obtained. R. J. W. LE FÈVRE.

Dihydroxy- and dichloro-ketohexahydrotriazines. J. B. EKELEY and A. A. O'KELLY (J. Amer.

Chem. Soc., 1928, **50**, 2731—2733).—The additive products of αβ-diketones with 2 mols. of sodium hydrogen sulphite yield with semicarbazide hydrochloride in hot water 5 : 6-dihydroxy-3-keto-5 : 6-dialkylhexahydro-1 : 2 : 4-triazines, the lower homologues of which are converted by phosphorus trichloride into 5 : 6-dichloro-3-keto-5 : 6-dialkylhexahydro-1 : 2 : 4-triazines. γδ-Diketo-β-methylpentane does not yield a triazine derivative by this method. The decomposition temperatures of the following are: (*a*) sodium hydrogen sulphite additive *compounds* of: *βγ-diketobutane*, 145—155°; *βγ-diketopentane*, 135—150°; *βγ-diketohexane*, 130—140°; *βγ-diketoheptane*, 100—110°, and *βγ-diketo-octane*, 95—100°; (*b*) derivatives of 5 : 6-*dihydroxy*-3-*ketohexahydro*-1 : 2 : 4-*triazine*, 265—270° : 5- or 6-*methyl*-, 250—255°; 5 : 6-*dimethyl*-, 240—245°; 5 : 6- (or 6 : 5)-*methylethyl*-, 230—235°; 5 : 6-*methylpropyl*-, 240—245°; 5 : 6-*methylbutyl*-, 230—235°, and 5 : 6-*methylamyl*-, 100—105°; (*c*) derivatives of 5 : 6-*dichloro*-3-*ketohexahydro*-1 2 : 4-*triazine*, 265—270° : 5- or 6-*methyl*-, 260—270 5 : 6-*dimethyl*-, 250—260°; 5 : 6-*methylethyl*-, 240 -245°; 5 : 6-*methylpropyl*-, 230—235°. H. E. F. NOTTON.

o-Aminophenylhydrazine and heterocyclic compounds derived from it. IV. Lengthened o-di-derivatives of benzene and their ring-closure. P. C. GUHA and T. N. GHOSH (J. Indian Chem. Soc., 1928, **5**, 439—451).—Reduction of 1-o-*nitrophenyl*-4-*phenylsemicarbazide*, m. p. 202°, with tin and concentrated hydrochloric acid gives a mixture of 1-o-*aminophenyl*-4-*phenylsemicarbazide* (I), m. p. 145° (*hydrochloride*, decomp. 250—251° after darkening; o-*nitrobenzylidene* derivative, m. p. 245—246°), and 3-*keto*-4-*phenyl*-1 : 2 : 3 : 4-*tetrahydrobenz*-1 : 2 : 4-*triazine* (II; R=Ph), m. p. 170—171°, also formed by the action of boiling acetic anhydride on I. 1-*Carbamido*-, m. p. above 290°, 1-*phenylcarbamido*-, m. p. above 290°, and 1-*phenylthiocarbamido*-, not melted at 290°, -2-*phenylsemicarbazidobenzenes* are described. Oxidation of I with ferric chloride gives the *compound* (III), not melted at 290°, whilst the action of hydrazine hydrate is to give the *compound* (IV), m. p. 90—91°. Reduction of 1-o-*nitrophenylsemicarbazide*, m. p. 225° (decomp.), gives 3-*imino*-1 : 2 : 3 : 4-*tetrahydrobenz*-1 : 2 : 4-*triazine* (II; R=H, O=:NH), m. p. 85° [*hydrochloride*, m. p. 248—



249° (decomp.); *acetyl* derivative, m. p. 182—183°], also formed during the reduction of 1-o-*nitrophenylthiosemicarbazide*, m. p. 200° (decomp.). o-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, m. p. 171°, is reduced to the *compound* (V), m. p. 217—218°; *glyoxal*-o-*nitrophenylosazone*, m. p. 279—280° (decomp.), to *bisbenziminazole*, not melted at 300° [*hydrochloride*, m. p. 253° (decomp.); *diacetyl* derivative, m. p. 183—184°]; *methyl* o-*nitrophenyldithiocarbazinate*, m. p. 113—114°, to the *compound* (VI), m. p. 199—200°; *di*-o-*nitrophenylcarbohydrazide*, m. p. 260—261°, to the *compound* (VII), isolated only as the *hydrochloride*, m. p. 251—252° (decomp.).

Ethyl o-*nitrophenylcarbazinate* has m. p. 185°.

H. BURTON.

Transformation of uric acid into carbamide by oxidation with chromic and sulphuric acids. (MLLE.) J. SCHWANDER and H. CORDEBARD (Bull. Soc. Chim. biol., 1928, **10**, 920—931).—The rate of hydrolysis of carbamide by aqueous sulphuric acid increases with rise of temperature, is greatest when the concentration of the acid is 0·5—0·1*N* (depending on the temperature), and increases with the duration of the operation and with the concentration of the carbamide. Addition of potassium dichromate to the mixture has no other effect than the formation of small amounts of nitric acid. By the use of these results to select favourable conditions, carbamide may be obtained from uric acid in more than 96% yield.

G. A. C. GOUGH.

Modifications of hydroxyhæmin. A. HAMSÍK (Z. physiol. Chem., 1928, **178**, 67—74; cf A., 1925, i, 1476; this vol., 1148).—The β- and ψ-hydroxyhæmins, formed by the action of acids and alkalis on the α-hydroxyhæmin derived directly from blood, are distinguished chiefly by increased solubility, weak attachment of chlorine in the corresponding chlorohæmins, and low yield of protoporphyrin on removal of iron, the ψ-modification showing these properties more strongly. Details are given of the preparation of β-hydroxyhæmin (i) by the action of alkalis (the prolonged action of methyl-alcoholic potassium hydroxide on blood coagulum, or the action of aqueous potassium hydroxide on defibrinated blood followed by extraction of the precipitate with alcohol containing oxalic acid), and (ii) by the action of acids (the prolonged action of sulphuric, hydrochloric, acetic, and oxalic acids on defibrinated blood, or the action of these acids on α-hydroxyhæmin).

R. K. CALLOW.

Preparation of hæmin derivatives by high-temperature reactions. II. Preparation of pyratin from hæmin by fusion with resorcinol. Preparation and properties of pyroporphyrin. Introduction of iron into porphyrins in the 'iron–phenol fusion,'' and transformation of iron porphyratins by phenols and phenol–sulphuric acid mixtures. O. SCHUMM (Z. physiol. Chem., 1928, **178**, 1—18; cf. this vol., 1148). When hæmin is fused with a large excess of resorcinol at 180—190°, the process being followed by spectroscopic observations, and the mixture is poured into water, pyratin is precipitated. It may be purified by reprecipitating it from very dilute alkali by the addition of acetic acid, and may be converted into pyratin chloride by Küster's method (A., 1904, i, 356). It is reduced to pyroporphyrin by hydrazine and acetic acid (cf. Papendieck and Donath, A., 1925, i, 711) and also when heated with pyruvic acid, hydriodic and acetic acids, phenol and oxalic acid, oxalic acid, 10% sulphuric acid, or 25% hydrochloric

acid. The spectroscopic comparison of pyroporphyrin and copratoporphyrin suggests complete identity, in concordance with the close similarity of composition and solubility and the apparent identity of pyratin and copratin. Treatment of pyroporphyrin with hydrogen chloride in methyl alcohol yields pyroporphyrin methyl ester, m. p. of different specimens 218°, 221°, and 223°, of the same composition as copratoporphyrin methyl ester, m. p. 221°.

Fusion of pyroporphyrin, copratoporphyrin, Nencki's hæmatoporphyrin, mesoporphyrin, or hæmateric acid with 100—200 parts of phenol and iron powder or ferrous oxide yields the corresponding iron compounds.

An account is given of preliminary investigations of the behaviour of hæmin when heated with various phenols and a little sulphuric acid. Spectroscopic observations show that under various conditions derivatives either with or without combined iron, or mixtures of these, are obtained.

R. K. Callow.

Benz*iso*thiazolone. A. Reissert [with H. Düsterdiek] (Ber., 1928, **61**, [*B*], 1680—1682).—In his recent publication (this vol., 883), the author has overlooked the priority of McClelland (J.C.S., 1922, **121**, 86, and subsequent papers) in the description of certain compounds. Attempts to convert benz*iso*thiazolone into the corresponding thiazole were unsuccessful. Thus, when distilled with zinc dust it yields benzonitrile. With phosphorus pentachloride it affords 3-*chlorobenz*iso*thiazole*, m. p. 40°, reduced by zinc dust to 3 : 3-*dibenz*iso*thiazolyl*, $\left[S{<}{\overset{C_6H_4}{\underset{N}{}}}{>}C\right]_2$, m. p. 100°. The thiazolone is completely resinified by fuming hydriodic acid at 230°. H. Wren.

Methylene bases from 1-methylbenzthiazole and 1-methylbenzselenazole methiodides; preparation of 1-substituted benzthiazoles. L. M. Clark (J.C.S., 1928, 2313—2320).—1-Methylbenzthiazole and 1-methylbenzselenazole methiodides react with ammonia and with sodium hydroxide solution, yielding, through the intermediate carbinol base, $C_6H_4{<}{\overset{X}{\underset{NMe}{}}}{>}C{<}{\overset{Me}{\underset{OH}{}}}$, mixtures of $C_6H_4{<}{\overset{X}{\underset{N}{}}}{>}C{:}CH_2$ and $C_6H_4{<}{\overset{X(NH_4 \text{ or } Na)}{\underset{NMeAc}{}}}$, where is sulphur or selenium (cf. Clark, A., 1925, i, 841; König and Meier, *ibid.*, 705). A much higher proportion of the methylene base is formed from 1-methylbenzselenazole methiodide than from the analogous sulphur compound. 2-Methyl-1-methylenebenzthiazoline condenses with *p*-dimethylaminobenzaldehyde, giving a highly-coloured product (cf. Mills and Raper, A., 1926, 77) which could not be isolated. *p*-Dimethylaminostyrylbenzthiazole methiodide is formed, however, when hydriodic acid is added to the reaction mixture. Selenocarbocyanines which, like the thiocarbocyanines, are powerful sensitisers of the photographic plate, are obtained in good yield by condensation of 1-methylbenzselenazole alkiodides with orthoformic ester in pyridine solutions (Hamer, this vol., 76).

An attempt to isolate the carbinol base from 1-phenylbenzthiazole methiodide by treatment with silver hydroxide resulted only in the formation of an insoluble compound containing silver (silver salt of *o*-benzoylmethylaminothiophenol ?).

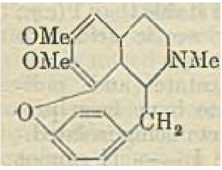
Acylation of 2 : 2′-diaminodiphenyl disulphide with the appropriate acid or acid chloride, followed by reduction of the product with sodium hyposulphite, gives rise to *o*-acylaminothiophenols, which suffer internal condensation to form the corresponding 1-substituted benzthiazoles. The following are described: 2-methyl-1-methylenebenzthiazoline, m. p. 170° (lit. 164°) (a dark red crystalline *substance* and a colourless *compound*, m. p. 164°, were obtained as by-products); *benzoyl* derivative, m. p. 87°, of *o*-acetmethylamidothiophenol; 1-methylbenzthiazole [*methopicrate*, m. p. 94°; *hydrogen sulphate*, m. p. 177—178°; *methochloroplatinate*, m. p. 224° (decomp.); *perchlorate*, m. p. 149°]; *benzoyl* derivative, m. p. 130—131°, of *o*-benzoylmethylaminothiophenol; 1-phenylbenzthiazole [*methochloroplatinate*, m. p. 243° (decomp.); *methopicrate*, m. p. 125—126°; *methoperchlorate*, m. p. 220°]; 1-*methylbenzselenazole*, b. p. 140°/51 mm., obtained by the action of acetyl chloride on the zinc salt of *o*-aminoselenophenol [*chloroplatinate*; *methiodide*, m. p. 221° (decomp.); *ethiodide*, m. p. 212° (decomp.); *methochloroplatinate*, m. p. 214° (decomp.)]; 2-*methyl*-1-*methylenebenzselenazoline*, m. p. 157—158°; 2 : 2′-*diacetmethylamidodiphenyl diselenide*, m. p. 141°; 2 : 2′-*dimethylselenocarbocyanine iodide*, m. p. 267—268° (decomp.); 2 : 2′-*diethylselenocarbocyanine iodide*, m. p. 270—271° (decomp.); 2 : 2′-*diacetamidodiphenyl disulphide*, m. p. 165—166°; 2 : 2′-*dipropionamidodiphenyl disulphide*, m. p. 138°; 1-*ethylbenzthiazole picrate*, m. p. 138°; 2 : 2′-*dibenzamidodiphenyl disulphide*, m. p. 143—144·5°.

M. Clark.

Reaction of eserine (physostigmine). M. Mokragnatz (Bull. Soc. Chim. biol., 1928, **10**, 905—908).—Solutions containing eserine (more than 0·002 mg.) yield a fairly permanent, intense violet coloration on treatment with a 2% solution of benzidine in 20% aqueous acetic acid (1—2 drops) followed by the addition of hydrogen peroxide (30%; 1 drop). Under these conditions 20 of the better-known alkaloids (in the free state) give a slight yellow colour and chlorides and bromides give a blue or bluish-green colour. Eserine may be detected in mixtures of alkaloids or in viscera by this method. Ptomaines give an evanescent green colour. G. A. C. Gough.

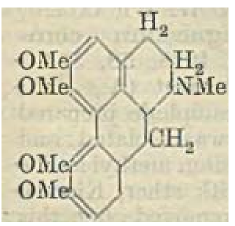
Curare alkaloids. I. Constitution of curine. E. Späth, W. Leithe, and F. Ladeck (Ber., 1928, **61**, [*B*], 1698—1709).—Curine, m. p. 221—221·5° in an evacuated tube, is isolated from the technical "tubocurare" according to the method of Boehm (A., 1898, i, 283). It is identified as the lævorotatory isomeride of *d*-bebeerine obtained by Scholtz (A., 1913, i, 87, 385) from *Radix Pareiræ bravæ*, in which it is shown to be present in very varying amount (0—30%), whereas from other samples of the root *l*-bebeerine is isolated. *l*-Curine has $[\alpha]_D^{20}$ −328° in pyridine, whereas for *d*-bebeerine the values, m. p. 221—221·5°, $[\alpha]_D^{20}$ +332° in pyridine, are now recorded. The latter alkaloid separates from ether, benzene (m. p. 161°), and methyl alcohol with solvent of crystallisation which is more or less firmly retained. Admixture of equal amounts of *l*-curine and *d*-bebeerine affords *r*-bebeerine, m. p.

299—300° (cf. Scholtz, *loc. cit.*). Analyses and determinations of mol. wt. by Rast's method support the formula $C_{18}H_{19}O_3N$ for the base. It contains one hydroxyl and one methoxyl group. *d*-Bebeerine is transformed by diazomethane into the amorphous *methyl ether*, which is converted by methyl iodide in benzene at 100° into the corresponding methiodide (cf. Scholtz, *loc. cit.*). The latter compound is transformed by successive treatment with silver chloride and sodium amalgam into the optically inactive methine base (*hydrochloride*, $C_{20}H_{26}O_3NCl$, m. p. 238—241° (decomp.) in an evacuated tube, which, by repetition of the treatments with methyl iodide, silver chloride, and sodium amalgam, is converted into trimethylamine and a *substance*, $C_{18}H_{20}O_3$, m. p. 186—187°; since this compound does not absorb hydrogen in the presence of palladised charcoal, an aliphatic double linking is probably not present. The Emde degradation of *l*-curine affords identical products. Distillation of demethylated *l*-curine or *d*-bebeerine with zinc dust affords 1-methyl*iso*quinoline instead of 1-methoxy*iso*quinoline described by Scholtz. Curine or the products of its degradation do not appear to be oxidised by nitric acid to benzene-1 : 2 : 3 : 4-tetracarboxylic acid so that a phenanthrene complex is probably not present in the alkaloid. Fusion of *d*-bebeerine or its demethylated derivative with potassium hydroxide, followed by methylation of the mixture of acids thus obtained, yields mainly veratric and anisic acids. If bebeerine is methylated and then oxidised with permanganate, neither veratric nor anisic acid is obtained, so that the 4-hydroxybenzyl or 3 : 4-dihydroxybenzyl complex as such or methylated does not appear pre-formed in bebeerine or its methyl ether. If, however, the oxidation is carried out under extremely mild conditions, *p*-hydroxybenzoic acid is produced, indicating the presence of a *p*-hydroxybenzyl complex in which the hydroxylic oxygen is linked to a benzene nucleus. The constitution I is provisionally suggested for bebeerine methyl ether in which the position of the methoxy-groups and the point of attachment of the oxygen bridge remain undecided.



H. Wren.

Alkaloids of *Corydalis cava*. XIII. Synthesis of *d*-corytuberine dimethyl ether. E. Späth and O. Hromatka (Ber., 1928, 61, [*B*], 1692—1698).—The structure, I, ascribed to corytuberine dimethyl ether by Gadamer (A., 1912, i, 46), is confirmed by synthesis.



2-Nitrohomoveratric acid is converted by thionyl chloride into 2-nitrohomoveratroyl chloride, m. p. 56°, which, with homoveratrylamine, gives the *amide*, $NO_2{\cdot}C_6H_2(OMe)_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, m. p. 72° after softening at 69° in an evacuated tube. The latter compound is converted by phosphoric oxide in the presence of boiling toluene into 6 : 7-*dimethoxy*-1-2′-*nitro*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 165—166°, transformed successively into the corresponding *methiodide*, m. p. 179—182° (decomp.) [also *sesquihydrate*, m. p. 102—104°], and *methochloride trihydrate*, m. p. 101—103°. Reduction of the chloride with tin and hydrochloric acid in presence of alcohol affords 6 : 7-*dimethoxy*-2-*methyl*-1-2′-*amino*-3′ : 4′-*dimethoxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, converted by diazotisation and subsequent treatment with copper powder into *dl*-corytuberine dimethyl ether. The product is purified by fractional distillation in a high vacuum and from it by means of *l*-tartaric acid, *d*-corytuberine dimethyl ether hydrogen *l*-tartrate, m. p. 213—215°, $[\alpha]_D^{25}$ +147° in water, is derived, identical with that obtained from natural sources. The synthetic product is also transformed into its methiodide, identical with that derived from corytuberine dimethyl ether from corydine.

H. Wren.

Composition of strychnine phosphomolybdate. C. Antoniani (Giorn. Chim. Ind. Appl., 1928, **10**, 408—410).—When washed with 10% nitric acid (this vol., 979), strychnine phosphomolybdate has a composition corresponding with the formula $11MoO_3,H_3PO_4,(Str.)_3,2HNO_3$, which is in agreement with the value 0·0257 for the ratio P_2O_5 : precipitate. The most favourable proportions for the precipitation are 350 parts of MoO_3, 2500 parts of HNO_3, and 10 parts of strychnine to 1 part of P_2O_5.

T. H. Pope.

Alkaloids of Kurchi bark (*Holarrhena antidysenterica*). I. Two new alkaloids in Indian Holarrhena. S. Ghosh and N. N. Ghosh (J. Indian Chem. Soc., 1928, **5**, 477—482).—Details are given for the extraction of conessine, and the new alkaloids *kurchicine*, m. p. 175°, and *kurchine*, m. p. 75°, from Kurchi bark (total alkaloids 1·2%). H. Burton.

Microchemistry of the alkaloids. H. Beckmann (Pharm.-Ztg., 1928, **73**, 1165—1166).—Two simple types of micro-sublimation apparatus and a scheme for the micro-chemical detection of alkaloids by colour reactions are described. E. H. Sharples.

Aryl arsenoxides and the corresponding dichloro- and di-iodo-arsines. G. Newbery and M. A. Phillips (J.C.S., 1928, 2375—2381).—Certain phenyl-dichloro- and -di-iodoarsine derivatives have been prepared for therapeutic investigation. The aminophenyldichloroarsines were obtained by sulphurous acid reduction of the corresponding arsinic acid in hydrochloric acid at the ordinary temperature, a trace of potassium iodide being present; some acetamido-derivatives were prepared by a modification of this method. The aminophenyldi-iodoarsine hydriodides were prepared from the corresponding chloro-derivatives by addition of hydriodic acid or potassium iodide in aqueous solution. In general, the attachment of the iodine atom to the arsenic atom appears to be firmer than that of the chlorine atom in the corresponding chloro-compound; this stability extends to concentrated nitric acid and in the case of 3 : 5-diamino-4-hydroxyphenyldi-iodoarsine dihydriodide, even to 5*N*-sodium hydroxide solution. The arsenoxides were obtained by aqueous hydrolysis of the halogen compounds. The following are described: 3-*nitro*-5-*acetamido*-2- (obtained by nitration of 5-acetamido-2-hydroxyphenylarsinic acid), 3-*amino*-5-*acetamido*-4- and 2-, and 3 : 5-*diacetamido*-2-*hydroxy*-

phenylarsinic acids; *3-amino-5-acetamido-4-hydroxyphenyl-dichloroarsine hydrochloride*, *-arsenoxide hydrochloride* and *hydriodide*, and *-di-iodoarsine hydriodide*; 3 : 5-*diamino-4-hydroxyphenyl-dichloroarsine dihydrochloride* and *-di-iodoarsine dihydriodide*; *3-amino-5-acetamido-2-hydroxyphenyl-di-iodoarsine hydriodide* and *-arsenoxide hydriodide*; 3 : 5-*diacetamido*-2- and -4-*hydroxyphenyldichloroarsines*; 3 : 5-*diacetamido-4-hydroxyphenylarsinous acid* (the arsenoxide apparently exists only in this form); 3 : 5-*diacetamido-2-hydroxyphenylarsenoxide*; *3-amino-4-hydroxyphenyl-di-iodoarsine hydriodide*; *3-acetamido-4-hydroxyphenyl-arsenoxide*; *5-amino-2-hydroxyphenyl-dichloroarsine hydrochloride*, *-di-iodoarsine hydriodide*, and *-arsenoxide hydrochloride* and *hydriodide*; *5-acetamido-2-hydroxyphenylarsenoxide*; *3-acetamido-4-hydroxy-* and *5-acetamido-2-hydroxy-phenyldichloroarsines*; *3-nitro-4-hydroxy-5-aminophenyldi-iodoarsine hydriodide*; *3-nitro-4-hydroxy-5-acetamidophenylarsenoxide*; *3-acetamido-4-hydroxy-* and *5-acetamido-2-hydroxy-phenylmethoxychloroarsines*, obtained by the action of methyl-alcoholic hydrogen chloride on the corresponding arsenoxides, which are regenerated by treatment with water; *3-acetamido-4-hydroxyphenyl-arsine* and *5-acetamido-2-hydroxyphenylarsine*.

The four compounds 3-amino-5-acetamido-2- and -4-hydroxyphenylarsenoxide hydrochlorides and hydriodides dissolve in water only after keeping for a few seconds; the formulation $NH_2\cdot C_6H_2(OH)(NHAc)\cdot AsCl\cdot OH$, hydrolysed by water to $HCl,NH_2\cdot C_6H_2(OH)(NHAc)\cdot AsO$, is suggested.

M. CLARK.

Organic compounds of arsenic. XIII. *cyclo*-Penta-*n*-propylpenta-arsine and the thermal decomposition of arseno-derivatives. W. STEINKOPF and H. DUDEK (Ber., 1928, **61**, [*B*], 1906—1911; cf. this vol., 654).—Magnesium *n*-propylarsinate is reduced by sodium hypophosphite and sulphuric acid to cyclo*penta*-n-*propylpenta-arsine*, $[C_3H_7As]_5$, b. p. 177—179°/1 mm. (slight decomp.), which contains about 5% of propylcacodyl. In freezing nitrobenzene the product has the expected mol. wt., thus affording indirect evidence in favour of the cyclic constitution assigned to the pentamethylpenta-arsine (*loc. cit.*). The compound is decomposed when distilled under 13 mm. pressure into arsenic and *propylcacodyl*, b. p. 165—167°/13 mm., converted by exhaustive methylation into *dimethyldi*-n-*propylarsonium tri-iodide*; this change explains the unavoidable presence of propylcacodyl in distilled *cyclo*penta-*n*-propylpenta-arsine. Similarly, *cyclo*pentamethylpenta-arsine is decomposed at 270°/atm. into arsenic and cacodyl. Arsenobenzene at 255° analogously yields arsenic and phenylcacodyl. H. WREN.

Mercuration of aromatic amines and the problem of substitution. I. A. F. ALBERT and W. SCHNEIDER (Annalen, 1928, **465**, 257—272).—On the basis of Wieland's addition theory of substitution, Kharasch and Jacobsohn (A., 1922, i, 189) postulated the production of complex salts in the mercuration of aromatic amines. Such salts have now been isolated. The action of mercuric acetate on an aromatic amine may be represented by the typical scheme: NH_2Ph (I) $[NH_2Ph\cdot Hg\cdot OAc]OAc \longrightarrow$ (II*a*) $NHPh\cdot Hg\cdot OAc$ + (II*b*) $NHPh\cdot Hg\cdot OH \longrightarrow$ (III) $NH_2\cdot C_6H_4\cdot Hg\cdot OAc$. With aniline, a methyl-alcoholic solution of the amine is treated with a methyl-alcoholic suspension of mercuric acetate; after addition of a little acetic acid the mixture becomes clear and on cooling deposits *aniline acetate* N-*mercuriacetate* (I), m. p. 87°. Similarly are obtained: p-*toluidine*, m. p. 155°, o-*toluidine*, m. p. 76°, m-*aminoacetophenone*, m. p. 104°, p-*anisidine*, m. p. 125°, and *bis*-o-*toluidine*, m. p. 96°, *acetate* N-*mercuriacetates*. These compounds are very unstable, changing slowly on keeping, or at once on melting, or heating in aqueous or alcoholic solution, into the mono- and di-nuclear-substituted products. (When aniline acetate *N*-mercuriacetate was kept in a vacuum, no change of composition occurred, but the m.p. changed.) In the cold, ammonium sulphide, sodium hydroxide, or sodium iodide solutions all give with I the corresponding mercuric compound. Sodium iodide may be employed to distinguish between the different stages of the reaction, since with I sodium acetate is formed in solution, but with II, sodium hydroxide also. At stage III alkalinity is developed only in so far as mercury is being removed from the nucleus.

The stage II compound is obtained, in the case of aniline, by shaking I with ether; *aniline* N-*mercuriacetate* is obtained impure, m. p. about 154°. Stage II is the first result of the action of mercuric acetate on ethyl *p*-aminobenzoate, which gives a *product*, m. p. 117°, estimated, from the analytical results, to contain 80% of II*a*, 12% of II*b*, and 8% of mercuric acetate. Stage II compounds have a great surface-activity, *e.g.*, in adsorbing impurities; the above product when prepared in ether yields a solid mass, which contains adsorbed ether, and becomes gelatinous in water. *p*-Aminoacetophenone and *m*-nitroaniline also give stage II products. These are more stable than I (*e.g.*, in water), but are converted by acetic acid into nuclear-substituted compounds.

p-Ethylaminophenylmercuric acetate and *p*-dimethylaminophenylmercuric acetate have been prepared, without intermediate products being isolated.

It is suggested that if the stage I $\longrightarrow$ II cannot take place at the ordinary temperature, mercuration will not occur (cf. mercuric chloride).

Attention is directed to the danger that, since impurities may be introduced by adsorption, pharmacological mercury compounds may be impure.

E. W. WIGNALL.

Constitution of organo-magnesium compounds. Q. MINGOIA (Gazzetta, 1928, **58**, 532—541).—Contrary to Kierzek's statement (A., 1927, 1176), the magnesium bromohydrosulphide prepared by the author (A., 1926, 388) was isolated and analysed. By decomposing magnesium methyl iodide with water and then extracting with ether, Kierzek found that magnesium iodide is removed, but this author's conclusion that the organo-magnesium compound and water react with formation of magnesium hydroxide and iodide in equimolecular proportions is fallacious, since by prolonged extraction with ether he was able to extract only 72·63% of the iodide, the residual compound still containing 25·25% of iodine, in spite of the appreciable solubility of magnesium

iodide in anhydrous ether. The change of colour from white to brown during the treatment with ether is explainable more readily by assuming gradual decomposition of the magnesium iodohydroxide into magnesium iodide and hydroxide. Further, treatment with pyridine of the organo-magnesium solution decomposed by water fails to yield $[Mg(C_5H_5N)_6]I_2$ or $[Mg(C_5H_5N)_4(Et_2O)_2]I_2$ (cf. Spacu, A., 1922, i, 859), this behaviour being in agreement with the predominant basic properties of magnesium iodohydroxide. On the other hand, if the decomposition is effected by means of hydrogen sulphide, treatment with pyridine yields the additive compound of pyridine and magnesium bromohydrosulphide, in accord with the distinctly saline properties of the latter compound. The asymmetric formula for the organo-magnesium compounds is upheld in preference to the doubled symmetrical formula. T. H. POPE.

Method of preparing selenophen. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1928, 2628—2629).—Selenium, in portions of 5 g., is heated in an inclined Pyrex tube, closed at the lower end, and provided with an axial inlet tube delivering acetylene some inches above the selenium and well below a side tube leading to a condenser. The middle of the tube is heated to redness, and the selenium is slowly vaporised by heating it from the surface downwards. Flashing of the acetylene, accompanied by deposition of carbon, takes place and a liquid condensate is formed thereafter at the rate of 3—4 c.c. in 4 hrs. Fractionation of the crude oil yields a high percentage of selenophen (cf. this vol., 1021). M. CLARK.

Attempted preparation of optically active derivatives of quadrivalent tin. F. B. KIPPING (J.C.S., 1928, 2365—2372; cf. Pope and Peachey, Proc. C.S., 1900, **16**, 42, 116).—The relative ease of removal by iodine of aromatic groups attached to a tin atom in mixed arylstannanes decreases in the following order: *o*-tolyl, *p*-tolyl, phenyl, benzyl. The tin aryls are also decomposed by boiling with concentrated hydrochloric acid, which frequently removes two aryl groups. The order in which this removal occurs is the same as that with iodine, except that whereas iodine removes one of the benzyl groups from tribenzylethylstannane, hydrochloric acid removes the ethyl group. Three compounds containing an asymmetric tin atom are described: phenyl-*p*-tolylbenzylstannic hydroxide, phenylbenzyl-*n*-butylstannic hydroxide, and benzylethyl-*n*-butylstannic iodide. Their salts with *d*-camphorsulphonic, *d*-α-bromo-π-camphorsulphonic, and tartaric acids have been prepared, but in no case could crystalline salts or any evidence of optical activity of the tin atom be obtained. The following are described: *phenyltribenzylstannane*, b. p. 290°/5 mm.; *tribenzylstannic iodide*, m. p. 102—103°; *triphenylbenzylstannane*, m. p. 90°, b. p. 250°/3 mm.; *phenylbenzylstannic chloride*, m. p. 83—84°; p-*tolyltribenzylstannane*; *triphenyl*-o-*tolylstannane*, m. p. 165°; *tri*-p-*tolyl*-o-*tolylstannane*, m. p. 168°; *tri*-m-*tolylstannic chloride*, m. p. 108—109°; *tri*-m-*tolyl*-p-*tolylstannane*, m. p. 103°; *phenyldi*-p-*tolylbenzylstannane*, b. p. 265—270°/2—3 mm.; *phenyl*-p-*tolylbenzylstannic hydroxide*, m. p. 136—137° (oily *iodide*, d-*camphorsulphonate*, d-α-*bromo*-π-*camphorsulphonate*; d-*tartrate*); *triphenyl*-n-*butylstannane*, m. p. 61—62°, b. p. 222°/3 mm.; *phenyl*-n-*butylstannic chloride*, m. p. 50°; *diphenylbenzyl*-n-*butylstannane*, b. p. 215°/2—3 mm.; *phenylbenzyl*-n-*butylstannic hydroxide*, m. p. 135—137° (*fluoride*, m. p. 218°, oily *chloride, bromide, iodide*, d-*camphorsulphonate*, d-α-*bromo*-π-*camphorsulphonate* and d-*camphorate*; d-*tartrate*); *dibenzylethyl*-n-*butylstannane*, b. p. 195—200°/3—5 mm.; *benzylethyl*-n-*butylstannic iodide*. M. CLARK.

Apparatus for chromic anhydride oxidations. W. F. SHORT (J.C.S., 1928, 2630).—A slight modification of Walker's apparatus (*ibid.*, 1892, **61**, 717) for the preparation of alkyl iodides is described, the adaptor and side-tube being sealed together as in a Soxhlet apparatus. A. I. VOGEL.

Partial decomposition of alkali chlorides in the incineration of organic matter (particularly nitrogenous organic matter). P. FLEURY and P. AMBERT (Bull. Soc. Chim. biol., 1928, **10**, 869—878).—Incineration of mixtures of sodium chloride and various organic substances (especially those of the purine group) results in the loss of chlorine (46—80%) and the formation of sodium hydroxide and carbonate. The presence of salts of nitrous, hydrocyanic, cyanic, or oxalic acids could not be detected.
G. A. C. GOUGH.

Micro-determination of sulphur in an organic compound. S. HANAI (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 915—919).—The substance is weighed into a platinum boat which is introduced into a Pregl micro-combustion tube containing freshly reduced, pure nickel (from the oxalate). After displacement of air by hydrogen the substance is gently heated to 200° and allowed to volatilise on to the nickel catalyst which retains all the sulphur as sulphide. The contents of the tube are dissolved in hydrochloric acid in an atmosphere of hydrogen and the hydrogen sulphide is passed into an ammoniacal solution of cadmium chloride; the cadmium sulphide is oxidised by iodine (liberated from permanganate and potassium iodide), and the excess of iodine is titrated with thiosulphate. J. W. BAKER.

Jaffe's picric acid reaction. W. WEISE and C. TROPP (Z. physiol. Chem., 1928, **178**, 125—138).—The picric acid reaction (red coloration in alkaline solution) first given for creatinine by Jaffe (A., 1886, 1056) is a particular case of a general reaction of compounds with active methylene or methine groups. It is distinct from Braun's reaction (1865) for dextrose and other reducing substances, in which the partial reduction of picric acid to red picramic acid takes place. Generally this reaction takes place only on warming. Jaffe's reaction, according to Reissert (A., 1904, i, 389), is probably a condensation process. In tests of a large number of compounds the following order was found for the power of groups in activating methylene or methine groups so that the compound gave Jaffe's reaction: NO_2, diazo->:CO>·CN, CH_2:CH·>·CO·NH_2, ·CO_2Et.
R. K. CALLOW.

Creatine-phosphoric acid and methods of determination. D. FERDMANN [with O. FEINSCHMIDT] (Z. physiol. Chem., 1928, **178**, 52—61).—The

creatine-phosphoric acid (phosphagen, cf. Eggleton and Eggleton, A., 1927, 271, 274; Fiske and Subbarow, *ibid.*, 990) of muscle is rapidly destroyed at the ordinary temperature by grinding the muscle, but this fermentative change can be inhibited by grinding with quartz sand and sodium borate, thus enabling a quantitative determination of the creatine-phosphoric acid to be made, using a modification of Eggleton's method. The formation of lactacidogen, as shown by the decrease in inorganic phosphate, still takes place when the creatine-phosphoric acid has been destroyed, and the presence of the latter is, therefore, not essential for this process. R. K. CALLOW.

Determination of pyruvic acid. B. H. R. KRISHNA and M. SREENIVASAYA.—See this vol., 1292.

Determination of carnosine. W. M. CLIFFORD and V. H. MOTTRAM.—See this vol., 1292.

Determination of tryptophan and tyrosine in proteins. J. TILLMANS, P. HIRSCH, and F. STOPPEL. —See this vol., 1278.

Biochemistry.

Gas and electrolyte equilibria in blood. XII. Value of pK' in the Henderson–Hasselbalch equation for blood-serum. A. B. HASTINGS, J. SENDROY, jun., and D. D. VAN SLYKE (J. Biol. Chem., 1928, **79**, 183—192).—Taking the solubility coefficient of carbon dioxide in blood-serum to be 0·510, as recently determined by Van Slyke and others (this vol., 1150), the value of pK' in the Henderson–Hasselbalch equation for blood-serum at 38° is 6·10; taking Bohr's value of 0·541 as the solubility coefficient, pK' becomes 6·13. C. R. HARINGTON.

Gas and electrolyte equilibria in blood. XIII. Distribution of chloride and hydrogen carbonate in blood of normal and pathological human subjects. A. B. HASTINGS, J. SENDROY, jun., J. F. MCINTOSH, and D. D. VAN SLYKE (J. Biol. Chem., 1928, **79**, 193—209).—In normal human blood the ratios $[Cl]_{cells}:[Cl]_s$ and $[BHCO_3]_{cells}:[BHCO_3]_{serum}$ are higher than those previously determined (A., 1923, i, 1249) for horse blood; this is ascribed to the higher base-binding capacity of the proteins of the latter. In a variety of pathological conditions, the distribution of the electrolytes in human blood was found to obey the same laws as in the normal. C. R. HARINGTON.

Determination of p_H [of blood] by hydrogen electrode and by colorimetric methods. C. G. JOHNSTON (J. Biol. Chem., 1928, **79**, 297—307).—Comparison of the p_H of blood as determined by the hydrogen electrode and by the colorimetric methods of Cullen (A., 1922, ii, 672), Hastings and Sendroy (A., 1924, ii, 869), and of Dale and Evans (A., 1921, i, 142) indicates that the results of the colorimetric determinations differ from those of the electrometric method by inconstant amounts, the range of variation being greater than that observed by previous workers; particularly inconstant values were obtained in dog's blood after hæmorrhage. It is therefore suggested that no colorimetric method is at present trustworthy for the determination of the p_H of blood with accuracy. C. R. HARINGTON.

Electrometric titration of hæmin and hæmatin. J. B. CONANT, G. A. ALLES, and C. O. TONGBERG (J. Biol. Chem., 1928, **79**, 89—93).—The conclusions of Hill and Holden and of Haurowitz (A., 1927, 686, 689) that the reduction of hæmatin involves one equivalent are confirmed by the electrometric titration of hæmin with titanous chloride in presence of tartrate. C. R. HARINGTON.

Blood-corpuscles of cows and fœtuses in hypertonic salt solutions. D. VON DESEÖ (Biochem. Z., 1928, **199**, 41—47).—Fœtal blood-corpuscles shrink more in hypertonic salt solutions, contain more free water, have a greater volume, and contain more colloidal material than those of the mother. J. H. BIRKINSHAW.

Blood-cell metabolism. II. Effect of methylene-blue and other dyes on glycolysis and lactic acid formation of erythrocytes. E. S. G. BARRON and G. A. HARROP, jun. (J. Biol. Chem., 1928, **79**, 65—87).—The glycolysis brought about by mammalian erythrocytes is essentially anaerobic in character, the proportion of lactic acid produced to dextrose destroyed being high; with avian erythrocytes a larger proportion of the dextrose is oxidised. In both cases the addition of small amounts of methylene-blue or of other dyes with similar oxidation–reduction potentials favours the oxidative part of the process. The effect of the dye is exercised over a considerable range of concentration and is probably catalytic in character. The rate of glycolysis is increased by rise of temperature up to 37°. The catalytic effect of methylene-blue is not affected by the presence of cyanides, but is increased by addition of phosphates and requires the presence of molecular oxygen, whence it is probable that the dye catalyses the oxidation of hexosephosphate. Damage or destruction of the surface of the erythrocytes inhibits partly or entirely their glycolytic activity. C. R. HARINGTON.

Blood glycolysis. I. General consideration of glycolysis in relation to the blood-cells, and the production of lactic acid and carbon dioxide. I. KATAYAMA (J. Lab. Clin. Med., 1926, **12**, 239—254).—The sugar content of shed blood decreases on keeping, most rapidly at 38° and least rapidly at 0°; that of plasma, serum, or hæmolysed blood is unaltered. Saturation of whole blood with carbon monoxide does not inhibit glycolysis. Glycolysis takes place when washed blood-cells are added to Ringer or physiological saline solution containing dextrose, lævulose, or galactose (order of decreasing effect). The rate of glycolysis is the

same for diabetic and non-diabetic blood. Insulin has no effect on the rate. Lactic and evidently other acids, but not carbon dioxide, are produced.

CHEMICAL ABSTRACTS.

Carbohydrate degradation and phosphoric acid in blood. W. A. ENGELHARDT and A. E. BRAUNSTEIN (Klin. Woch., 1928, 7, 215).—Of the two processes contributing to the phosphoric acid balance in blood observed *in vitro*, the separation of inorganic phosphate is independent of glycolysis, whilst the union of phosphoric acid as an organic stabilisation product is directly connected with the disappearance of sugar. Conditions diminishing or inhibiting glycolysis cause a corresponding diminution of phosphoric acid stabilisation. Addition of dextrose to erythrocyte suspensions reduces the speed of liberation of phosphoric acid, but such addition is without influence in systems where glycolysis cannot occur. Addition of arsenate prevents phosphoric acid stabilisation when disappearance of sugar is proceeding. A. A. ELDRIDGE.

Catalytic decomposition of hydrogen peroxide by blood. I. Chemical dynamics of blood-catalase. II. Effect of temperature on blood-catalase. III. Catalytic activity of the red cells. IV. So-called heat-activation and influence of some organic substances on the red blood-cell catalysis. K. NOSAKA (J. Biochem. Japan, 1928, **8**, 275—299, 301—309, 311—330, 331—340).—I. The catalytic decomposition of hydrogen peroxide (0·009—0·036N) by blood solutions is not unimolecular, but corresponds with Yamazaki's formulation, $-dc/dt=kEC$; $-dE/dt=k'EC$, where E is the concentration of catalase and C that of hydrogen peroxide. Variation of values of k with variable quantities of enzyme is corrected by $k_1/k_2=(E_1/E_2)^m$, where m is constant (1·07) for different temperatures. Blood-serum has no catalytic effect, but is protective. The optimal p_H for blood-catalase is 7; the p_H has practically no influence on the destruction of catalase by the hydrogen peroxide.

II. The temperature curve for blood-catalase shows a wide optimum range at about 40°; between 0° and 20° the coefficient is 1·49 per 10°. The temperature curve for the destruction of the catalase by hydrogen peroxide is very steep and has no optimum; between 0° and 35° the coefficient is 2·22 per 10°. Inactivation by heat is not a unimolecular reaction. Blood-catalase is inactivated by heating for 30 min. at 65° or 15 min. at 70°.

III. A suspension of red blood-cells in physiological sodium chloride solution decomposes hydrogen peroxide unimolecularly provided there is no hæmolysis; serum and plasma have a stimulating effect. The reaction is regarded as a special case of hydrogen peroxide catalysis without the intervention of catalase.

IV. The catalytic effect of the red-cell suspension on hydrogen peroxide is considerably increased, owing to hæmolysis, by heating at 45°. Activation by various protoplasmic poisons is similarly occasioned.

CHEMICAL ABSTRACTS.

Effect of carbon monoxide on the metabolism of leucocytes. A. FUJITA (Biochem. Z., 1928, **197**, 189—192).—When the ratio $CO/O_2=18$ the respiration of leucocytes and of white bone-marrow cells as well as that of blood-platelets is checked, the effect being very strong in the case of the last two. Illumination with a metal-filament lamp diminished the effect, especially in the case of the marrow cells and platelets. W. MCCARTNEY.

Peroxidase properties of leucocytes. K. NICOLAJEV (Zhur. exp. biol. Med., 1928, **8**, 33—41).—Leucocytic extracts have peroxidase properties which disappear on boiling. The intensity of the oxidation process has no relation to the iron content.

CHEMICAL ABSTRACTS.

Decomposition of uric acid in blood. M. GOMOLINSKA (Biochem. J., 1928, **22**, 1307—1311).—Uric acid is quantitatively oxidised by blood to allantoin, urea, and ammonia within 48 hrs. at 37°. Stromata and blood-plasma are inactive in this respect. Hæmoglobin is most probably the uricolytic agent present in blood. The reaction of uricolysis is inhibited by propyl and butyl alcohols but not by cyanides. S. S. ZILVA.

Precipitation of blood-calcium by lead. F. BISCHOFF and L. C. MAXWELL (J. Biol. Chem., 1928, **79**, 5—17).—Addition of lead acetate to blood-serum at p_H 6·9—8·3 causes precipitation of an equivalent amount of calcium and of phosphoric acid sufficient to form the phosphates of both the lead and the calcium. The reaction is independent of the concentration of calcium, carbonate, and phosphate, and is a specific effect of lead. C. R. HARINGTON.

Electrical transference of calcium in blood-serum protein solutions. D. M. GREENBERG (J. Biol. Chem., 1928, **79**, 177—182).—Blood-serum was freed from electrolytes by electrodialysis, and the resulting solution was treated with varying amounts of calcium hydroxide alone or together with sodium hydroxide. Measurement of the electrical transport numbers of such solutions affords evidence of the formation of complex calcium–protein ions, although this complex ion formation is not so marked as with caseinogen (this vol., 241). C. R. HARINGTON.

Calcium and inorganic phosphorus in the blood of rabbits. III. Periodic and progressive variations in normal rabbits. W. H. BROWN and M. HOWARD (J. Exp. Med., 1928, **47**, 637—662).—Periodic variations of calcium and the calcium/inorganic phosphorus ratio, and progressive variations of inorganic phosphorus and the same ratio, were observed. CHEMICAL ABSTRACTS.

Determination of chloride in blood and serum. D. W. WILSON and E. G. BALL (J. Biol. Chem., 1928, **79**, 221—227).—The method of Van Slyke (A., 1924, ii, 271) for the determination of chloride yields better results if the material be treated first with silver nitrate in aqueous solution and then with concentrated nitric acid. C. R. HARINGTON.

Iron content of blood-serum. G. BARKAN (Z. physiol. Chem., 1928, **177**, 205—207).—A comment on the work of Abderhalden and Moller (this vol., 913). J. H. BIRKINSHAW.

[Iron content of blood-serum.] E. ABDERHALDEN (Z. physiol. Chem., 1928, **177**, 207—210).—A reply to Barkan (cf. preceding abstract).

J. H. BIRKINSHAW.

Determination of sulphur in blood and organic products. A. LESURE and A. DUNEZ (Bull. Soc. Chim. biol., 1928, **10**, 879—890).—After removal of the protein with acetic acid, the residue is oxidised with boiling, fuming nitric acid and the product decolorised with hydrogen peroxide. A 4% solution of benzidine in 4% hydrochloric acid is then added and the benzidine sulphate washed with pure acetone. The sulphate is finally determined by titration with sodium hydroxide solution. G. A. C. GOUGH.

Irradiated proteins. IV. Effect of short-wave radiation on the ultra-violet absorption of serum and of serum-protein. M. SPIEGEL-ADOLF (Biochem. Z., 1928, **197**, 197—209).—The absorptive power of irradiated serum-albumin is independent of the presence of oxygen. Serum-albumin kept in an atmosphere of nitrogen exhibits quantitatively and qualitatively the same changes, and serum-albumin free from electrolytes, under the same conditions, also remains insoluble after treatment with alkali (cf. A., 1927, 893; this vol., 190, 659). Serum diluted with physiological salt solution and also pseudoglobulin irradiated in presence of alkali show an increase in absorbing power after irradiation. Euglobulin, under the same conditions, exhibits no such change. As regards the extent of change in absorbing power undergone, the substances form the descending series: serum-albumin, serum, pseudoglobulin, euglobulin. The permeability of irradiated and unirradiated solutions of these substances by light of short wave-length provides confirmation of the results determined spectrographically.

W. McCARTNEY.

Presence of polypeptides in blood-plasma and -serum. Application of erepsin and trypsin-kinase for their detection. E. ABDERHALDEN and E. ROSSNER (Fermentforsch., 1928, **10**, 102—110).—Serum dialysates contain at most only very small amounts of compounds giving rise to free amino-groups when subjected to the action of purified erepsin or trypsin-kinase. W. O. KERMACK.

Composition of the compounds containing residual carbon and nitrogen; oxyproteic acids in blood. O. DEUTSCHBERGER (Biochem. Z., 1928, **198**, 268—295).—The residual carbon of blood (horse) filtrates is 182·5 mg./100 c.c. The sum of the carbon contents of known constituents is 165·6 mg. of carbon per 100 c.c. of blood, made up of sugar 38·4, lactic acid 6·5, amino-acids 47·0, carbamide 4·7, creatine and creatinine 3·2, oxyproteic acids 65·8 mg. The residual nitrogen is 44 mg./100 c.c. of blood, made up of oxyproteic acids 19, amino-nitrogen 11, carbamide 11, and creatine and creatinine 3 mg. The whole of the nitrogen and most of the carbon of the filtrates are therefore accounted for in terms of known substances. The mean values for the oxyproteic acid fractions of the filtrate were residual carbon 66, hydrogen 8, and nitrogen 19 mg. per 100 c.c. of blood.

P. W. CLUTTERBUCK.

Micro-method for determination of fats and lipins of blood. J. A. MILROY (Biochem. J., 1928, **22**, 1206—1211).—The extracted compounds of the blood are hydrolysed and the amount of fatty acids is determined colorimetrically, using Nile-blue hydrochloride as the stain. In the case of the total fatty acids the blood (0·1 c.c.) is extracted with alcohol and ether, and in that of the fatty acids from neutral fats with alcohol and light petroleum.

S. S. ZILVA.

[Non-]effect of splenectomy on the blood-sugar. A. M. BLINOV (Zhur. exp. biol. Med., 1928, **8**, 467—470). CHEMICAL ABSTRACTS.

Conversion of blood- into bile-pigments. E. POLLAK (Biochem. Z., 1928, **198**, 311—316).—The pigment previously obtained by Brugsch and Pollak (A., 1924, i, 1127) by the action of pyrocatechol on hæmin and claimed to be bilirubin has now been obtained in quantity; it has mol. wt. 300—330, empirical formula $C_{16}H_{16}N_2O_4$, and gives a blue hydrochloride showing an absorption band in the orange. The substance is not bilirubin, since it cannot be extracted from chloroform solution with sodium hydroxide or ammonia, the mol. wt. is not reconcilable, and the substance does not appear to be a pyrrole derivative. P. W. CLUTTERBUCK.

Keeping properties of specific anti-sera for the precipitin test. F. BAMFORD (Analyst, 1928, **53**, 531—532).—Anti-sera prepared by the Lister Institute and kept in Cairo in an ice-chest for nearly 5 years showed a very definite reaction with fowl blood-serum diluted to 1 in 2000. Another set of anti-sera, with the utmost precautions against temperature changes, was quite unsatisfactory from the first, but a third set had good specificity although kept for about 12 days at 30—35°. Temperature variations alone are regarded as insufficient causes of instability in anti-sera. D. G. HEWER.

Hæmolysis of chicken blood. G. E. SHATTUCK (J. Gen. Physiol., 1928, **12**, 17—28).—The hæmolytic action of saponin, sodium taurocholate, and sodium oleate on nucleated erythrocytes from chicken blood has been studied and comparison is made between the action of these lipins on nucleated and on non-nucleated blood-cells. E. A. LUNT.

Hæmolysis by saponin and sodium taurocholate with special reference to the series of Ryvosh. J. F. YEAGER (J. Gen. Physiol., 1928, **11**, 779—787).—The resistances of the red blood-corpuscles of various animals to hæmolysis by sodium taurocholate do not follow the order found by Ryvosh (Arch. ges. Physiol., 1907, **116**) and confirmed by Ponder (Brit. J. Exp. Path., 1927, **8**, 267) for resistance to hæmolysis by saponin.

W. O. KERMACK.

Hæmolytic action of inorganic acids. Lipoid solubility, permeability, and hæmolytic action of saturated fatty acids. M. BODANSKY (J. Biol. Chem., 1928, **79**, 229—239, 241—255).—Red blood-corpuscles are very readily permeable to mineral acids; the hæmolytic powers of phosphoric, sulphuric, hydrochloric, and nitric acids are in descending order of magnitude. The effect of these acids is one of

destruction of the cell membrane rather than of osmosis. Human erythrocytes are less resistant to hæmolysis than those of the dog, but erythrocytes from normal and anæmic individuals are equally resistant.

Curves are given showing the relationship between and hæmolytic action for a number of fatty acids; since increase in the osmotic concentration of the outer fluid diminishes the hæmolytic action, the latter must be, in part at least, an osmotic effect. The power of the fatty acids to penetrate the erythrocyte increases approximately with the mol. wt., and the effectiveness as a hæmolytic agent runs parallel to the lipoid solubility as determined from the partition coefficient between olive oil and water. C. R. Harington.

Second protein (livetin) of egg-yolk. H. D. Kay and P. G. Marshall (Biochem. J., 1928, **22**, 1264—1296; cf. Plimmer, J.C.S., 1908, **93**, 1500).—After removing the vitellin from the yolk the protein is precipitated and reprecipitated several times by half saturation with ammonium sulphate. The lipins are removed by extraction with alcohol and ether at —15° and the ammonium sulphate is eliminated by dialysis at 3° and p_H 5·0. The protein contains 5·2% of tyrosine, 2·1% of tryptophan, 3·9% of cystine, 0·067% of phosphorus, and 1·8% of sulphur. It has its isoelectric point at about p_H 4·8—5·0 and $[\alpha]^{20}_{5461}$ —55·5°. In the fresh yolk the ratio vitellin/livetin is fairly constant from one egg to another. Between one quarter and one fifth of the yolk-proteins of the hen's or duck's egg is livetin. A method based on the above technique is described for determining the amount of this protein in a single egg-yolk. S. S. Zilva.

Reaction of tissues. A. B. Carlstrom, R. Ege, and V. Henriques (Biochem. Z., 1928, **198**, 442—462).—A colorimetric method is elaborated for determining the reaction of tissues and a correction employed for a systematic protein error. The glass electrode is also used with satisfactory results. The formation of lactic acid takes place in the cellular tissue and not in the tissue extract. Formation of the acid is detectable in finely minced muscle at 0°. The buffer curve of cross-striated rabbit's muscle and the *post mortem* changes in reaction are determined. The p_H of muscle is displaced from 7 to 6 by 0·055M-acid, corresponding with the presence of 525 mg. of lactic acid per 100 g. of muscle. The temperature correction for the reaction of tissue is determined, an increase of 1° causing the p_H to be decreased by 0·007. The p_H of resting muscle at 37° is 6·8—6·95, that of muscle when the production of lactic acid is prevented is 7·0, that of muscle free from lactic acid is calculated as 7·1 and that of muscle in rigor is 5·9. P. W. Clutterbuck.

Relative reactions within living mammalian tissues. X. Litmus constituents as vital stains. R. Elman, D. R. Drury, and P. D. McMaster (J. Exp. Med., 1928, **47**, 777—796).—Erythrolitmin is advantageous as a vital stain, but erythrolein is useless and azolitmin is toxic. Methods for the separation of these substances from litmus are described. Chemical Abstracts.

Coloration of animal membranes with copper sulphate solutions. M. Chanoz (Compt. rend. Soc. Biol., 1927, **97**, 1539—1541; Chem. Zentr., 1928, i, 1972).—Animal membranes are coloured by copper sulphate solutions less acid than $10^{-5}N$. It is considered that in acid solutions a colourless protein–sulphate salt is formed, whilst in more alkaline solutions a green copper–protein compound is produced. A. A. Eldridge.

Cystine content of keratins. T. Takeda (Bul. Sci. Fak. Terkultura Kjusu, 1926, **2**, 262—272).—A comparison of human and monkey hair, wool, and feathers. Chemical Abstracts.

Occurrence of gold in food and organs. R. Berg (Biochem. Z., 1928, **198**, 424—427).—A method for determining traces of gold is outlined and the following values are obtained: oat flakes, 0·2 mg.; commercial oat flakes, 0·04 mg.; natural honey, none; grape and apple juice, trace; apple-juice concentrate, 0·1 mg.; finest wheat meal, none; whole-meal bread, 0·03 mg.; whole-meal rye bread, 0·1 mg.; hazel nuts, 0·1 mg. per 100 g. in each case; drinking water, 0·046 mg. per litre; human urine, 0·1 mg. per day; human fæces, 1·0 mg. per day; human blood up to 0·3 mg. per 100 g.; ox liver, 0·2 mg. per kg.; ox brain, 1·4 mg. per 100 g. (surprisingly large). P. W. Clutterbuck.

Volatile sulphide from muscle. W. A. Osborne (Biochem. J., 1928, **22**, 1312).—Volatile sulphide is formed in the muscle of well-nourished guinea-pigs when kept for about 24 hrs. even if precautions are taken to avoid bacterial decomposition. The volatile sulphide can be detected immediately after killing in the muscles of guinea-pigs which have previously been starved for 48 hrs. The flesh of sheep but not beef has been found to emit sulphide. S. S. Zilva.

Artificial preparation of the principal constituent of bones and teeth. T. Gassmann (Z. physiol. Chem., 1928, **178**, 62—66).—The preparation is described of phosphatocalcium carbonate (cf. A., 1911, ii, 129) by the treatment of calcium oxide under special conditions with atmospheric carbon dioxide, sodium phosphate solution, and acetic acid, followed by extraction with alcohol. The substance thus prepared had the composition and properties of the natural material (cf. A., 1913, ii, 320; 1914, i, 773). R. K. Callow.

Composition of bone. I. Analytical methods. M. J. Shear and B. Kramer. **II. Pathological calcification.** B. Kramer and M. J. Shear. **III. Physico-chemical mechanism.** M. J. Shear and B. Kramer. **IV. Primary calcification.** B. Kramer and M. J. Shear. **V. Properties of calcium citrate.** M. J. Shear and B. Kramer (J. Biol. Chem., 1928, 79, 105—120, 121—123, 125—145, 147—160, 161—175).—I. Bone was crushed and extracted in a Soxhlet apparatus with a mixture of alcohol and ether to which was added some sodium hydroxide to retain acid vapours; 50 mg. of the dried extracted powder were used for the determination of (*a*) carbonate by the method of Van Slyke and Neill (A., 1924, ii 872), (*b*) calcium by the method of Kramer and Tisdall (A., 1921, ii, 595), (*c*) phosphorus

by the method of Briggs (A., 1922, ii, 718). The average ratio of non-carbonate calcium to total inorganic phosphorus was 2·0.

II. In pathologically calcified tissues the above ratio is the same as for normal bone except in calcified uterine fibroids, in which it is 2·2.

III. The probable mechanism of calcification is considered from a physico-chemical point of view. It is pointed out that there is no evidence for the existence of tertiary calcium phosphate in bone. Previous experiments on calcification *in vitro* and *in vivo* lead to the conclusion that the important factor is the ionic product $[Ca]^{++}\times[HPO_4]^{=}$; it is at least evident that no calcification occurs when the value of this product is less than that of the solubility product of secondary calcium phosphate, and this compound may first be precipitated and may be subsequently changed to one with a higher proportion of calcium.

IV. In primary calcification in rats undergoing healing of rickets, the non-carbonate calcium : inorganic phosphorus ratio is higher than in normal rat bones, indicating the presence of a basic calcium salt in the freshly-deposited bony tissue. The proportion of carbonate in rat bones increases with age, and in the condition of rickets. The theory expressed in the previous paper is modified to the view that, from an alkaline medium such as blood-serum, calcium is deposited as a mixture of secondary calcium phosphate and calcium hydroxide, which would give rise to the high Ca : P ratios observed.

V. Mixtures of sodium chloride and sodium citrate solutions have electrical resistances intermediate between those of solutions of the pure salts. Addition of sodium citrate to calcium chloride solution produces, however, anomalous results, the resistance first increasing and then decreasing; this affords evidence for the binding of the calcium ions by the sodium citrate. C. R. Harington.

***Bombyx mori*. I. Effect of hydrogen-ion concentration on the coagulation of liquid silk. II. Quantitative changes of cystine, tryptophan, and tyrosine in proteins of silkworms.** S. Nakajima (Bul. Sci. Fak. Terkultura Kjusu, 1926, **2**, 20—32).—I. "Liquid silk" is negatively charged and is readily coagulated by addition of some acids. The optimal coagulation points are p_H 1·3 and 3·9; the latter approximates to the isoelectric point of sericin.

II. The cystine and tryptophan content gradually decreases during the development of the worms or silk formation, whilst that of tyrosine increases.

Chemical Abstracts.

Significance of composition of the secreting and dry mammary gland to milk secretion. J. W. Gowen and E. R. Tobey (J. Gen. Physiol., 1928, **12**, 123—128).—Values are given for the composition of the dry and lactating udder of the cow, and of the milk from the latter, with reference to fat, ash, nitrogen, and lactose. At all times there is a large excess of fat, ash, and nitrogen in the udder in proportion to that necessary for milk formation. This excess does not obtain during lactation in the case of lactose, and the non-lactating udder contains no lactose. These results are held to indicate that lactose in milk is formed from the blood only as needed in the formation of milk. E. A. Lunt.

Influence of freezing of milk on its acid fermentation. V. W. Winter (Chem. Listy, 1928, **22**, 357—361).—The solid fraction of partly frozen milk has a lower specific gravity and a higher acidity than the original milk, whilst the contrary is the case with the liquid fraction. Both fractions on incubation at the ordinary temperature for 2—3 weeks exhibit a lower acidity than milk not previously frozen.

R. Truszkowski.

Bufodeoxycholic acid in the bile of *Bufo vulgaris Japonica*. I. T. Okanura (J. Biochem. Japan, 1927, **8**, 351—360).—The *bufodeoxycholic acid*, $C_{24}H_{36}O_4$, stimulates lipase action and is hæmolytic.

Chemical Abstracts.

Fish bile. II. *Tetrodon porphyleus*, Sieb. N. Teraoka (J. Biochem. Japan, 1928, **8**, 341—350).—The bile contains about 9% of taurocholic acid.

Chemical Abstracts.

Solubility of cystine in urine. G. Blix (Z. physiol. Chem., 1928, **178**, 109—124).—The causes of the relatively high solubility of cystine in urine as compared with water were investigated. The effect of different hydrogen-ion concentrations is small (cf. Sano, A., 1926, 345). Inorganic salts present in urine increase the solubility considerably; *e.g.*, in 0·25*N*-calcium chloride it is increased by 59%. The principal cause of the increased solubility is, however, the presence of colloids which inhibit the crystallisation of the cystine.

The influence of neutral salts on the solubility of amino-acids is discussed from the point of view of the activity theory. The effects are accounted for by Bjerrum's theory of the "zwitterion," which also accounts for changes in optical activity and depression of the f. p., rather than by Pfeiffer's theory. Pfeiffer's observation of the salting-out of cystine by ammonium sulphate (A., 1924, i, 378) could not be confirmed.

A method of determining sulphur, applicable to the determination of cystine, by oxidation with alkaline permanganate and precipitation with barium chloride in acid solution, is described.

R. K. Callow.

Excretion of creatinine and the energy demand. L. Garot (Arch. Int. Physiol., 1927, **29**, 326—341; Chem. Zentr., 1928, i, 1788).—The quantity of creatinine excreted per kg. body-weight falls with increasing age. The quantity is related to the muscle mass, and not to the energy demand.

A. A. Eldridge.

Uric acid and creatinine in the urine of infants. O. S. Rougichitch (Amer. J. Dis. Children, 1926, **31**, 504—513).—For infants, aged 1—22 months, on a diet free from purine, 14—25 mg. of uric acid per kg. of body-weight were excreted daily; the creatinine varied from 10 to 15 mg. per kg.

Chemical Abstracts.

Uric acid in the urine of infants. O. S. Rougichitch (Amer. J. Dis. Children, 1926, **32**, 530—535).—In boys aged 6—12 weeks the purine metabolism was regular throughout 24 hrs.

Chemical Abstracts.

Test for alkalis [in urine]. C. Mitchell (Clin. Med., 1928, **35**, 167).—The urine is poured on to 20% nickel sulphate solution; in presence of alkalis a white ring or cloudiness appears at the interface. Albumin and sugar do not interfere.

Chemical Abstracts.

Dextrose in normal urine. A. Hassan (Biochem. J., 1928, **22**, 1332—1340).—Normal urines give crystal mixtures consisting of two simple osazones—glucosazone and an osazone which agrees in m. p. but not in crystalline structure with *iso*maltosazone. Examination of urines of more than 700 persons revealed that 20—30% of urines voided 1—2 hrs. after an ordinary meal yielded typical glucosazone crystals. The percentage dropped to 12—15 in urines passed 4—5 hrs. after meals. The presence of dextrose in the urine is not due to abnormal carbohydrate metabolism. 1 mg. of dextrose per 100 c.c. of water or urine from which the normal sugars have been removed could be detected by the method employed for the preparation of osazones.

S. S. Zilva.

Detection of sugar in urine. J. Schmid and E. Glorius (Süddeut. Apoth.-Ztg., 1928, **68**, 98—99; Chem. Zentr., 1928, i, 1896—1897).—In Schmidt and Rubner's reaction the mixture of urine, ammonia, and lead acetate is preferably heated at 85° at one point, or immersed in water at 40—50°, when the development of a salmon-pink colour will detect 0·05%; under these conditions lactose does not react similarly.

A. A. Eldridge.

Determination of sugar in normal urine. M. R. Everett and M. O. Hart (J. Lab. Clin. Med., 1927, **12**, 579—589).—Irregularities are recorded.

Chemical Abstracts.

Piperazine in the analysis of urine and blood. R. Gros (J. Pharm. Chim., 1928, [viii], **8**, 313—316). —By adding piperazine to urine, suspended uric acid and urates are dissolved, the bacteriological examination is simplified, and the determination of uric acid, purine bases, urea, chlorine, and phosphates by the usual methods is improved. In the preparation of standard uric acid solution in Grigaut's method for the determination of uric acid in blood, the addition of piperazine facilitates dissolution of the uric acid and has no effect on either the stability of the solution or the colorimetric determination.

E. H. Sharples.

Modifications of Katayama's formulæ for computing the fæcal nitrogen and fæcal organic matter in chicken excrement. H. W. Titus (Poultry Sci., 1928, **7**, 145—150).—Fæcal nitrogen= 0·9784×excrement-nitrogen−1·0253×uric acid nitrogen−1·2641×excrement ammonia-nitrogen−0·0554; urinary organic matter in the excrement=2·16×(urinary nitrogen %)+27·53%.

Chemical Abstracts.

Changes in composition of blood in pernicious anæmia treated by a diet rich in liver. W. P. Murphy, R. T. Monroe, and R. Fitz (J. Amer. Med. Assoc., 1927, **88**, 1211—1214).—Corpuscular-protein increased with increasing hæmoglobin concentration; no changes in plasma-protein or -non-protein-nitrogen were observed.

Chemical Abstracts.

Anaphylaxis in man and animals. VII. Potassium and calcium content of the blood and organs of the rabbit and dog and its changes in sensitised and anaphylactic animals. A. Schittenhelm, W. Erhardt, and K. Warnat (Z. ges. exp. Med., 1928, **58**, 662—682; Chem. Zentr., 1928, i, 1787).

Chemistry of healthy and of atherosclerotic aorta. II. Quantitative chemical changes in the atherosclerotic aorta. III. Atherosclerotic lipin mixture. R. Schönheimer (Z. physiol. Chem., 1928, **177**, 143—157).—II. The values for cholesterol, cholesteryl ester, and phosphatides in the atherosclerotic aorta support the infiltration theory previously advanced (A., 1926, 1269); the hypothesis of calcium deposition by way of the calcium salts of the hydrolysed fatty acids of the cholesteryl esters is rejected. The calcium salt corresponds in composition with that of bone.

III. From the lipins were isolated free cholesterol and the stearate, palmitate, and oleate. Indications of doubly-unsaturated esters were obtained. A galactoside, and substances not precipitated by digitonin, but apparently no neutral fats, were present.

J. H. Birkinshaw.

Composition of the blood of animals under pathological conditions. I. Broncho-pneumonia in cows. A. A. Horvath and R. B. Little (J. Clin. Invest., 1928, **5**, 541—546).—The blood-plasma chlorine is diminished and the globulin and fibrin fractions are increased.

Chemical Abstracts.

Analyses of blood in patients having senile cataract. C. S. O'Brien and V. C. Myers (Arch. Int. Med., 1928, **42**, 376—378).—Analyses made on the blood of 54 cases of cataract indicate no abnormality of composition except in the cholesterol content, which was high in 54% of the cases observed.

E. A. Lunt.

Effect of Karlsbad mineral water on diabetes mellitus. O. Kauffmann-Cosla and R. Zörkendörfer (Münch. med. Woch., 1928, **75**, 396—399; Chem. Zentr., 1928, i, 2103).

Diabetes. Mathematical derivation of the blood-dextrose curve. D. M. Ervin (J. Lab. Clin. Med., 1926, **12**, 318—325).—A mathematical expression for the blood-dextrose curve depends on the absorption from the intestinal tract, formation of glycogen, and oxidation. The curve depends only on a decreased rate of glycogen formation; there is no evidence of failure of dextrose combustion.

Chemical Abstracts.

Mechanism of the inflammatory process. III. Electrophoretic migration of inert particles and blood-cells in gelatin sols and gels with reference to leucocyte emigration through the capillary wall. H. A. Abramson (J. Gen. Physiol., 1928, **11**, 743—756).—The cataphoresis of particles of quartz and of silver as well as of air bubbles from 1·0 to 50·0 μ in diameter has been studied in 1·0% gelatin sols and gels. The apparent viscosity η' (measured using small shearing stresses) as well as the true viscosity η (measured using large shearing stresses) have also been determined for the

sols and soft gels employed. The cataphoretic velocity remains constant during gelation, whilst the apparent viscosity is rapidly increasing. It appears therefore that the cataphoretic velocity in these sols and soft gels is dependent on the true viscosity which remains constant for a sol during the process of gelation. Leucocytes traverse soft gelatin-serum under cataphoresis with approximately the same velocity as quartz, viz., 0·5 μ per volt per cm., whilst red blood-cells move with double that speed. In both cases the velocity of migration remains constant during the process of gelation. With stiffer gels all three types of particles move at first with the same slow velocity which gradually increases as cataphoresis is continued, especially in the case of the red blood-cells. When leucocytes move in a fibrin gel they are frequently completely stopped apparently as the result of obstruction by the fibrin strands. Nickel particles suspended in a soft gelatin gel and acted on by a magnetic field show only elastic displacement if the field is sufficiently weak and apparently experience more resistance than the particles of the same size undergoing cataphoresis in a similar gel. The bearing of these results on the theory of the migration of leucocytes through the capillary walls is discussed. W. O. KERMACK.

Blood-uric acid in nephritis. W. P. HOLBROOK and H. D. HASKINS (J. Lab. Clin. Med., 1926, **12**, 10—15).—A diagnostic study.
CHEMICAL ABSTRACTS.

Value of the diazo-test on blood. S. M. ROBSON and L. JACOBS (Arch. Int. Med., 1928, **42**, 386—389). —Evidence is cited against the use of the diazo-test on blood as a specific means of differentiation between uræmic coma and that of other origin. A high creatinine content of the blood usually accompanies a positive diazo-test, although no definite creatinine value can be established as the point at which the positive diazo-test appears. E. A. LUNT.

Phosphorus and calcium in the blood in Parkinsonism after injection of ergotamine and hyoscine. C. I. URECHIA and G. POPOVICIU (Compt. rend. Soc. Biol., 1927, **97**, 1573—1575; Chem. Zentr., 1928, i, 1786).

Physiology of glands. L. ASHER. **Prevention of over-compensation for loss of iron, through blockade of the reticulo-endothelial system, after extirpation of the spleen.** Y. KOJIMA (Biochem. Z., 1928, **197**, 84—104).—In order to find whether the decreased excretion of iron after splenectomy in guinea-pigs depends on over-compensation by the liver the method of blockade of the reticulo-endothelial system was employed. In normal guinea-pigs blockade with Chinese ink causes only insignificant increase in the amount of iron excreted daily. After splenectomy the blockade causes quite considerable increase in the excretion of iron, and this increase may become so great that all over-compensation is prevented and excretion is restored to its normal value. These results support the view that the spleen plays a part in the control of iron metabolism.
W. MCCARTNEY.

Physiology of glands. L. ASHER. **Exchange of material between blood and tissues in [animals with] normal and denervated thyroid glands.** T. HONDA (Biochem. Z., 1928, **197**, 72—83).—The change in the chloride content of the blood of rabbits and also the change in the volume of red blood-corpuscles following injection, at the same time, of sucrose solution and of solutions of a specific diuretic ("Euphyllin") have been followed. (The sugar was injected intraperitoneally, the diuretic intramuscularly.) After denervation of the thyroid gland the chloride content of the blood changed more rapidly and to a greater extent than before denervation. Complete removal of the gland caused only insignificant changes in the chloride content of the blood. W. MCCARTNEY.

Potassium, calcium, and choline content of the blood of dogs and its alterations following extirpation of the thyroid gland. M. MAXIM and C. VASILIU (Biochem. Z., 1928, **197**, 237—240).—There was a constant decrease in the potassium content in the first 4—7 days after the operation. The amount of calcium remained unchanged at first and then began to rise. There was also an immediate increase in the choline content, and during tetanic convulsions and also during respiratory crises it reached very high values, as also did the potassium. All analyses were made with whole blood.
W. MCCARTNEY.

Co-enzyme of glycolysis from tumours. H. KRAUT and E. BUMM (Z. physiol. Chem., 1928, **177**, 125—142).—A highly active co-enzyme has been prepared from carcinomata and sarcomata capable of promoting glycolysis by sections of rat's kidney washed free from co-enzyme. A preparation of the tumour dried with acetone and ether is extracted with 0·01N-ammonia and precipitated by alcohol. The precipitate still contains an inhibitor which is removed by adsorption from concentrated solution by aluminium hydroxide. The final product is 125 times as active as the dried preparation. The co-enzyme content of extracts of liver, kidneys, embryo, and tumour increases in the order given. J. H. BIRKINSHAW.

Carbohydrate metabolism of certain pathological overgrowths. H. G. CRABTREE (Biochem. J., 1928, **22**, 1289—1298).—The magnitude and relationships of the respiratory and glycolytic processes found by Warburg to be characteristic of malignant tissues are not specific for these tissues, but are a common feature of pathological overgrowth. Thus the magnitude of the respiration and aerobic and anaerobic glycolysis of the reactive tissue in experimental vaccinia in young chickens, in fowl pox and human warts approximates to that found for tumours. In the case of vaccinia lesions in rabbits where little or no epithelial hyperplasia is evident lower quotients are obtained, probably due to leucocytic invasion. In the brain of guinea-pigs dying of rabies where no abnormal cell division occurs there is no deviation from the normal metabolism. The metabolic activity of fowl-pox lesions exhibits a rough parallelism in its magnitude to the state of development or regression of the lesion. There is great variability in the values for respiration in the Rous chicken-sarcoma. After the injection of Rous sarcoma cell-free filtrate in the muscle of fowls a

slight rise in the metabolism was noticed during $4\frac{1}{2}$ hrs. followed by a return to the normal values obtained for resting muscle. During the subsequent development of the tumour in its early stages, the cells of this tumour assume on their first appearance the high metabolic activity characteristic of the fully grown tumour. S. S. Zilva.

Action of naturally occurring iron compounds on metabolism. Active iron. M. Kochmann and H. Seel (Biochem. Z., 1928, **198**, 362—378).—In prolonged experiments with young rats, a considerable acceleration of growth was obtained on administration of a naturally occurring mineral ("Liebenstein") water containing ferric hydrogen carbonate. This acceleration of growth was accompanied by increased oxygen utilisation. Animals receiving the same amount of ferrous sulphate showed a smaller acceleration of growth, but this was still greater than when distilled water free from iron was administered. No support could be obtained for the view that there exists a special form of iron, not as yet characterised, which shows great biological activity. P. W. Clutterbuck.

Growth-promoting influence of inorganic iron compounds. A. Bickel (Biochem. Z., 1928, **199**, 60—68).—Rats fed on a diet containing "siderac" (a magnetic benzidine-active ferric oxide) showed a greater increase in body-weight than controls receiving no "siderac." A second magnetic benzidine-active ferric oxide and a non-magnetic benzidine-active ferrous–ferric carbonate had no growth-promoting effect. "Siderac" also increased the iron content of the body. J. H. Birkinshaw.

Can the growth-promoting influence of iron be increased by ultra-violet irradiation? P. M. Suski (Biochem. Z., 1928, **199**, 69—71).—Irradiation of ferrous sulphate produced no improvement in growth-promoting power. J. H. Birkinshaw.

(*a*) Inorganic iron of the organism. (*b*) Fate of inorganic iron in surviving organs. (*c*) Fate of inorganic iron in the organism after administration of ferrous and ferric compounds. E. Starkenstein and H. Weden (Arch. exp. Path. Pharm., 1928, **134**, 274—287, 288—299, 300—316).—(*a*) The inorganic iron present in the animal organism is only partly extracted by water or by dilute hydrochloric acid, but is almost completely extracted by boiling with $5N$-hydrochloric acid followed by precipitation with trichloroacetic acid, a method which does not remove any hæmoglobin iron. The distribution of inorganic iron in the blood and organs of various animals has been investigated and the percentage present in the ferric and ferrous states has been ascertained. Inorganic iron for the most part appears to be present in a form insoluble in water. Of that extracted by hydrochloric acid, the greater portion is in the ferrous state, but of that extracted by water most is in the ferric state.

(*b*) The effect of the addition of ferrous chloride and of ferric hydroxide to blood has been investigated and the quantities of ferrous and ferric iron present at various times have been determined. Ferrous iron is oxidised to ferric and the ferric iron is reduced to ferrous, but the ferric iron formed from ferrous in the blood appears to have different physical and chemical properties from the ferric iron added as ferric hydroxide and in the same way the ferrous iron formed by reduction in blood of ferric hydroxide behaves differently from ferrous iron added as ferrous chloride.

(*c*) The various changes which ferrous chloride and ferric hydroxide undergo in the blood and in various organs have been investigated. W. O. Kermack.

Change of soluble ferrous salts in organisms. M. Messini (Arch. exp. Path. Pharm., 1928, **135**, 346—361).—The minimal lethal dose for colloidal ferrous phosphate was determined by intravenous injections into rabbits and compared with both simultaneous and consecutive injections of sodium phosphate and ferrous sulphate. The relative equivalence of the doses is assumed to justify the hypothesis that soluble ferrous salts are converted into insoluble ferrous phosphate *in vivo*. Subcutaneous injections of ferrous sulphate were made, the animals killed after measured time intervals, and the injection sites tested for iron and phosphate. The phosphate reaction increased with increase of time between injection and death to a maximum and then both iron and phosphate reactions decreased. This is claimed to support the hypothesis of conversion of soluble ferrous salts into phosphate *in vivo*. H. R. Ing.

Raw and prepared milks as sources of calcium and phosphorus for the human subject. M. M. Kramer, E. Latzke, and M. M. Shaw (J. Biol. Chem., 1928, **79**, 283—295).—Better retention of calcium and phosphorus in children was secured with fresh milk than with dried milk; for adults, fresh and condensed milks were about equally good, whilst pasteurised and dried milks were definitely poorer.
C. R. Harington.

Relation of carbon quotient to oxidation quotient of urine. A. Bickel (Biochem. Z., 1928, **199**, 195—201).—The carbon quotient denotes the ratio total carbon/total nitrogen. The oxidation quotient is the reciprocal of that employed by Müller (A., 1927, 996) and denotes the ratio "oxygen requirement"/total nitrogen. J. H. Birkinshaw.

Carbon- and oxidation-quotients of urine after calcium administration. E. Goldschmidt (Biochem. Z., 1928, **199**, 207—211).—Rabbits received daily 0·03 g. or 0·06 g. of calcium *per os*. Whilst the carbon quotient in the first and second calcium periods was below normal, the oxidation quotient was above normal. J. H. Birkinshaw.

Carbon- and oxidation-quotients of urine after dextrose administration. T. Taslakowa (Biochem. Z., 1928, **199**, 212—215).—The daily oral administration to rabbits of 3 g. of dextrose per kg. body-weight caused a general movement of the two quotients in the same direction, both tending to increase. J. H. Birkinshaw.

Action of hypertonic dextrose solutions on the excretion of water and chlorides by the kidneys. I. J. M. Goldberg, S. M. Gamerow, and M. L. Pinchassik **Action of hypertonic dextrose solutions on the excretion of water and chlorides**

by the kidneys in thyroidectomised animals. II. J. M. GOLDBERG, M. L. PINCHASSIK, and S. M. GAMEROW (Biochem. Z., 1928, **199**, 107—114, 115—120).—I. Hypertonic dextrose solutions introduced into the blood of rabbits cause the water content of the muscles to decrease, that of the blood and liver to increase. The chloride content remains unchanged. The secretion of urine usually diminishes, and the chloride content of the urine varies according to the total volume.

II. Hypertonic dextrose solutions have much less influence on the water distribution between blood, liver, and muscles of thyroidectomised rabbits than of normal animals; the decrease in the quantity of urine is, on the other hand, much more marked.

J. H. BIRKINSHAW.

Carbohydrate metabolism. H. SCHUR and A. LOW (Wien. klin. Woch., 1928, **41**, 225—229, 261—266; Chem. Zentr., 1928, i, 1886).—It is considered that the minimal quantity of carbohydrate for metabolism is smaller than is supposed. The function of the islets is discussed. A. A. ELDRIDGE.

Overnutrition and the blood-sugar content. C. SCHWARZ and J. SMUTNY (Biochem. Z., 1928, **198**, 243—249).—The fasting blood-sugar value in normal dogs never exceeds 0·12% even after a period in which the diet has been increased by 200%.

P. W. CLUTTERBUCK.

Carbohydrate metabolism in dried muscle. H. VON EULER, E. BRUNIUS, and S. PROFFE (Z. physiol. Chem., 1928, **177**, 170—176).—Previous experiments had indicated that dried muscle preparations which were capable of producing glycolysis on addition of boiled yeast juice were not activated by purified co-zymase. A repetition of the work with new muscle preparations shows no difference between the action of boiled juice and that of chemically purified co-zymase. J. H. BIRKINSHAW.

Enzyme experiments with dried muscle. E. BRUNIUS (Z. physiol. Chem., 1928, **177**, 201—204).—Experiments were carried out on lactic acid formation from dextrose by means of the activator prepared according to Meyerhof. The best phosphate concentration was 1—1·3%; the presence of toluene had no effect. Extraction of the active preparation with water weakened its power; the filtrate was inactive. On treatment with alcohol and hydrochloric acid the dried muscle lost its activity and this was not restored by addition of the extract.

J. H. BIRKINSHAW.

Regulation of carbohydrate metabolism. II. Rôle of lactic acid in intermediary carbohydrate metabolism. III. Action of electrolytes on blood-sugar. A. PARTOS (Fermentforsch., 1928, **10**, 50—65, 66—71; cf. this vol., 1049).—II. The rate of glycogenolysis which occurs in minced liver *in vitro* is increased by the presence of lactic acid and also by adrenaline and extracts of the pituitary and ovary. Insulin has a retarding action, whilst thyroxine has no material influence. In presence of the above substances, lactic acid has always an accelerating influence *in vitro*, but *in vivo* it accentuates the hypoglycæmia brought about by insulin and decreases or converts into a hypoglycæmia the hyperglycæmia resulting from the administration of adrenaline, or extracts of pituitary or ovary. On the other hand, the hyperglycæmia resulting from administration of thyroxine is scarcely affected by lactic acid.

III. The action which is exhibited by certain acids in raising the concentration of sugar in the blood is not dependent on an increase in hydrogen-ion concentration, but is rather a specific effect of the anion and is exhibited by the sodium salt as well as by the acid itself. W. O. KERMACK.

Determination of lactic acid in the vessels of the uterus and umbilicus. F. WIND and K. VON OETTINGEN (Biochem. Z., 1928, **197**, 170—174).—A method of measuring the lactic acid metabolism of tissues in the living animal is described.

W. MCCARTNEY.

Metabolism of body-cells. A. FUJITA (Biochem. Z., 1928, **197**, 175—188).—Suprarenal, pituitary, and parathyroid glands, sympathetic ganglia, embryonic lenses, testes, ovaries, placentas, spleens, and bone-marrow were investigated. The animals used were rats, rabbits, mice, and guinea-pigs. The serum method of determination was employed. Except the lenses, all the organs and cells investigated, under anaerobic conditions, display glycolysis, but this disappears almost completely on saturation with oxygen. This holds also for placenta and leucocytes, neither of which is comparable with carcinoma cells as regards metabolism.

W. MCCARTNEY.

Behaviour of aldol in the animal body and in fresh organ pulp. F. LIEBEN and G. EHRLICH (Biochem. Z., 1928, **198**, 317—327).—Ripper's method for the determination of aldehydes (A., 1900, ii, 319) may be used for aldol and paraldol, the presence of acetone interfering but of sugar not. The presence of aldol does not interfere with the determination of sugar by the Pavy–Kumagawa–Suto method. Aldol administered subcutaneously does not pass into the urine in significant amounts either in normal or phloridzinised dogs. The conversion of aldol into sugar in phloridzinised dogs is possible, but owing to the high excretion of sugar and the small permissible amount of aldol administered (high toxicity), the extra sugar cannot be determined. The D/N ratio is not affected by these small amounts of aldol, and no increase in urinary β-hydroxybutyric acid occurs. Aldol must therefore either be burnt or built up into glycogen or fat. It does not appear to be detoxicated by combination with glycuronic acid. Organ pulp has the power to destroy aldol in large or small concentration, β-hydroxybutyric acid being in part formed; the activity of the organs decreases in the following order: liver, spleen, muscle of warm-blooded animals, muscle of cold-blooded animals. Aldol is very quickly destroyed on perfusion through a surviving tortoise. P. W. CLUTTERBUCK.

Importance of lipins in cell permeability. N. OKUNEFF (Biochem. Z., 1928, **198**, 296—310).—Lecithin and cholesterol are shown to be capillary-active at benzene–water and water–olive oil interfaces both when dissolved in the lipin solvent and when emulsified or suspended in water, the activity being in general greater in the former case. Lecithin is

considerably more active than cholesterol, especially at a water–benzene interface, concentrations of 1 in 400,000 still causing a lowering of surface tension. When trypan-blue is added to the aqueous layer and lipin simultaneously to the benzene or olive oil the surface tension developed at the interface is only that of the constituent which is most capillary-active at the concentration employed. P. W. CLUTTERBUCK.

Lipoid metabolism of the stomach. S. M. LING, A. C. LIU, and R. K. S. LIM (Chinese J. Physiol., 1928, **2**, 305—327).—Although subcutaneous injection of histamine results in a considerable increase in gastric secretion in dogs, the concentration of total fatty acid remains unchanged, whereas that of the lipoid phosphoric acid decreases. Calculation of the phospholipin fatty acid from the lipoid and acid-soluble phosphoric acid shows it to be only 9% of the total fatty acids. Phospholipin appears to be derived chiefly from the peptic secreting cells and the non-phosphorus fatty acid from the oxyntic cells. The total lipoid content of gastric mucosa before and after injection of histamine is constant, but the phospholipin content increases and the phosphorus-free fat decreases after injection.

The phospholipin fraction of mucosa lipoid appears to consist of lecithins and kephalins, since about 70% is fatty acid, and of these 50% are liquid fatty acids which become more unsaturated during activity.

L. C. BAKER.

Chloride metabolism of the stomach. C. L. HOU, T. G. NI, and R. K. S. LIM (Chinese J. Physiol., 1928, **2**, 299—303).—The average basal chlorine intake of the viviperfused stomach is 0·029 mg./g. of gastric mucosa per min. and is greater than can be accounted for by the amount in the basal secretion. Injection of histamine increases the chlorine intake two- to fifteen-fold, which is again greater than the secretion demands. Since the maximum intake is reached before the maximum output occurs, there is an accumulation of chlorine in the tissues, although as it falls the intake may finally be less than the output. L. C. BAKER.

Degradation of fatty acid in surviving dog's muscle. W. GRIESBACH (Z. ges. exp. Med., 1928, **59**, 123—132; Chem. Zentr., 1928, i, 1788).—The lower extremities and the liver of dogs were perfused with blood to which *iso*valeric and *n*-butyric acid were added. Only in liver perfusion were acetic and β-hydroxybutyric acids formed; the acids formed were rapidly decomposed when the liver perfusion blood was passed through the lower extremities.

A. A. ELDRIDGE.

Nitrogen metabolism of man after total resection of the stomach. L. SOLOVIEV (Biochem. Z., 1928, **199**, 121—135).—The removal of the stomach had no marked effect on protein assimilation or on the excretion of the chief products of nitrogen metabolism. After 6 months, nitrogen retention was observed and a progressive increase in body-weight. The proportion of bound sulphate to total sulphate in the urine was twice that of the normal subject.

J. H. BIRKINSHAW.

Decomposition of *d*- and *l*-alanine, glycyl-*dl*-alanine, and *dl*-alanylglycine by the organism of the dog. E. ABDERHALDEN and K. FRANKE (Fermentforsch., 1928, **10**, 39—49).—*d*-Alanine administered to a dog is completely decomposed, whilst *l*-alanine is only partly decomposed, part of it being excreted in the urine unchanged. From experiments in which *dl*-alanylglycine and glycyl-*dl*-alanine were administered it appears that the peptides containing *d*-alanine are utilised by the animal organism, whilst the peptides containing *l*-alanine are excreted in part unchanged. The observation was made that the lead salt of *d*- or *l*-alanine has an optical rotation greater than the original acid and opposite in sign. The same appears to be true for other α-amino-acids, whereas lead salts of dipeptides have an increased rotation but of the same sign as that of the original dipeptide. W. O. KERMACK.

Purinolytic enzymes of the leech (*Hirudo medicinalis*) and the fresh-water mussel (*Anodonta*). R. TRUSZKOWSKI (Biochem. J., 1928, **22**, 1299—1301).—From the determinations of purine-nitrogen before and after autolysis of the tissues of leeches and of fresh-water mussels, it is concluded that the end-product of their purine catabolism is xanthine, or hypoxanthine, or a mixture of the two.

S. S. ZILVA.

Absorption of uric acid by tissue. II. Relation between absorbed urate and concentration of perfusion liquid. S. LA FRANCA (Ann. Inst. Physiol., 1927, **29**, 291—297; Chem. Zentr., 1928, i, 1788).

Action of the sympathetic on the formation of ammonia in muscle. H. E. BUTTNER (Biochem. Z., 1928, **198**, 478—486).—The traumatic formation of ammonia in frogs is about 50% higher on the sympathectomised side than on the control and, on stimulating electrically, is about 60% greater on the denervated side. The resting ammonia values are not regularly increased after sympathectomy.

P. W. CLUTTERBUCK.

New aminophosphoric acid [in invertebrate muscle]. O. MEYERHOF and K. LOHMANN (Naturwiss., 1928, **16**, 47; Chem. Zentr., 1928, i, 1674—1675).—Argininephosphoric acid, analogous to creatinephosphoric acid in vertebrate muscle, is present in invertebrate (crab) muscle. The latter is less readily decomposed, especially at the neutral point, by the muscle enzyme, and at slightly alkaline reaction is more readily resynthesised from its components; it contains a free amino-group. The effect of increasing acid concentration and of catalysts (molybdate) on the rate of decomposition is reversed in the two cases. A. A. ELDRIDGE.

Transformation of phosphagen in muscle. O. MEYERHOF and O. NACHMANSOHN (Naturwiss., 1928, **16**, 726—727).—The reversible decomposition of phosphagens (guanidino-, creatine-, and arginine-phosphoric acids) has been shown to be concerned in muscle activity (cf. A., 1927, 75, 274, 990; this vol., 917). The decomposition is now shown to occur only or at least principally in the excitation process rather than in the contraction. The ratio of the amount of phosphagen decomposed to the amount of lactic acid formed is much reduced by curarising the

muscle. Paralysing the nerves with tetramethylammonium chloride further hinders the phosphagen decomposition; muscle treated in this way shows a transient decomposition on contraction, but resynthesis occurs practically completely on relaxation. Indirect confirmation of the view that the normal excitation process is intimately connected with the phosphagen decomposition is given by suspending muscle in a phosphate concentration higher than the inorganic phosphate content of the muscle itself; excitability and phosphagen concentration are thereby increased. R. A. MORTON.

Tryptophan and the thyroid gland. H. C. CHANG and W. C. MA (Chinese J. Physiol., 1928, **2**, 329—335).—Addition of tryptophan to the food of rats fed on a gelatin diet did not improve the condition of the thyroid gland, except in one case where the loss in body-weight was small. There was usually a loss in body-weight as in inanition and the appearance of the glands in both cases is similar. L. C. BAKER.

Determination of tryptophan and tyrosine in proteins: application to the most important food-proteins. J. TILLMANS, P. HIRSCH, and F. STOPPEL (Biochem. Z., 1928, **198**, 379—401).—A method is described for the determination of tryptophan and tyrosine in proteins, the protein being nitrated and the colour tones at two widely different being compared with those of solutions containing known amounts of these acids similarly nitrated. A table summarises the tyrosine and tryptophan contents of a large number of proteins along with the values obtained by the methods of other authors. The albumin and globulin fraction of human, cow's, and goat's milk contains about the same amounts of tyrosine and tryptophan, but the whey protein of human milk contains more tryptophan and less tyrosine than that of goat's and cow's milk. The tyrosine and tryptophan contents of the myosin of the muscle of different animals are about the same. The protein extractable by saline from wheat meal contains a large amount of tryptophan, but this is absent from zein. Considerable differences were obtained between the tyrosine and tryptophan contents of rye and wheat proteins. The globulin fraction of legumes contains 1—2% of these acids. Of the food proteins egg- and blood-albumins contain 4—5% of tyrosine, but other albumins and globulins have a low content (0·7—2%). Gliadin and glutelin have a high tyrosine content (5—8%). P. W. CLUTTERBUCK.

Muscle-protein. V. Nutritive value of the muscle-protein. 2. Amount of lysine in the muscle-protein and its effect on the growth of young rats. H. SEKINE (J. Imp. Fish. Inst., 1926, **22**, 42—43).—Experiments with proteins from *Oncorhynchus masou* and *Meretrix meretrix* indicate that the lysine, but not the tryptophan or histidine, content of muscle-protein is directly related to the growth of young animals. CHEMICAL ABSTRACTS.

Quantitative methods of measuring the nutritive value of proteins. H. H. MITCHELL (Biochem. J., 1928, **22**, 1323—1326).—Polemical. The author objects to Kon's statement (this vol., 324) that it is inherent in the author's method to give higher biological values in the periods immediately following the standardising nitrogen-free or low-nitrogen periods and also that the method is not a measure of the capacity of a protein to build new tissues. S. S. ZILVA.

Determination of coefficients of utilisation of foodstuffs. V. G. HELLER, C. H. BREEDLOVE, and W. LIKELY (J. Biol. Chem., 1928, **79**, 275—282).—The method of Bergeim (A., 1926, 1170) for determining the coefficients of utilisation of foodstuffs compares well with standard methods so long as the mixing of the ferric oxide with the diet be perfectly even; this is difficult to obtain, and since most diets contain sufficient iron for the purpose, the best results are obtained by applying the method of analysis of Bergeim without the addition of any extraneous iron. C. R. HARINGTON.

Effect of varying amounts of oxygen, anoxæmia, and anæsthetics on the sugar metabolism of animal cells. A. M. ESTES and W. E. BURGE (Amer. J. Physiol., Proc. Amer. Physiol. Soc., 1927, **81**, 474).—Experiments on paramœcia are described. CHEMICAL ABSTRACTS.

Lactic acid and carbohydrate in sea-urchin eggs under aerobic and anaerobic conditions. W. A. PERLZWEIG and E. S. G. BARRON (J. Biol. Chem., 1928, **79**, 19—26).—The mature unfertilised eggs of the sea-urchin, *Arbacia punctulata*, contain 2—5 mg. of lactic acid per g. of protein; this amount is considerably increased by treatment of the eggs with potassium cyanide, and a smaller increase is observed after fertilisation. No free reducing sugars were detected in the eggs, nor was glycogen isolated, but acid hydrolysis of the eggs yielded dextrose in amounts more than sufficient to serve as precursor for the lactic acid. C. R. HARINGTON.

Effect of certain electrolytes and non-electrolytes on permeability of living cells to water. M. MCCUTCHEON and B. LUCKE (J. Gen. Physiol., 1928, **12**, 129—138).—Permeability to water in unfertilised eggs of *Arbacia punctulata* is found to be greater in hypotonic solutions of dextrose, sucrose, and glycine than in sea-water of the same osmotic pressure. The addition to dextrose solution of small amounts of calcium or magnesium chloride reduces the permeability approximately to the value obtained in sea-water. Further addition of sodium or potassium chloride increases the permeability. E. A. LUNT.

Retarding action of metallic silver on the development of sea-urchin eggs. A. DRZEWINA and G. BOHN (Compt. rend. Soc. Biol., 1927, **97**, 1522—1524; Chem. Zentr., 1928, i, 1789).

Changes in the cholesterol content of rabbit's serum after intracardial injection of peptone. X. CHAHOVITCH, V. ARNOVLJEVITCH, and M. VICHNJITCH (Arch. Int. Physiol., 1927, **29**, 298—301; Chem. Zentr., 1928, i, 1786).—A fall in the cholesterol content is followed by persistently high values. A. A. ELDRIDGE.

Activity and toxicity of the vapours of the lower aliphatic alcohols. H. WEESE (Arch. exp. Path. Pharm., 1928, **135**, 118—130).—The narcotic and toxic action of the vapours of methyl, ethyl,

propyl, *iso*propyl, *n*-, *sec*-, *tert*.-, and *iso*-butyl alcohols have been investigated by ascertaining their action on white mice. W. O. KERMACK.

Toxic action of fatty acids in relation to the adaptation of the organism. J. BELEHRADEK and F. SCHWARZ (Bull. Soc. Chim. biol., 1928, **10**, 909—919).—The toxic action of normal fatty acids (formic to valeric) on *Anguillula aceti*, *Daphnia*, and the larvæ of *Rana fusca* and similar organisms is examined. The time of survival may be expressed as the reciprocal of a constant power of the concentration of the acid. The toxic action is apparently not determined by adsorption or by surface tension. G. A. C. GOUGH.

Alimentary glycæmia in phloridzin diabetes. Action of phloridzin on the liver. C. SCHWARZ and H. SASSLER (Biochem. Z., 1928, **198**, 250—258).—Blood-sugar values are tabulated for dogs over prolonged periods with normal diet, after phloridzin and fasting. Hypoglycæmia becomes strongly developed during administration of phloridzin to fasting animals, whilst in subsequent fasting the blood-sugar values rise again, but the glycogen-forming capacity of the liver is still disturbed, as is seen by the administration of a carbohydrate-rich diet, which causes a considerable glycæmia. P. W. CLUTTERBUCK.

Influence of section of the vagus and of morphine on the respiratory exchange. H. MELTZER and M. STEUBER (Arch. exp. Path. Pharm., 1928, **134**, 259—273).—Subcutaneous administration of morphine accelerates the breathing, decreases the absolute respiratory volume, strongly increases the alveolar carbon dioxide tension, and markedly decreases the intake of oxygen. W. O. KERMACK.

Influence of narcotics on the blood-sugar concentration. K. STEINMETZER and F. SWOBODA (Biochem. Z., 1928, **198**, 259—267).—All the narcotics (ether, morphine, chloral hydrate, "hedonal") investigated caused hyperglycæmia in dogs which on the average persisted for 6 hrs. and always lasted longer than the duration of narcosis. The mean blood-sugar was 30—50% above normal. Hyperglycæmia caused by small doses of chloral hydrate and "hedonal" persists for a considerable time. P. W. CLUTTERBUCK.

Effect of various substances of the quinine group on the enzymic functions of the organism. IX. Effect of quinine on the dynamics of carbohydrate and fat metabolism. I. A. SMORODINCEV (Biochem. Z., 1928, **197**, 160—169).—In general, carbohydrate metabolism is increased in the presence of quinine. The hydrolysis of starch is, in most cases, accelerated by quinine, but that of sucrose and of maltose is almost unaffected. At p_H 8·0 and higher quinine checks the hydrolysis of fats, but the process is accelerated if the medium in which it takes place is acid. Probably the inhibition is produced by adsorption of free quinine on the enzyme molecule, whilst the accelerating effect is due to the action of quinine salts. W. MCCARTNEY.

Effect of parasympathetic poisons on the blood-sugar. II. T. SAKURAI (J. Biochem. Japan, 1928, **8**, 365—370).—The combined effect of ergotoxin and pilocarpine is to lower the blood-sugar; the effect can be prevented by atropine. CHEMICAL ABSTRACTS.

Effect of illumination on the proteins of the lens of the eye. F. LIEBEN and P. KRONFELD (Biochem. Z., 1928, **197**, 136—140).—On illuminating lenses of fresh intact pig eyes with diffused daylight in the presence of a sensitising agent and with a quartz lamp with and without the presence of the agent no decrease in the tryptophan content of the proteins of the lenses could be observed. Under the same conditions, in solutions of the lenses in sodium hydroxide containing the equivalent of 0·5% of proteins, considerable destruction of tryptophan took place, but, since such destruction did not occur in solutions four times as concentrated, it may be assumed that the protein material in the lens is able to protect itself, by its high concentration, from chemical changes caused by light. Normal human lenses and lenses affected by cataract exhibit no differences in so far as the tryptophan content of their proteins is concerned. W. MCCARTNEY.

Influence of peroral and intravenous administration of radium bromide on the urinary C : N quotient. A. A. GOLDBLOOM (Biochem. Z., 1928, **197**, 14—19).—Daily peroral administration to rabbits of radium bromide increases the urinary C : N quotient, whilst single intravenous injections cause a gradually developing increase; in both cases this is mainly due to decrease of nitrogen excretion. There is great similarity between radium and radiothorium as far as their actions on metabolism are concerned. W. MCCARTNEY.

Prophylactic and sterilising properties of organic arsenicals and mercurials in syphilis. G. E. WAKERLIN and A. S. LOEVENHART (J. Pharm. Exp. Ther., 1928, **34**, 15—22).—One intravenous injection of the following drugs 24 hrs. after the inoculation of rabbits with *Treponema pallidum* showed their protective power to run parallel to their sterilising power; 25 mg./kg. of salvarsan, 40 mg./kg. of neosalvarsan, and 750 mg./kg. of tryparsamide afforded complete protection, 200 mg./kg. of proparsanol (monosodium salt of *p*-γ-hydroxypropylaminophenylarsinic acid) delayed symptoms 2 weeks and 30 mg./kg. of "flumerin" and 100 mg./kg. of sodium 1-mercuribis-3-nitronaphthalene-8-carboxylate did not protect. The determination of prophylactic power requires only 3 months, as against 8 months for sterilising power, and is therefore recommended for assessing the therapeutic efficacy of these drugs. L. C. BAKER.

Therapeutic action of organic mercurials in syphilis. G. E. WAKERLIN and A. S. LOEVENHART (J. Pharm. Exp. Ther., 1928, **34**, 23—28).—Mercuric salicylate shows definite healing power of syphilitic lesions in rabbits with 3 weekly intramuscular injections of 10 mg./kg. (one third of the tolerated dose), but little sterilising power, whilst the maximum dose tolerated affords no protection. Two doses of 15 mg./kg. (half the tolerated dose) and two of 7·5 mg./kg. of "flumerin" are effective in healing, but one fourth of the tolerated dose is much less effective; it has no sterilising or protective power. Sodium

1-mercuribis-3-nitronaphthalene-8-carboxylate shows no healing power in two doses of 25 mg./kg. and two of 50 mg./kg. (half the tolerated dose) and it has no sterilising or prophylactic properties.

L. C. BAKER.

Toxicity of lead compounds. F. BISCHOFF, L. C. MAXWELL, R. D. EVANS, and F. R. NUZUM (J. Pharm. Exp. Ther., 1928, **34**, 85—109).—Details are given for the preparation of colloidal suspensions of various lead compounds by adding the sodium salt of the particular anion required to a solution of lead chloride containing 1·5—2·0% of gelatin. The toxicity of lead given intravenously to rabbits depends entirely on the form of lead and four groups may be distinguished. Most toxic is ionic lead such as colloidal lead hydroxide, metallic lead, and lead glycerophosphate, oleate, and stearate, for which the lethal dose is 3—10 mg./kg. body-weight. To produce a fall in hæmoglobin comparable to that produced by a dose of ionic lead, two to four times that dose of colloidal lead oxychloride, oxycarbonate, or carbonate is necessary, 4—16 mg. being the lethal dose. Lead tetraethyl and lead triethyl chloride produce only a very slight fall in hæmoglobin even when the lethal dose, which, except in pregnancy, for lead tetraethyl is of the same order as for lead oxycarbonate and for lead triethyl chloride as for ionic lead, is approached. Tri- and di-lead phosphate and lead sulphide do not appear to affect the red cells nor does the first appear to be toxic. Lead phosphate and ionic lead are practically removed from the blood-stream in 2 hrs. Colloidal lead phosphate and lead tetraethyl seem suitable for trial in cancer therapy.

L. C. BAKER.

Toxicology of bismuth. R. FABRE and M. PICON (J. Pharm. Chim., 1928, [viii], **8**, 249—258, 297—308).—The distribution of bismuth in the organism after intramuscular and intravenous injection of an oil solution of bismuth camphocarbonate into dogs and rabbits has been examined. The method of destruction of the organs for bismuth determination is given and colorimetric and micro-electrolytic methods for the determination of bismuth are described and compared. Whatever method of injection is used most of the bismuth is found in the liver and kidneys and a notable proportion is present in the blood. The salivary secretion, teeth, and hair contain considerable amounts and evidently act as auxiliaries to the usual methods of elimination, especially in animals in which perspiration does not play a large part. The brain retains only a small amount of bismuth even after long treatment.

E. H. SHARPLES.

Structure and enzyme reactions. VII. The system glycogen–amylase–liver tissue. S. J. PRZYLECKI and J. WÓJCIK (Biochem. J., 1928, **22**, 1302—1306).—Liver tissue has an exceptionally high adsorptive action on glycogen which, as in the case of egg-white, is reversible, elution taking place when the concentration of glycogen in solution falls. The addition of protein to the system glycogen–amylase retards but does not inhibit the reaction of glycogenolysis. The biological reaction is: adsorbed glycogen $\rightleftharpoons$ free glycogen dextrose.

S. S. ZILVA.

Inter-relation of hydrogen-ion activity and concentration of salt in the activation of pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 2529—2535).—The above inter-relation was investigated for pancreatic amylase in presence of buffers of sodium phosphate, which salt, like sodium sulphate, does not influence the activity. The optimum hydrogen-ion activity depends on the nature and concentration of the salt, or salts, present. It decreases with increasing salt concentration until the latter reaches a certain value depending on the nature of the salt, beyond which the activity is practically uninfluenced. Sodium salts and potassium chloride were used.

S. K. TWEEDY.

Influence of concentration of neutral salt on the activation of pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 2535—2537).—The optimum concentrations for certain sodium salts and potassium chloride together with the corresponding optimum hydrogen-ion activities for pancreatic amylase are recorded. The activity of pancreatic amylase is favoured by more acid solutions in the presence of those salts which must be present in higher concentrations to produce complete activation.

S. K. TWEEDY.

Quantitative comparison of the influence of neutral salts on the activity of pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 2538—2543).—This comparison was made in the presence of chlorides of sodium, potassium, and lithium and several sodium salts, each at its optimum concentration. The anions have much more influence than the cations. If sodium sulphate, or more especially sodium nitrate, is added to amylase containing sodium chloride, the activity of the enzyme is diminished to an extent which increases as the concentration of the added salt is increased. The salt concentration necessary for producing the optimum hydrogen-ion activity seems to be independent of the concentration of the enzyme solution and of the starch present (2—4%). The presence of a neutral salt is essential to the activity of pancreatic amylase; its effect may be due to some influence on the colloidal state of the enzyme, since, except in the case of sodium sulphate, those neutral salts having the most favourable influence on the activity are also the most effective precipitating agents for proteins. In all probability the effect is the result of a specific reaction between the enzyme and the salt rather than of the influence of salt on the total ionic strength and activity of the solution.

S. K. TWEEDY.

Complement of the amylases. VI. H. PRINGSHEIM, J. BONDI, and E. THILO (Biochem. Z., 1928, **197**, 143—151).—In order that proteins may become energetic activators of the amylases it seems to be necessary for the proteins to undergo digestion with trypsin.

W. MCCARTNEY.

Glycogenase in fish muscle. I. T. OYA and K. SHIMADA (J. Imp. Fish. Inst. Tokyo, 1926, **22**, 24—28).—The action of glycogenase in muscle of

Scomber japonicus, *Paralichthus olivaceus*, and *Pagrosomus mayor* is optimal at p_H 7.

CHEMICAL ABSTRACTS.

Specific nature of invertase. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 406—418).—The sucrose-splitting enzymes in *Aspergillus oryzæ* (the source of taka-diastase), *A. niger*, *Penicillium glaucum*, and pigs' intestine are all capable of decomposing raffinose into melibiose and lævulose at rates which are of the same order as those observed in the hydrolysis of sucrose. There are therefore no grounds for assuming that the invertase of taka-diastase or the other materials mentioned represents a different type (gluco-invertase) from that present in yeast (fructo-invertase).

J. H. LANE.

Hydrolysis of sucrose by enzymes. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 539—542).—A more detailed account of work already published (this vol., 1157).

Preparation of substance taking part in the enzymic decomposition of dextrose to lactic acid (Meyerhof's "activator"). E. BRUNIUS and S. PROFFE (Z. physiol. Chem., 1928, **178**, 164—168).—A strain of top-yeast, treated according to Meyerhof's method (A., 1927, 590), yielded no substance capable of forming lactic acid from dextrose unless autolysis of the yeast was previously carried out in presence of dextrose. A second strain of bottom-yeast, however, did not need this preliminary treatment. The explanation of the difference is uncertain. A solution of the "activator" was found to possess undiminished activity after dialysis.

R. K. CALLOW.

Succinoxidase. II. Influence of phosphate and other factors on the action of succinodehydrogenase and the fumarase of liver and muscle. P. W. CLUTTERBUCK (Biochem. J., 1928, **22**, 1193—1205; cf. A., 1927, 693).—The fumarase activity of rabbit's liver pulp is about eight times that of the same weight of muscle pulp. An amount of the enzyme with an activity approximately equal to that of the tissue pulp itself can be removed from liver or muscle by steeping in water or 0·25% saline solution. Succinodehydrogenase could not be detected in these extracts, possibly because it became inactivated in the manipulation. After this extraction a further quantity of fumarase equal in activity to about six times the original pulp can be obtained from the muscle residue, but not from the liver residue, by elution with M/15-phosphate. 0·052M-Phosphate activates fumarase from muscle and liver, but not succinodehydrogenase. The temperature coefficient for fumarase activity of liver pulp is 2—2·4, and of muscle pulp 1—4, but the coefficient of the aqueous extract of the latter tissue is nearer normal. Sodium chloride inhibits the action of succinodehydrogenase considerably, but of fumarase only slightly. Sodium fluoride inhibits the action of fumarase considerably. The presence of fumarase has been detected in the muscle of *Pecten maximus* and *Anodonta cygnea*, but not in baker's yeast. It was present in the corpuscles but absent from the serum of fresh defibrinated blood. A very active fumarase solution is obtained by precipitating the phosphate extract of washed muscle with ammonium sulphate, filtering, and dialysing the solution of the precipitate.

S. S. ZILVA.

Specificity of the dehydrases. Separation of the citric acid dehydrase from liver and of the lactic acid dehydrase from yeast. F. BERNHEIM (Biochem. J., 1928, **22**, 1178—1192).—The finely-minced liver tissue is extracted with acetone and dried in a vacuum. The dried powder is extracted with water, the extract is dialysed and precipitated by half saturation with ammonium sulphate, leaving the hæmoglobin in solution, and the active precipitate is finally dissolved in water. A further yield of the enzyme can be obtained from the hæmoglobin solution by fully saturating with ammonium sulphate. The citric acid dehydrase thus prepared did not act with the sodium salts of the following acids as donators: succinic, malic, fumaric, lactic, tartaric, formic, glutamic, maleic, acetic, α-hydroxybutyric, oxalic, saccharic acids, or with acetaldehyde. It also did not utilise aconitic acid as a donator, but this compound, like citric acid, is capable of inhibiting the citric acid–enzyme system beyond certain concentrations.

The lactic acid dehydrase was prepared by treating baker's yeast with acetone, extracting the zymin thus obtained with M/15-disodium hydrogen phosphate for 4 hrs., and dialysing the active solution against distilled water. The enzyme is specific for lactic and α-hydroxybutyric acids. The following did not act as hydrogen donators: β-hydroxybutyric, malic, maleic, formic, citric, glutamic, succinic, fumaric, oxalic, acetic, tartaric, and pyruvic acids and acetaldehyde and dextrose. Pyruvic acid is the product of the action of the enzyme on lactic acid, but not on α-hydroxybutyric acid. Pyruvic, oxalic, and lactic acids inhibit the action of the dehydrase. Oxygen could not replace methylene-blue as a hydrogen acceptor, nor did the enzyme produce pyruvic acid when, instead of the dye, xanthine oxidase, hypoxanthine, and a concentrated solution of peroxidase were added to the system and oxygen was bubbled through the solution for several hours at 37°.

S. S. ZILVA.

Dehydrogenation of lactic acid. A. HAHN, E. FISCHBACH, and W. HAARMAN (Z. Biol., 1928, **88**, 89—90).—Washed, minced muscle in presence of methylene-blue as hydrogen acceptor was able to dehydrogenate lactic acid to pyruvic acid. Semicarbazide was used to protect the pyruvic acid from further oxidation by the formation of semicarbazone. The pyruvic acid was finally isolated and weighed as the phenylhydrazone.

J. H. BIRKINSHAW.

Dehydrogenation of malic acid. A. HAHN and W. HAARMAN (Z. Biol., 1928, **88**, 91—92).—Washed muscle in presence of methylene-blue was shown to dehydrogenate malic to oxalacetic acid, which was isolated as the semicarbazone. On hydrolysis of the latter the free acid formed lost carbon dioxide, giving pyruvic acid, which was isolated as the phenylhydrazone.

J. H. BIRKINSHAW.

Influence of intravenous injections of hepatocatalase on the catalase and anticatalase content of rabbit tissues. I. Catalase and anticatalase content of tissues from normal rabbits.

L. G. Belkina, L. L. Kremlev, and R. V. Falk. **II. Changes in the catalase and anticatalase content of blood and tissues following injection of massive doses of catalase into the blood.** L. G. Belkina and L. L. Kremler (Zhur. Exp. Biol. Med., 1928, **8**, 322—328, 329—341).—I. Considerable variations are observed. The order of catalase content is: blood, kidney, liver, spleen, lungs, heart, brain, muscles. The order of anticatalase content is nearly the same.

II. The injected catalase disappears completely in 3 hrs. The catalase accumulates chiefly in the kidneys and muscles. Anticatalase changes are not parallel with catalase changes.

Chemical Abstracts.

Oxidising enzymes. X. Relationship of oxygenase to tyrosinase. M. W. Onslow and M. E. Robinson (Biochem. J., 1928, **22**, 1327—1331).—The view of Pugh and Raper (this vol., 202) that, since tyrosinase has all the properties ascribed by Onslow to oxygenase, it seems unnecessary to retain the term oxygenase, is opposed. S. S. Zilva.

Tyrosinase of *Beta vulgaris*. R. Weidenhagen and F. Heinrich (Z. Ver. deut. Zucker-Ind., 1928, 499—538).—The tyrosinase–tyrosine reaction is best followed by the disappearance of tyrosine as determined by the bromine absorption method of Raper and Wormall. Haehn and Stern's rapid modification (A., 1927, 699) is not trustworthy, but the following gives good results. The test portion is heated with acetic acid, made alkaline without filtration, kept for 1 day, re-acidified, and the necessary potassium bromide added. On filtration a water-white liquid is obtained, in which the tyrosine can be readily determined. The tyrosinase–tyrosine reaction is not unimolecular, the velocity coefficient usually increasing with time. The velocity increases from p_H 5 to 8 in phosphate-buffered solutions. Borate buffers are unsuitable, as strong acidity is developed by boric acid in presence of dihydroxyphenylalanine, the first product of the reaction. Phosphate buffers exert an inhibiting effect at concentrations much above $M/15$. Tyrosinase is inactivated by heating in solution for 5—10 min. at 70—80°, and slightly weakened in 7 hrs. at 30°. The reaction proceeds more slowly at 40° or 30° than at 20°; in the former case the velocity coefficient decreases with time, indicating probable destruction of enzyme. The relative velocity is greater with low concentrations of substrate, but not in strict proportion, and at the highest concentration employed, 0·1% of tyrosine, the coefficient decreased with time. The time value for tyrosinase is defined as the time taken to bring about the disappearance of 50 mg. of tyrosine from a solution containing 100 mg. in 200 c.c. of phosphate buffer of p_H 6·81. Beet tyrosinase cannot be purified by precipitation by alcohol, or by adsorption on kaolin or alumina. It is precipitated with the proteins, but damaged by the use of metallic salts or tannin for this purpose. Precipitation with phosphotungstic acid (p_H 4·4), rapid separation and washing of the precipitate, and elution with very dilute ammonia (p_H 7·5—8) gives a 7·5-fold increase in activity calculated on the dry matter, with a 45% loss of total activity. Better results are obtained by treating beet slices with the phosphotungstic acid, and after washing and pulping, treating with dilute ammonia, evaporating in a vacuum, and dialysing. This treatment gives a forty-fold increase in the activity of the preparation. It is essential to use fresh material, and the use of rootlets from seed germinating in sand is recommended. The sap from these after dialysis shows a higher tyrosinase activity than the raw sap, apparently owing to removal of inhibiting impurities. F. E. Day.

Stalagmometric determination of lipases. B. J. Krijgsman (Natuurwetensch. Tijdschr., 1928, **10**, 137—144).—The apparatus and method of Rona and Michaelis (A., 1911, ii, 302) have been modified to permit of quicker and more accurate determination of lipase. An examination of the hydrolysis of tributyrin by lipase from the middle intestine of the snail, *Helix pomatia*, showed that at first the time required to hydrolyse a definite quantity of the fat was inversely proportional to the quantity of enzyme used. The quantity of fat hydrolysed was directly proportional to the time. Magnesium chloride had no influence on the speed of the reaction within the limits of concentration used. S. I. Levy.

Acceleration of lipase activity by substances containing vitamin-*A*. B. L. Johnson (Iowa State Coll. J. Sci., 1928, **2**, 145—153).—Addition of vitamin-*A* concentrates to a mixture of ethyl butyrate, lipase, and sea sand greatly increases the amount of butyric acid liberated. Sodium oleate and palmitate accelerate lipase activity. Chemical Abstracts.

Metaphosphatase. T. Kitasato (Biochem. Z., 1928, **197**, 257—258).—Sodium hexametaphosphate in 2% solution in the presence of 1·5% of takaphosphatase and toluene gives in 68 hrs. at 37° a yield of 20% of orthophosphate, whereas in this time a solution of the metaphosphate alone gives only traces of orthophosphate. This change can also be produced by animal organs (liver and kidney) and by yeast. W. McCartney.

Action of rennin on the proteins of milk. IV. Enzymes in the stomach contents of calves of various ages. J. Zaykovski, O. Fedorova, and V. Ivankin (Fermentforsch., 1928, **10**, 83—87).—Pepsin and rennin are both present in the stomach of embryonic calves. Both are increased in amount after birth, but pepsin proportionately more than rennin, from which it appears that rennin and pepsin are not identical. W. O. Kermack.

Nature of proteases. I. Behaviour of amino- and carboxyl groups in various pepsin preparations. J. A. Smorodincev and A. N. Adova (Z. physiol. Chem., 1928, **177**, 187—200).—A relationship was found to exist between the total nitrogen, the ratio of amino- to carboxyl groups, the amino-acid and polypeptide content, and the effect on the p_H of the solvent on the one hand and the proteoclastic action of various pepsin preparations on the other. The activity is directly proportional to the nitrogen, amino-nitrogen, and carboxyl group content. The ratio NH_2/CO_2H varies from 0·75 in strong to less than 0·5 in weak preparations, the ratio polypeptide-

CO_2H/amino-acid CO_2H varies from 2·64—3·41 in strong to 0·8—1·5 in weak preparations.

J. H. BIRKINSHAW.

Modification of Congo-red method for determination of pepsin. E. BEER and O. PECZENIK (Fermentforsch., 1928, **10**, 88—90).—A modification of the method of Kawahara (Arch. ges. Physiol., 1924, **206**, 360) for the determination of pepsin is described, consisting in the substitution of rose-bengal B for Congo-red. A solution of albumin coloured by rose-bengal B is not decolorised by the addition of hydrochloric acid. If, however, hydrolysis of the protein by pepsin is allowed to take place, the rose-bengal becomes decolorised when insufficient protein is left to keep it in the coloured form. By this modification the time required for a determination is reduced from 16 to 2—4 hrs. W. O. KERMACK.

Degradation of caseinogen, serum-globulin, and serum-albumin by dilute alkali, dilute acid, pepsin and hydrochloric acid, and pancreatic enzymes. E. ABDERHALDEN and W. KRONER (Fermentforsch., 1928, **10**, 12—35).—The hydrolyses have been followed using Sørensen's formol titration in order to determine the degree of decomposition which occurs after various periods of time. Albumin is split more slowly by alkali than is caseinogen or serum-globulin. *N*-Hydrochloric acid effects no detectable hydrolysis in the cases of caseinogen or of serum-globulin, although with these proteins the results are complicated owing to the precipitation of the proteins by the acid. Caseinogen is hydrolysed slowly by pepsin and hydrochloric acid, with the production of equal numbers of free amino- and of free carboxyl groups, whilst serum-albumin and especially serum-globulin are practically unattacked. Caseinogen and serum-globulin are extensively hydrolysed by pancreatic enzymes, whereas serum-globulin is unattacked. Protein previously treated with pepsin and hydrochloric acid is more extensively hydrolysed by *N*-sodium hydroxide solution than is untreated protein. Caseinogen after treatment with trypsin is more intensively hydrolysed than is fresh caseinogen, but serum-albumin is not affected by previous treatment. The action of *N*-hydrochloric acid is not greater on caseinogen and serum-albumin after the action of tryptic enzymes. Preliminary treatment with pepsin and hydrochloric acid increases the susceptibility of all proteins to tryptic digestion, a phenomenon particularly noticeable in the case of serum-globulin, which by the method used shows no evidence of decomposition by pepsin and hydrochloric acid, or by trypsin separately. Trypsin is also effective to some extent if the globulin is previously treated with 0·1*N*-hydrochloric acid alone. In the case of no protein is pepsin and hydrochloric acid rendered more effective by previous treatment with trypsin. Trypsin causes no increase in amino-nitrogen when it acts on serum-albumin or serum-globulin previously treated for a considerable time with *N*-sodium hydroxide solution and only a slight increase in the case of serum-globulin. W. O. KERMACK.

Action of erepsin and of trypsin-kinase on *l*-leucylpentaglycyl-*l*-tryptophan. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, **10**, 91—94).—l-*Leucylpentaglycyl*-l-*tryptophan* is hydrolysed by purified erepsin in such a way that no tryptophan is set free, whereas when this polypeptide is acted on by pure trypsin-kinase, tryptophan is liberated. α-Bromo*iso*hexoyltetraglycylglycine, decomp. 210°, $[\alpha]_D^{20}$ +12·21°, is converted into the acid *chloride* and allowed to react with *l*-tryptophan in dilute sodium hydroxide solution under definite conditions with the formation of *α-bromoisohexoylpentaglycyl*-l-*tryptophan*, and this is converted into l-*leucylpentaglycyl*-l-*tryptophan* by treatment with liquid ammonia at the ordinary temperature. This amorphous polypeptide begins to decompose at 135°, but has no definite m. p., is precipitated by mercuric salts and by phosphotungstic acid, and gives the biuret reaction. W. O. KERMACK.

Action of erepsin and trypsin-kinase on polypeptides containing *d*-glutamic acid. E. ABDERHALDEN and E. ROSSNER (Fermentforsch., 1928, **10**, 95—101).—The three new polypeptides, d-valyl-*l*-leucylglycyl-*d*-glutamic acid, *d*-alanyl-*d*-valyl-*l*-leucylglycyl-*d*-glutamic acid, and *l*-leucyl-*d*-alanyl-*d*-valyl-*l*-leucylglycyl-*d*-glutamic acid as well as the phenylcarbimide derivative of the last have been prepared and subjected to the action of purified erepsin and of trypsin-kinase. The tetrapeptide was almost completely resistant to erepsin, whilst the pentapeptide was slightly, and the hexapeptide considerably, attacked by that enzyme. All three polypeptides were hydrolysed by trypsin-kinase. The phenylcarbimide compound was not attacked by erepsin, but was definitely hydrolysed by trypsin-kinase. α-Bromo*iso*valeryl chloride and *l*-leucylglycylglutamic acid react in dilute sodium hydroxide solution with the formation of *α-bromoisovaleryl*-l-*leucyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +16° in absolute alcohol, which by the action of aqueous ammonia is converted into d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +11·4° in water. Similarly, d-*α-bromopropionyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +0·36° in alcohol, −18·2° in water, is converted by aqueous ammonia into d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{19}$ −10·7 in water, and d-*α-bromoisohexoyl*-d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{21}$ +12·6° in alcohol, is converted into l-*leucyl*-d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D$ −9·5° in water, which couples normally with phenylcarbimide to yield the *compound* $C_{34}H_{53}O_{10}N_7$.

W. O. KERMACK.

Proof of the enzymic nature of the phenomena underlying the Abderhalden reaction. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1928, **10**, 111—144).—Serum dried at a low temperature is treated with 87% glycerol, which extracts the enzymes responsible for the Abderhalden reaction. The enzymes can be purified by adsorption on kaolin or alumina followed by elution with ammonium phosphate solution. Of sera from cases of pregnancy 76% gave extracts showing the presence of enzymes, whilst of other sera none gave a positive result.

W. O. KERMACK.

Urease. M. JACOBY (Fermentforsch., 1928, **10**, 1—11).—Discussion and bibliography.

W. O. KERMACK.

Relation between protein and urease. H. ISHIBASHI (Bul. Sci. Fak. Terkult. Kjusu, 1928, **2**, 287—291).—Pepsin and trypsin produce from urease some amino-acid, and the activity of the urease is diminished, although not proportionally. Urease is closely related to proteins. CHEMICAL ABSTRACTS.

Influence of structure on the kinetics of desmolases. I. Uricase. Systems uricase–uric acid–active and inactive charcoal or protein. S. J. VON PRZYŁECKI (Z. physiol. Chem., 1928, **178**, 19—38).—See this vol., 1055.

Enzymes and biocatalysts in relation to adaptation and inheritance. I. Effect of iron-containing media on yeast. H. VON EULER and E. ERIKSSON (Z. physiol. Chem., 1928, **178**, 39—51).—Yeast was grown in media containing iron as ferrous sulphate, and the iron and the amino-, peptide-, and cyclic nitrogen contents, rate of fermentation, rate of reduction of methylene-blue, and oxygen absorption were measured. By growth in a succession of media containing ferrous sulphate the iron content of the yeast was raised to 0·04%. The rate of reduction of methylene-blue and the oxygen absorption decreased with increasing iron content. A decrease in the peptide-nitrogen appeared to take place, but was not definitely established. The rate of reduction of methylene-blue by normal yeasts treated with sulphur, hydrogen sulphide, or thiolactic acid was little affected. R. K. CALLOW.

Yeast amylase. A. GOTTSCHALK (Z. physiol. Chem., 1928, **178**, 139—147; cf. A., 1926, 759).—A juice poor in co-zymase, prepared by maceration of dried yeast, fermented glycogen very slowly in comparison with dextrose, showing that glycogen requires a relatively larger quantity of co-zymase. On the other hand, a juice rich in co-zymase, prepared by maceration of dried yeast with an extract of yeast by hot water, fermented glycogen more rapidly, but still at a lower rate than dextrose. The results were affected by the concentration of carbohydrate and by the age of the yeast. The induction period of the glycogen fermentation was longer. The aqueous extract supplies, in addition to co-zymase for the fermentation of the hexoses from glycogen, an activating agent for the action of the amylase. The amylase, as previously shown (*loc. cit.*), is extracted with difficulty from yeast, and the addition of a little of the residue from maceration accelerated the fermentation of glycogen considerably. Takadiastase fermented glycogen nearly as rapidly as dextrose, but the results obtained with saliva were similar to those with yeast amylase. Comparison was made of the autolysis of fresh yeast with that of yeast the structure of which had been destroyed by chemical or mechanical treatment. No difference was found, and it was concluded that the yeast-cell contained no excess of diastase adsorbed on the cell-wall. R. K. CALLOW.

Second form of fermentation of sugar under the influence of carbamic acid hydrazide and thiocarbamic acid hydrazide. Isolation of acetaldehyde and glycerol. M. KOBEL and A. TYCHOWSKI (Biochem. Z., 1928, **199**, 218—229).—Carbamic acid hydrazide and thiocarbamic acid hydrazide were used as interceptors of acetaldehyde in the second form of fermentation; yields of acetaldehyde up to 15% of the theoretical were attained. Acetaldehyde and glycerol were formed in equivalent amounts. Where the sulphur content of the mash prevented a direct determination of the glycerol by the original Zeisel–Fanto method the *iso*propyl iodide was absorbed in pyridine. The pyridine solution was treated with silver nitrate solution, strongly acidified with nitric acid, and boiled for 2—3 hrs. The excess of silver in solution was then determined by Volhard's method. J. H. BIRKINSHAW.

Supposed interception of methylglyoxal in alcoholic fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, **199**, 230—231).—Kostytschev and Soldatenkov (this vol., 923) have now retreated from their original position with regard to the isolation of methylglyoxal as the disemicarbazone, but still claim the isolation of pyruvic acid as the semicarbazone. This has been anticipated by several authors. J. H. BIRKINSHAW.

Difference between the processes of alcoholic fermentation and of acetaldehyde dismutation. C. NEUBERG and E. SIMON (Biochem. Z., 1928, **199**, 232—247).—Boiled suspensions of acetic bacteria capable of producing strong dismutation (*B. ascendens* and *B. pasteurianum*) were quite unable to replace co-zymase. When the suspension was added to a system of washed dried yeast (apo-zymase) and dextrose no fermentation occurred until co-zymase was added. Thus the view of Euler and Myrbäck (A., 1927, 484) that the initiator of fermentation (co-zymase) and the agent causing dismutation of acetaldehyde are of the same nature is not substantiated. J. H. BIRKINSHAW.

Co-zymase and its determination. K. MYRBÄCK (Z. physiol. Chem., 1928, **177**, 158—169).—Recent work casting doubt on the existence of Harden's co-zymase is criticised. According to the author the essentials for cell-free fermentation are: the enzyme system (apo-zymase); inorganic phosphate; small amounts of hexosediphosphate; co-zymase; a suitable acidity. For quantitative measurements of fermentation velocity the experiments must be carried out at constant temperature and the vessels shaken. J. H. BIRKINSHAW.

Mechanism of enzyme action. II. Action of ethylene. F. F. NORD and K. W. FRANKE (J. Biol. Chem., 1928, **79**, 27—51).—Treatment of a zymase solution (which could be preserved in the cold with unimpaired activity for 65 days), or of yeast suspensions with ethylene caused an increase in the ability to ferment dextrose; in the latter case the increase was observed after contact with ethylene during 1 min. only, and is regarded as being due to formation of a film of ethylene on the cells with increasing permeability of the latter. A similar increase in the activity of the catalase of tobacco leaves was found after treatment of these with ethylene. In the fermentation of pyruvic acid by yeast, preliminary ethylene treatment increased both the permeability

(and hence the enzymic activity of the yeast) and its power of resisting the harmful effects of high concentrations of the acid. C. R. HARINGTON.

Trehalosemonophosphoric ester isolated from the products of fermentation of sugars with dried yeast. R. ROBISON and W. T. J. MORGAN (Biochem. J., 1928, **22**, 1277—1288).—The *ester* $C_{12}H_{21}O_{11}\cdot PO_3H_2$, $[\alpha]_{5461}$ +185° (*barium* salt, $[\alpha]_{5461}$ +132°; *brucine* salt, $[\alpha]_{5461}$ +31°), was isolated from the products of fermentation of lævulose in presence of phosphate by zymin and dried yeast by fractional alcohol precipitation (30—70%) of the aqueous solution of the barium salts and by purification as the brucine salt. It is also produced by fermentation of dextrose in the presence of phosphates. It is non-reducing and from it the bone phosphatase liberates trehalose. Hydrolysis with boiling mineral acid slowly converts the ester into dextrose and dextrosemonophosphoric ester, the latter being still more slowly hydrolysed to dextrose and phosphoric acid. Barium dextrosemonophosphate was isolated, but in a slightly impure condition. Trehalosemonophosphoric ester is readily fermented by dried yeast and more slowly by yeast juice and zymin. The examination of dried yeast used in the fermentation showed that neither trehalosemonophosphoric ester nor free trehalose was present in quantities sufficient to account for the amount of the ester found in the fermentation products. This ester was not found in the products of fermentation by yeast juice.
S. S. ZILVA.

Alcoholic fermentation of sugars by acetic acid bacteria. C. NEUBERG and E. SIMON (Biochem. Z., 1928, **197**, 259—260).—When *B. ascendens* or *B. pasteurianum* was allowed to act, under anaerobic conditions, on a 1·2% dextrose solution typical alcoholic fermentation occurred, the yield of alcohol amounting to 25% of the theoretical quantity. Addition of sterile extract of bottom yeast doubled this yield. Since the amounts of alcohol and carbon dioxide produced were nearly equivalent and since only about 45% of the unfermented sugar was recovered, part of it had apparently been decomposed in some other way. W. MCCARTNEY.

Respiratory pigment, cytochrome, in bacteria. H. YAOI and H. TAMIYA (Proc. Imp. Acad. Tokyo, 1928, **4**, 436—439).—The absorption spectra of the respiratory pigment cytochrome have been examined microspectroscopically in a large number of strains of aerobic, facultative aerobic, and anaerobic pathogenic bacteria. The first class exhibit all four bands (*a*) (614—593 μμ), (*b*) (567—561 μμ), (*c*) (550 μμ), and (*d*) (532 and 521 μμ), the second show only (*b*) and (*d*) and occasionally (*a*), whilst the pigment is absent in anaerobic bacteria. In addition, in all strains of *B. dysenteriæ*, excluding the Shiga bacillus, and in *B. coli*, a new characteristic band at 623—637 μμ was detected. J. W. BAKER.

Formation of catalase by *Bacillus coli*. O. FERNANDEZ and T. GARMÉNDIA (Z. Hyg. Infekt.-Krankh., 1928, **108**, 329—335; Chem. Zentr., 1928, i, 1783).—In aerobic cultures of *B. coli* in synthetic media containing various sugars (2%) and amino-acids (0·5%), the formation of catalase depends on the sugar. It is particularly marked with lævulose in presence of alanine, asparagine, or glycine, and with tyrosine and ammonium lactate. With leucine, optimal catalase formation takes place in presence of galactose and dulcitol; with glutamic acid, in presence of sucrose. In anaerobic cultures peroxidase, but seldom catalase, is formed. A. A. ELDRIDGE.

Quantitative enzyme measurements with micro-organisms. II. Effect of some factors on the catalase content of bacteria. A. I. VIRTANEN and A. O. WINTER (Biochem. Z., 1928, **197**, 210—221).—The factors considered were: effect of hydrogen-ion concentration, effect of concentration of iron, effect of different sources of carbon and nitrogen, and effect of aerobic and anaerobic growth. Inconclusive results were obtained as regards the effect of concentration of iron, but catalase formation by *B. coli* is independent of the other factors. The great decrease in the catalase content of bacteria grown in media containing dextrose is due to destruction of the catalase resulting from the formation of acid. No agreement could be found with the general view that the catalase content of cells grown under aerobic conditions is greatly increased.
W. MCCARTNEY.

Sulphate-reducing bacteria in Californian oil waters. R. GAHL and B. ANDERSON (Zentr. Bakt. Par., 1928, II, **73**, 331—338; Chem. Zentr., 1928, i, 1783).

Oxidations by *Bacterium xylinum*. I. Formation of dihydroxyacetone from glycerol. K. BERNHAUER and K. SCHÖN (Z. physiol. Chem., 1928, **177**, 107—124).—A bacterium resembling *B. xylinum* can convert quantitatively glycerol into dihydroxyacetone. In order to prevent mould contaminations, it was found advisable to acidify the medium. Acetic acid was found to be superior to formic, propionic, and butyric acids for this purpose, the best concentration being 0·02—0·03*N*. The process gives the highest yields when the medium is in shallow layers (1—2 cm.) and contains not more than 6—8% of glycerol. J. H. BIRKINSHAW.

Biochemical nature of *B. paratyphosus B.*, Schottmüller, and *B. enteritidis*, Breslau, and a new differentiating medium for these. M. N. FISCHER and A. J. BUNTE (Biochem. Z., 1928, **198**, 428—441).—Autoclaving milk or Seitz's medium causes the condensation of amide-nitrogen with sugar, giving a humin-like substance the nitrogen of which is difficultly assimilable by micro-organisms, *B. paratyphosus*, Schottmüller, being probably unable and *B. enteritidis*, Breslau, able to assimilate it.
P. W. CLUTTERBUCK.

Pyocyanine, the blue colouring matter of *Bacillus pyocyaneus*. III. Constitution of hemipyocyanine. F. WREDE and E. STRACK (Z. physiol. Chem., 1928, **177**, 177—186).—In continuation of previous work (A., 1925, i, 844) the authors prepared a further quantity of hemipyocyanine by the action of sodium hydroxide solution on pyocyanine and purified it by sublimation. It had m. p. 158° and the formula $C_{12}H_8ON_2$. Its constitution as 1-*hydroxyphenazine* was proved by synthesis. The 1-methyl ether of pyrogallol was oxidised with lead peroxide in

benzene solution to the *o*-quinone and the latter treated with *o*-phenylenediamine in acetic acid. Condensation occurred with elimination of 2 mols. of water, the monomethyl ether of 1-hydroxyphenazine being produced. This was identical with hemipyocyanine monomethyl ether. It was demethylated by hydrobromic acid. J. H. BIRKINSHAW.

Influence of the medium on the growth of tubercle bacilli. V. M. KULIKOV and Z. I. NIKOLSKAJA (Zhur. exp. biol. Med., 1928, 8, 73—77).—Copper ions and guaiacol are much more toxic to tubercle bacilli in an alkaline than in an acid medium. CHEMICAL ABSTRACTS.

Chemotherapy of tuberculosis. I. E. HESSE, G. MEISSNER, and G. QUAST (Arch. exp. Path. Pharm., 1928, **135**, 82—110).—Certain dyes of the triphenylmethane, azine, and thiazine series show special affinity for the tubercle bacillus and stain the living organism. When tested under particular conditions certain of these dyes have marked bactericidal power. Experiments are described the aim of which is to correlate such results obtained *in vitro* with the chemotherapeutic activity of the dye administered to the animal organism. W. O. KERMACK.

Influence of ultra-violet radiation on some physico-chemical and biological properties of tuberculin. S. M. MIKHAILOVSKI (Zhur. Exp. Biol. Med., 1928, 9, 12—22).—The of solutions is shifted towards the acid side, and the surface tension increases. CHEMICAL ABSTRACTS.

Oxidation-reduction equilibria in biological systems. I. Reduction potentials of sterile culture bouillon. C. B. COULTER (J. Gen. Physiol., 1928, **12**, 139—146).—The time-potential curves of sterile culture bouillon during deaeration with nitrogen indicate a negative drift to −0·060 volt as a limiting value. It is suggested that this is due to the glutathione, from the chopped meat, acting as a catalyst in the oxidation of the muscle residue by molecular oxygen. E. A. LUNT.

Isoelectric state of bouillon containing toxin. A. S. RAEWSKY (Biochem. Z., 1928, **197**, 8—13).—The point at which the precipitate of maximum toxicity is obtained should not be regarded as the isoelectric point of the toxin itself, and the isoelectric points found by the author were those either of the proteins of the bacillus or of a compound of these with the proteins of the bouillon. The proteins of the nutrient medium, when they react with the proteins of the bacilli, displace the isoelectric point of the latter, the degree of displacement being proportinal to the amount of protein present in the medium. W. MCCARTNEY.

Diphtheria toxin. A. LEULIER, P. SÉDALLIAN, and J. GAUMONT (Compt. rend. Soc. Biol., 1927, **97**, 1543—1545; Chem. Zentr., 1928, i, 1973).—By acidification of the filtrate from bouillon cultures of the diphtheria bacillus with hydrochloric or acetic acid to p_H 4—7, a precipitate containing all the toxic principle is obtained. This is considered to be a nucleoprotein; it contains 0·5—1·5% P. A. A. ELDRIDGE.

Action of adrenaline. I. Carbohydrate metabolism of fasting rats. II. Carbohydrate metabolism of rats in the post-absorptive state. III. Utilisation of absorbed dextrose. C. F. CORI and G. T. CORI (J. Biol. Chem., 1928, **79**, 309—319, 321—341, 343—355).—I. During the second 24 hrs. of a fasting period, the total glycogen content of rats is decreased by only 22 mg.; the authors explain this small deficit on the basis of intermediary formation of sugar from fat in the course of oxidation, a process distinct from true gluconeogenesis in which the sugar newly formed is stabilised in the body. Injection of adrenaline into 24-hr. fasting rats produced a rise in oxygen consumption, but no change in the respiratory quotient; the liver-glycogen was increased and the muscle-glycogen decreased by a more than equivalent amount. In view of the facts that oral administration of lactic acid leads to increased deposition of glycogen, and that the disappearance of muscle-glycogen could not be accounted for by oxidation, it is thought that the action of adrenaline may involve the degradation of muscle-glycogen to lactic acid, and the re-synthesis of the latter into liver-glycogen.

II. Whilst in the normal rat in the post-absorptive state the glycogen which disappears from the animal is derived partly from the liver and partly from the muscles, after injection of adrenaline the whole of the glycogen disappearing comes from the muscles, and after insulin a larger proportion comes from the liver than in the normal. The hyperglycæmia following adrenaline administration is due in part to mobilisation of muscle-glycogen and in part to diminished utilisation of blood-sugar; in the latter respect, therefore, adrenaline and insulin are directly antagonistic.

III. The above hypothesis is confirmed by the observation that rats injected with adrenaline fail to utilise as much dextrose (both by oxidation and by conversion into liver-glycogen) after feeding with dextrose as do normal animals. The extra heat production of the adrenaline-treated rats is accounted for entirely by oxidation of fats. C. R. HARINGTON.

Relation between concentration and action of adrenaline. D. WILKIE (J. Pharm. Exp. Ther., 1928, **34**, 1—14).—The isometric and isotonic response to adrenaline of strips of sheeps' carotid arteries, prepared by cutting 5 mm. rings of the artery longitudinally, may be expressed by the formula $Kx=y/(A-y)$, where x is the concentration of adrenaline, A maximum response, y response produced, and K is a constant. The arterial flow, rise in blood-pressure, and cardiac frequency are also fairly well expressed by this formula. L. C. BAKER.

Action of insulin. IV. Effect on the metabolism of the tortoise. B. V. ISSEKUTZ and F. V. VEGH (Magyar Orvosi Arch., 1928, **29**, 1—7).—Insulin increases the oxygen consumption and carbon dioxide production. The respiratory quotient does not change. CHEMICAL ABSTRACTS.

Action of insulin. I and II. H. HANDOVSKY (Arch. exp. Path. Pharm., 1928, **134**, 324—338, 339—346).—I. Administration of insulin to rabbits causes a decrease in the carbohydrate present in the muscle and particularly in the muscle-glycogen.

II. The action of insulin is greater in animals to which calcium dithioglycollate has been administered

than in untreated animals. It is suggested that the sulphydryl group of insulin plays an important part in its action. W. O. KERMACK.

Pancreatic hormone and mineral metabolism. I. Influence of the pancreatic hormone on the excretion of different urinary constituents (particularly inorganic salts) by normal and by pancreas-diabetic dogs. S. TAKEUCHI (Tôhoku J. Exp. Med., 1928, **10**, 388—407).—Subcutaneous injection of pancreatic hormone into dogs increased the daily excretion of chlorine, potassium, and nitrogen. In two depancreatised dogs the daily quantity of urine, phosphorus, chlorine, calcium, magnesium, potassium, sodium, nitrogen, sulphate, and sodium/potassium ratio were decreased and the phosphoric acid/nitrogen ratio was increased by injection of the hormone. CHEMICAL ABSTRACTS.

Relation between hormonal and enzymic phenomena in the mechanism of regulation of the carbohydrate metabolism. V. A. ENGELHARDT and A. N. PARSHIN (Zhur. exp. biol. Med., 1928, **8**, 573—580).—Fatal doses of insulin caused an average increase of only 10% in the blood-amylase. CHEMICAL ABSTRACTS.

Physiological changes of the inner secretion of the pancreas. I. Proof of the existence of a physiological insulinæmia. II. Vagus as nerve inducing insulin secretion. III. Rôle of the nervous system in regulation of physiological insulinæmia. J. LA BARRE. **IV. Hyperinsulinæmia after hyperglycæmia caused by injection of dextrose. V. Hyperinsulinæmia after injection of adrenaline.** E. ZUNZ and J. LA BARRE (Arch. Int. Physiol., 1927, **29**, 227—290; Chem. Zentr., 1928, i, 1785).

Hormonal action of dextrose on production of insulin. E. GEIGER (Arch. exp. Path. Pharm., 1928, **134**, 317—323).—A sodium chloride or urea solution isotonic with 60% dextrose solution is as effective as the latter in stimulating the production of insulin by the pancreas. The conclusions of Grafe and Meythaler (A., 1927, 1115; cf. this vol., 925) that dextrose specifically stimulates the production of insulin is not rigorously proved. This conclusion is supported by the fact that if dextrose is administered in a concentration isotonic with blood no stimulation of insulin production is apparent. W. O. KERMACK.

Destructive action of heat on insulin solutions. A. KROGH and A. M. HEMMINGSEN (Biochem. J., 1928, **22**, 1231—1238).—The destruction of insulin at a constant temperature follows fairly well the law of unimolecular reactions. The relation of rate of destruction to temperature can be expressed by the formula of Arrhenius. The critical thermal increment amounts to 28,300. The rate of destruction is not appreciably altered by changes in the p_H between 2 and 4. S. S. ZILVA.

Behaviour of the urinary C : N quotient following parenteral administration of extract of the anterior lobe of the pituitary body. A. A. GOLDBLOOM (Biochem. Z., 1928, **197**, 20—30).—The chief effect produced is a limitation of the oxidations, but the extract also has a certain hyperoxidising function. Almost always there is increase in the amount of dysoxidisable carbon in the urine, whilst the nitrogen generally increases in amount with small doses but decreases with large ones. W. MCCARTNEY.

Carbon- and oxidation-quotients of urine after injection of "praephysone." A. A. GOLDBLOOM (Biochem. Z., 1928, **199**, 202—206).—Rabbits receiving a daily subcutaneous injection of "praephysone" (extract of anterior lobes of the pituitary corresponding to 0·66 g. of fresh organ) showed a general increase in both carbon- and oxidation-quotients, but the increases were irregular. J. H. BIRKINSHAW.

[Lack of] effect of pituitary preparations on phosphorus and calcium metabolism. F. NAKAZAWA (Biochem. Z., 1928, **198**, 350—361).—In dogs which have been fed on a diet of sugar, starch, fat, and salts sufficient calorifically but practically free from nitrogen, calcium, and phosphorus, the daily excretion (urine and fæces) of phosphorus is 14—26 mg./kg. and of calcium 2—6 mg./kg. Subcutaneous injection of various pituitary preparations did not affect the excretion of phosphorus and calcium. P. W. CLUTTERBUCK.

Parallelism in behaviour of the pancreatic secretin and of enterokinase at the b. p. I. P. RASENKOW (Fermentforsch., 1928, **10**, 72—77).—From the observation that the behaviour of enterokinase and secretin at the b. p. under various conditions of reaction shows very great similarity, it is considered possible that these two substances are identical. W. O. KERMACK.

Influence of boiling on pancreatic secretin. I. P. RASENKOW (Fermentforsch., 1928, **10**, 78—82).—Secretin resembles enzymes in that under certain conditions it is largely destroyed by boiling. W. O. KERMACK.

Tissue respiration. IV. Influence of thyroxine, adrenaline, and insulin on the oxygen consumption of surviving liver-cells. H. REINWEIN and W. SINGER (Biochem. Z., 1928, **197**, 152—159).—Both thyroxine and commercial extract of thyroid gland cause increase in the oxygen consumption of surviving liver-cells. Adrenaline in concentrations above 10^{-5} checks the consumption of oxygen by the cells, and there is no stimulating effect on the consumption even at the lowest concentrations. In high concentrations insulin has a damaging effect on tissue respiration, and an increase, due to insulin, in the respiratory activity of surviving liver-cells is never observed. W. MCCARTNEY.

Thyroid and tissue respiration. M. MAEDA (Fol. pharmacol. japon., 1927, **3**, 796—824).—The thyroid hormone promotes tissue respiration of almost all organs except the thyroid. CHEMICAL ABSTRACTS.

Thyroid gland and mineral metabolism. Influence of disodium hydrogen phosphate and calcium salts on the action of the thyroid. I. ABELIN (Biochem. Z., 1928, **199**, 72—106).—The action of thyroid substances on the basal metabolism of the rat is increased by phosphate and diminished by calcium, although these have no

effect without thyroid. The over-excitability caused by thyroid feeding is diminished by calcium. Glycogen formation by the liver can often be maintained, in spite of thyroid administration, if calcium is supplied, preferably as carbonate; the chloride is unsuitable. Attention is directed to the old lime theory of goitre, since there is actually an antagonism between thyroid gland function and excess of calcium.

The action of adrenaline on the basal metabolism is not noticeably influenced by calcium.

J. H. Birkinshaw.

Role of the iodine component of the thyroxine molecule. B. Zavadovski, N. Raspopova, T. Rolitch, and E. Umanova-Zavadovski (Zhur. exp. biol. Med., 1928, **8**, 600—611).—The minimum quantity of iodine necessary to produce metamorphosis in axolotls (8—15 g.) is 0·5 mg., and of thyroxine 0·003—0·010 mg. Di-iodotyrosine cannot replace thyroxine; hence it is doubtful if the former is an intermediate in the synthesis of the latter. Chemical Abstracts.

Extraction of ovarian hormone. II. S. Thayer, C. N. Jordan, and E. A. Doisy (J. Biol. Chem., 1928, **79**, 53—64).—The ovarian hormone is readily destroyed by traces of peroxides; it is necessary therefore that the ether and light petroleum employed in its extraction (A., 1926, 1064) should be free from these compounds, and that the stages of the preparation involving the use of these solvents should be carried through as rapidly as possible. A clear aqueous solution of the hormone may be obtained by diluting the concentrated alcoholic solution of the purified material with water, distilling off the alcohol, flocculating the colloidal impurities by addition of a little hydrochloric acid, and finally filtering through asbestos. Crude extracts are stable in ethereal solution, but the purified material deteriorates more or less rapidly in solution in ether or light petroleum; the more active preparations are best stored in aqueous or alcoholic solution, in which, provided that no oxidising agent be present, they are stable at least for 3—4 years. C. R. Harington.

Avitaminosis. VIII. Influence of avitaminosis of normal and thyroidectomised rabbits on the nitrogen-, creatine-, and creatinine-excretion and on the blood-sugar. A. Palladin, A. Utewski, and D. Ferdmann (Biochem. Z., 1928, **198**, 402—419).—Thyroidectomised rabbits when placed on a diet free from vitamins develop the usual symptoms of avitaminosis, and the duration of life and the course of the blood-sugar curve are the same as with normal rabbits on the same diet. The excretion of nitrogen by thyroidectomised rabbits in avitaminosis is lower than for non-operated animals under the same conditions. Creatine appears in the urine of thyroidectomised animals in avitaminosis 2—3 days, and in non-operated animals 1·5—2 weeks, before death. P. W. Clutterbuck.

Rickets in rats. VII. Calcium and phosphorus metabolism of rats on non-rachitic diets. A. T. Shohl, H. B. Bennett, and K. L. Weed. **IX.** p_H **of the fæces.** A. T. Shohl and F. C. Bing (J. Biol. Chem., 1928, **79**, 257—267, 269—274).—VII. To a basal rachitic diet were made graded additions of phosphates and vitamins-*A* and -*D*, and the behaviour of young rats on the various diets so produced was observed. The gradual improvement in the quality of the diet was accompanied by increased intake of food, resulting in better growth, and there was increased retention of calcium and phosphorus with improved histological condition of the bones.

IX. The cure of rickets in rats by agents other than cod-liver oil is not necessarily accompanied by change in the p_H of the fæces from alkaline to acid (cf. Jephcott and Bacharach, this vol., 332).

C. R. Harington.

Protein and vitamin-*B*. G. A. Hartwell (Biochem. J., 1928, **22**, 1212—1220).—Many young rats die on a diet containing 20% of edestin and 5 g. of yeast extract per 100 g. of dry solid, showing typical kidney abnormality. Older rats are not affected by this diet. These symptoms can be prevented by the addition of more yeast extract to the diet. The "protective" factor in yeast extract is not destroyed by autoclaving at 120° for 4½—5 hrs. Edestin requires more yeast extract than either caseinogen or egg-albumin for normal metabolism in young growing rats. S. S. Zilva.

Minimum amount of vitamin-*D* required for a positive antirachitic effect in the "line" test. K. H. Coward (Biochem. J., 1928, **22**, 1221—1222).—The daily dose which gives this positive result is 2×10^{-5} mg., which confirms the prediction of Fosbinder, Daniels, and Steenbock (this vol., 557).

S. S. Zilva.

Photochemical activation of sterols in the cure of rickets. II. S. K. Kon, F. Daniels, and H. Steenbock (J. Amer. Chem. Soc., 1928, **50**, 2573—2581).—Cholesterol purified by fractional oxidation with permanganate in acetone cannot be activated antirachitically by irradiation (cf. Bills, Honeywell, and McNair, this vol., 332). The results of Bills (A., 1926, 645) on activation by means of "floridin" are confirmed. The photochemical formation of vitamin-*D* from ergosterol has been studied quantitatively (cf. this vol., 557). The minimum amount of radiation necessary to produce sufficient vitamin to cause deposit of calcium in the bones of a rachitic rat is 700—1000 ergs, corresponding with the formation of 6×10^{-8} g. of vitamin-*D*. For monochromatic light from the mercury lines 256, 265, 280, and 293 μμ, the quantum efficiency is independent of the wave-length and of the continuous or intermittent nature of the irradiation. The same value is obtained with ergosterol, solid or in alcoholic solution, and with ergosteryl acetate. The quantum efficiency of ordinary cholesterol is variable and may be nearly as high as that of ergosterol. H. E. F. Notton.

Irradiation of ergosterol. T. A. Webster and R. B. Bourdillon (Biochem. J., 1928, **22**, 1223—1230).—Ergosterol was irradiated at 77·8°, 30·6°, 1°, −18°, −183° (approx.), and −195° (approx.). With the exception of the products obtained at the last two temperatures, which were less active, all the activated products showed about equal activity. 0·1% Solutions of ergosterol irradiated by rays which were passed through a filter which cut off all rays of

wave-length shorter than 265 $\mu\mu$ showed a maximum activity after exposure for 1 or 4 hrs., whilst after 63 hrs. they were less than one quarter as active. The products remaining after removal of unchanged ergosterol by precipitation with digitonin show strong absorption for wave-lengths shorter than 290 $\mu\mu$ with no maximum between 265 and 280 $\mu\mu$, in contrast to ergosterol and other products which have a maximum between 300 and 330 $\mu\mu$. The absorption is much greater than that of ergosterol. Ergosterol examined after short periods of irradiation shows an increase in absorption which is at a maximum after a period depending on the concentration of the solution and on the intensity of radiation. On further irradiation the absorption decreases steadily to almost complete disappearance. The antirachitic activity and absorption are produced at approximately the same rate. On further irradiation of active products after the removal of ergosterol, the antirachitic activity and absorption decrease and eventually disappear entirely after irradiation for 3—5 hrs. The irradiation of ergosterol probably produces two substances in succession, one with maximum absorption at 280 or 290 $\mu\mu$ and a second with a maximum at about 230 $\mu\mu$, the former of which is probably vitamin-*D*. S. S. ZILVA.

Factor *H* in the nutrition of trout. C. M. McCAY and W. E. DILLEY (Trans. Amer. Fish Soc., 1927, **57**, 250—260).—Fresh meat contains a thermolabile factor (*H*) which is essential for life and growth. Raw liver (5%) causes marked increase in growth. Lactose cannot replace starch. The factor in liver responsible for growth is different from that concerned in blood regeneration.

CHEMICAL ABSTRACTS.

Spectrophotometric studies of penetration. IV. Penetration of trimethylthionine into *Nitella* and *Valonia* from methylene-blue. M. IRWIN (J. Gen. Physiol., 1928, **12**, 147—165).—Spectrophotometric measurements indicate that the dye present in the sap extracted from uninjured cells of *Nitella flexilis* and *Valonia macrophysa* which have been placed in methylene-blue solution, is chiefly trimethylthionine. The mechanism of the penetration is discussed. E. A. LUNT.

Photo-oxidation with anthraquinone. K. PFEILSTICKER (Biochem. Z., 1928, **199**, 8—11).—Anthraquinone in the light acts as oxygen carrier, the carbonyl groups becoming reduced to carbinol. On shaking with air the anthraquinone is regenerated. This action can also occur in the dark with dextrose as oxygen acceptor. J. H. BIRKINSHAW.

Theory of photo-synthesis. K. PFEILSTICKER (Biochem. Z., 1928, **199**, 12—20).—The view is held that chlorophyll-*B*, activated by four quanta, produces electrolysis of aqueous protein–carbon dioxide solution. Two carbonyl and two methine groups add on four hydrogen atoms, and a hydrogen carbonate and three hydroxyl ions are electrically discharged at the magnesium anode. Dipercarbonic acid is formed which decomposes catalytically, giving formaldehyde and oxygen. The chlorophyll-*A* regenerates chlorophyll-*B* with the formation of hydrogen peroxide from which catalase liberates oxygen.

J. H. BIRKINSHAW.

Maintenance of seeds in a medium deprived of oxygen as a means of prolonging their germinative faculty. A. GUILLAUMIN (Compt. rend., 1928, **187**, 571—572).—An atmosphere from which oxygen has been removed is as efficient as a vacuum for the purpose of prolonging the germinative faculty of seeds (soya). J. GRANT.

Angiosperm seeds and factors in germination. III. Surface-active substances. A. NIETHAMMER (Biochem. Z., 1928, **199**, 175—185).—Various seeds were shown to contain saponins. The influence of saponin substances on the germination of saponin-containing and of saponin-free seeds was examined, but no marked differences were found between the two types. The action of various alkaloids was also tested. J. H. BIRKINSHAW.

Enzyme content of germinating wheat. N. PROKOPENKO (Nauch. Agron. Zhur., 1927, **4**, 346—354).—Catalase, peroxidase, and amylase values were determined. CHEMICAL ABSTRACTS.

Carbohydrate metabolism and its relation to growth in the edible canna. J. C. RIPPERTON (Hawaii Agric. Exp. Sta. Bull., 1927, **56**, 1—35).—The distribution of sugars in the leaves, stem, and root is recorded. The hexoses are considered to be sugars of translocation and the starch in the rootstocks to be formed from sucrose.

CHEMICAL ABSTRACTS.

Nutrition of plants with aldehydes. VIII. T. SABALITSCHKA (Biochem. Z., 1928, **197**, 193—196).—The author discusses results communicated in the previous papers and comments on the views of Bodnar and co-workers (this vol., 207).

W. McCARTNEY.

Enzymic oxidation of oxalic acid by higher plants. V. ZALESKI and A. KUCHARKOVA (Ukraine Chem. J., 1928, **3**, 139—152).—The velocity of aerobic or anaerobic oxidation of oxalic acid by wheat seeds, as measured by the quantity of carbon dioxide produced, is unaffected by the addition of hydrogen acceptors, such as methylene-blue, potassium nitrate, or hydrogen peroxide, whilst quinone and quinol have a distinctly inhibitory influence on oxalase, the enzyme responsible for this oxidation. The inhibitory action of the latter is due probably to their greater affinity for oxygen, the supply of which is thereby greatly diminished for the oxidation of oxalic acid. Cyanides and ethylurethane do not inhibit the action of this enzyme, showing that neither surface action nor active centres containing iron are responsible for its action. Potassium iodide has a marked inhibitory influence, probably as a result of combination with the enzyme. It is concluded that, in spite of the above observations, oxalase is a dehydrogenase, able to use only molecular oxygen as a hydrogen acceptor. R. TRUSZKOWSKI.

Carbohydrate transformations in carrots during storage. H. HASSELBRING (Plant Physiol., 1927, **2**, 225—243).—On storage at 0—14° inversion of sucrose and hydrolysis of dextrins and hemicelluloses took place; little change took place after 10 weeks. CHEMICAL ABSTRACTS.

Losses in mangels during storage. G. T. Pyne (J. Dep. Lands Agric. Ireland, 1927, **27**, 33—35).—The losses (5 months) were: water 8·8, dry matter 27·0, protein 22·2, fibre 3·8%. The sucrose decreased 29·5% during 2 months. Chemical Abstracts.

Origin of camphor in camphor trees. T. Yahagi (Japan. J. Chem., 1928, **3**, 109—129).—The different parts of the camphor tree have been chemically examined at various stages of growth. It is shown that the formation of camphor, and of the oil of which it is the chief constituent, takes place, even in the earliest stages of growth, in nearly all tissues of active growth, especially just beneath the cambial layer. The sap, however, contains no appreciable amount of camphor. The rate of formation of camphor and oil is very closely related to the growth of the tree; the more vigorous the growth the more rapid is the rate of formation. Once the formation of oily matter is started in the cell it proceeds fairly rapidly until the cell is filled with camphor products. The lining of the oil cells has been shown to contain an enzyme, of the nature of a peroxidase, which appears to be responsible for the formation of the oil and disappears when the cell is full of oil. The peroxidase lining has been found in the cells of other oil-bearing plants. M. S. Burr.

Flower coloration and nitrogen fertilisation. M. von Wrangell and H. von Bronsart (Naturwiss., 1928, **16**, 169—172; Chem. Zentr., 1928, i, 1973).—Unlike that of leaves, the colour of flowers is not markedly brightened by nitrogen fertilisation. A. A. Eldridge.

Behaviour of cyanogenetic glucosides of cherry laurel during starvation. H. Godwin and L. R. Bishop (New Phytol., 1927, **24**, 295).—The cyanogenetic glucosides represent a fairly large fraction of the stored carbohydrate of the leaves. During starvation, the glucoside disappears, the rate of disappearance becoming maximal, and then decreasing. Protoplasm is present as gel in young cells; hence the available water at enzyme centres may be so small that accumulation of enzyme results. Chemical Abstracts.

Relation of boron to the growth of the tomato plant. W. H. Dore (Science, 1928, **67**, 324—325).—The presence of boron is essential for the normal growth of tomato plants. Plants deficient in boron exhibit an excessive accumulation of sugar in the leaves, which become purple. A. A. Eldridge.

Influence of sulphur on the nitrogen and phosphoric acid utilisation of plants. A. Kalushski (Nauch. Agron. Zhur., 1927, **4**, 643—656).—By addition of 0·03—0·04% S the p_H of soil was changed from 7 to 6·6—6·8. Utilisation of nitrogen, and particularly of phosphoric acid, was increased. Chemical Abstracts.

Nitrate reduction by plant roots. A. Schmuck (Nauch. Agron. Zhur., 1927, **4**, 155—170).—Marked reduction of nitrate to nitrite takes place in the root substrate. Aromatic nitrogen compounds are also reduced. Chemical Abstracts.

Effect of light on nitrate assimilation in wheat. W. E. Tottingham and H. Lowsma (J. Amer. Chem. Soc., 1928, **50**, 2436—2445).—Comparative experiments show that the absorption of nitrate and the synthesis of protein by maize in water-cultures is decreased by the removal from sunlight of those rays which are absorbed by ordinary greenhouse glass. The growth of wheat in sand- or water-cultures has been followed at a total intensity of illumination of 200—8000 ft.-candles, using various distributions of spectral energy. When the blue, violet, and long ultra-violet rays of the tungsten lamp are increased some 50—400% by the use of carbon arcs, absorption of nitrate and, to a smaller extent, synthesis of protein are increased, whilst sugar content and total dry matter are decreased. The same effects are observed when an intensity of illumination greater than that required for maximum tissue formation is employed. Using as standard this combined illumination from which light of lower wave-length than 4000 Å. has been excluded, the effect of successive extensions of the spectrum into the ultra-violet are: 4000—3700 Å., no change; 3700—3000 Å., increase in absorption, but not in assimilation of nitrates; 3000—2800 Å., decrease in formation of tissue and protein. H. E. F. Notton.

Microchemistry of *Illicium verum*, Hook, and *I. religiosum*, Sieb. E. Siersch (Pharm. Zentr., 1928, **69**, 581—585, 601—605).—The crystals obtained by extraction with solvents of the carpel and seeds of *I. verum* and *I. religiosum* have been examined microchemically and their solubilities and colour reactions are described. Shikimic acid, m. p. 184°, was isolated from the carpel of both plants, but those from *I. verum* contained much smaller quantities than those of *I. religiosum*. The acid could not be detected in the seeds of either plant but from the seeds of *I. religiosum* a crystalline substance was isolated which agreed in colour reactions with the shikimin of Eykman (A., 1891, 919). Combe's saponin reaction indicated the presence of a saponin in the fruits of *I. religiosum* but in much smaller amount than in *I. verum*. E. H. Sharples.

Seed of *Euphorbia verrucosa*, Jacq. P. Gillot (Mat. grasses, 1928, **20**, 8166—8168).—The seed contains: water 8·84, fat 25·74, crude protein 21·12, nitrogen-free extract 1·30, ash 5·80, crude fibre 37·20%. Cold-pressed oil has α (200 mm.)+0° 10′, d_{15}^{15} 0·9356, n^{22} 1·4855, Crismer value (alcohol d 0·7967) 65°, f. p. −24°, acid value 2·4, acidity (as oleic) 1·24%, soluble fatty acids (Planchon) 0·7 c.c. 0·1*N*-potassium hydroxide per 150 c.c., soluble fatty acids (as butyric) 0·12%, Hehner value 95·60%, Reichert–Wollny value 0·2 c.c. 0·1*N*-potassium hydroxide (soluble), 0·3 c.c. (insoluble), saponification value 190·4, acid [? iodine] value 209·0, acetyl value (André) 10·4, unsaponifiable matter 1·04%, ether-insoluble brominated glycerides (Hehner and Mitchell) 60·56%, degree of oxidation (Bishop) 21·20%. The total fatty acids have n^{22} 1·4740, iodine value 218·1, neutralisation value 197·5, solid acids 2·5%, liquid 97·5%; the liquid acids have n^{22} 1·4745, iodine value 222·3. Chemical Abstracts.

Variations in the constants of the oils of certain *Leguminosæ*. G. Halden (Mat. grasses, 1928, **20**, 8168—8171).—A discussion. Chemical Abstracts.

Jerusalem artichoke. L. E. Dunton (Forecast, 1927, **34**, 295—296, 332).—Average values are: moisture 81·2, ash 1·26, phosphorus 0·099, calcium 0·023, iron 0·003%. Chemical Abstracts.

Chemical constituents of the fruit of *Ginkgo biloba*. I. J. Kawamura (Japan. J. Chem., **3**, 89—108).—From the ethereal extract of the fruit of *Ginkgo biloba* the unsaturated acid, *ginkgolic acid*, $C_{21}H_{30}(OH)\cdot CO_2H$, m. p. 42—43°, has been isolated. On catalytic reduction with palladium or platinum-black this acid yields dihydroginkgolic acid, $C_{21}H_{34}O_3$, m. p. 86—88° (identical with *cyclo*galliparic acid, cf. Kunz-Krause and Schelle, A., 1904, i, 587; acetyl derivative, m. p. 73—74·5°; p-*nitrobenzoyl* derivative, m. p. 87—89°; *methyl* ester, m. p. 41—42·5°; *silver*, *lead*, and *alkali* salts), which on nitration yields the *derivatives* $C_{21}H_{33}O_3\cdot NO_2$, m. p. 66—68°, and $C_{15}H_{22}N_2O_5$, m. p. 55—56°. Ginkgolic acid possesses an aromatic nucleus and a phenolic hydroxyl group. When heated at 240° it loses carbon dioxide with the formation of *ginkgol*, $C_{20}H_{31}\cdot OH$, b. p. 221—223°/4 mm., which when reduced catalytically in presence of platinum-black yields dihydroginkgol, $C_{20}H_{33}\cdot OH$ (identical with *cyclo*gallipharol, *ibid.*, 588; p-*nitrobenzoyl* derivative, m. p. 60—61·5°). Methylation of ginkgol yields *ginkgol methyl ether*, $C_{20}H_{31}\cdot OMe$, b. p. 200—203°/3 mm., which on oxidation with potassium permanganate gives rise to a *dihydroxy*-derivative, $C_{20}H_{31}(OH)_2\cdot OMe$, m. p. 98—98·5°, as well as to a compound probably identical with butyric acid.

Besides ginkgolic acid the ethereal extract contains (*a*) a secondary alcohol, *ginnol*, $C_{27}H_{55}\cdot OH$, m. p. 82·5°, which on oxidation with potassium dichromate yields a ketone, *ginnone*, $C_{27}H_{54}O$, m. p. 74—75° (*oxime*, m. p. 49·5°; *semicarbazone*, m. p. 45—46°); (*b*) *bilobol*, $C_{21}H_{32}(OH)_2$, m. p. 36—37°, which on catalytic reduction using platinum-black yields *dihydrobilobol*, m. p. 89—90° (*dinitro*-derivative, m. p. 68—71° with previous sintering; *diacetyl* derivative, m. p. 56°); (*c*) an *acid*, $C_{21}H_{42}O_3$ (?), m. p. 63°.

The alkali salts of ginkgolic acid are strong hæmolytic agents. Ginkgolic acid, ginkgol, and ginkgol methyl ether strongly inflame the skin, whilst bilobol is even more active in this respect than ginkgolic acid.

[With N. Fujita.] Phosphoric acid and asparagine have also been isolated from the fruit juice of *Ginkgo biloba*. W. O. Kermack.

Nuclear materials in *Nostoc*. F. A. Mockeridge (Brit. J. Exp. Biol., 1927, **4**, 301—304).—Nucleic acid was not found, but phosphate, pentose, adenine, guanine, cytosine, and uracil were identified.
Chemical Abstracts.

Influence of temperature on the growth of fungi. R. Meyer (Biochem. Z., 1928, **198**, 463—477).—Curves show the growth of *Aspergillus niger* (dry weight plotted against time) on a medium containing different amounts of ammonium sulphate at different temperatures. With rising temperature the time to attain maximal growth decreases, more strongly with larger than with smaller amounts of ammonium sulphate. Curves showing minima are obtained by plotting the time to attain maximal values against the temperature for a particular concentration of ammonium sulphate.
P. W. Clutterbuck.

Dependence of the slope of the nitrogen growth curve on the phosphoric acid supply for *Aspergillus niger*. R. Meyer (Biochem. Z., 1928, **199**, 171—174).—The Mitscherlich law defining action of growth factors cannot be reconciled with the author's results showing influence of nitrogen and phosphorus supply on the yield of *A. niger*.
J. H. Birkinshaw.

New enzyme, glucose-oxidase. I. D. Müller (Biochem. Z., 1928, **199**, 136—170).—Active enzyme preparations were obtained from *Aspergillus niger* capable of promoting dextrose oxidation. These were (1) the expressed juice from the ground mycelium, (2) a dry powder obtained by treating the juice with 12 vols. of 96% alcohol-ether (2 : 1), (3) a dried mycelium preparation obtained by treating the pressed mass with alcohol-ether. Approximately one atom of atmospheric oxygen was absorbed per mol. of dextrose, giving rise to 1 equivalent of fixed acid. This was shown to consist, probably entirely, of *d*-gluconic acid. J. H. Birkinshaw.

Effect of stimulation on [the production of] invertase by *Penicillium glaucum*. II. Z. I. Kertesz (Fermentforsch., 1928, **10**, 36—38; cf. this vol., 1063).—*P. glaucum* was grown first on dextrose, then on sucrose, and again on dextrose solution. The invertase activity of the solution measured during the last period rises during the first 8 days and then decreases. It appears therefore that the production of invertase within the mould is stimulated by sucrose and that this enzyme slowly diffuses into the dextrose solution. W. O. Kermack.

"Lead disease" [of plants]. C. M. Albizzati (Anal. Soc. cient. Argentina, 1927, **103**, 38—42; Chem. Zentr., 1928, i, 1973).—In "lead disease" the leaves contain more soluble and less insoluble oxalate than normally, and a greater quantity of a diastase.
A. A. Eldridge.

Spike disease of sandal (*Santalum album*, L.). II. Analysis of leaves from healthy and spiked trees. II. Physico-chemical study of the leaf sap. A. V. V. Iyengar (J. Indian Inst. Sci., 1928, **11A**, 97—102, 103—109).—Sandal leaves affected with spike disease have a higher content of reducing sugars, total carbohydrates, starch, total nitrogen, and dry matter and a lower moisture content than healthy leaves. Diseased leaves are also deficient in calcium, potassium, and ash content.

The p_H values of the sap of healthy and diseased leaves were 5·15—5·71 and 4·69—4·99, respectively. The titratable acidity and osmotic pressure are higher in diseased leaves, and the specific conductivity and the ratio of specific conductivity to f.-p. depression lower in "spiked" sap than in normal.
A. G. Pollard.

New respirometer apparatus. S. Steffenburg (Z. physiol. Chem., 1928, **178**, 75—80).—An apparatus is described consisting of a capillary gas-burette attached to a reaction vessel, by means of which absorption or evolution of gas during fermentation etc. may be measured at constant pressure.

The accuracy is fifty times that of the Euler-Myrback apparatus. R. K. CALLOW.

Micro-determination of carbon dioxide tension. A. BECK (Biochem. Z., 1928, **199**, 21—28).—Into a syringe containing the sample of liquid (5—10 c.c.) an air bubble (0·05—0·1 c.c.) is introduced. Equilibrium is attained by shaking and the bubble is then transferred by way of an intermediate vessel to the absorption apparatus, where the gas is contained in a graduated capillary tube and enclosed by mercury. After absorption of the carbon dioxide by potassium hydroxide the contraction is measured. An accuracy of 0·1% is claimed.

J. H. BIRKINSHAW.

Two-colour colorimetry. E. KAUFMANN (Biochem. Z., 1928, **197**, 141—142).—A description of a modified form of the Autenrieth colorimeter is given. The instrument may be used for the determination of blood-sugar and of the oxygen capacity of blood.

W. MCCARTNEY.

Measurement of chlorine-ion potentials in the presence of proteins. R. S. AITKEN (Biochem. J., 1928, **22**, 1239—1245).—The chlorine-ion potentials in pure potassium chloride solutions as measured by means of silver-silver chloride electrodes are steady and reproducible. The readings obtained in potassium chloride solutions containing serum-protein are steady but not reproducible and indicate a higher concentration of chlorine ions than is known to be present. The readings obtained in oxalated human plasma were neither steady nor reproducible. Immersion in plasma "poisoned" the electrode.

S. S. ZILVA.

Determination of soluble carbohydrates. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1927, **2**, 195—204).—A report of a committee of the American Society of Plant Physiologists.

CHEMICAL ABSTRACTS.

Behaviour of various sugars in the Bang micro-method. Reducing power of lævulose in the Bertrand method. B. RÓHNY (Biochem. Z., 1928, **199**, 48—52, 53—59).—The Bang factor corresponding with c.c. of 0·01*N*-residual thiosulphate/mg. of sugar was determined for xylose, lævulose, galactose, lactose, and maltose. This is compared with Bertrand's factor representing mg. of copper/mg. of sugar for the same series.

The Bertrand factor for pure lævulose is found to be lower than that for dextrose, contrary to the statement of Bertrand; however, in presence of dextrose both lævulose and galactose factors become identical with that for dextrose. Thus invert-sugar and inverted lactose have the same factor as dextrose.

J. H. BIRKINSHAW.

Determination of pyruvic acid. B. H. R. KRISHNA and M. SREENIVASAYA (Biochem. J., 1928, **22**, 1169—1177).—The proteins are eliminated from biological fluids either by the Folin and Wu method or by precipitation with alcohol. Acetone, acetaldehyde, or other volatile compounds are removed from the neutralised solution by evaporation under diminished pressure at 40—50°. After acidification and extraction with ether the extract is treated with sodium hydrogen sulphite and extracted again with ether, which removes lactic acid, β-hydroxybutyric acid, phenols, etc. The residue containing the pyruvic acid is reduced by sulphuric acid and zinc with a trace of copper to lactic acid and the latter compound determined by Friedemann, Cotonio, and Shaffer's modification of Fürth and Charnass' method (A., 1927, 800). S. S. ZILVA.

Determination of nitrogen in relatively simple compounds. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1927, **2**, 205—211).—A report of a committee of the American Society of Plant Physiologists. CHEMICAL ABSTRACTS.

Determination of carnosine. W. M. CLIFFORD and V. H. MOTTRAM (Biochem. J., 1928, **22**, 1246—1252; cf. Hunter, A., 1922, ii, 328, 885; 1924, i, 791).—A reinvestigation of Clifford's method of determination of carnosine (A., 1921, ii, 604) shows that the method is accurate to within 1%. The carnosine content of skeletal muscle of a species is constant but varies from species to species. S. S. ZILVA.

Determination of small amounts of bismuth in urine and organs. J. BODNAR and A. KARELL (Biochem. Z., 1928, **199**, 29—40).—The bismuth is determined colorimetrically in presence of potassium iodide. Since the chloride ion has a detrimental effect the organic matter is ashed in presence of nitric acid. The ash from 20—100 g. of material is heated with 5 c.c. of 10% nitric acid to boiling, to the cooled filtrate and washings are added 6 drops of 1% sodium hydrogen sulphite solution, 3 drops of 1% starch solution (to be certain that the solution contains no free iodine), 2 c.c. of 20% potassium iodide solution, and water to 20 c.c. The yellow colour produced is compared with the standards; 0·02 mg. of bismuth can be determined.

J. H. BIRKINSHAW.

Detection of minute traces of lead in biological material. R. BERG (Biochem. Z., 1928, **198**, 420—423).—The ash after heating with sulphuric acid and igniting is treated with nitric acid and electrolysed, when the lead, as peroxide, is deposited on a platinum wire, acting as the positive pole, which becomes brownish-black. The method detects 0·01 mg. of lead (cf. A., 1922, ii, 659). P. W. CLUTTERBUCK.

Micro-determination of potassium. A. T. SHOHL and H. B. BENNETT (J Biol. Chem., 1928, **78**, 643—651).—Organic matter is destroyed by incineration with sulphuric acid in presence of hydrogen peroxide; from the hydrochloric acid solution of the ash potassium is precipitated as chloroplatinate; the precipitate is re-dissolved and treated with potassium iodide, the colour of the potassium iodoplatinate formed being determined against standards. Alternatively, the excess of iodide may be titrated with thiosulphate. The error of the method is ±4% for 0·1 mg. and ±2% for 0·4 mg. of potassium.

C. R. HARINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1928.

General, Physical, and Inorganic Chemistry.

Ballistic method of ionisation measurement with a quadrant electrometer. D. L. WEBSTER and R. M. YEATMAN (J. Opt. Soc. Amer., 1928, **17**, 248—253).—The method of using the quadrant electrometer by taking the reading when the needle has stopped swinging is open to the objection that the time required is long. The method described is to read the farthest point of swing. The accuracy of the method depends on (1) linearity of the differential equation of motion; (2) homogeneity, except for the term proportional to the ionisation; (3) initial values of deflexion and velocity must be zero; (4) the exposure time must be constant. In practice, the last can easily be satisfied, whilst (2) and (3) can be satisfied by introducing a constant current opposite to that of the ionisation chamber. The first condition depends on the instrument. Tests on a Compton electrometer showed that all the conditions could be satisfied and that the method has no systematic errors large enough to detect in the presence of a 1% erratic error. For large deflexions there is a deviation of 1% from linearity, but calibration by means of a potentiometer enables the comparison of ionisation currents to be carried out accurately.

A. J. MEE.

Proof of Schrodinger's theory. J. L. SNOEK, jun., and L. S. ORNSTEIN (Z. Physik, 1928, **50**, 600—608).—Measurements have been made of the fine structure of the absorption in the H_α and H_β lines. The ratio of the total absorption of the H_α line to that of the line is 5·25, a value in good agreement with that deduced theoretically from Schrodinger's theory (5·37). The ratio of the absorption maxima in the two lines also agrees with that calculated from the theory. J. W. SMITH.

Promotion of the emission of the Balmer lines by the addition of argon. E. HIEDEMANN (Z. Physik, 1928, **50**, 609—617).—It has been shown that the addition of argon produces a very marked effect on the relative intensities of the lines and bands in the hydrogen spectrum. The action of argon on the dissociation of the hydrogen molecule into ions and on the recombination of the latter is discussed. A theory is developed which is claimed to agree with the observed phenomena.

J. W. SMITH.

Fulcher spectrum of hydrogen. E. HIEDEMANN (Z. Physik, 1928, **50**, 618—625).—From a discussion of the existing data the conclusion is reached that the Fulcher bands in the hydrogen spectrum are set up by the H_2 molecule, and not by H_3. It is also concluded that the continuous hydrogen spectrum is due to excited hydrogen molecules as suggested by Blackett and Franck (A., 1925, ii, 1097) and not to the decomposition of H_2^+ ions as supposed by Herzberg (this vol., 1). J. W. SMITH.

Extinction of the *D*-lines in flames by [the addition of] chlorine compounds. J. FRANCK and G. E. GIBSON (Z. Physik, 1928, **50**, 691).—By observing the behaviour of a salted flame to which small amounts of carbon tetrachloride vapour were added it has been shown that a complete parallelism exists by the extinction of the emission of the *D*-lines and their disappearance in the absorption spectrum. This is held to indicate that the disappearance of the *D*-lines is due to the disappearance of the free sodium atoms which pass under these conditions into sodium chloride molecules. J. W. SMITH.

Spectra of neon, argon, and krypton (additional lines). W. GREMMER (Z. Physik, 1928, **50**, 716—724).—A number of new lines in the red and infra-red regions have been observed in the spectra of neon and argon. Most of these have been shown to be members of the *sp*-, *ps*-, or *pd*-series. The spectrum of krypton, like those of neon and argon, shows certain constant vibrational differences. These regularities enable a considerable number of the spectral lines of krypton to be classified.

J. W. SMITH.

Breadth of some lines of the mercury spectrum. A. CARRELLI (Atti R. Accad. Lincei, 1928, [vi], **7**, 1014—1018).—A discussion of the results of the measurement, by the interferometer method, of the breadth of eleven lines of the mercury spectrum.

F. G. TRYHORN.

Spectra of ionised neon (Ne II) and ionised argon (A II). II. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 593—602). —A comparison is made between the quadruplet terms of ionised neon (Ne II) and ionised argon (A II). A table of terms is given. Nearly all the terms predicted by the theory of Heisenberg and Hund have been detected and identified. The Zeeman effect was investigated in order to check the term scheme, the calculated effect being compared with that observed.

A. J. MEE.

Intensity of reflexion of *X*-rays by crystals and the Compton effect. G. E. M. JAUNCEY (Physical Rev., 1927, [ii], **29**, 206).—A correction factor, introduced by the Compton effect, is applied

to Bragg, Darwin, and James' formula (A., 1926, 663) for the case of an ideally imperfect crystal.

A. A. ELDRIDGE.

X-Ray spectrographic measurements in the L and M series of rhenium. H. BEUTHE (Z. Physik, 1928, **50**, 762—768).—The wave-lengths of a number of $L\alpha$, β, and γ and of $M\beta$ and γ lines of rhenium have been determined, and the corresponding term values have been calculated.

R. W. LUNT.

Intensities of K-series X-rays from thin targets. D. L. WEBSTER, H. CLARK, R. M. YEATMAN, and W. W. HANSEN (Proc. Nat. Acad. Sci., 1928, **14**, 679—686).—Experimental data have been obtained for targets of silver so thin as to cause no appreciable retardation of most of the cathode rays. These data give the relative intensity of K-series X-rays, and, therefore, the relative probability of direct K-electron ionisation, as a function of cathode-ray energy from the excitation energy to 3·3 times that amount.

W. E. DOWNEY.

Relation between chemical constitution and K-absorption spectra. VII. General review. O. STELLING (Z. Physik, 1928, **50**, 506—530).—Following a review of the various experimental methods now employed, the author analyses the results obtained with the compounds of phosphorus, sulphur, and chlorine. In the phosphorus compounds it is shown that the displacement of the absorption limit depends only on the nature of the atom or radical directly linked to the phosphorus, and that the displacement is proportional to the number of such atoms or radicals. The limit for sulphur shifts towards shorter wave-lengths as the valency is increased; the influence of metals in sulphides is specific to the metal, but the position of the limit is constant in organic compounds of sulphur. Metallic chlorides with water of crystallisation are characterised by a shorter wave-length limit than the corresponding anhydrous substances; the limit is constant for a number of cobaltaminochlorides, and also constant, although different in value, for organic compounds containing chlorine. The relationship between the displacement of the absorption limit, ion distance, grating type, and electron configuration is also discussed.

R. W. LUNT.

Variation of X-ray absorption spectra in crystal gratings. K. FAJANS (Z. Physik, 1928, **50**, 531—536).—The data of Stelling (cf. preceding abstract) have been used to show that the displacement of the absorption limit varies inversely as the fourth power of the ionic distance, and that therefore the absorption limit is determined by the electron configuration of the ions in the grating.

R. W. LUNT.

Ultra-violet band spectra of nitrogen. R. T. BIRGE and J. J. HOPFIELD (Physical Rev., 1927, [ii], **29**, 356).—The system previously analysed (A., 1925, ii, 737) has been extended to include sixty bands between 1250 and 2025 Å. The system is not now ascribed to nitric oxide, but is the resonance system of nitrogen. Two other progressions of emission bands between 1030 and 1520 Å. have been identified.

A. A. ELDRIDGE.

Excitation of the arc spectrum of nitrogen. R. A. WOLFE and O. S. DUFFENDACK (Physical Rev., 1927, [ii], **29**, 209—210).—When the arc spectrum of nitrogen was excited by an interrupted low-voltage arc in a mixture of helium and nitrogen, nitrogen arc lines were very strong in a limited region, whereas in other regions helium lines or nitrogen bands strongly predominated. Existing data are largely confirmed.

A. A. ELDRIDGE.

Absorption spectrum of antimony vapour. R. V. ZUMSTEIN (Physical Rev., 1927, [ii], **29**, 209).—The arc lines 2311·50, 2175·88, and 2068·38 were strongly, and 2023·86, 2127·46 less strongly, absorbed. All five absorption lines come from the $3d_2$ state, which is doubtless the normal state of the atom.

A. A. ELDRIDGE.

Resonance glow in a hydrogen discharge tube. R. D. RUSK (Physical Rev., 1927, [ii], **29**, 213—214).—A study of the blue haze obtained in a hot-filament discharge tube. A close relationship between the life of the excited molecule and its collision frequency is suggested.

A. A. ELDRIDGE.

Absorption of the mercury line 1941·5 A. in the positive column and the optical determination of the concentration of mercury ions. W. DE GROOT (Z. Physik, 1928, **50**, 559—569).—Radiation of 1941·5 Å. emitted from a low-voltage arc in a neon–mercury vapour mixture was allowed to pass through the positive column of a low-voltage discharge in a mixture of argon (16 mm.) and mercury vapour (3 mm.); the ratio of the intensity of the incident to the transmitted radiation, I_0/I, has been measured as a function of the current in the positive column. A theoretical expression for this ratio has been derived from the analyses of Lorentz, Voigt, and Minkowski in terms of the most probable velocities, assuming a Maxwellian distribution, of the ions in the light source, w_e, and in the positive column, w, of the widths of the line 1941·5 Å. in the source, ω_e, and in the positive column, ω, of the density of ionisation, N, and of the apparent temperature of the ions in the positive column T. Values of w, w_e, ω_e, and ω were then chosen so that the theoretical and experimental curves relating I_0/I with the current coincided, assuming that N is proportional to the current. Values are thus obtained for N in terms of $w\omega$, and by assuming on the basis of Langmuir's experiments (this vol., 342) that the currents used in the discharge tube correspond with values of T from 1000° to 5000° Abs. N is found to range from $1·6$ to $3·2\times10^{10}$ ions/c.c. as the current is increased from 5 to 100 ma. These values are in agreement with the recent values obtained by Compton, Turner, and McCurdy (A., 1925, ii, 86) using search electrodes.

R. W. LUNT.

Arc spectrum of iron under reduced pressure over the range 2270—3900 Å. P. MARING (Z. wiss. Phot., 1928, **26**, 47—86).—A large Rowland grating was used, giving results claimed to be accurate to one thousandth of an Ångstrom unit. Full experimental details are given for obtaining accurate measurements of wave-length shifts.

A table is given comparing corresponding wave-lengths in air and in a vacuum, respectively, for some

hundreds of lines, and shows that the vacuum displacement, which is usually towards the red, never exceeds 1—2 Å. The vacuum lines are generally sharper than the corresponding air lines; occasionally a line is simple in the air and inverted in the vacuum spectrum. The intensity of the vacuum line is greater only when the corresponding air line is inverted. Many lines occur only in the vacuum spectrum; occasionally two apparently independent lines in the air spectrum unite to give a single line in the vacuum.

Contrary to expectation, the vacuum spectrum does not give any better results for the frequency differences between successive pairs in multiplets than the air spectrum.

In spite of the greater sharpness of the lines and the certainty of avoiding pole-effects, the vacuum spectrum of iron cannot replace the air spectrum as a standard owing to the far greater care required in operation. S. J. GREGG.

Spectrum temperature of magnesium- and flash-light. H. ARENS and J. EGGERT (Z. wiss. Phot., 1928, **26**, 95—96).—The spectrum temperatures of the magnesium flame and of flash-light are 3700° and 2900° Abs., respectively. On an Agfa colour plate flash-light showed normal distribution of intensity, whilst the magnesium flame was strong in the blue. This was confirmed by spectrum observations. S. J. GREGG.

First spark spectrum of krypton. P. K. KICHLU (Proc. Roy. Soc., 1928, **A**, **120**, 643—649; cf. this vol., 808).—With the aid of the data of Bloch, Bloch, and Déjardin (A., 1924, ii, 286) and of Abbink and Dorgelo (this vol., 338), an analysis has been made of the spark spectrum of krypton over the region 783·72—6768 Å. The calculated ionisation potential of the krypton ion is 26·4 volts. The discrepancy between this value and that found by Déjardin (28·25 volts) is perhaps due to the fact that the present value was calculated by taking only the first two members of a Rydberg sequence.
L. L. BIRCUMSHAW.

Absorption spectrum of cæsium. (MISS) I. M. MATHEWS (Proc. Roy. Soc., 1928, **A**, **120**, 650—654).—The light from a carbon arc was passed through cæsium vapour, produced in an electrically-heated steel tube from dried cæsium carbonate in the presence of powdered magnesium, and focussed on the slit of a Rowland grating. The wave-lengths and classification of the principal lines in the spectrum over the region 3888·622—3193·172 Å. are tabulated. The values are in close agreement with those obtained by Bevan (*ibid.*, 1912, **A**, **86**, 320). As far as the *s* and *p*-terms are concerned, no support is found for the view of Sowerby and Barratt that the present accepted term values are inaccurate (cf. A., 1926, 213). L. L. BIRCUMSHAW.

Zeeman effect for spectrum of tantalum. J. C. MCLENNAN and A. M. I. A. W. DURNFORD (Proc. Roy. Soc., 1928, **A**, **120**, 502—510).—The magnetically resolved components of 55 of the more important wave-lengths of the tantalum arc spectrum between 5548 and 6700 Å. have been determined. Several of the Zeeman patterns confirm the previous work on atomic states and spectral terms (McLennan, McLay, and Smith, A., 1926, 874), giving the lowest spectral term for tantalum as $4F_2$, and thus indicating a quadruplet system for the arc spectrum.
L. L. BIRCUMSHAW.

New regularities in the helium band spectrum. G. H. DIEKE, T. TAKAMINE, and T. SUGA (Z. Physik, 1928, **49**, 637—669).—The band spectrum of helium has been re-examined using a concave grating of 15 ft. radius leading to an accuracy of 0·008, 0·004, and 0·003 Å. in the first, second, and third orders, respectively. The helium used contained a small amount of neon; the conditions under which the spectrum was excited are not described. A large number of new bands was observed, the last members of which are $2p$-terms; the characteristics of these bands differ widely from those of others previously recorded. The newly-observed lines have been classified and co-ordinated, and the parameters of the equations for the vibrational bands have been evaluated. R. W. LUNT.

Mathematical relationships between fine structure and the Doppler effect. G. DOETSCH (Z. Physik, 1928, **49**, 705—730).—Following an analysis of the variation of intensity throughout a spectral line due to thermal agitation, two methods are derived for the calculation of the fine structure of a line from measurements of the width and of the total intensity of a line. R. W. LUNT.

Intensity ratios for the doublets of the principal series of the alkali metals. S. SAMBURSKY (Z. Physik, 1928, **49**, 731—739).—The intensity of a number of doublets of the principal series of sodium, potassium, rubidium, and cæsium have been determined. The ratio of the intensities $1s-np_1 : 1s-np_2$ (n—2, 3, . . .) varies linearly with the logarithm of the effective quantum number, but only in the case of sodium is the theoretical constant value of 2 attained; in the other cases the ratio increases with the logarithm of the quantum number. R. W. LUNT.

Gurney theory of the origin of the helium lines in the spectrum of the chromosphere. W. ANDERSON (Z. Physik, 1928, **48**, 749—782).—Calculations are made which show that the distance of fall of a Ca^{++} ion in the sun's gravitational field necessary to excite the 5876 Å. line of helium is in good agreement with the observed region of emission of this line relative to the sun's surface. R. W. LUNT.

Spectrum of the hydrogen molecular ion. C. J. BRASEFIELD (Proc. Nat. Acad. Sci., 1928, **14**, 686—689).—By spectroscopic examination of a luminous canal-ray beam in hydrogen, it has been found possible to separate the lines due to the hydrogen molecular ion. W. E. DOWNEY.

Series spectra of cadmium-like atoms. J. B. GREEN and R. J. LONG (Proc. Nat. Acad. Sci., 1928, **14**, 706—710; cf. Lang, this vol., 99).—The spectrum of Sb IV has been measured and analysed.
W. E. DOWNEY.

Spark spectrum of neon. A. S. GANESAN (Physical Rev., 1928, [ii], **32**, 580—582).—A list of lines in the spark spectrum of neon between 2300 and

1850 Å. is given. Many of the lines seem to belong to Ne III. N. M. BLIGH.

Intensities of the lines in the spectrum of mercury. E. O. HULBURT (Physical Rev., 1928, [ii], 32, 593—599).—The total radiation in the spectral region 6000—2300 Å. from a small quartz mercury lamp was $1 \cdot 85 \times 10^{-10}$ erg per atom per sec. From this and the intensities of the lines, the average emission of quanta per second by each atom was found as 11·4, 8·9, 5·0, 2·3 of yellow, green, blue, and violet light, respectively. The intensities of twenty-four lines of the spectrum were measured. Plotting the logarithm of the intensity against the frequency for the lines of a series gave roughly straight lines of about the same slope for the sharp series ($2^3P_n - m^3S_1$) and for the diffuse series ($2^3P_n - m^3D_{1,2,3}$). The temperatures of the excited atoms derived from the slopes were 3900° and 2600° Abs. for the sharp and diffuse series, respectively. N. M. BLIGH.

29 and 30-Electron-system spectra of arsenic and selenium. R. A. SAWYER and C. J. HUMPHREYS (Physical Rev., 1928, [ii], 32, 583—592).—New vacuum-spark data in the extreme ultra-violet have been obtained for arsenic and selenium. Extrapolation methods are used to predict the location of and to identify the lines arising from transitions between the lowest levels in the spectra of As IV, As V, Se V, and Se VI. The ionisation potential of As V is determined as 62·4 volts, that of Se VI as 81·4 volts. The $(4P^2)^3P$ separation of the 30-electron-system spectra shows a rapid increase with respect to the separation both of $(4s4p)^3P$ term and $(4p)^2P$ term of the next ion. The theoretical significance of this effect, first observed here and not appearing in the corresponding iso-electronic spectra of the lighter elements, is discussed. The effect is believed to be due to a change of coupling of the quantum vectors with increasing nuclear charge. N. M. BLIGH.

Spectrum of potassium excited during its spontaneous combination with chlorine. L. A. RAMDAS (Indian J. Physics, 1928, 3, 31—36).—The light emitted by potassium burning in chlorine gives a spectrum showing the arc lines of potassium, an intense, broad red band due to potassium molecules, and a few feeble lines which appear to be the enhanced lines in the violet region. The possibility of thermal excitation of this spectrum is discussed.
W. E. DOWNEY.

Horizontal comparison in the location of spectra of elements. M. SAHA and K. MAZUMDAR (Indian J. Physics, 1928, 3, 67—76).—Theoretical.
W. E. DOWNEY.

Ultra-violet absorption bands of oxygen. A. S. GANESAN (Indian J. Physics, 1928, 3, 95—104).—The structure of five ultra-violet absorption bands of oxygen between 1953 and 1864 Å. has been experimentally determined. W. E. DOWNEY

Excitation of Cu II spectrum by positive neon ions. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1927, [ii], 29, 925).—The spectra of low-voltage arcs maintained in mixtures of argon and copper and of neon and copper in a tungsten furnace were studied. The argon mixture gave no spark lines. In neon the lines from the levels corresponding with the $(3d)^9(4p)$ and $(3d)^9(5s)$ configurations were strongly developed. The results accord with Shenstone's analysis (A., 1927, 389). A. A. ELDRIDGE.

Nature of the nitrogen afterglow. A. G. WORTHING (Physical Rev., 1927, [ii], 29, 907—908).—The observations described do not support the view that the afterglow originates in impacts of neutral unexcited nitrogen atoms and molecules.
A. A. ELDRIDGE.

Zeeman effect of the fine structure components of mercury radiation λ 2536 Å. W. A. MACNAIR (Physical Rev., 1927, [ii], 29, 915).—The five fine structure components split into triplets, the effects of a magnetic field on the components of which is recorded. A. A. ELDRIDGE.

X-Ray absorption and valency. W. B. MOREHOUSE (Physical Rev., 1927, [ii], 29, 924).—The absorption of heterogeneous X-rays by an element depends on its valency; the effect may differ for different wave-lengths. If the screening constant changes the absorption coefficient will change. With change of valency there must be a slight change in the electronic configuration of the atom.
A. A. ELDRIDGE.

Secondary absorption edges in X-rays. B. B. RAY (Nature, 1928, 122, 771—772).—An explanation of the anomalous position of secondary edges is advanced; it is assumed that the same quantum can be absorbed successively by two or more electrons occupying different energy levels in the atom.
A. A. ELDRIDGE.

Stark effect in neon. J. S. FOSTER and W. ROWLES (Physical Rev., 1927, [ii], 29, 925).—The observed symmetrical Stark patterns for the line groups of higher order were remarkably hydrogen-like in character. Each of the lines $2p_j$—$4f$ and $2p_j$—$5f$ appears as a doublet, and the two members of the doublet present nearly identical Stark effects.
A. A. ELDRIDGE.

Unclassified lines of oxygen in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 923—924).—The triplet 988·67, 990·13, 990·73 Å. is possibly an unresolved group similar to the sulphur group at 1480 Å., which contains eight lines. The aurora line 5577·35 Å. is apparently related to the two ultra-violet lines of oxygen 1217·62 and 999·47 Å.; possibly the ultra-violet lines have a common initial or final state and the aurora line represents the transition between their respective final or initial states. A. A. ELDRIDGE.

Characteristics of the neutral and of the singly- and doubly-ionised spectra of cerium. A. S. KING (Physical Rev., 1927, [ii], 29, 366).—Approximately 1600 lines between 3000 and 4700 Å. in the spectrum of neutral cerium have been measured in furnace spectrograms. More than 3000 neutral lines may now be listed. The spectrum of ionised cerium is common to the arc and spark, whilst in the ultra-violet a condensed spark discharge gives many doubly-ionised lines. A. A. ELDRIDGE.

Series limits. A. G. SHENSTONE (Nature, 1928, 122, 727—728).—The predictions of Hund's theory

of the limits of component series are invalid, since they do not take into account the fact that a magnetic field which is, in the usual sense, strong may still be weak from other points of view. A. A. ELDRIDGE.

Fine structure of the Compton effect. M. DE BROGLIE (Compt. rend., 1928, **187**, 697).—If the experiments of Davis (this vol., 1168) are considered in the light of the diffused photon theory of the Compton effect, then the continuous background diffused under the influence of an exciting source containing rays of all wave-lengths should be banded, and in the curve connecting the total absorption of an element with the wave-length, a portion of the absorption should be attributed to diffusion. J. GRANT.

Spectrum of bromine in the electrodeless discharge. N. SIRACUSANA (Atti R. Accad. Lincei, 1928, [vi], 7, 835—838).—The spectrum of bromine excited by the electrodeless discharge under unspecified electrical conditions has been examined to 2000 Å.; this is characterised by a number of lines belonging to arc spectrum many of which are new, and a faint continuous background. R. W. LUNT.

Extension of the group theory of terms. M. DELBRÜCK (Z. Physik, 1928, **51**, 181—187).—Mathematical. R. W. LUNT.

Spectra of boron. R. A. SAWYER (Physical Rev., 1927, [ii], **29**, 357).—Twenty-five out of ninety new "vacuum spark" boron lines have been classified. A. A. ELDRIDGE.

Stages in the excitation of the spectrum of indium. J. G. FRAYNE (Physical Rev., 1927, [ii], **29**, 357).—At 3·3 volts the lines $2p_1$—$2s$ and $2p_2$—$2s$ appeared; at 4·2 volts the additional lines $2p_1$—$3d$ and $2p_2$—$3d$ appeared. At 7 volts higher members of the series appeared, whilst at 13·2 volts lines additional to the recognised series lines appeared. At this potential a second electron may have been detached from the atom, assuming that ionisation occurred at 7 volts. Most of the lines which appeared at 23 volts have been recognised as air lines. At 600—800° the lines from the $2p_1$ level were consistently stronger than those from the $2p_2$ level. A. A. ELDRIDGE.

Energy level studies on metallic vapours using a high-temperature tungsten furnace. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1927, [ii], **29**, 358).—New absorption lines were observed with copper vapour at 2618·37, 2824·39, 2882·81, 2961·19, 3010·87, 3194·09, and 5782·08 Å., all originating in the metastable $^2D_{2,3}$ level. The copper lines 3247, 3274, 5106, 5700, 5782 Å. originating in the $2^2P_{1,2}$ level and several copper hydride bands were obtained in emission. The $^2D_{2,3}$ level is reached by thermal action and the $2^2P_{1,2}$ level by absorption of resonance radiation. A. A. ELDRIDGE.

Relations in the spectra of stripped atoms. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], **29**, 359).—It has been possible to recognise the first pair of doublets in the principal series for stripped atoms as far as Mn VII in the first long period, Zr IV in the second, and Pr V in the third. The first pairs of inverted diffuse doublets with satellite have been located for Sc III, Ti IV, and V V. A. A. ELDRIDGE.

Two electron multiplets of the first and second long periods. H. E. WHITE and R. C. GIBBS (Physical Rev., 1927, [ii], **29**, 359).—Three characteristic multiplets arising from two-valency electron systems of the first and second long periods of the periodic system follow the regular and irregular doublet laws. A. A. ELDRIDGE.

Intensity of scattered X-rays and the Compton effect. G. E. M. JAUNCEY (Physical Rev., 1927, [ii], **29**, 605).—It is assumed that all the electrons in the U state in a given atom co-operate in the unmodified scattering, which therefore varies as F^2 and the modified scattering as $Z—F$, where F is Williams and Jauncey's atomic structure factor and Z is the atomic number. A. A. ELDRIDGE.

Vibrational levels in the blue-green band system of sodium. F. W. LOOMIS (Physical Rev., 1927, [ii], **29**, 607).—The following assignment is made: $\nu=20301{\cdot}7+(124{\cdot}13n'-0{\cdot}84n'^2)-(158{\cdot}5n''-0{\cdot}73n''^2-0{\cdot}0027n''^3)$. The bands to which the fluorescence lines belong can be identified approximately. A. A. ELDRIDGE.

Fine structure of the helium arc spectrum. W. V. HOUSTON (Physical Rev., 1927, [ii], **29**, 749).—The sharp series line 7065 Å. and the diffuse series line 5876 Å. of the orthohelium spectrum are triple. Hence the helium spectrum is not anomalous. A. A. ELDRIDGE.

Photo-electric properties of thin films of the alkali metals. N. R. CAMPBELL (Phil. Mag., 1928, [vii], 6, 633—648).—The sensitivity of a photo-electric cathode has been shown to depend on the thickness of the metallic deposit, the nature of this deposit, and the material on which the deposit is made. Potassium photo-electric cathodes produced by depositing the metal on copper, driving it off by heat, and then subjecting the remaining film to a discharge in hydrogen show remarkable and stable sensitivity to red light, the photo-electric currents obtained with a wave-length of 8000 Å. being of the same order as those obtained in normal potassium cells under a wave-length of 4500 Å. Similar but less regular effects were obtained with films of sodium, cæsium, and rubidium on various other metals. It is suggested that to obtain maximum photo-electric sensitivity over the range of the visible spectrum a combination of the normal potassium cell and that with the new potassium-on-copper anode should be employed. The results indicate that the films in question consist of a succession of unimolecular layers analogous to those of cæsium and oxygen on tungsten examined by Langmuir and others. A. E. MITCHELL.

Critical potentials of the spark lines of mercury. J. A. ELDRIDGE (Physical Rev., 1927, [ii], **29**, 213).—From measurements of the intensities of 30 spark lines as a function of voltage, three critical values <150 volts have been found at about 18, 24, and 57 volts. A. A. ELDRIDGE.

Possible relation between radiation and ionisation potentials of iron. O. STUHLMAN (Physical

Rev., 1927, [ii], 29, 354).—Published values are considered. The critical radiation potentials can probably be attributed to multiple impact.

A. A. ELDRIDGE.

29-Volt critical potential of hydrogen. R. D. RUSK (Physical Rev., 1927, [ii], 29, 354).—The results of determinations of striking and breaking potentials of illuminated arcs in hydrogen suggest that 29 volts represents a molecular excitation level capable of sustaining intense cumulative ionisation and having a critical excitation period of the order of 10^{-8} sec. A. A. ELDRIDGE.

Direction of ejection of photo-electrons by polarised *X*-rays. C. J. PIETENPOL (Physical Rev., 1928, [ii], 32, 564—569).—The lateral distribution of photo-electrons ejected by polarised *X*-rays was studied by means of the Geiger point counter which could rotate about the polarised beam, and results supported the theoretical relation due to Auger and Perrin (A., 1925, ii, 618). N. M. BLIGH.

Photo-electric thresholds and fatigue. G. B. WELCH (Physical Rev., 1928, [ii], 32, 657—666).—Causes affecting threshold values were investigated, using highly purified elements the surfaces of which were prepared in a vacuum by an electromagnetic filing device. A linear relation was found between the logarithm of the photo-electric current and the logarithm of the time elapsed since polishing the surface. The rate of fatigue increases with the pressure and depends on the element used and for a given substance increases numerically as the threshold is approached. Thresholds were found as formerly (cf. A., 1927, 603) and the values obtained were: calcium 4475, iron 3155, cobalt 3165, nickel 3040, copper 2955, zinc 3180, and germanium 2880 Å. The results are in harmony with the patch theory of Richardson and Young (A., 1925, ii, 343).

N. M. BLIGH.

Distribution in space of the initial directions of photo-electrons produced by monochromatic *X*-rays. P. AUGER (J. Phys. Radium, 1928, [vi], 9, 225—230).—The apparatus used is described. Measurements have been made using monochromatic *X*-rays to excite a mixture of hydrogen with 10% of argon. The results are represented by a method previously described (cf. *ibid.*, 1927, [vi], 8, 85—112) and it is found that when ω, the angle between the emitted photo-electric ray and the incident *X*-ray, is plotted against the total number of emitted rays between 0 and ω, the curve closely follows that of $\sin^3\omega$. The results are discussed and it is pointed out that their difference from those given in the previous paper is due to the fact that monochromatic *X*-rays had not then been used. J. L. BUCHAN.

Electric emission of incandescent platinum in an atmosphere of iodine. S. KALANDYK (J. Phys. Radium, 1928, [vi], 9, 231—235).—Both the positive and negative emission have been studied in an apparatus which is described. The latter only is influenced by the presence of iodine vapour. The intensity of the negative emission has been measured at various temperatures and pressures of the iodine vapour and for different temperatures of the emitting platinum filament. The influence of the iodine is shown to be greater the lower is the temperature of the filament and finally disappears as the temperature is raised. The results are discussed, and the increase in intensity of emission is attributed to the formation of a film of platinum iodide on the filament.

J. L. BUCHAN.

Heat of condensation of electrons and positive ions on molybdenum. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1927, [ii], 29, 909).—The heat of electron condensation on a molybdenum sphere is 4·76 volts in argon, 4·77 or 5·01 in nitrogen, and 4·04 or 4·35 volts in hydrogen, according to the surface treatment. The heating effect of a positive ion of argon is about 1 volt. A. A. ELDRIDGE.

Effect of oxygen on photo-electric emission from potassium. L. R. KOLLER (Physical Rev., 1927, [ii], 29, 902—903).—Variations in the effect of the admission of oxygen are ascribed to adsorption phenomena. A. A. ELDRIDGE.

Critical potentials of copper. R. HAMER and S. SINGH (Physical Rev., 1927, [ii], 29, 901—902).—The following were observed: 3·3, 7·9, 14·2, 19·5, and 25·3 volts. A. A. ELDRIDGE.

Simultaneous ionisation and excitation of molecules on collision with foreign ions. O. S. DUFFENDACK and H. L. SMITH (Physical Rev., 1927, [ii], 29, 914—915).—A study of the spectrum of the low-voltage arc in mixtures of helium, neon, or argon and carbon monoxide or nitrogen leads to the conclusion that an ion can ionise a molecule and excite the resulting ion to the degree represented by the difference in the ionising potentials.

A. A. ELDRIDGE.

Surface layers produced by activated nitrogen. C. KENTY and L. A. TURNER (Physical Rev., 1927, [ii], 29, 914).—The decrease in resistance of a tungsten wire in the presence of activated nitrogen is attributed to the formation of a surface layer which increases the emissivity of the filament, thereby lowering its temperature. The effect is apparently produced by a neutral substance. A. A. ELDRIDGE.

Infra-red spectrum of mercury. V. P. LUBOVICH (Physical Rev., 1927, [ii], 29, 355).—McLennan and Shaver have ascribed higher order lines to the infra-red spectrum of mercury, photographed in the first order of a diffraction grating. Certain new lines have been observed; the line 10141 Å. is not a doublet.

A. A. ELDRIDGE.

Critical potentials of iron. R. HAMER and S. SINGH (Physical Rev., 1927, [ii], 29, 608).—Critical potentials were observed as follows 3·7, 7·15, 11·2, 16·3, 19·4, 24·5, 29·0, 33·9, 38·8, 42·1, 45·7, 48·4, 51·4, 54·8, 61·6, 72·7, 89·6, 103·1, 111·6, 125·8 volts.

A. A. ELDRIDGE.

Ionisation of mercury vapour by 2537 Å. radiation. P. D. FOOTE (Physical Rev., 1927, [ii], 29, 609).—The relation between illumination (I) and photo-current (Δi) was of the form $\Delta i = AI^2/(1+BI)^2$, where A and B are constants for a given vapour pressure. Admixture of nitrogen increases, and that of hydrogen effaces, the effect. Two separate excited atoms are involved in the ionisation process. A. A. ELDRIDGE.

Excitation of mercury vapour by positive ions. E. J. Jones (Physical Rev., 1927, [ii], **29**, 611).—Saturated mercury vapour at 90° was bombarded with positive potassium ions, and the lines appearing at various voltages were observed. The efficiency of excitation by positive ions is far less than that by electrons. Up to 1200 volts the probability of excitation to the $2p_2$ level is greater than that to higher levels; excitation to levels higher than $3d_{1,2,3}$ was not observed. A. A. Eldridge.

Inelastic collisions in ionised gas mixtures. G. P. Harnwell (Physical Rev., 1927, [ii], **29**, 611).—The variation with pressure of the ionisation by electron impact in mixtures of the rare gases with hydrogen and nitrogen was studied. The number of rare gas ions decreased rapidly after a pressure of about 0·05 mm. was reached. Similar effects were observed with mixtures of nitrogen and the rare gases. The results support evidence for the existence of a type of collision of the second kind resulting in ionisations by positive ions.

A. A. Eldridge.

Recombination of ions in the chamber of an *X*-ray spectrometer. D. L. Webster and R. M. Yeatman (J. Opt. Soc. Amer., 1928, **17**, 254—259).—It is shown that under proper conditions the fraction of ions lost by recombination is independent of the total number of ions produced, for any loss up to about 10%. This allows the use of a much lower chamber voltage in the comparison of ionisation currents. The fact that the fraction lost is practically constant indicates that probably the recombination is columnar, *i.e.*, in the case of *X*-rays, an ion recombines only with another ion produced by the same photo-electron. This will be best satisfied with weak rays, and not with strong ones. A. J. Mee.

Reflexion of electrons from an aluminium crystal. D. C. Rose (Phil. Mag., 1928, [vii], **6**, 712—729).—An apparatus similar to a Bragg *X*-ray spectrograph has been used in the examination of the reflexion of electrons from the surface of an aluminium crystal. Four different orders of reflected beams were found, the positions of which agreed fairly closely with those predicted from wave theory when the refractive index of aluminium is assumed to be unity. Two other orders of another set of reflected beams, attributed to an aluminium oxide film or to some other contamination, were found. The accelerating potential, spacing constant of the crystal, and angle of reflexion are connected by the usual relationships applicable to *X*-rays. Similar experiments on nickel by Davisson and Germer (cf. this vol., 102) did not yield results in accordance with the wave theory, and it is suggested that the discrepancies are due to the magnetic effects of the nickel but more probably to the exhibition of a definite refractive index by the nickel. A. E. Mitchell.

Collisions of the second kind between zinc and mercury atoms. J. G. Winans (Physical Rev., 1927, [ii], **29**, 213).—Additional evidence (cf. A., 1926, 768) has been obtained that mercury atoms in the $2P$ state are effective in collisions of the second kind with zinc atoms. In the experiment, an excited mercury atom with an associated metastable state was probably about twice as effective in producing collisions of the second kind as one with no metastable state near it. A. A. Eldridge.

Dependence of the free path of potassium ions in various gases on their velocity. F. M. Durbin (Physical Rev., 1927, [ii], **29**, 215).—Curves showing the dependence of the free path of potassium ions on the velocity in air, hydrogen, nitrogen, helium, oxygen, and argon show an approach to a constant high value of the free path at the higher velocities and a decrease to a kinetic theory value at the lowest velocities.

A. A. Eldridge.

Secondary electron emission produced by positive cæsium ions. J. M. Hyatt (Physical Rev., 1927, [ii], **29**, 214).

Distribution of electrons in a metal. J. E. Lennard-Jones and H. J. Woods (Proc. Roy. Soc., 1928, **A**, **120**, 727—735).—Thomas (A., 1927, 290) has applied the new statistics of Fermi and Dirac to the distribution of electrons in heavy atoms. The basic idea is that the "electron gas" surrounding a nucleus is "degenerate," so that every cell of extension h^3 of a six-dimensional phase space contains two electrons, spinning in opposite directions to one another. A differential equation is obtained which has been solved by Thomas and Fermi by numerical methods. Another application of the statistics has been made by Sommerfeld to the free electrons of a metal (this vol., 467). Sommerfeld's work is criticised on the ground that he has neglected the interaction of the electrons and the atomic cores. The object of the present investigation is to find the average distribution of electrons (by the means employed by Thomas and Fermi for isolated atoms) when the metal is regarded as a whole. The same differential equation as that of Thomas and Fermi is obtained, but the boundary conditions are different. The differential equation inside a cube subject to the simple boundary conditions that $Vr \longrightarrow E$ at the centre and $\partial V/\partial n=0$ at the boundary proves to be insoluble, and the problem has been further simplified to give a kind of two-dimensional metal, where the nuclei are replaced by a series of parallel line-charges so arranged as to intersect a plane perpendicular to them in a square array. The following equation is ultimately obtained: $(\partial^2 V/\partial x^2)+(\partial^2 U/\partial y^2)-k^2 V$, where $k^2=16\pi^2 me^2/dh^2$, m being the mass of the electron, e the charge, and U the potential field. This is solved subject to certain conditions. By this means the work required to move an electron from any point in the crystal is obtained, and a number of equipotential lines for a crystal are plotted. Near a nucleus the equipotential lines are approximately circles, which are gradually deformed until a critical curve is reached. This extends throughout the crystal and encloses another system of closed curves. The electrons in these regions may be regarded as "shared," the "shared" electrons forming a lattice array which interpenetrates that of the nuclei. This provides some justification for the model of a metal proposed by Lindemann and Thomson.

L. L. Bircumshaw.

Magnetic moment of the electron. C. G. Darwin (Proc. Roy. Soc., 1928, **A**, **120**, 621—631;

cf. this vol., 570).—Starting from the wave equations for an electron and the associated electric density and current, it is shown how part of the magnetic field of a moving electron can be attributed to an electric convection current and part to its intrinsic magnetisation. The relation between the wave constants and the magnetisation is shown by a geometrical construction. The formulæ are first worked out for slow motions, then generalised by relativity principles for high speeds. A comparison is made between an electron wave and a light wave; the relation of light to electricity may be loosely described by saying that a light-quantum is an electron without charge or mass. L. L. BIRCUMSHAW.

Diffraction of the magnetic electron. C. G. DARWIN (Proc. Roy. Soc., 1928, **A**, **120**, 631—642).—The problem is solved of the diffraction of an electron wave by a line grating, supposed made out of a periodic distribution of electric or magnetic material. The electric and magnetic forces of the grating are limited in such a way that there shall only be first-order spectra on each side, two reflected and two transmitted. When a polarised electron wave falls on such a grating, the direction of magnetisation may be changed in the diffracted rays. In the case of pure electric forces and of some magnetic forces, the effect is to rotate the direction of magnetisation through a definite angle about an axis perpendicular to the incident and diffracted rays, and no polarisation can be produced by the diffraction. In cases where there are simultaneous electric and magnetic fields some polarisation may occur, but the case has not been worked out in detail.

L. L. BIRCUMSHAW.

Motion of electrons in gases. J. S. TOWNSEND (Proc. Roy. Soc., 1928, **A**, **120**, 511—523; cf. A., 1926, 3, 878).—A reply to the criticisms of Atkinson (this vol., 809) and others of the author's work on the ionisation of gases by collision. In the method of investigation adopted by Atkinson, no account has been taken of the motion of agitation of the gas in finding the loss of energy in the simplest case where the molecules or atoms of the gas are supposed to be perfectly elastic spheres. L. L. BIRCUMSHAW.

Theory of ferromagnetism. W. HEISENBERG (Z. Physik, 1928, **49**, 619—636).—Mathematical.

R. W. LUNT.

Vertical deflexion of slow electrons by gas molecules. R. KOLLATH (Ann. Physik, 1928, [iv], **87**, 259—284).—The cross-section of a molecule is considered from three different points of view, a cross-section involving absorption of an electron, a cross-section involving loss of velocity with or without deflexion of the electron, and finally a cross-section involving elastic reflexion or deflexion without a change in velocity. An experimental arrangement is described whereby the last-named section can be measured in relation to the primary electron velocity for the angle range 87·1—92·9° to the direction of the primary beam. Over the velocity range 1—6 volt^{½}, helium, neon, argon, krypton, hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, and methane exhibit vertical deflexion without marked loss in velocity, and the deflexion–velocity curves show a single maximum in all cases. When the curves are compared with those showing the effective cross-sectional area against electron velocity, the gases fall into three groups: (*a*) argon, neon, krypton, and methane, in which the two types of curves show maxima which are at greater velocities for the effective than for the deflexion cross-section, (*b*) hydrogen and helium, in which the curves run parallel, (*c*) the remaining gases, in which the maxima for the deflexion curves occur at the same velocity as the first maxima in the "effective" curves. R. A. MORTON.

Recombination of argon ions and electrons. C. KENTY (Physical Rev., 1928, [ii], **32**, 624—635).—The afterglow of the arc spectrum of argon was investigated. Lines involving jumps from high energy levels are relatively much stronger in the afterglow than in the arc. Evidence is given for the view that the excited atoms producing the afterglow must be formed by the recombination of ions and electrons. The effect of applied potentials on the afterglow was studied. In the case of accelerating voltages of 3—10 volts, the electronic velocities are increased, and the recombination velocity is decreased, resulting in a quenching of the afterglow. Retarding after-voltages up to 90 volts had practically no effect. The intensity of the afterglow is shown to be directly related to the concentration of positive ions, and the quenching to a saving up of ions. Measurements show positive ion concentrations in the afterglow of the order 10^{12} per c.c. The mean energy of the electrons is 0·4 volt. The coefficient of recombination is approximately 2×10^{-10}. N. M. BLIGH.

Diffusion of metastable atoms in mercury vapour. J. H. COULLIETTE (Physical Rev., 1928, [ii], **32**, 636—648).—The change in the rate of arrival of metastable atoms at the outer boundary of a spherical volume of gas was determined as a function of the time elapsed after a number of atoms had been formed at the centre. Detection of metastable atoms was based on the fact that they free electrons from a nickel surface. Observations were made over a vapour-pressure range of 3×10^{-9} to 0·33 mm. and a temperature range of −80° to 103°. The average duration of the metastable state is proportional to the distance travelled by the metastable atom to the walls of the tube, and this duration increased with the increase of vapour pressure of the mercury. It is also found that the effective radius of the metastable mercury atom is about 1·5 times as large as that of the normal atom, and that metastable and normal mercury atoms obey the same general laws of diffusion. Evidence of the loss of energy of excitation as the result of collision between normal and metastable mercury atoms was found. N. M. BLIGH.

Dissociation of hydrogen chloride by positive ion impact. W. M. NIELSEN (Physical Rev., 1927, [ii], **29**, 907).—Positive ions from heated sodium phosphate were projected between electrodes P_1 and P_2 to P_3. No negative current to P_1 was observed below 34 volts; above this value of the driving potential the ratio of negative current to total positive ion current increased rapidly with increase in the driving potential. The products of dissociation are not indicated. A. A. ELDRIDGE.

Magnetic moment of atomic iodine. J. B. Taylor and T. E. Phipps (Physical Rev., 1927, [ii], **29**, 904).

Magnetic moment of helium and molecular hydrogen. I. H. Solt (Physical Rev., 1927, [ii], **29**, 904).—No influence of the magnetic field on a beam of atoms or molecules was observed for a gradient of $1{\cdot}5\times10^5$ gauss/cm. A. A. Eldridge.

Magnetic moment of the electron. G. Breit (Nature, 1928, **122**, 649).—Theoretical.
A. A. Eldridge.

Reflexion of electrons from molybdenum. W. R. Ham (Physical Rev., 1927, [ii], **29**, 908).—When the percentage of reflected electrons relative to incident electrons is plotted against the velocity of reflected electrons, a large percentage of reflexion occurs at the velocity corresponding with 2900 volts. Peaks of reflexion occur as the impressed *P.D.* passes the critical potentials for the *L*-levels and probably also the *K*-level of molybdenum.
A. A. Eldridge.

Recombination of positive ions with electrons. R. d'E. Atkinson (Z. Physik, 1928, **51**, 188—203). —An attempt has been made to measure the change in intensity of a beam of cæsium ions of 220 volts velocity when allowed to traverse a cloud of electrons. No change in intensity, within the limits of experimental error, was observed, from which it is deduced that the upper limit for the effective distance, measured from the centre of the ion, in which recombination can occur is 7×10^{-7} cm. R. W. Lunt.

Metastable neon and argon. R. Rudy (Physical Rev., 1927, [ii], **29**, 359—360).

Explanation of long life of metastable atoms. G. Breit (Physical Rev., 1927, [ii], **29**, 361).—Theoretical. A. A. Eldridge.

Formation of negative ions. A. P. Alexeievsky (Physical Rev., 1927, [ii], **29**, 752).—Theoretical.
A. A. Eldridge.

Separation of isotopes and a further separation of mercury by evaporative diffusion. W. D. Harkins and B. Mortimer (Phil. Mag., 1928, [vii], **6**, 601—631).—The apparatus developed by Harkins and Mulliken (A., 1922, ii, 295) has been modified to allow of more rapid working and an extensive fractionation of mercury has been made. It is shown that the change in atomic weight ΔM depends largely on the separation coefficient, the cut, and the efficiency. The time required to build up any extreme fraction, allowing for the time necessary for the intermediate fractions, is $t-K(\Delta M)^3Q_0DE^3B^3$, where K is constant, B the separation coefficient, E the efficiency, D the rate of production of the lighter fraction, and Q_0 the constant minimum mass of the intermediate fractions. It then follows that in the case of mercury, where B is small, the time taken to achieve large values of ΔM must be great. The extreme fractions obtained showed a difference in atomic weight of 0·189 unit, the greatest difference so far reported. This separation corresponds with changes of 27 and 20%, respectively, in the initial proportions of isotopes 204 and 198.
A. E. Mitchell.

Isotope effect in iodine monochloride bands in the neighbourhood of the convergence limit. G. E. Gibson (Z. Physik, 1928, **50**, 692—696).—A new band series has been discovered in the iodine monochloride absorption spectrum with the same convergence limit (5144 Å.) as that previously discovered (Gibson and Ramsberger, this vol., 6). This series is attributed to the second isotope of chlorine (37). The coincidence of the convergence limits of the two series is to be expected, since the heats of dissociation must be identical. The relative positions of the corresponding vibration terms are in accordance with the theory of Sommerfeld. J. W. Smith.

Separation of the isotopes of chlorine. W. D. Harkins and C. E. Broeker (Z. Physik, 1928, **50**, 537—547).—Hydrogen chloride was allowed to flow through a series of porous porcelain tubes so that only one twentieth of the original gas did not diffuse through the porous walls; this procedure was repeated on the undiffused residue twice; finally the resulting 1/8000th of the original gas was absorbed in water. Measurements of the density and of the acidity of the resulting solution gave data from which the mean value, 0·055 unit, was obtained for the apparent increase in the atomic weight of chlorine. The method is sensitive to a change of 0·002 unit of atomic weight. R. W. Lunt.

Atom models [nucleus] for isotopes. II. G. Beck (Z. Physik, 1928, **50**, 548—554).—The theoretical considerations previously advanced (cf. this vol., 344), leading to a derivation of the periodic system from the Pauli principle, have been extended to devise atomic models for isotopes.
R. W. Lunt.

Mass deficiencies and nuclear dimensions. L. Strum (Z. Physik, 1928, **50**, 555—558).—It is claimed that the recent data of Aston on mass deficiency, μ, can be related more simply to the number of protons in the nucleus, A, than to the atomic weight relative to oxygen; the results then fall very closely on the line $\mu=8{\cdot}4\times10^{-3}m_HA$, where m_H is the mass of a proton. By assuming point charges in the calculation of the internal energy of the nucleus and by adopting Lenz's model of the helium nucleus the value $1{\cdot}4\times10^{-14}$ cm. has been obtained for the diameter of the nucleus. R. W. Lunt.

Experimental evidence of the existence of aggregates of active deposit atoms in gases containing radon. E. L. Harrington (Phil. Mag., 1928, [vii], **6**, 685—695).—The existence of aggregates of active atoms, both in the gas and on the walls of the containers, in radon–air mixtures freed from dust has been demonstrated by subjecting tubes containing them to centrifugal action, when it is found that the activity becomes greatest in regions subjected to the greatest centrifugal forces. The existence of such aggregates has been further demonstrated in the gas by the Wilson cloud method. The effects persisted in tubes which were both saturated and unsaturated with water vapour. It has been shown by a migration experiment that particles of both positive and negative sign occur in the gas. It is suggested that the aggregates originate from the combination of molecules and ions in the highly-ionised gas con-

taining radon, whilst in the case of gas saturated with water the effects will be enhanced by the droplets of water. A. E. MITCHELL.

Theory of the origin of the actinium series. T. R. WILKINS (Physical Rev., 1927, [ii], 29, 352).—The actinium series is considered to arise from an isotope of uranium-I (actino-uranium-I), the decay-constant of which is several times that of uranium-I. The parent isotopes were originally in radioactive equilibrium, but in geological time actino-uranium has largely disappeared. The ages of rocks, computed on the basis of this theory, may differ from those calculated from the lead or helium content by 40%. A. A. ELDRIDGE.

Velocity distribution of β-particles after passing through thin foils. P. WHITE and G. MILLINGTON (Proc. Roy. Soc., 1928, A, 120, 701—726).—Using the photographic method, a study has been made of the dispersion of the retardations of β-particles after passing through thin foils. The source (Ra-*B* and -*C* initially in equilibrium with Ra-*A*) was partly covered by a straggling foil of mica, pierced at equal distances by two or three holes adjusted to give nearly equal maximum photographic densities to each of a corresponding pair of traces. A thorough investigation was made with the three strong lines of the Ra-*B* spectrum 1410, 1677, and 1938 $H\rho$, using sheets of mica of 2·25, 2·65, 3·95, and 5·72 mg./sq. cm. The distribution of optical density along each plate was measured by means of a microphotometer. A process is worked out for computing the shape of the straggled curve which would have been obtained with an ideally fine unstraggled line, and this is applied to the experimental curves, after correction for the background due to the continuous spectrum and chemical fog and for the characteristics of the plates used (cf. Ellis and Wooster, A., 1927, 324). It is found that all the curves obtained can be summarised into a single fundamental straggling curve, for which the equation is $y=(\beta^3/\sigma)g(\beta^3x/\sigma)$, where β is the ratio of the initial velocity to the velocity of light, and σ is the thickness of the foil in centigrams per cm. The relation between most probable loss of velocity and thickness of stopping material is investigated for $H\rho$ 1410—5904 and surface density 2—14 mg./sq. cm., and a small systematic divergence from Bohr's theory, outside the limits of experimental error, is observed. The same is found for the relation between initial velocity and most probable loss of velocity. L. L. BIRCUMSHAW.

Absorption of β-rays. J. A. GRAY and B. W. SARGENT (Physical Rev., 1927, [ii], 29, 351—352).—The absorption of the β-rays of radium-*E* and uranium-*X* in carbon, aluminium, copper, tin, and lead has been studied. The energy lost in an atom by the β-rays of uranium-*X* is, on an average, proportional to the atomic number. A. A. ELDRIDGE.

Atomic disintegration with α-rays. W. BOTHE and H. FRANZ (Naturwiss., 1928, 16, 204—205; Chem. Zentr., 1928, i, 2232).—Experiments with beryllium, carbon, aluminium, and iron, and with aluminium, boron, magnesium, and paracyanogen, support the results of Rutherford and Chadwick rather than those of Kirsch and Pettersson. With boron the absorption curve showed two separate groups of hydrogen particles, of differing range, possibly to be attributed to the isotopes of boron. When the Geiger counter was filled with air or argon instead of hydrogen, greater effects, ascribed to the *K*-rays of aluminium, iron, and zinc, excited by the α-rays, were observed. A. A. ELDRIDGE.

Light quantum theory. T. TAKEUCHI (Z. Physik, 1928, 50, 697—700).—Mathematical. Schrodinger's wave equation is applied to the motion of photons in a gravitational field, and a relation is deduced for the dependence of the refractive index of a medium on the curvature of space. The phase and group velocities of de Broglie waves and their dependence on the curvature of space are calculated and Brewster's law is deduced. J. W. SMITH.

Synthesis and disintegration of atoms as shown by an application of the Wilson cloud-track method. W. D. HARKINS and H. A. SHADDUCK (Physical Rev., 1927, [ii], 29, 207).—In two cases (in 265,000 tracks) union of a fast α-particle with a nitrogen nucleus, and release of a hydrogen nucleus, have been observed. A. A. ELDRIDGE.

Dissociation of pure mercury. R. S. BRADLEY (Nature, 1928, 122, 573).—Theoretical. It is computed that for cadmium analgams and zinc amalgams respectively 0·13 and 0·12 of the mercury is ionised. A. A. ELDRIDGE.

Origin of penetrating radiation. W. PERSCHKE (Z. Physik, 1928, 48, 740—751).—By assuming the validity of the Bohr model the orbital number of an electron in the nucleus of a helium atom can be shown to be 10^{-4}. If this value be inserted in the Balmer formula applied to calculate the wave-length associated with the transition of an electron from a hydrogen atom to the nucleus of a newly-formed helium atom, the value 10^{-13} cm. is obtained. This value corresponds with the lower limit for penetrating radiation, and it is therefore suggested that this may arise from the formation of helium from hydrogen. R. W. LUNT.

Evolution of heat in the condensation of electrons on metals. R. VIOHL (Ann. Physik, 1928, [iv], 87, 176—196).—An arrangement is described whereby the heat of condensation of electrons on nickel is found to be 97,800(±9800) g.-cal. per mol. R. A. MORTON.

Polarisation of the resonance radiations of [the] zinc [family]. P. SOLEILLET (Compt. rend., 1928, 187, 723—725).—The author's method (this vol., 930) has been used to investigate the resonance radiations of the zinc atom ($1^1S_0-2^3P_1$), λ=3076, and ($1^1S_0-2^1P_1$), λ=2139, the polarisations obtained with the magnetic field in the directions of the exciting and observed rays being discussed from the point of view of Larmor's theory. The approximate mean life in the excited state (τ) of the zinc atom was found to be 10^{-5} sec. for the ray 3076. Comparison with the values obtained for cadmium and mercury (λ=3261 and 2537, $\tau=2\times10^{-6}$ and $1\cdot13\times10^{-7}$, respectively) shows that the stability of the excited atoms increases as the atomic number decreases, *i.e.*, as the electronic edifice becomes simpler. J. GRANT.

Life-history of an adsorbed atom of cæsium. J. A. Becker (Physical Rev., 1927, [ii], 29, 364).—The average life of an absorbed atom under equilibrium conditions is N/A, where N is the number of absorbed atoms and A the arrival rate. The behaviour of cæsium adsorbed on tungsten is considered. A. A. Eldridge.

Anomalies in the position of the innermost ring in pleochroic uranium haloes. F. Lotze (Zentr. Min. Geol., 1928, A, 87—89; Chem. Zentr., 1928, i, 1754).—The anomalies are ascribed to changes in the range of α-particles owing to changes in the physical properties (cohesion) of the material. A. A. Eldridge.

Current according to Dirac's electron theory. W. Gordon (Z. Physik, 1928, **50**, 630—632).—Mathematical. J. W. Smith.

Wave mechanics of an alkali metal atom in an electric field. F. Rasetti (Atti R. Accad. Lincei, 1928, [vi], 7, 1010—1014).—From a calculation of the behaviour in an electric field of an atom of the lithium type a value is obtained for the dielectric constant of the vapour which is of the same order of magnitude as approximate experimental values. F. G. Tryhorn.

Impact polarisation and spinning electron. A. Ellett (Physical Rev., 1927, [ii], **29**, 207).—A theoretical note. A. A. Eldridge.

Spectroscopic interpretation of the magneton numbers in the iron group. A. Sommerfeld and O. Laporte (Physical Rev., 1927, [ii], **29**, 208).—A formula for the magneton number is given. A. A. Eldridge.

Electronic theory of passivity. W. D. Lansing (Physical Rev., 1927, [ii], **29**, 216—217).—Under normal conditions the electrons of iron are probably distributed among the energy levels as 2, 8, 14, 2; under strongly oxidising conditions this may become 2, 8, 8, 8, the iron then being passive and non-magnetic. Thin films of iron produced by cathode sputtering are passive and possibly non-magnetic, although apparently not throughout their whole thickness. A. A. Eldridge.

Theory of diffraction of electrons in crystals. H. Bethe (Ann. Physik, 1928, [iv], **87**, 55—129).—Mathematical. The observations of Davisson and Germer, and others, on the diffraction of electrons in crystals are treated from the point of view of wave-mechanics. It is shown that the observed difference between X-ray and electron diffraction can be explained by means of a refractive index. The dynamics of the field of the de Broglie waves in crystals and the conditions at the surface are investigated. On the basis of the theory the deviations occurring with respect to X-ray reflexion are settled. A. J. Mee.

Life period of excited mercury atom. I. Asada (Physikal. Z., 1928, **29**, 708—711).—The mean life period of the $^3P_0$-state, obtained by resonance in pure nitrogen, is about 0·001 sec. at a few mm. of nitrogen. Impurities in the gas greatly reduce the intensity of the fluorescence (cf. this vol., 1065). R. A. Morton.

Origin of the cosmic rays. R. A. Millikan and G. H. Cameron (Physical Rev., 1928, [ii], **32**, 533—557).—Theoretical. Ionisation–depth curves previously found (cf. this vol., 811) indicate a band spectrum, the existence of which demands that cosmic rays originate in some nuclear act having sharply-defined energy values translatable like quantum jumps into spectral line frequencies. Quantitative arguments, based on Aston's mass spectrograph curve and Einstein's equation, are given against the possibility of the production of rays having the observed penetrating power, from any atomic disintegration process, and in support of the view that the only possible transformations capable of yielding the rays are those corresponding with the building up of abundant elements such as helium, oxygen, silicon, and iron out of hydrogen, or, in the case of the last two elements, out of helium. Calculations in these cases, for which alone sufficient mass disappears to create the observed rays, are in satisfactory agreement with the results of experimental observation, except for iron, which is less definite. Kinetic and other evidence is suggested for supposing that the rays do not originate in the stars but in interstellar space, where the atom building is favoured by extremely low temperature and density. In this connexion a theory is advanced concerning the relation of cosmic processes to the second law of thermodynamics. N. M. Bligh.

Duration of atomic hydrogen. J. Kaplan (Physical Rev., 1927, [ii], **29**, 920).—The Welsbach mantle test was observed 3 sec., and infected spots on the glass 6 sec., after the discharge was discontinued. A. A. Eldridge.

Evolution of the chemical elements. B. Cabrera (Anal. Fís. Quím., 1928, **26**, 186—205).—A discussion of atomic evolution in the light of Aston's work on atomic structure. H. F. Gillbe.

Experimental test of Schrodinger's theory. E. Gaviola (Nature, 1928, **122**, 772).

Quantum mechanics and chemical combination. F. Hund (Z. Elektrochem., 1928, **34**, 437—442).—The importance of the new quantum mechanics in chemistry is discussed with particular reference to the recent work of London (this vol., 344). S. K. Tweedy.

Wave mechanics of alkali metal atoms in an electric field. F. Rasetti (Atti R. Accad. Lincei, 1928, [vi], 7, 839—844).—Mathematical. R. W. Lunt.

Calculation of M-terms from the statistical atomic potential. F. Rasetti (Atti R. Accad. Lincei, 1928, [vi], 7, 915—918).—Mathematical. R. W. Lunt.

Degeneration of electron gases in the interior of stars. W. Anderson (Z. Physik, 1928, **50**, 874—877).

A possible generalisation of the Planck radiation law. L. Strum (Z. Physik, 1928, **51**, 287—291).

System of structures for atomic nuclei. W. W. Nicholas (Physical Rev., 1927, [ii], **29**, 612—613).—A theory is based on a "neutron" structure, the evolution of light elements from complex to simple, and a geometrical structure in which protons and neutrons are on alternate cube corners in a cubic lattice. A. A. Eldridge.

King's classical theory of atomic structure. B. Podolsky (Physical Rev., 1927, [ii], **29**, 750).—King's theory ("A classical theory of atomic structure and radiation," Montreal) is criticised.
A. A. Eldridge.

Absorption spectra of liquid crystals. D. Vorländer (Naturwiss., 1928, **16**, 759—760).—Whilst there is a considerable difference between the absorption spectra of substances in the crystalline state and in the liquid crystalline state, there is practically no difference between them for the substance in the liquid crystalline state and the amorphous liquid state. A. J. Mee.

Collisions of the second kind between molecules. Excitation of the Lyman band and non-combination of symmetrical with asymmetrical term systems in the hydrogen molecule. H. Beutler (Z. Physik, 1928, **50**, 581—599).—The hydrogen spectrum is discussed from the point of view of wave mechanics. J. W. Smith.

Band fluorescence of mercury vapour. S. Mrozovski (Z. Physik, 1928, **50**, 657—690; cf. Wood and Gaviola, this vol., 1065).—Further investigations have been made on the conditions of excitation and the structure of the mercury fluorescence bands. It has been shown that any spectral line which lies in the absorption region of mercury vapour will excite fluorescence, but that the structure of the fluorescence spectrum so obtained depends markedly on the mode of excitation. The change in intensity of certain bands with changing density of mercury vapour is attributed to reabsorption in the vapour. The bands in the short-wave ultra-violet region have been studied in detail and their series structure has been partly elucidated. The destruction of certain fluorescence bands on superheating the vapour is shown to be due to a diminished absorption of the exciting radiation. The $2P$ series bands have been classified, and from their convergence limits the heat of dissociation of the mercury molecule has been calculated as about 15 kg.-cal. The effect of adding water vapour and other gases to the fluorescing vapour has also been investigated. J. W. Smith.

[Absorption spectra of] potassium ferro- and ferri-cyanides. S. H. C. Briggs (J. Physical Chem., 1928, **32**, 1422).—In view of Getman's conclusions (this vol., 345), attention is directed to the author's previous work (J.C.S., 1920, **117**, 1026).
L. S. Theobald.

Fluorescence spectra in metallic vapours excited by the light of the mercury arc. J. C. McLennan and I. Walerstein (Physical Rev., 1927, [ii], **29**, 208).—Sulphur vapour gives a set of bands extending over the visible spectrum. Selenium at 325° gives a fluorescence spectrum from 2200 to 6500 Å., whilst at 425° it gives nine broad bands between 4178 and 4829 Å., this latter spectrum disappearing at high temperatures. The fluorescence spectrum of tellurium consists of regularly spaced bands in the visible region. Bismuth emits a band spectrum in the region 4400—4900 Å. The fluorescence of tellurium vapour was produced by mercury radiation between 2536 and 3655 Å.
A. A. Eldridge.

Some hydrocarbon bands. F. C. McDonald (Physical Rev., 1927, [ii], **29**, 212).—Two new bands, 2264 and 2367 Å., observed when methane was introduced into a Wood tube and excited by a condensed discharge, and when acetylene mixed with helium was excited by a transformer discharge, have been analysed. The possibility of a CH ion as carrier is considered. A. A. Eldridge.

Fine structure of three infra-red absorption bands of ammonia. G. A. Stinchcomb and E. F. Barker (Physical Rev., 1927, [ii], **29**, 213).—The fine structure of bands at 1·98, 2·2, and 3·0 μ has been studied. A. A. Eldridge.

Titanium bands. R. T. Birge and A. Christy (Physical Rev., 1927, [ii], **29**, 212).—Twenty-eight of the well-known titanium bands have been arranged in one system, and vibrational quantum numbers have been assigned. The bands are attributed to TiO. A. A. Eldridge.

Fluorescence and chemiluminescence of cod-liver oil. J. W. Woodrow and G. M. Wissink (Physical Rev., 1927, [ii], **29**, 219).—Faint bluish-green chemiluminescence of cod-liver oil has been obtained by oxidation of the heated vapour. The fluorescence spectrum of cod-liver oil illuminated by light from a quartz mercury-vapour arc is of maximal intensity at about 5000 Å. A. A. Eldridge.

Quenching of mercury vapour fluorescence by the addition of other gases. O. Oldenberg (Z. Physik, 1928, **49**, 609—618).—The quenching produced by the addition of nitrogen or of argon has been investigated at the ordinary temperature and at 750°. In the former case the quenching disappears as the temperature is raised to 750°, whilst for argon the quenching increases with rise of temperature. It is thought that the behaviour in the case of nitrogen is due to a resonance phenomenon between the first vibrational frequency of the nitrogen molecule, 0·29 volt, and the transition $2^3P_1 \longrightarrow 2^3P_0$ of the mercury atom, 0·218 volt. In support of this view it has been observed that an addition of carbon monoxide, the first vibrational frequency of which corresponds with 0·265 volt, produces an increase of fluorescence as the temperature is raised. The increased quenching in the case of argon can be explained by postulating that the probability of collisions of mercury atoms in the 2^3P_1 state with argon atoms, resulting in the transition of the mercury atoms to the normal state, increases with the kinetic energy of the colliding argon atoms. This assumption is discussed at length and held to be in general accord with current theory and experiment. R. W. Lunt.

Absorption spectra of iron carbonyl. I. Drechsler (Arh. Hemiju, 1928, **2**, 175—197).—See this vol., 1075.

Ultra-violet absorption spectra of simple benzene derivatives. F. W. Klingstedt (Z. physikal. Chem., 1928, **B**, **1**, 74—93).—The ultra-violet absorption spectrum of acetanilide in hexane and ethyl alcohol, up to 2060 Å., has been examined and compared with the spectra of aniline and aniline salts. The normal absorption spectrum of acetanilide in hexane, like that of aniline, has two

regions of selective absorption in the ultra-violet. The one of longer wave-length, between 2900 and 2630 Å., is made up of a succession of narrow bands. Only two of these bands could be measured, because the outer absorption region overlaps the inner. Not only the long-wave band system, but also the outer broad band, which is present in a number of aromatic amines, appears to be due to the amine radical. In alcoholic solution a marked change occurs, resulting in the disappearance of the narrow bands and indicating a disturbance of the vibrations of the nucleus. The change of spectrum cannot be ascribed to the isomeric form, but must depend on a solvent influence of another kind. The introduction of acetyl into the amino-group results in a very definite change in the aniline spectrum. The selective absorption of the anilide begins at much shorter wave-lengths. The longer wave absorption region is shifted towards the shorter and the short wave in the opposite direction. The frequency of the nuclear vibrations increases from 450 to about 950 cm.$^{-1}$ and reaches a value characteristic for several other mono-derivatives of benzene. The intensity of the selective absorption in the longer-wave ultra-violet falls by about 20%, whilst in the short-wave region, on the contrary, it is doubled. Acetylation apparently causes a closer union in a phenyl radical combined with an amino-group, but not to the same extent as salt formation. This behaviour is probably connected with the polar nature of the nitrogen atom in combination in the benzene nucleus. The atom acquires a polarity through dissymmetry in the distribution of its charge within the molecule. This will be greater in aniline salts than in the anilide. M. S. BURR.

Absorption spectrum of nitrogen dioxide. L. HARRIS (Proc. Nat. Acad. Sci., 1928, **14**, 690—694).—The absorption spectrum of single nitrogen dioxide molecules consists of bands between 6000 and 2250 Å. The absorption due to double molecules, N_2O_4, in the gaseous phase is continuous. W. E. DOWNEY.

Relation of hydrolysis to the validity of Beer's law. R. C. GIBBS and C. V. SHAPIRO (Proc. Nat. Acad. Sci., 1928, **14**, 694—700).—It has been found experimentally that, with substances of the phenolphthalein type, the hydrolysis which occurs at low concentrations results in a complete modification of the absorption spectrum. This modification invalidates Beer's law. W. E. DOWNEY.

"Line" absorption of crystalline chrome alums. H. SAUER (Ann. Physik, 1928, [iv], **87**, 197—237; cf. Joos, this vol., 345).—The absorption spectra at 18°, −78°, and −190° of crystals of the types $R^ICr(SO_4)_2,12H_2O$ (R^I=K, Rb, Cs, Tl^I, NH_4, NH_3OH, and NH_3Me) and $R^ICr(SeO_4)_2,12H_2O$ (R^I=K, Rb, Tl^I, and NH_4) have been studied in the visible region, using a continuous light source and a registering microphotometer. Solid chrome alums show considerable absorption throughout the visible region except at 6300—6800 Å. The unresolved absorption (Konig–Martens photometer) shows a maximum near 5700 Å. and a flat minimum near 4750 Å., followed by a region of rapidly increasing absorption extending beyond the blue limit of visibility. The intensity of absorption is about 50% greater for crystals than for solutions. In the region 6300—6900 Å., crystals of the chrome alums exhibit selective absorption showing a high degree of resolution, especially at very low temperatures. The positions and intensities of the component bands vary with the cations and anions, but the absorption is fundamentally unaltered in type, since corresponding lines can be identified in the different alums. The cæsium and methylamine alums are anomalous. Most of the alums investigated exhibit sequences of sharp bands separated by constant frequency differences, *e.g.*, in the potassium chromium selenate $\Delta\nu$=43 cm.$^{-1}$ and for the rubidium analogue $\Delta\nu$=44·2 cm.$^{-1}$ The vibration is attributed to a normal lattice constituent giving an oscillation corresponding with a residual ray of 232 μ. Raising the temperature shifts the band towards the red and causes a loss in definition. The changes in wave-length are irregular, but the half-breadth increases as $T^{\frac{1}{2}}$. The alums show a well-defined doublet band near 6700 Å. For different alums $\Delta\nu$ varies from 2·0 to 24·0 cm.$^{-1}$

The number of absorbing centres is very small but approximately constant. The ratio absorbing/total chromium atoms (or complexes) is 3×10^{-8} for the characteristic doublet and not more than 10^{-3} for the unresolved absorption in the visible and ultra-violet. The conclusion is reached that the absorbing entity for the banded structure is a non-electrostatically bound, homopolar Cr–(H_2O) complex.

R. A. MORTON.

Wide absorption bands among the halogens. P. BOVIS (Ann. Physique, 1928, [x], **10**, 232—344).—Methods are described of obtaining extremely thin layers of bromine and iodine between quartz plates and of the measurement of their thickness by an interferometric method. The absorption of such films and of aqueous solutions of copper sulphate, copper chloride, copper acetate, cobalt sulphate, cobalt chloride, nickel sulphate, nickel chloride, potassium chromate, and of certain mixed solutions of these substances has been measured between 2000 and 4500 Å. These solutions are suggested for photometric standards. With rise of temperature the opacity of liquid bromine decreases, the decrease being seven times as great as would be anticipated from the thermal expansion of the liquid. Absorption curves were determined for solutions of bromine in water, chloroform, carbon tetrachloride, ethyl alcohol, and carbon disulphide. The positions of the two bands of bromine do not vary greatly in these solutions, the maxima of the violet and characteristic ultra-violet solution bands being in the neighbourhood of 0·414 and 0·260 μ, respectively. The ultra-violet band is narrow but very persistent. Thin films of solid iodine showed a wide band with a maximum at 0·255 μ which appears to be related to the wide absorption near 0·206 μ of iodine vapour. F. G. TRYHORN.

Beryllium hydride band spectra. W. W. WATSON (Physical Rev., 1928, [ii], **32**, 600—606).—Measurements were made at high dispersion of two new band systems appearing in a beryllium arc in hydrogen, one in the green from 4800 to 5120 Å., the other from 3700 to beyond 2200 Å. in the ultra-violet. The quantum analysis is given. The green band group

belongs probably to the $^2P \longrightarrow {}^2S$ class due to BeH molecules, and consists of the 0—0, 1—1, etc. bands, degrading to the violet, but all branches exhibit a marked shift to the red for $j>30$. The analysis gives $I_0'=2\cdot6833\times10^{-40}$ g.-cm.^{2} and $I_0''=2\cdot7212\times10^{-40}$ g.-cm.^{2} for the moments of inertia, $r_0''=1\cdot35\times10^{-8}$ cm., $\omega_0'=2053\cdot4$, $\omega_0''=2025\cdot7$. The ultra-violet system consists of singlet P,R branch bands degrading to the red. For this system $I_0'=3\cdot85\times10^{-40}$ g.-cm.^{2} and $I_0''=2\cdot50\times10^{-40}$ g.-cm.^{2}, $r_0''=1\cdot29\times10^{-8}$ cm. The probable electronic transition for the ultra-violet bands is discussed. N. M. BLIGH.

Less refrangible bands in the spectrum of tin monochloride. W. F. C. FERGUSON (Physical Rev., 1928, [ii], **32**, 607—610).—Four groups of bands previously obtained by Jevons (A., 1926, 222) in a discharge through stannic chloride vapour are now found also in streaming active nitrogen. Two groups, α and β, were classified by Mulliken (A., 1926, 1079) as a $^2S \longrightarrow {}^2P$ transition in SnCl. It is concluded from new measurements and from an examination of the band structure that the other two groups, λ 3500 and 3800, are a $^2D \longrightarrow {}^2P$ transition with the same ^2P state as the α and β bands. The chlorine isotope effect confirms the identity of the emitter as SnCl, and confirms the vibrational quantum number assignments. The vibrational intensity distribution (intensity concentrated in $\Delta n=0$ sequence) is in qualitative agreement with theory, for the ratio of ω_0'' to ω_0'. No new bands were obtained in an attempt to obtain analogous bands by introducing stannic iodide vapour into active nitrogen. N. M. BLIGH.

Absorption band spectrum of iodine monochloride. E. D. WILSON (Physical Rev., 1928, [ii], **32**, 611—617).—The visible spectrum has been photographed and measured, and eight new members have been located in the two series described by Gibson and Ramsperger (this vol., 6) as corresponding with $n''=1$ and $n''=2$. The convergence limit of the former series is at $\nu=17430\pm5$ cm.$^{-1}$, making the heat of dissociation 49650 15 g.-cal. per mol. Four members of a new series, $n''=3$, have been found, also a further series of five members. The ratio c_p/c_v for gaseous iodine monochloride is calculated as 1·30, in agreement with empirical results. The fine structure of three consecutive bands has been measured. Approximate values for the moment of inertia have been computed. N. M. BLIGH.

Absorption spectrum of liquid benzene. J. BARNES and W. H. FULWEILER (Physical Rev., 1928, [ii], **32**, 618—623; cf. this vol., 458).—A precision method is described for measuring the wavelengths of radiation in the near infra-red region of the spectrum using a 6-ft. Rowland concave grating with a Thalofide cell. The wave-length of a further outstanding absorption band was determined as 0·6060 μ. The absorber of these radiations is considered to be a linear anharmonic oscillator, the energy states of which are represented by odd multiples of half quanta. N. M. BLIGH.

Potential of photo-active cells containing fluorescent electrolytes. H. W. RUSSELL (Physical Rev., 1928, [ii], **32**, 667—675).—A theory is developed and expression obtained for the variation of potential with time of illumination for the photo-active cell. It is assumed that the exciting light produces a chemical change in the electrolyte. Experiments made with a cell containing rhodamine-B gave results in good agreement with the theory, and diffusion was shown to play an important part. N. M. BLIGH.

Fluorescence and photo-chemical change. K. G. MATHUR and S. S. BHATNAGAR (Indian J. Physics, 1928, **3**, 37—52).—From a study of the decay of fluorescence of certain fluorescent solutions when exposed to sunlight in the presence of air it is concluded that this photo-decomposition is probably an oxidation phenomenon which may have nothing to do with fluorescence. W. E. DOWNEY.

New phenomenon of light scattering in crystals. G. LANDSBERG and L. MANDELSTAM (Naturwiss., 1928, **16**, 772).—A better photograph of the dispersed light and comparison spectra (this vol., 936) is given. J. W. BAKER.

Raman spectra of scattered radiation. R. W. WOOD (Phil. Mag., 1928, [vii], **6**, 729—743).—Results similar to those obtained by Raman and Krishnan for the spectra of light scattered by transparent media have been obtained for ten liquids and for quartz. Both Stokes and anti-Stokes lines have been observed. The scattered light shows, in addition to lines of the illuminating radiation, other bright lines having constant differences in frequency from the exciting lines. These frequency differences correspond with frequencies in the infra-red, and in some cases agree closely with observed infra-red absorption bands. The experimental arrangements are fully described. The results are in accordance with the quantum theory, the incident light quantum giving up a portion of its energy to the molecule, thus raising it to an excited state, and then passing off with diminished energy exhibited in lines of greater wave-length. The results obtained with calcite do not correspond with the known infra-red absorption bands. No modified lines were obtained with sodium chloride. A. E. MITCHELL.

Raman effect in glycerol and glycerol–water mixtures. S. VENKATESWARAN (Indian J. Physics, 1928, **3**, 105—122).—When light from a quartz–mercury lamp is diffused through glycerol, the spectrogram of the scattered light contains a bright continuous spectrum and a number of modified lines, including one of enhanced frequency. The shifts of frequency of the modified lines correspond with certain characteristic infra-red frequencies of the molecule. W. E. DOWNEY.

Raman effect in xylene. C. E. BLEEKER (Z. Physik, 1928, **50**, 781—786).—The wave-lengths and intensities of the Raman lines excited by the light from a mercury arc have been determined. The frequency differences correspond with a number of infra-red frequencies, many of which lie very close to those observed by Coblenz. R. W. LUNT.

Influence of temperature on the Raman effect. K. S. KRISHNAN (Nature, 1928, **122**, 650).

Raman effect in crystals. I. R. RAO (Indian J. Physics, 1928, **3**, 123—135).— The Raman effect has

been studied in the cases of ice and quartz. Compared with water, the bands observed with ice are sharper and of shorter wave-length. This result is in agreement with the corresponding infra-red absorption data. W. E. DOWNEY.

Raman effect in gases and vapours. L. A. RAMDAS (Indian J. Physics, 1928, 3, 131—136).—The Raman effect has been obtained with ether vapour and with liquid ether at the ordinary temperature. The intensity of the modified radiation is smaller in the case of the vapour than in that of the liquid. Some experiments have been made on the effect in carbon dioxide liquid and vapour at and near the critical temperature. W. E. DOWNEY.

Raman effect in organic liquids. P. PRINGSHEIM and B. ROSEN (Z. Physik, 1928, 50, 741—755).—The Raman spectra of the following liquids, in addition to quartz, have been examined using a mercury arc as light source: methylene chloride, chloroform, carbon tetrachloride, dichloroacetylene, tetrachloroethylene, acetylene tetrachloride, benzene, chlorobenzene, toluene, and silicon tetrachloride. For each liquid every observed Raman line has been identified as corresponding with a known infra-red frequency, although the converse does not hold. No similarity can be traced between the spectra of carbon and silicon tetrachlorides. A number of lines have been observed for quartz, but only some of these appear to be related to the known infra-red frequencies; fused quartz does not give a Raman spectrum. R. W. LUNT.

Cause of the luminescence of phosphorus. A. PETRIKALN (Naturwiss., 1928, 16, 205; Chem. Zentr., 1928, i, 2235—2236).—The excitation of phosphorus trioxide vapour yields the same band spectrum as is obtained by the oxidation of phosphorus and phosphorus trioxide. Absorption experiments also support the view that the luminescence spectrum of phosphorus is to be attributed to the trioxide. With the pentoxide the spectrum of the glow of phosphorus, either in emission or in absorption, was not obtained. Emeléus and Purcell's band, 3270 Å. (A., 1927, 497), arises from impure phosphorus pentoxide.

A. A. ELDRIDGE.

Spectra of intermetallic compounds. J. M. WALTER and S. BARRATT (Nature, 1928, 122, 684—685).—Most of the "mercury–thallium" spectrum described by Waring (this vol., 603, 1166) is identical with that listed by Mohler and Moore (A., 1927, 917) as the "cadmium" molecular spectrum; the true origin of the system appears to be the molecule of thallium chloride. Similarly, Waring's "indium–cadmium" spectrum appears to coincide with another set of cadmium bands found by Mohler and Moore; these appear to arise from an association of cadmium and oxygen, although they may be totally unconnected with cadmium. A. A. ELDRIDGE.

Chemiluminescence of aminophthalic hydrazide. H. O. ALBRECHT (Z. physikal. Chem., 1928, 135, 321—330).—The strong chemiluminescence observed when 3-aminophthalic hydrazide and its diacetyl derivative are oxidised in alkaline solution has been investigated. Most oxidising agents which may be used in alkaline solution are active, especially hypochlorites and ferricyanides. The action of hydrogen peroxide alone is feeble, but the maximum effect is obtained with a mixture of hydrogen peroxide and hypochlorite or ferricyanide. The luminescence is visible even at concentrations of $10^{-8}M$. Of the various *cyclo*hydrazides and hydrazine derivatives investigated, only those related in some manner to phthalic acid exhibit this highly developed luminescence. H. F. GILLBE.

Vitamin-*D* and *iso*ergosterol. A. VAN WIJK and E. H. REERINK (Nature, 1928, 122, 648).—Similarities in the absorption curves of ergosterol, *iso*ergosterol, and vitamin-*D* suggest that ergosterol has two types of absorption bands connected with different parts of the molecule. On irradiation and formation of vitamin-*D* the first system (293, 281, 270 μμ) gives place to the characteristic absorption band of *iso*-ergosterol, indicating constitutional change, whilst another part of the molecule is unchanged constitutionally, since the bands 262, 250 μμ are permanent.

A. A. ELDRIDGE.

Intensity relations and band structure in bands of the violet CN type. R. S. MULLIKEN (Physical Rev., 1927, [ii], 29, 923).—Theoretical intensity formulæ applicable to bands of the violet CN ($^2S \rightarrow {}^2S$) type are obtained, assuming Hund's case *b*. Their predictions are verified with CaH, N_2^+, and violet CN bands. A. A. ELDRIDGE.

Infra-red reflexion spectra of some carbonates. E. K. PLYLER (Physical Rev., 1927, [ii], 29, 923).—A study of the structure of the band of selective reflexion of calcium carbonate indicated maxima at 6·36, 6·54, and 6·62 μ. These maxima are probably due to the isotopes of calcium. Iron carbonate and dolomite showed two maxima. A. A. ELDRIDGE.

Infra-red spectrum of ammonia. W. F. COLBY and E. F. BARKER (Physical Rev., 1927, [ii], 29, 923).—The ammonia absorption band consists of two overlapping bands with zero branches at 10·3 μ and 10·7 μ. About 12 lines have been observed in each branch, the spacing differing somewhat. Ammonia bands are interpreted in terms of two different types of transition: one in which the second rotational quantum number changes, and the other in which it does not change. A. A. ELDRIDGE.

Shift in a near infra-red absorption band of some benzene derivatives. J. BARNES (Physical Rev., 1927, [ii], 29, 922).—The following wave-lengths (Å.) are recorded: benzene 8741, toluene 8758, ethylbenzene 8772, *o*-xylene 8781, *m*-xylene 8793, *p*-xylene 8808, diethylbenzene 8799, mesitylene 8844.

A. A. ELDRIDGE.

Ultra-violet absorption and emission spectra of carbon monoxide. J. J. HOPFIELD and R. T. BIRGE (Physical Rev., 1927, [ii], 29, 922).—Nine absorption systems between 920 and 2064·5 Å. have been obtained, representing transitions from the normal level to all of the previously known excited electronic levels, and to four new levels. Other absorption systems do not permit of definite analysis. Certain band systems are also found in emission.

A. A. ELDRIDGE.

Band structure and intensities, atomic and molecular electronic states, in diatomic hydrides. R. S. MULLIKEN (Physical Rev., 1927, [ii], 29, 921).—Theoretical intensity formulæ applicable to $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2P$ molecular electronic transitions have been obtained for Hund's case *b*. Observations on CaH, MgH, OH, and CH (λ 3900) bands are in agreement with the theory. A. A. ELDRIDGE.

Structure and isotope effect in the α-bands of boron monoxide. F. A. JENKINS (Physical Rev., 1928, [ii], 29, 921).—New observations on the α-bands of boron monoxide support Mulliken's interpretation of the structure as due to a $^2P \longrightarrow {}^2S$ transition. The ^2P doublet is inverted. The origins of the ($\frac{1}{2}$, $\frac{1}{2}$) bands of $B^{10}O$ and $B^{11}O$ are separated by 1·547 Å., the amount required for half-integral vibrational quantum numbers. Analysis of the $B^{10}O$ band gives smaller moments of inertia than those obtained for $B^{11}O$, but identical internuclear distances, $r_0'=1{\cdot}352\times10^{-8}$ and $r_0''=1{\cdot}208\times10^{-8}$ cm. A. A. ELDRIDGE.

Theoretical relation between infra-red and ultra-violet bands. R. T. BIRGE and J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 365—366).—Measurements with carbon monoxide show that the frequency of infra-red (vibration–rotation) bands of a diatomic molecule can be calculated from the measured frequencies of certain ultra-violet (electronic) bands correlated with the normal state of the molecule.
A. A. ELDRIDGE.

Fluorescence of mercury vapour under low excitation. (LORD) RAYLEIGH (Nature, 1928, 122, 725).—When dense mercury vapour is excited by radiation of wave-length 3000 Å., the spectrum shows, besides the visual maximum, the broad maximum at about 3300 Å. The fluorescence can be distilled away from the place of origin (cf. this vol., 935).
A. A. ELDRIDGE.

Absorption of ultra-violet light by organic vapours. A. W. SMITH, C. E. BOORD, and C. S. PEASE (Physical Rev., 1927, [ii], 29, 355).—The characteristics of bands observed with benzene, diethyl ether, methyl *n*-amyl ether, and ethylene chlorohydrin are described. A. A. ELDRIDGE.

New series in the spectrum of fluorescent iodine. F. W. LOOMIS (Physical Rev., 1927, [ii], 29, 355).—The constants *d* and γ of new series in Wood's spectra of fluorescent iodine afford nearly integral values of the vibrational quantum number of the fluorescent molecule before excitation. Values of n' and n'' are obtained for each doublet in the series. A. A. ELDRIDGE.

Absorption spectra in the extreme ultra-violet. J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 356).—Nitrogen, air, acetylene, and carbon monoxide show selective absorption and a region of continuous absorption on the short wave-length side. Acetylene shows band absorption beginning at 2300 Å. Nitrogen shows Sponer's bands and continuous absorption beginning at 990 Å. The principal lines of the four ultra-violet series of N I and a group of lines at 1085 Å. due to ionised nitrogen were observed. Some carbon lines (probably resonance), the Cameron bands (arising from the normal state) of carbon monoxide, and some bands of a new system in carbon monoxide were observed with that gas.
A. A. ELDRIDGE.

Quantitative test of Hund's theory of doublet bands of the OH type. E. C. KEMBLE and F. A. JENKINS (Physical Rev., 1927, [ii], 29, 607).—A study, for doublets, of the effect of molecular distortion on the rotational term formula, and an application of the results to NO β-bands confirm Hund's theory. A. A. ELDRIDGE.

Activation of hydrogen by the contact action of palladium. M. POLJAKOV (Naturwiss., 1928, 16, 131; Chem. Zentr., 1928, i, 1743).—When hydrogen is circulated over a palladium plate which has been heated in hydrogen at 700—800° and cooled at 1—5 mm. to 300—400°, a violet luminescence is observed beyond the palladium towards the pump and at the walls of the tube. A. A. ELDRIDGE.

Absorption and fluorescence of iodine vapour. P. PRINGSHEIM (Naturwiss., 1928, 16, 131—132; Chem. Zentr., 1928, i, 1750).—In view of Wychodil's observation that iodine vapour under suitable conditions exhibits surface fluorescence, the supposition that all collisions between excited and unexcited iodine molecules cause extinction of fluorescence is invalid. Also a resonance spectrum was obtained in iodine vapour at 100 mm. above 600° by mercury radiation 2537 Å.; it consisted of twelve positive and four anti-Stokes members. Between 2100 and 3000 Å. and below 500°, iodine vapour is almost completely transparent. On progressive rise of temperature increasingly strong absorption bands appear.
A. A. ELDRIDGE.

Striking potentials of metallic arcs in a vacuum. S. H. ANDERSON (Physical Rev., 1927, [ii], 29, 750—751).—The striking potential is dependent on a gaseous atmosphere as well as on the nature of the electrodes (cf. Simeon, Phil. Mag., 1923, 46, 816).
A. A. ELDRIDGE.

Carbon monoxide band excitation potentials. A. B. HEPBURN (Physical Rev., 1927, [ii], 29, 212).—Birge's computation that the lines 4511, 4880, 2190, and 3794 Å. should be produced by electrons having a minimum velocity corresponding with 10·7, 16·7, 19·8, and 19·8 volts, respectively, is experimentally confirmed within 0·1 volt. A. A. ELDRIDGE.

Relation between dipole moment and constitution. J. ERRERA (Physikal. Z., 1928, 29, 689—690).—Chloroiodoethylene forms compounds in which the iodine is tervalent; *cis*- and *trans*-dichloro-derivatives of this type have been prepared and their molecular polarisations determined. The results confirm the view that the iodine atom is positively charged relative to the chlorine atom, since the dipole moment of the *trans*-derivative is more than twice that of the *cis*-derivative. R. A. MORTON.

Electrical symmetry of the molecular structure of methane derivatives. L. EBERT, R. EISENSCHITZ, and H. VON HARTEL (Z. physikal. Chem., 1928, B, 1, 94—114).—The physical methods for the determination of the symmetry of molecules in gaseous form or in dilute solution are discussed. By measurements of the change in dielectric constant when

solution is substituted for pure solvent, determinations of the molecular polarisation of derivatives of $C(OH)_4$, $C(CH_2{\cdot}OH)_4$, and $C(CO_2H)_4$ of the form CX_4 have been made in benzene and carbon tetrachloride solutions. In a number of cases it was found that the orientation polarisation, as measured by the difference between the molecular polarisation in the dissolved and solid states, respectively, had a value far beyond the limits of experimental error. This is regarded as indicating that the following substances examined possess a fixed dipole moment: $C(OMe)_4$, $C(OEt)_4$, $C(CH_2{\cdot}CO_2Me)_4$, $C(CH_2{\cdot}O{\cdot}NO_2)_4$, $C(CO_2Me)_4$, and $C(CO_2Et)_4$. These substances appear to possess a normal mol. wt. in solution as determined by Beckmann's f.-p. method. The results supplement Weissenberg's theory (A., 1926, 934) that the molecule CX_4 shows greater variety of form than is in accordance with the requirements of classical stereochemistry, since if it is to be regarded as a symmetrical pyramid it could not have a dipole moment. M. S. Burr.

Dielectric constants and dispersion of some organic compounds and shattering of light by the molecules. W. Lautsch (Z. physikal. Chem., 1928, B, 1, 115—133).—The degree of depolarisation of the Tyndall beam, diffracted by the molecules of pure liquid, has been determined for 15 organic liquids. In order to determine whether a large depolarisation is due to a departure of the simple molecule from the spherical form or to association, the influence of temperature on the function $(\varepsilon-1)/(\varepsilon+2)d$, where ε is the dielectric constant and d the density, has been determined in a number of cases. From the constancy of this expression for the liquid hydrocarbons, diphenyl, dibenzyl, triphenylmethane, and decalin, these appear to possess no dipole moment, but its existence is indicated in the case of the ethyl esters of stearic, palmitic, lauric, and oleic acids. For the last the moment increases with diminishing length of chain. The double linking in the oleic ester apparently increases the moment. When hydrocarbons are arranged in the order of degree of depolarisation certain conclusions with regard to the influence of molecular structure are indicated. The closed ring is not necessarily productive of large depolarisation, but a double linking appears to give a certain amount of rigidity to the molecule which tends to make the value high. The position of the substituents in the benzene nucleus may have a marked influence, the depolarisation by *o*-xylene being much less than by *p*- and *m*-xylene. The value for dibenzyl is distinctly less than for diphenyl, which is similar to the value for naphthalene. Possibly the benzene rings in the two last compounds lie more nearly in the same plane. For triphenylmethane the value is relatively small, which may be explained by the arrangement of the groups round the methane carbon atom. From the dispersion in the visible region the ultra-violet and the ultra-red portion of the characteristic frequency of the molecules may be calculated. M. S. Burr.

Electrical dipole moment of organic molecules. J. Estermann (Z. physikal. Chem., 1928, B, 1, 134—160).—The methods employed for the calculation of the electrical dipole moment from dielectric constant measurements are discussed and it is shown that the error obtained by employing the molecular refraction or the polarisation in the solid state, instead of the deformation or dielectric fraction of the molecular polarisation, may be considerable. In non-associated liquids the dipole moment may be determined from the variation of dielectric constant with temperature. This method has been employed for a number of ethers, diphenyl derivatives, and esters of amino-acids in dilute benzene solutions. Symmetrical ethers have all, apparently, the same dipole moment, so that its value must depend on the oxygen atom. The asymmetric ethyl amyl ether has a larger moment. The mixed ethers, anisole and phenetole, have different values of molecular polarisation according to whether they are in the pure liquid state or in solution. Diphenyl, which has a small moment, is not much influenced by the introduction of a CH_2 group, but the O, NH, and CO groups give an increasingly larger moment. The methyl esters of aminobenzoic acids contain a positive group and a negative group, and it is found that the moment of the *o*-compound is less than that of either aniline or methyl benzoate, whereas the moment of the *p*-ester is approximately equal to the sum of the two. The moments of the methyl esters of α- and δ-aminovaleric acid appear to indicate that a straight aliphatic chain is obtained and not a curved one. M. S. Burr.

Electrical dipole moments of organic molecules by the molecular ray method. J. Estermann (Z. physikal. Chem., 1928, B, 1, 161—169).—The method of comparison of electrical dipole moments by the deviation of a molecular ray in a non-homogeneous electric field has been improved. The relationship between the dipole moments of the series diphenyl, diphenylmethane, benzophenone, and diphenyl ether, and also of *o*-, *m*-, and *p*-aminobenzoic esters obtained by this method agrees with that found by measurements of the dielectric constant. M. S. Burr.

Anomalous dispersion in calcium, strontium, and bromine vapour. V. Prokofiev (Z. Physik, 1928, 50, 701—715; cf. this vol., 577).—The anomalous dispersion in calcium, strontium, and bromine vapours has been investigated with respect to the changes $1^1S_0 \longrightarrow 2^1P_1$ and $1^1S_0 \longrightarrow 2^3P_1$. The ratio of the number of dispersion centres of these two lines diminishes very strongly with increasing atomic number. When the probability of the spontaneous transition $2^1P_0 \longrightarrow 1^1S_0$ is taken as unity, the probability A_2 of the spontaneous combination change $2^3P_1 \longrightarrow 1^1S_0$ is given by $A_2=(\Delta\nu/\delta\nu)^{2\cdot44}$, where $\Delta\nu$ and $\delta\nu$ indicate the term differences $2^3P_2-2^3P_0$ and 1^1S_0—centre of gravity of the $2^3P_{0,1,2}$ term in $cm.^{-1}$ The results obtained by other investigators for cadmium and mercury also follow this relation. Predictions of the relative probabilities for the intercombination lines of magnesium and zinc are also made from this relation. J. W. Smith.

Reflecting power of carbon between the ordinary temperature and 1500°. K. Warmuth (Wiss. Veroff. Siemens-Konz., 1928, 7, 307—320).—The reflecting power of carbon for light of wavelengths 0·538 and 0·663 μ has been determined by Pirani's method with an accuracy of 4—5%. The

results show that the reflecting power of carbon varies only slightly between 20° and 1470° from 0·034 to 0·028. Assuming that the latter value remains constant for higher temperatures, the true temperature of the positive crater of the carbon arc is 3740° Abs. On this basis a new vapour-pressure curve for carbon has been constructed from which the mean heat of vaporisation of carbon at 3900° Abs. under 1—5 atm. pressure has been calculated as 125·54 kg.-cal./g.-mol. A. R. POWELL.

Molecular theory of diffusion of light in fluids. I. Without consideration of the intermolecular field. II. The intermolecular field. Y. ROCARD (Ann. Physique, 1928, [x], **10**, 116—179, 181—231).—I. A mathematical consideration of the diffusion of light by a hypothetical atom built up of isotropic oscillating ions.

II. The previous treatment of the problem is modified by taking into account the effect of the intermolecular field on the diffusion of light, and it is shown that the results predicted by the author's theory are in closer accord with experiment than those deduced from the Einstein–Gans theory.

F. G. TRYHORN.

Refractive index of sodium vapour and the width of the *D*-lines in absorption. J. Q. STEWART and S. A. KORFF (Physical Rev., 1928, [ii], **32**, 676—680).—A theoretical relation is developed by classical methods between the refractivity of sodium vapour near the *D*-lines and their observed width in absorption. The theory is approximately verified by preliminary results of experiments described, involving observation of the wave-lengths of interference fringes produced by sodium vapour, using a Michelson interferometer in conjunction with a spectroscope and a source of white light.

N. M. BLIGH.

Anomalous magnetic rotation in excited neon. R. N. JONES (Physical Rev., 1928, [ii], **32**, 681—688).—Measurements were made of the angle of rotation for different frequencies of light near strong lines in the yellowish-red region of the neon spectrum. These lines show anomalous dispersion, and the dispersion constants are calculated from the angle of rotation using Kuhn's formula; hence the relative transition probabilities were found. N. M. BLIGH.

Internal field of polarisation. R. DE MALLEMANN (Compt rend., 1928, **187**, 720—722).—The author's general method for the calculation of the internal field of the molecules of a substance (this vol., 1172) indicates that the field is essentially a heterogeneous effect. This contradicts the classic reasoning of Lorentz, and a new expression is derived for the refractive power (n) of a spherical isotropic body in which the Lorentz or Gladstone factor is replaced by $3K/(2K+1)$, where K is the inductive power of the medium. The new factor gives values of n in close agreement with experimental values and with those derived from Gladstone's formula. J. GRANT.

Chemical constitution and rotatory power. III. S. BERLINGOZZI (Atti R. Accad. Lincei, 1928, [vi], **7**, 925—929).—Measurements have been made of the specific rotatory power and the dissociation constant of a number of aminosuccinic acid monoamides in which an acyl group is introduced into the amino-group. The following derivatives were examined: anisoyl, cuminoyl, *p*-toluoyl, *p*-chlorobenzoyl, *p*-nitrobenzoyl, *m*-toluoyl, *m*-nitrotoluoyl, *o*-chlorobenzoyl, *o*-bromobenzoyl, *p*-toluenesulphonyl, and 2-nitrotoluene-3-sulphonyl. The data are thought to show that a diminution in rotatory power is associated with an increase in the dissociation constant. R. W. LUNT.

Anomalous dispersion of lithium and mercury. E. SEGRÈ and E. AMALDI (Atti R. Accad. Lincei, 1928, [vi], **7**, 919—921).—The ratio of the intensity of the lithium lines 6708 ($2S-2P$) and 3232 ($2S-3P$) and that of the mercury lines 2537 ($^{6_1}S_0-^{6_3}P_1$) and 1849 Å. ($^{6_1}S_0-^{6_1}P_1$) has been determined from measurements of the anomalous dispersion of these lines by the interferometer method of Rasetti. The data obtained show that the ratio of the number of "dispersion" electrons associated with 6708 to that associated with 3232 Å. is 135 ± 27, and that the ratio for the mercury lines 2537, 1849 Å. is approximately 100. R. W. LUNT.

Variation with state of the optical constants of cæsium. J. B. NATHANSON (Physical Rev., 1927, [ii], **29**, 369—370).—For liquid cæsium at 33° values of the coefficient of absorption, the refractive index, and reflecting power are, for 5400 Å., respectively, 3·66, 0·310, 0·588, whilst for solid cæsium (23°) corresponding values are: 3·74, 0·308, 0·595.

A. A. ELDRIDGE.

Covalency, the paramagnetism of oxygen, and stereochemistry. H. F. BIGGS (Phil. Mag., 1928, [vii], **6**, 659—664).—London's theory of covalency (cf. this vol., 344) is shown to be applicable to the structure of oxygen, since if his model be accepted and one Bohr magneton be assigned to each *p*-orbit, the calculated value of the paramagnetic susceptibility accords with the accepted observed value. Van Vleck's theory (cf. this vol., 572), whilst requiring only slight modification for oxygen and nitrogen, is not applicable to nitric oxide when tested on the susceptibility criterion. London's theory is used to explain some points in the structures of graphite, diamond, and the aliphatic compounds, whilst it accounts also for the apparent anomaly that the addition of two extra hydrogen atoms to benzene leads to a more unsaturated substance, since such addition, displacing the hexagonal symmetry of the carbon atoms, destroys the unstrained plane structure of the ring and leads to a reversion of the carbon atoms from tervalent to quadrivalent. By analogy with the results for oxygen and nitric oxide, the effect of adsorbed hydrogen in diminishing the paramagnetism of palladium (Biggs, A., 1916, ii, 412) is attributed to the neutralisation of two palladium magnetons per molecule of hydrogen adsorbed. A. E. MITCHELL.

Electronic symmetry and polyatomic molecules. P. VINASSA (Atti R. Accad. Lincei, 1928, [vi], **7**, 975—979).—To account for the inactivity of the nitrogen molecule compared with that of the chlorine molecule it is suggested that in these molecules the centre consists of the pair of nuclei, each carrying the two electrons of the innermost orbit, and that the residue of the electrons is distributed

in orbits about this centre. Thus the electron distribution of the fluorine molecule is (2+2).2.8.2.2, and of the chlorine molecule (10+10).2.8.2.2. These molecules possess perfect electronic symmetry, but not that typical of the inert gas atoms, and in consequence exhibit chemical activity. The distributions in the oxygen and nitrogen molecules are, respectively, (2+2).2.8.2 and (2+2).2.8. The inertness of the latter molecule is due to the fact that the two nuclei, each possessing the stability of the helium type, are surrounded by electrons having the stable neon configuration. Ozone is regarded as a compound of molecular and atomic oxygen, since its electronic formula, based on the assumption of a molecule O_3, (2+2+2).2.8.8, possesses the symmetry of an inert gas and is not in accord with the properties of ozone. Sulphur is assumed to form true allotropes, *e.g.*, S_3, (10+10+10).2.8.8, with an electronic symmetry similar to that of argon. The probable constitution of a number of more complex molecules is discussed from this point of view. F. G. TRYHORN.

Co-ordination and atomic structure. P. RÂY (Z. anorg. Chem., 1928, **174**, 189—192).—The main factors governing complex formation are: (1) the volume occupied by the central ion, and its charge; (2) the tendency of the central ion to assume the atomic structure of the next higher inert gas; (3) the electronic arrangement in the central atom; (4) the co-ordinating group must be of such a nature that for each co-ordinated linking two electrons must be transferable to the central ion. H. F. GILLBE.

Constitution of hydrated crystals. M. A. RAKUZIN (Bull. Soc. chim., 1928, [iv], **43**, 984—988; cf. A., 1927, 948).—The nature of the linkings which hold the molecules of water of crystallisation in a hydrate is considered from the point of view of the theory of Wurtz (1879), according to which the water molecules are joined in a closed chain directly to the metallic atom of the salt. The importance of distinguishing between water of crystallisation and water of constitution is emphasised. O. J. WALKER.

Desiccation and the density of magnesium nitrate. L. LE BOUCHER (Anal. Fís. Quím., 1928, **26**, 223—227).—Dehydration of magnesium nitrate hexahydrate over sulphuric acid at the ordinary temperature yields a stable dihydrate without loss of nitric acid. The densities and m. p. of the hexa- and di-hydrates are 1·6363, 89°, and 2·0256, 120—125°, respectively. The density of the hexahydrate as given in the literature is thus erroneous. H. F. GILLBE.

Rule of additive volumes. E. MOLES (Anal. Fís. Quím., 1928, **26**, 228—233).—Satisfactory calculated values for the molecular volume of lanthanum, cerium, praseodymium, neodymium, and samarium nitrates are obtained if the general formulæ $[M^{\cdot\cdot}(NO_3)_2(H_2O)_6]_3$ and $[M^{\cdot\cdot\cdot}(NO_3{\cdot}H_2O)_3]_2$ be employed. Insufficient data are extant for the calculation to be applied to gadolinium. For the tervalent rare-earth metals there is a systematic decrease of molecular volume as the atomic weight of the central atom increases. H. F. GILLBE.

Magnetic moments of iron in complex salts. L. A. WELO and O. BAUDISCH (Physical Rev., 1927, [ii], **29**, 612).—Iron salts are grouped according to the magnetic moment of the iron atoms.

A. A. ELDRIDGE.

Effective cross-section of gas molecules in the presence of alkali ions of 1—30 volts velocity. C. RAMSAUER and O. BEECK (Ann. Physik, 1928, [iv], **87**, 1—30).—The magnetic method already used for the determination of the effective cross-section of gas molecules in the presence of slow electrons is here applied to slow alkali ions. The ions were obtained from a platinum or platinum–iridium filament coated with alkali-metal amalgam. The alkali metals used were lithium, sodium, potassium, rubidium, and cæsium, and the gases used were helium, neon, argon, hydrogen, oxygen, and nitrogen. It was found that for all combinations the effective cross-section of the gas molecule in the presence of alkali ions increases as the velocity of the ions is reduced at first slowly and then more rapidly. There is a turning point in the cross-section–voltage curve between 1 volt and 2 volts. The alkali ions show an increasing cross-section with increasing atomic number. The same behaviour was obtained with hydrogen, oxygen, and nitrogen as with the rare gases. Here the effective cross-section increased with the gas-kinetic size of the molecule. The results obtained were compared with those obtained using electrons instead of alkali ions. The ionic radius was also compared with the radius of the outer electron shell. A. J. MEE.

Temperature of the cathode as a factor in the sputtering process. L. R. INGERSOLL and L. O. SORDAHL (Physical Rev., 1928, [ii], **32**, 649—656).—Cathodic sputtering was investigated over an extreme temperature range of 150—1350° and a relatively low potential of 500—800 volts. Gold, platinum, and nickel show an increase in the rate of sputtering in argon with rise in cathode temperature. The lower the sputtering voltage the more pronounced is the effect. Films sputtered from a hot cathode suffer less change in resistance on baking and show a more definite crystal structure than those from a cold cathode. Results are consistent with the explanation of sputtering as essentially a vaporisation process.

N. M. BLIGH.

Effect of molecular form and association on light scattering in liquids. I. Fatty acids and alcohols. II. Some aromatics. S. R. RAO (Indian J. Physics, 1928, **3**, 1—30).—The variations of intensity of the transversely scattered light, the depolarisation factor, and the optical molecular anisotropy have been determined in the cases of four primary alcohols, three fatty acids, and four polar aromatic compounds. W. E. DOWNEY.

Magnetic properties of some substances in the adsorbed state. S. S. BHATNAGAR, K. N. MATHUR, and P. L. KAPAR (Indian J. Physics, 1928, **3**, 53—66).—Iron, nickel, cobalt, and manganese lose their paramagnetism and become diamagnetic when adsorbed on charcoal. Adsorption is not analogous to mixing, but would appear rather as a chemical combination. Adsorption by silica gives a slight increase in paramagnetism in the case of iron. W. E. DOWNEY.

Types of [chemical] combination. H. G. GRIMM (Z. Elektrochem., 1928, **34**, 430—437).—A

general account. The characteristics of the individual types of combination are discussed and the various types compared and contrasted. S. K. TWEEDY.

Significance of atom models [in the types of chemical combination]. A. SOMMERFELD (Z. Elektrochem., 1928, **34**, 426—430).—A general account of the recent theories of atom mechanics. S. K. TWEEDY.

Crystal structure and the types of chemical combination. V. M. GOLDSCHMIDT (Z. Elektrochem., 1928, **34**, 453—463).—A general account in which previous work on crystal structure is collated from the point of view of chemical combination. S. K. TWEEDY.

***X*-Ray absorption spectra and chemical combination.** O. STELLING (Z. Elektrochem., 1928, **34**, 520—522).—The author summarises his work on the subject (cf. A., 1927, 391). S. K. TWEEDY.

Inversion point of the second order. W. JAZYNA (Z. Physik, 1928, **51**, 292—307).

Close agreement between the *X*-ray spectra of a substance in the liquid and liquid crystalline states. J. R. KATZ (Naturwiss., 1928, **16**, 758—759).—The *X*-ray spectra of various substances were investigated just above and just below the transition from the liquid to the liquid crystalline state. It was found that there were no characteristic differences between the two diagrams. The molecules in the liquid must therefore be arranged in the same way as in the liquid crystals of the same substance. A. J. MEE.

***K*-Series *X*-ray absorption spectrum of potassium in various compounds.** O. STELLING (Z. Physik, 1928, **50**, 626—629).—The investigations of Lindh (Arkiv Mat. Astron. ock Fysik, 1924, **18**, No. 14) on the dependence of the *X*-ray absorption spectrum of potassium compounds on the nature of the anion have been confirmed and extended, data for 27 potassium salts having been obtained. It has been shown that the compounds cannot be divided into groups, according to the wave-length of the absorption line observed, as suggested by Lindh, but that there is a continuous transition from metallic potassium to potassium hydrogen tartrate, in which the change in wave-length is most marked (5·5 X-units). The normal halides all show the same wave-length, which is surprising in view of the great differences in atomic distances to be observed in this group. There is a great difference in many cases between the values given by the normal and acid salts, but the phenomenon is not general. J. W. SMITH.

***X*-Ray coloration of kunzite and hiddenite.** P. L. BAYLEY (Physical Rev., 1927, [ii], **29**, 353).—A spectrographic study. The green colour in both minerals is probably due to a similar physical cause. A. A. ELDRIDGE.

$K\beta_2$-Lines of the elements potassium to manganese. T. WETTERBLAD (Z. Physik, 1928, **49**, 670—673).—In view of the doubt thrown by the work of Druyvestyn (A., 1927, 804) on the values of $\beta_1-\beta_2$ given by Hjalmar (cf. A., 1920, ii, 655), new determinations of this difference have been made, with an estimated accuracy of 0·3X-unit, for the elements potassium to manganese. The difference β_2, determined for the oxides, shows a maximum at 21 (scandium) when plotted against the atomic number; this relationship is similar to that already traced for the difference $\alpha_{12}-\beta_1$ (Wetterblad, A., 1927, 491). The spectrograms show that in the case of calcium the β_2 line occurs as a doublet in the metal, and only the longer wave-length member of this doublet in the oxide. The difference between the doublet members is 3·3X-units, corresponding with 4·4 volts. This value agrees well with that previously observed by the author for the influence of oxygen in the elements sodium to chlorine, 4·3 volts. Druyvesteyn has recorded a β'''-line for calcium and potassium; these values cited are now shown to be but mean values of doublets of wave-length 3404·5, 3396·3 and 3047·6, 3043·9, respectively. R. W. LUNT.

Theory of *X*-ray diffraction in liquids. G. W. STEWART (Physical Rev., 1928, [ii], **32**, 558—563).—The assumption of myriads of non-crystalline and non-permanent molecular groupings in liquids at any instant, a condition termed cybotaxis, makes possible the use of the crystal powder theory as an idealised one for liquids, and is shown to give a simple explanation of a number of experimental results in the diffraction of *X*-rays in liquids not otherwise adequately explained by a single theory. N. M. BLIGH.

Thermal degeneration of the *X*-ray haloes in liquids and amorphous solids. S. S. RAMASUBRAMANYAM (Indian J. Physics, 1928, **3**, 137—149).—*X*-Ray diffraction in *cyclo*hexane, pentane, and glycerol at different temperatures has been studied. On raising the temperature a contraction of the ring, a broadening of the ring and diffuseness at the edges, and a large amount of internal scattering occur. The theory of these changes is discussed. W. E. DOWNEY.

Diffraction of cathode rays by calcite. S. NISHIKAWA and S. KIKUCHI (Nature, 1928, **122**, 726).—The pattern obtained by reflexion of cathode rays at a cleavage face of calcite is described. The structure factor for *X*-ray reflexion appears to have a similar influence on cathode-ray reflexion, since the relative intensities of lines due to different orders are similar in the two cases. Similar patterns were obtained with mica, topaz, zinc blende, and quartz. A. A. ELDRIDGE.

Polarisation of ions in a crystal lattice. A. E. VAN ARKEL (Z. Physik, 1928, **50**, 648—656).—On the supposition that an ion is equally polarisable in all directions, the energy of polarisation in different crystal forms is calculated. Among binary compounds, this energy is least in the cæsium chloride lattice and increases with decreasing co-ordination number. This accounts for the decreasing readiness of polarisation in passing from the cæsium chloride type to the sodium chloride type and thence to the zinc-blende type. Among alkali halides the cæsium chloride type is found only with compounds of very low polarisation energy. Potassium fluoride and cæsium fluoride appear to be somewhat anomalous cases. J. W. SMITH.

Crystal structure of calcium. C. D. NIVEN (Phil. Mag., 1928, [vii], **6**, 665—666).—Calcium has

been crystallised by condensation of the vapour and the crystals have been shown to be rhombic dodecahedra and not hexagonal as concluded by Moissan (A., 1898, ii, 578). A. E. MITCHELL.

Symmetry and structure of the cubic nitrates of calcium, strontium, barium, and lead. F. M. JAEGAR and F. A. VAN MELLE (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 651—655).—There are a number of discrepancies in the crystal structure of the cubic nitrates of calcium, strontium, barium, and lead. In order to settle some of these, rotation spectrograms, as well as Laue spectrograms of the nitrates, were made. The great majority of diffraction spots obtained were compatible with holo-cubic symmetry. Vegard's conclusion that these nitrates have a dyakisdodecahedral symmetry is confirmed. A. J. MEE.

Arsenides of magnesium and zinc. G. NATTA and L. PASSERINI (Gazzetta, 1928, **58**, 541—550).—An investigation of the physico-chemical properties of the compounds As_2Zn_3 and As_2Mg_3. The densities are 5·578 and 3·165, respectively. The magnesium compound melts at 800°. *X*-Ray investigations by the powder method show that both substances have a cubic lattice containing two molecules of As_2M_3 in the unit cell, the side of which is 5·81 Å. ($d_{calc.}$ 5·854) in zinc arsenide and 6·10 Å. ($d_{calc.}$ 3·26) in magnesium arsenide. The arrangement of the atoms in the lattice represents a new type of structure defined by the co-ordinates: As ($\frac{1}{4}$, $\frac{1}{4}$), ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$), ($\frac{1}{4}$, $\frac{3}{4}$, $\frac{3}{4}$), ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4}$); M ($\frac{1}{2}$, 0, 0), (0, $\frac{1}{2}$, 0), (0, 0, $\frac{1}{2}$), (0, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, 0, $\frac{1}{2}$), ($\frac{1}{2}$, $\frac{1}{2}$, 0). The structure is not ionic. This is confirmed by the low heat of formation, which in the case of zinc arsenide is found to be 30·3 g.-cal. O. J. WALKER.

Symmetry of the pentaerythritol nucleus. H. SEIFERT (Z. anorg. Chem., 1928, **174**, 318—320).—Polemical (cf. Schleede and Hettich, this vol., 694). H. F. GILLBE.

Solid solutions of chromium and nickel and of iron and nickel. F. C. BLAKE, J. LORD, and A. E. FOCKE (Physical Rev., 1927, [ii], **29**, 206—207).—Chromium enters the nickel lattice up to 63% Cr; from 63 to 100% Cr the nickel is in the face-centred chromium lattice. This lattice is metastable at the ordinary temperature, and most of the chromium separates in the body-centred form. Iron distorts the nickel lattice up to 74% Fe; from 74 to 100% Fe the nickel is in the face-centred iron lattice which is stable only at high temperatures. A. A. ELDRIDGE.

Theory of the mechanism of crystal growth. W. P. DAVEY (Physical Rev., 1927, [ii], **29**, 206).—Experimental evidence is quoted in support of the view that crystallisation proceeds along a three-dimensional lattice structure, which is later filled in with crystalline material, instead of uniformly along a plane surface. A. A. ELDRIDGE.

Crystal structure of potassium chloroplatinate. W. A. FREDERIKSE and H. J. VERWEEL (Rec. trav. chim., 1928, **47**, 904—908).—By means of the powder method the distance between the chlorine and platinum ions in the compound K_2PtCl_6 has been found to be 2·29 Å. O. J. WALKER.

Crystal structure of copper–gold alloys. C. S. SMITH (Min. and Met., 1928, **9**, 458—459).—The lattice parameters of gold–copper alloys, annealed at 600° and quenched to retain the homogeneous solid solution, lie on a smooth curve slightly concave to the axis of composition and rising from 3·603 Å. for pure copper to 4·064 Å. for pure gold. Very slow cooling from 400° to 365° results in a gradual decomposition of alloys containing 50 at.-% Au with the separation of the compound CuAu which has a tetragonal lattice. Evidence of the non-existence of Cu_3Au is afforded by *X*-ray examination of an alloy containing 24·36 at.-% Au which on annealing shows only the face-centred cubic lattice of copper and traces of the tetragonal lattice of CuAu. A. R. POWELL.

Lattice constants for the mixed crystal series KCl–KBr. F. OBERLIES (Ann. Physik, 1928, [iv], **87**, 238—258).—The lattice constants *d* 3·1362 and 3·2952 Å. have been found for potassium chloride and bromide, respectively. The change in *d* with changing composition has been followed for the mixed crystal series, and Vegard's additivity formula found to reproduce the data accurately. No new interference lines (corresponding with a regular distribution of the components) were detected. R. A. MORTON.

Positions of adjacent rings in carbocyclic and heterocyclic molecules. H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1928, **40**, 233—242).—The position of the rings in two-ring compounds is discussed with reference to the views of van 't Hoff (symmetrical distribution of carbon valencies) and of Weissenberg (symmetrical structure of the whole molecule independent of symmetrical carbon valency distribution; cf. A., 1926, 934). According to *X*-ray measurements the elementary cells of anthracene and naphthalene have the following respective dimensions: 8·58, 6·02, 11·18 Å., and 8·34, 6·05, 8·69 Å. They thus differ in length only and by an amount 2·5 Å. which is the length of the additional benzene ring. Hence in anthracene all three rings lie in one plane, the 9 and 10 carbon atoms being bent out of it. In the combination of quinol and benzoquinone to quinhydrone the salt formation of the substances in alkaline solution of increasing p_H has been determined colorimetrically, using borate buffer solutions of known p_H and working in an atmosphere of hydrogen. With quinol, a yellow colour appears which increases in intensity up to p_H 10 and then remains constant at 3·0 Lovibond units. Benzoquinone gives a yellow which increases fairly rapidly with increasing p_H, being 3·3 Lovibond units at p_H 9·40 and 20 at p_H 10·6. The colour of quinhydrone increases much more rapidly with increasing p_H, being 4·4 at p_H 8·07, 34 at p_H 9·40, and undeterminable at p_H 10·6. Thus quinhydrone forms a salt in alkaline solution giving ions which possess a characteristic absorption in the visible which is stronger than that of the quinol ions. Thus quinhydrone is not a mere molecular compound, but probably has a diplanar formula. The position of the rings in dihexoses and their derivatives is discussed in the light of the *X*-ray data and is confirmed by reference to the structure of the anhydrides (glucosans and cellobiosans). S. J. GREGG.

Strongly birefringent crystal species. P. Terpstra (Physica, 1928, **8**, 95—100).—1 : 6 : 8-Trinitro-2-ethylaminonaphthalene, monoclinic, has $a:b:c=2\cdot2913:1:1\cdot1027$, β 106° 29′; n_α 1·5177, n_β 1·854, n_γ 2·316. Chemical Abstracts.

Oscillation method of *X*-ray analysis of crystals. Analcite. J. W. Gruner (Amer. Min., 1928, **13**, 123—141, 174—193).—Analcite has a cubic holohedral lattice, space-group O_h^{10}. The unit cube of edge 13·64 Å. contains 16 mols. of $NaAlSi_2O_6,H_2O$. Chemical Abstracts.

Determination of the magnetic saturation of iron carbide. F. Stäblein and K. Schroeter (Z. anorg. Chem., 1928, **174**, 193—215).—A ballistic method of saturation determination is described, whereby the test-piece is removed from the field and from the induction coil by withdrawal through a hole of about 10 mm. diameter bored centrally through the pole pieces of the field magnet. The necessary corrections have been experimentally determined. By filling a copper tube of the requisite dimensions with a ferromagnetic powder, magnetic data for the latter may be obtained. Iron carbide powder, obtained by dissolving Swedish iron in cold *N*-sulphuric acid, and having *d* 7·15 and composition 91·0% Fe, 6·7% C (combined), 0·5% C (free), has a saturation value of about 12,400 gauss, as compared with 12,300 gauss obtained for Fe_3C by extrapolation from the values obtained for two specimens of carbon steel containing, respectively, 0·46 and 0·95% of carbon. H. F. Gillbe.

Piezoelectricity of crystal quartz. L. H. Dawson (Physical Rev., 1927, [ii], **29**, 216).—The piezoelectric charge of quartz is maximal at 60° and disappears at 576°. The piezoelectric charges on surfaces variously oriented with respect to the optical axis show an unexplained distribution. A. A. Eldridge.

Magnetic susceptibility of rare-earth metals. E. H. Williams (Physical Rev., 1927, [ii], **29**, 218).—The susceptibilities of cerium, lanthanum, praseodymium, and yttrium range from 20 to 50×10^{-6} dyne/cm./g.; the value decreases as the magnetic field is increased from 10 to 4000 gauss. A. A. Eldridge.

Magnetostriction. A. Schulze (Z. Physik, 1928, **50**, 448—505).—An exact method for determining the magnetostriction coefficient, $\Delta l/l$, is described based on the Whiddington heterodyne method for determining small changes in spacings. The coefficient has been measured for iron and nickel of various purities, cobalt, bismuth, manganese steels, iron–nickel alloys, permalloy, iron–silicon, iron–aluminium, and iron–manganese alloys. No general relationship between magnetostriction and other physical properties could be traced. R. W. Lunt.

Magnetic properties of evaporated films of nickel. K. J. Miller (Physical Rev., 1928, [ii], **32**, 689—690).—A supplementary note to previous work (A., 1927, 299). Nickel films were tested in fields up to 167 gauss. The coercive force reached a value approximately three times that for hard-drawn wire, and decreased with decreasing deposit-temperature and increasing thickness. Retentivity as high as 65% was observed. N. M. Bligh.

Magnetic susceptibility of single-crystal metals. C. Nusbaum (Physical Rev., 1927, [ii], **29**, 905).—The magnetic susceptibility for bismuth and antimony, respectively, in a direction parallel to the principal axis is $1\cdot13\times10^{-6}$ and $0\cdot497\times10^{-6}$ dyne cm., and in a perpendicular direction $1\cdot32\times10^{-6}$ and $1\cdot38\times10^{-6}$ dyne cm. A. A. Eldridge.

Electrical conductivity in solid sodium chloride at the ordinary temperature. J. Gingold (Z. Physik, 1928, **50**, 633—643).—The electrical conductivity of solid sodium chloride has been measured with the salt in the forms of single natural crystals, blue rock salt, artificially prepared crystals, and compressed blocks of different types. Charge and discharge currents through the salt have also been investigated. The phenomena are explained on the supposition that the conductivity is occasioned by defects in the space lattice. J. W. Smith.

Electrical conductivity of arsenic and antimony at low temperatures. J. C. McLennan, C. D. Niven, and J. O. Wilhelm (Phil. Mag., 1928, [vii], **6**, 666—672).—A convenient method for crystallising arsenic by subliming the substance into a furnace tube which is not at an even temperature over its whole length is described. The crystals grow on the cooler portions of the tube. The electrical conductivities of an arsenic crystal, a crystal of antimony, and a piece of massive antimony have been measured down to 2·42° Abs. The two samples of antimony gave almost identical results. Both arsenic and antimony gave resistance–temperature curves similar to those of pure metals. Both showed evidence of maintaining definite residual resistances at low temperatures and neither showed superconductivity. Arsenic behaves similarly to most pure metals except that its resistance is by no means proportional to the absolute temperature. Neither arsenic nor antimony exhibits the abnormally high residual resistance found by Clay for bismuth. A. E. Mitchell.

Resistance of cæsium, cobalt, and chromium at low temperatures. J. C. McLennan, C. D. Niven, and J. O. Wilhelm (Phil. Mag., 1928, [vii], **6**, 672—677).—Cæsium appears to be unique amongst the alkali metals in that its resistance continues to decrease at temperatures below 4° Abs., whilst those of sodium, potassium, and rubidium examined by McLennan and Niven (A., 1927, 925) reach constant values close to that temperature. The metal is not superconducting down to 2·2° Abs. It is suggested that the persistence of the temperature gradient of electrical resistance in the case of cæsium is due to the fact that if the valency electron is stripped off, the fourteen 4_4 electrons are missing, whilst in the other alkalis the core is left complete. Neither chromium nor cobalt is superconducting down to 2·5° Abs., whilst below the temperature of liquid hydrogen the resistance of each is practically independent of temperature. Calculations of specific resistance at 20·6° Abs. indicate that although iron is a poorer conductor than either cobalt or nickel at the ordinary temperature, it is superior at low temper-

atures. From electronic structural considerations it is suggested that for a metal to be a good conductor the electron systems of the core must be completed and the relative conductivities must depend on the relative stabilities of the electronic arrangements of the cores. A. E. MITCHELL.

Effect of cadmium as an impurity in lead on the conductivity of lead. J. C. McLENNAN, C. D. NIVEN, and J. O. WILHELM (Phil. Mag., 1928, [vii], **6**, 678—685).—Measurements of the electrical conductivities of lead–cadmium alloys, containing up to 5·19% of cadmium, have been made at low temperatures. The specific resistances of the alloys at constant temperatures show a general increase with increasing proportions of cadmium except in the case of the cadmium-richest alloy, where irregularities were observed. The resistance of each alloy falls suddenly at the superconductivity temperature of lead (7° Abs.), but they do not become superconducting until 0·2—0·4° below this temperature. Considerable differences were found in the specific conductivities determined before and after cooling to the lowest temperatures. These are attributed to the "ageing" of the alloys at the low temperatures. The persistence, in its cadmium alloys, of the superconductivity phenomenon of lead and its inception at or close to the superconductivity temperature of lead are probably due to the existence of a continuous chain of lead atoms in the superconducting state of the alloy.

A. E. MITCHELL.

Electrophoretic mobility formula. M. MOONEY (Physical Rev., 1927, [ii], **29**, 217).—The formula, which accords approximately with experiment only below 0·01*N*, is based on the observation that with oil drops immersed in water there is a definite variation in mobility with the diameter of the drop.

A. A. ELDRIDGE.

Rate of evaporation of molten cadmium in a high vacuum. A. A. SUNIER (J. Physical Chem., 1928, **32**, 1516—1521).—The average rates of evaporation of molten cadmium in a vacuum over the range 340—425° are recorded, and are compared with the theoretical rates calculated from the equation of Herz (Ann. Phys. Chem., 1882, **18**, 177). The low experimental results are attributed to a contaminated surface. Two types of apparatus are described.

L. S. THEOBALD.

"Alteration of the legal temperature scale." The international temperature scale (Paris, 1927) and the Physikalisch-Technische Reichsanstalt (1924) scale. F. HENNING and J. OTTO (Z. Physik, 1928, **48**, 742—748).—The temperature scale of Physikalisch-Technische Reichsanstalt established in 1924 has been compared with the international scale adopted at Paris in 1927. It is shown that throughout the range −190° to 1063° and up to 4000° the difference between the two scales is less than the experimental error. R. W. LUNT.

Rotational and vibrational specific heat of a diatomic gas, the molecules of which have a doublet *P* normal state. E. E. WITMER (Physical Rev., 1927, [ii], **29**, 918).—In addition to the initial rise in the neighbourhood of the absolute zero, the specific heat curve shows a secondary rise at temperatures at which molecules begin to exist in the upper component of the doublet in appreciable numbers. The curve thereafter falls, tending towards the value *R*. A. A. ELDRIDGE.

Critical temperature measurements on carbon dioxide in small capillaries. H. T. KENNEDY and C. H. MEYERS (Refrigerating Eng., 1928, **15**, 125—130).—The critical temperature of carbon dioxide, measured in capillary tubes of diameter 0·004 and 0·060 mm., respectively, is 30·96±0·01°.

CHEMICAL ABSTRACTS.

Equation of state of a perfect gas. R. D. KLEEMAN (Phil. Mag., 1928, [vii], **6**, 743—744).—Alternative deductions are indicated of the equation of state of a perfect gas, $pv-MRT\xi$, where p is the pressure and ξ is a function of the volume v, the absolute temperature T, and the mass M (cf. this vol., 955). A. E. MITCHELL.

Entropy of vaporisation of non-associated liquids. J. CHIPMAN (J. Physical Chem., 1928, **32**, 1528—1531).—Equations of previous investigators connecting the entropy of vaporisation of a normal liquid with its b. p. are compared graphically with recent experimental data. Kistiakovski's equation (J. Russ. Phys. Chem. Soc., 1921, **53**, 256) holds over a wide range of temperature and is considered to be the best. It accords with Hildebrand's rule (A., 1915, ii, 416). L. S. THEOBALD.

Volume isobars of water up to the melting curve. G. TAMMANN and W. JELLINGHAUS (Z. anorg. Chem., 1928, **174**, 225—230).—New measurements have been made of the specific volume of water at pressures up to 1500 kg./cm.^{2} and temperatures from −14° to +15°. Bridgman's values at 1500 kg./cm.^{2} and temperatures below 0° are considerably too high, as are those at 500° and 1000 kg./cm.^{2}; his results for the temperature of maximum density at various pressures are therefore incorrect.

H. F. GILLBE.

Entropy and thermodynamic potentials of real gases and mixtures of real gases and a mass-action law for chemical reaction between real gases. II. Integrated equations. III. Relations for pure gases, and the equilibrium pressure of a gas in a mixture. J. A. BEATTIE (Physical Rev., 1928, [ii], **32**, 691—698, 699—705; cf. this vol., 589).—II. Mathematical. The general thermodynamic equations previously derived are integrated by means of a new equation of state for gas mixtures.

III. Mathematical. Assuming that the pressure of a real gas approaches nRT/V as the volume approaches infinity, the general thermodynamic equations are developed for a pure gas, and integrated by a new equation of state. General expressions are obtained for the density and pressure of a gas in equilibrium at constant temperature through a semipermeable membrane with a mixture containing the gas in question. N. M. BLIGH.

Thermal expansion of beryllium. P. HIDNERT and W. T. SWEENEY (Physical Rev., 1927, [ii], **29**, 616).—The coefficients of expansion of beryllium in ten temperature ranges between −120° and +700° are recorded; those between −50° and +20°, and

between 20° and 100° are 9·8 and $12·3 \times 10^{-6}$, respectively. A. A. ELDRIDGE.

Molecular cohesion. G. A. TOMLINSON (Phil. Mag., 1928, [vii], 6, 695—712).—Experiments are described in which the forces of adhesion between glass or quartz fibres and between glass spheres have been measured. It is assumed that in such contacts only the surface molecules exert cohesive attraction. An attempt is made to interpret the results on the basis of a simple inverse law of attraction and it is found that they are best satisfied by an inverse fourth power relationship between the forces and the distances between the molecules. The calculated value of the tenacity of drawn glass is in good agreement with the observed values of Griffith, but is considerably higher than those usually found by tensile methods. The results are not inconsistent when the law is applied to the calculation of the tenacities of some metals. A. E. MITCHELL.

Elastic constants of single-crystal aluminium wire. G. SUBRAHMANIAM (Nature, 1928, **122**, 650).—The values y $6·779 \times 10^{11}$, n $2·432 \times 10^{11}$, obtained at 28°, are slightly smaller than those given by ordinary specimens. A. A. ELDRIDGE.

Compressibility and pressure coefficients of resistance of ten elements. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1927, **62**, 207—226).—Values are recorded for the compressibility of praseodymium, lanthanum, cerium, beryllium, barium, thorium, chromium, vanadium, sulphur, and phosphorus (red and black), and for the electrical resistance of the first six elements. Cerium is polymorphic at high pressures. Beryllium has d^{20} 1·820. Lanthanum has m. p. 826°. CHEMICAL ABSTRACTS.

Viscosity of mercury under pressure. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1927, **62**, No. 8, 187—206).—The absolute viscosities at 30° and 75°, respectively, are: 1 kg./cm.², 0·01516, 0·01341; 2000, 0·01588, 0·01399; 4000, 0·01663, 0·01463; 6000, 0·01742, 0·01528; 8000, 0·01825, 0·01599; 10,000, 0·01913, 0·01675; 12,000, 0·02008, 0·01757. Some kind of interlocking mechanism between the molecules of a liquid is postulated.

CHEMICAL ABSTRACTS.

Internal friction and flow-point in lead. W. D. KUSNETZOV (Z. Physik, 1928, **51**, 239—262).—A number of experiments on the tensile strength and mechanical deformation of lead are described, together with an analysis of the conditions most appropriate to the determination of the coefficient of inner friction. R. W. LUNT.

Molecular association. Relation between the vapour pressures of binary liquid mixtures and the polarity of the molecules of the constituents. J. ERRERA (Compt. rend., 1928, **187**, 727—730).—The vapour pressures of liquids afford a measure of the total association, whilst polarity measurements indicate only dipolar association, homopolar association being an effect of the second order. When the azeotropism is negative, or the vapour-pressure curve concave, the two components are always polar or partly ionised, but when one or both of the two components are non-polar, the vapour-pressure curve can be only a straight line or convex, and azeotropism, if it exists, is positive. The curves indicate that the forces of association diminish with rise in temperature. J. GRANT.

[Formation of] solid solutions by precipitation. G. NATTA and L. PASSERINI (Gazzetta, 1928, **58**, 579—618).—Solid solutions can be obtained by the simultaneous precipitation of metallic hydroxides from aqueous solution by means of alkalis. The formation of solid solutions is shown by an *X*-ray examination of the precipitates. The following systems have been studied: $Ni(OH)_2$–$Co(OH)_2$, $Ca(OH)_2$–$Cd(OH)_2$, $Cd(OH)_2$–$Ni(OH)_2$, $Mg(OH)_2$–$Co(OH)_2$, $Mg(OH)_2$–$Ni(OH)_2$, $Cd(OH)_2$–$Mn(OH)_2$, $Zn(OH)_2$–$Mg(OH)_2$, $Zn(OH)_2$–$Ni(OH)_2$, and $Zn(OH)_2$–$Co(OH)_2$. The lattice constants of the pure hydroxides and of mixtures have been measured. Solid solutions are formed only in those cases where the cations of the two hydroxides do not differ widely in radius. For example, nickel hydroxide forms solid solutions with the hydroxides of magnesium, zinc, and cobalt, but not with those of cadmium and calcium. The lattice constants of the solid solutions vary directly with the composition and therefore obey Vegard's law. The method of obtaining solid solutions by simultaneous precipitation may be applied to other types of compounds. O. J. WALKER.

Electrolytic solution tensions and the ionic state. III. Solubility and solvent forces, solvent and ionising powers. K. FREDENHAGEN (Z. physikal. Chem., 1928, **134**, 33—56; cf. A., 1927, 936).—Mainly theoretical. The solubility of a substance is related to the distribution between gas and liquid phases, and the distribution numbers (cf. *loc. cit.*) measure the solution forces concerned between the solvent and solute. Solution forces are independent of concentration only at low concentrations. With binary compounds, three distribution numbers, viz., those of the undissociated compound and the dissociated components, must be taken into account. When electrolytic dissociation occurs in the liquid state, the distribution numbers of the neutral products of decomposition in the gaseous phase in relation to their ions are given by the electrolytic distribution numbers. The ionic product of a compound AB is given by the expression $c'_{(A^+)} . c'_{(B^-)} = c_A c_B P_A P_B$, where c_A and c_B are the concentrations of the dissociation products in the gaseous phase, and P_A and P_B are the electrolytic distribution numbers previously defined (*loc. cit.*). These latter have been calculated for a number of elements in various solvents, and their sequence differs from that of the normal potentials of the elements. The ionic products calculated for various compounds in different solvents agree with the values obtained when the Nernst heat theorem is used to calculate the dissociation constant in the gaseous phase. Generalisations concerning the magnitude of the distribution numbers of undissociated compounds cannot yet be made, but in all cases it appears that the order of magnitude is far less than that indicated by the electrolytic numbers.

L. S. THEOBALD.

Charcoal as an adsorbent. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1928, **60**, 859—869).—Nitric acid, ammonium, potassium, and barium nitrates, chloric acid, and sodium hydroxide solutions remove adsorbed chlorine ions almost quantitatively from charcoal. This is not due to preferential adsorption, for acetic acid, which is more strongly adsorbed than nitric acid, does not show this effect. A very highly adsorbent charcoal, containing practically no adsorbed acid, is prepared by heating ordinary charcoal at 850° for 1 hr., and then wetting it with 4N-nitric acid. After 3—4 hours excess of nitric acid is removed by filtration, and the charcoal boiled for 2 hrs. with 2 litres of water. The product is dried and heated on the blow-pipe for half an hour in a closed porcelain crucible, when the adsorbed nitric acid is decomposed with oxidation of part of the charcoal. The resulting product strongly adsorbs acid and neutral salts, but not alkalis. R. TRUSZKOWSKI.

Expansion of charcoal accompanying sorption of gases and vapours. D. H. BANGHAM and N. FAKHOURY (Nature, 1928, **122**, 681—682).—The expansion of charcoal on sorption of water vapour is not directly proportional to the quantity of vapour sorbed; the curve obtained on plotting the variables is concave to the expansion axis. This result supports the chemical theory of sorption at the pressures employed, and indicates that the mechanical disturbance suffered by the solid during the sorption of a given quantity of gas becomes greater as the absorption proceeds. In experiments with water and carbon dioxide the expansion was directly proportional to the square of the sorption value. The difference in the expansion caused by equal numbers of molecules of water and carbon dioxide is not proportional to the difference of molecular size. A. A. ELDRIDGE.

Absorption of mercury, mercury oxide and chloride, bromine, and carbon disulphide by chabasite. O. WEIGL and E. BEZNER (Sitzungsber. Ges. Naturwiss. Marburg, 1927, **62**, 57—108; Chem. Zentr., 1928 i, 2168).—In presence of air, mercury vapour at 400° is absorbed by chabasite. Mercuric chloride and bromine are absorbed at 360—370° and 90—95°, respectively, to equilibrium values. Carbon disulphide at 100—135° reacts with residual water: $CS_2+3H_2O=2H_2S+H_2CO_3$; unchanged carbon disulphide colours the crystals yellow. If too high a temperature is employed sulphur is obtained.
A. A. ELDRIDGE.

Dipolar nature of adsorbed gas molecules. A. MAGNUS (Z. Elektrochem., 1928, **34**, 531—533).—If gas adsorption which does not follow Henry's law, $\pi S=RT$ (π is surface pressure of the adsorbed layer and S area on which one mol. is adsorbed), is represented by a van der Waals equation $(\pi-\alpha/s^2)(s-\beta)=RT$, α being a repulsion constant and β double the total cross-section of the molecules in one mol., the constant α may be calculated on the assumption that the adsorbed molecules consist of vertically disposed dipoles, and is found to be of the order of 10^{20}, in agreement with the value obtained from the adsorption isotherms and heat of adsorption. This and other evidence show that the adsorbed gas molecules are dipolar in nature; conversely, strongly adsorbed vapours, *e.g.*, water and ammonia, are all dipolar. S. K. TWEEDY.

Adsorption of gases by sodium chloride and aqueous sodium chloride solution. F. DURAN (Ann. Physik, 1928, [iv], **87**, 307—384).—The sodium chloride was purified by melting in a vacuum and powdered in an atmosphere of nitrogen. Measurements were made at 0·4 mm. and at atmospheric pressure. Adsorption isotherms for nitrogen, hydrogen, carbon dioxide, oxygen, and nitric oxide were measured for unheated salt. The adsorption of carbon dioxide by salt outgassed at 480° was less than that by unheated salt. The adsorption increases with the b. p. of the adsorbed substance. Sulphur dioxide is the only gas which is adsorbed to the extent of the formation of a complete unimolecular layer.
W. E. DOWNEY.

Adsorptive combination. H. CASSEL (Z. Elektrochem., 1928, **34**, 536—538).—The behaviour of the molecules of a solid adsorbent in the interfacial layer between the solid and the gas is considered. According as repulsive or attractive forces are exerted between the different surface molecules there appear to be two extreme limiting cases in which either the adsorbent molecules are partly turned out of the layer into the solid surface or *vice versa*. In general, both these effects will occur simultaneously. This conception is discussed very briefly.
S. K. TWEEDY.

Detection of protons in metals. A. COEHN (Naturwiss., 1928, **16**, 183—184; Chem. Zentr., 1928, i, 2232).—It is said that hydrogen adsorbed in palladium, iron, etc. is partly dissociated into electrons and protons. Diffusion experiments support this view. A. A. ELDRIDGE.

Influence of quartz lamp irradiation on adsorptive power of certain adsorbents. E. V. ALEKSEEVSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 1173—1178).—The irradiation of active charcoal and of Patrick's silica gel, using a quartz lamp, slightly enhances the adsorptive power of these substances.
R. TRUSZKOWSKI.

Thermal and magnetic researches on adsorbed gases. F. SIMON (Z. Elektrochem., 1928, **34**, 528—530).—The adsorption isotherms for argon on dehydrated chabasite at 90° Abs., and magnetic susceptibility measurements with chabasite containing adsorbed oxygen, show that the gas molecules are evenly distributed over the cells in the adsorbent. The specific heat of hydrogen adsorbed in this material suggests that the molecules within each cell are in a comparatively free state, although the possibility of their passing from one cell to another is very small.

According to Sommerfeld's theory the specific heat of electron gas in iron should equal the specific heat of the metal at about 6° Abs.; experimental results agree with theory only if the latter is modified to take into account the forces between the electrons and the metal ions. S. K. TWEEDY.

Adsorption and constitution: adsorption of organic acids on animal charcoal. K. M. GRIFFIN, H. L. RICHARDSON, and P. W. ROBERTSON (J.C.S., 1928, 2705—2709; cf. A., 1925, ii, 383).—The adsorption of aliphatic and aromatic acids from

ethyl-alcoholic solution by animal charcoal has been determined. Since the activity of different samples of charcoal was found to vary, the results are expressed in terms of a standard acid (acetic for the aliphatic series, benzoic for the aromatic). In general the relative adsorption tends to increase with mol. wt., but this increase is subject to marked constitutive effects. In the normal fatty acid series the odd-numbered members are less adsorbed than the even. Aromatic acids are much more strongly adsorbed than aliphatic acids; substitution, especially in the *para*-position, increases the adsorption.

R. N. KERR.

Adsorption of mixtures of electrolytes from dilute aqueous solution. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1928, **60**, 951—963).—A linear relation is found for solutions containing two electrolytes, viz., $y=b-kx$, where b and x measure the adsorption of each electrolyte alone, and y is that of one of them when in solution with the other. This expression holds for solutions containing hydrochloric or nitric and oxalic acids, and hydrobromic or hydrochloric and nitric acids, and is also applicable to such mixtures as hydrochloric or acetic acid and acetone. Practically no adsorption of the chlorine ion takes place from solutions containing nitrates and chlorides in equivalent proportions, although when nitrates are replaced by nitric acid the adsorption of chlorine ion is little less than normal. R. TRUSZKOWSKI.

Adsorptive power of aluminium silicates used pharmaceutically. R. PORTILLO (Anal. Fís. Quím., 1928, **26**, 271—286).—The percentage of silica and water and the adsorptive power for methylene-blue have been determined for a number of commercial preparations of kaolin. There is no apparent connexion between chemical composition and adsorptive power. The adsorptive power falls to a low value, which is practically the same for all the samples examined, when the kaolin is dehydrated by heating, and in general decreases on treatment with alcohol.

R. K. CALLOW.

Absorption phenomena. J. RATELADE and M. TSCHETVERGOV (Rev. gén. Mat. col., 1928, **32**, 302—305).—The absorption of dyes from mixed solvents by filter-paper and by artificial silk has been investigated with reference to the percentage composition of the solvent. With "direct diamine" dyes on filter-paper, minima were found using water–methyl alcohol, water–ethyl alcohol, and water–pyridine mixtures, but not with ethyl alcohol–methyl alcohol or ethyl alcohol–pyridine mixtures. In the case of diphenylmethane and triphenylmethane dyes no minima were found. Similar results were obtained with viscose. The extraction of direct colours from filter-paper by water–alcohol and water–pyridine mixtures also showed a minimum (cf. Schilov and Pevsner, A., 1926, 238). C. W. GIBBY.

Adsorption of iron from ferric hydroxide sols and ferric chloride solutions by kaolin and by talc. A. FODOR and A. ROSENBERG (Kolloid-Z., 1928, **46**, 91—95).—Kaolin and talc adsorb ferric hydroxide from colloidal solutions and also from hot solutions of ferric chloride, but do not adsorb aluminium hydroxide from a colloidal sol or from a hot solution of aluminium chloride. Pulverised sand does not adsorb ferric hydroxide under these conditions. A separation of iron and aluminium may be effected by the preferential adsorption by kaolin or talc of iron from a hot solution of the mixed chlorides. The colloid content of ferric chloride solutions was checked by measuring the rate of hydrolysis of sucrose by the hydrolytically produced hydrochloric acid. Kaolin adsorbs iron hydrolytically from a ferric chloride solution and the free acid remains behind. On the other hand, the adsorption of iron from a hot ferric chloride solution by talc is mainly a secondary process; the first process is an exchange-adsorption between magnesium and hydrolytically formed hydrogen ions, magnesium ions gradually appearing in the solution. The amount of colloidal ferric hydroxide subsequently adsorbed is proportional to the amount of adsorbed hydrochloric acid.

E. S. HEDGES.

Adsorption and swelling. II. V. KUBELKA and J. WAGNER (Kolloid-Z., 1928, **46**, 107—114; cf. Kubelka and Taussig, A., 1926, 900).—The gross adsorption of hydrochloric acid by hide powder is characterised by a maximal value of the equilibrium adsorbed amount (x/m) in very dilute solutions (0·06 millimol.). With increasing concentration of acid the value of x/m remains practically constant. The gross adsorption of sulphuric acid does not exhibit such a maximum, but a steady rise with increasing acid concentration. The swelling of hide powder in water has a maximal value at which 7 g. of water are taken up by 1 g. of the air-dried substance. In hydrochloric acid, the swelling is considerably greater than in pure water and reaches a maximal value in quite dilute solutions. A swelling maximum was not observed in sulphuric acid solutions; in dilute solutions, the degree of swelling is approximately the same as in pure water, and at higher concentrations the swelling is less than that in water. The corrected adsorption curves have the characteristic form of the adsorption isotherm, but show that for both acids the logarithmic adsorption equation holds only for a definite range of concentrations.

E. S. HEDGES.

Adsorption at crystal–solution interfaces. III. Individual macroscopic ammonium alum crystals grown in the presence of gelatin and dyes. G. W. BENNETT and W. G. FRANCE (J. Amer. Ceram. Soc., 1928, **11**, 571—581; cf. this vol., 358, 472).—Preliminary qualitative experiments showed that striking "hour-glass" figures are obtained when potassium alum coloured with diamine-sky-blue is recrystallised from hot water, and that adsorption of the dye takes place only during the growth of crystals. All quantitative experiments were conducted in an air-thermostat at 30·0±0·1°. The crystallisation cell was filled with ammonium alum solution, saturated at 30°, and weighed quantities of the desired foreign material, *i.e.*, dyes, gelatin, or amino-acids, were added to it. A carefully selected seed crystal. fastened to a platinum wire, was introduced into the solution, and an initial exposure of the film immediately made. Photographic records were continued every half hour over periods of 20—30 hrs., and the distances between cube faces and between octahedral

faces were measured on the magnified film. The ratio between the corresponding perpendicular displacements of the cube and the octahedral face, which for the pure ammonium alum crystal was found to be 1·53, varies with the extent of adsorption. Thus, diamine-sky-blue, oxamine-blue, and anthraquinone-green are adsorbed on the cube faces only and at the same time repress the displacement of these faces.

The hydrogen-ion concentrations of the solutions were practically constant. The dyes, both in pure water and in alum solutions, were examined for state of dispersion. Some colloid particles were detected, but there appeared to be no relationship between the number of particles and the action of the dye in repressing face displacement. It is, therefore, suggested that individual dye molecules rather than colloidal aggregates of them are responsible for the observed effects. The mechanism of adsorption is explained on the basis of residual valencies, polar groups in the adsorbed material, and interionic distances in the lattice. This explanation is extended to include the specific nature of the adsorption.

A. T. Green.

[Adsorption and crystallisation.] Calcite and aragonite. C. H. Saylor (J. Physical Chem., 1928, **32**, 1441—1460).—It is shown that foreign substances are adsorbed preferentially on certain crystal faces, the adsorption retarding the growth perpendicular to the faces, and resulting ultimately in their enlargement. All crystalline substances adsorb from the mother-liquor ions of electrolytes, molecules of solvent and of dissolved non-electrolytes. The preferential adsorption of a cation on one face species is accompanied by a similar adsorption of the anion on the other principal crystal faces. The development of octahedral faces on sodium chloride is favoured by the presence of sodium, potassium, and ammonium hydroxides, and sodium carbonate. Mercuric chloride, antimony chloride in hydrochloric acid, and carbamide act similarly. Ethyl alcohol, which is known to decrease the adsorption of anions, counteracts the tendency to form octahedra when added to the mother-liquor in the above-mentioned cases. No true octahedral faces could be observed on crystals of sodium chloride grown from pure salt solutions, or from solutions containing nickel or ferric chloride, or hydrochloric acid, as has been claimed by previous investigators. The adsorption of anions on the cubic faces of the alums and on the end forms of sodium nitrate favours their enlargement, and that of cations on the cubic faces of barium nitrate, and on the side forms of sodium nitrate acts in a similar way. Experiments with acidic and basic dyes are also recorded. Preferential adsorption on an allotropic modification may spoil each crystal nucleus as a centre for crystal growth, and will tend to suppress the modification, allowing an unstable form to be temporarily stabilised. This view is supported by crystallisations of the three forms of calcium carbonate from solutions of potassium carbonate and calcium chloride, and is shown to explain various findings of previous workers. Aragonite and μ-calcium carbonate are capable of existence because certain ions, *e.g.*, the hydrogen carbonate and acetate ions, carbamide, the high-temperature form of water, and organic material (in the case of molluscs) are preferentially absorbed on calcite and prevent its growth. L. S. Theobald.

Passivity of metals. W. J. Müller (Z. Elektrochem., 1928, **34**, 571—586).—A general account of the previously published work of this author and his co-workers (cf. this vol., 714). A consequence of the author's theory is that the " passivating " power of an electrolyte may be expressed numerically. It is proposed to call " coating passivity " that kind of passivity which is characterised by the metal passing into solution at stronger polarisation with the valency of the active metal. S. K. Tweedy.

Surface energy of solid sodium chloride. III. Heat of dissolution of finely-ground sodium chloride. S. G. Lipsett, F. M. G. Johnson, and O. Maass (J. Amer. Chem. Soc., 1928, **50**, 2701—2703; cf. A., 1927, 954).—Finely-ground sodium chloride has a smaller (negative) heat of dissolution than the coarsely ground salt. Results obtained with finely-ground material are not suitable for the calculation of surface energy. S. K. Tweedy.

Permeability of metals towards gases. V. Lombard (J. Chim. phys., 1928, **25**, 587—604; cf. this vol., 1085).—Using the apparatus described previously, measurements have been made of the permeability, d, of nickel membranes for nitrogen, argon, and helium, and of iron and platinum for hydrogen (d=number of c.c. of gas measured at 0° and 760 mm. passing per hour through a membrane 1 cm.² in area). With nickel membranes at about 500° the permeabilities for nitrogen and argon are very small—about one hundredth of the permeability for hydrogen; the permeability for helium is somewhat greater, but the results for this gas are untrustworthy. The diffusion of hydrogen through iron and platinum follows the same general laws as in the case of nickel. For these three metals the relationship between permeability towards hydrogen, temperature (t), and pressure (p) is $d=k\sqrt{p}/h\times a^{\alpha t}$, where h=thickness of membrane, a is an arbitrary number, and k and α are constants characteristic of the metal. The temperature ranges studied were for nickel 350—750°, for iron 350—520°, and for platinum 400—700°.

O. J. Walker.

Permeability of membranes. V. Diffusion of non-electrolytes through the dried collodion membrane. A. A. Weech and L. Michaelis (J. Gen. Physiol., 1928, **12**, 55—81).—The rates of diffusion of acetone, carbamide, glycerol, and dextrose through dried collodion membranes decrease in the order given. For each substance the rate of diffusion varies directly with the difference in concentration between the solutions on either side of the membrane.

E. A. Lunt.

Permeability of gelatin membranes. R. Collander (Protoplasma, 1927, **3**, 213—222).—Experiments with substances such as lævulose and methyl citrate indicate that molecular size, as measured by molecular refraction, is the main factor governing the rate of diffusion through gelatin membranes 0·8—1 mm. thick. The results are considered in relation to those obtained with protoplasm; they support the lipoid theory. Chemical Abstracts.

Pore size of compressed carbon and silica membranes. F. E. BARTELL and H. J. OSTERHOF (J. Physical Chem., 1928, **32**, 1553—1571).—Methods for the determination of membrane pore radii based on capillary rise and on Poiseuille's law are discussed. Experimental work with membranes formed by the compression of finely-powdered carbon and silica show that when certain conditions are satisfied both methods give results which are in close agreement. The capillary rise method is more convenient for finding pore radii in determinations of the adhesion tension of a solid against a liquid by the pressure displacement method. L. S. THEOBALD.

Light absorption in solution and the transition between different types of combination. G. SCHEIBE (Z. Elektrochem., 1928, **34**, 497—502).—The absorption of light by solutions of some organic compounds including ethyl iodide and of metal iodides in water, alcohols, and hexane is described. The two maxima exhibited by the iodide ion in water are attributed to an iodine atom and also a metastable iodine atom, formed by the iodide ion losing its electron. Solvation has also an influence on the absorption in this case. Observations on solutions of cadmium bromide in alcohol support this theory. Zinc, cadmium, and mercury halides may contain both homo- and hetero-polar linkings, between which, in solution, an equilibrium exists. S. K. TWEEDY.

Molecular state of salts in solutions. H. ULICH and E. J. BIRR (Z. angew. Chem., 1928, **41**, 443—446, 467—472, 1075—1078, 1141—1144).—In the first place, infinitely dilute solutions are considered and the application of Stokes' law to the calculation of ionic radii is examined. With reference to the solvation of ions in non-aqueous solutions it is pointed out that for alkali ions, as well as for halogen ions, the solvation number falls with increasing ionic weight, a fact which may be accounted for by supposing that the dipole group of the solvating molecule can get nearer to the centre of a lighter and smaller ion, and that therefore the attractive force will be greater. For sodium and potassium the solvation numbers are approximately the same for all solvents, but for halogen ions they are greater in solvents which contain the hydroxyl group. This must be connected with the dipole nature of the solvent. It is not the solvent molecule as a whole which influences the ion, but only certain atoms or groups which have a semi-polar character, *e.g.*, hydroxyl in alcohol, and carbonyl oxygen in acetone. In considering the interaction of ions and solvent molecules, and that between the ions themselves, it is possible to distinguish between an "electrical" and a "chemical" interaction. In very dilute salt solutions there is a region in which the effect of electrical interaction between free ions greatly exceeds the chemical effect. This region is that in which the Debye–Hückel theory holds. This theory is considered in its relation to activities, and the influence of the electric force on the osmotic effect is investigated. When moderately dilute solutions are investigated, the Debye–Hückel theory shows considerable deviations. Three reasons are given for these deviations. The properties of these solutions, and indeed those of concentrated solutions, can be made clear by assuming that for "weak" salts as the concentration is increased undissociated molecules predominate in solution, and for "strong" salts free, but largely associated, ions are formed. The relationship between the dielectric constant of the solvent and the osmotic coefficient for "strong" salts is considered. The dielectric constant of the solution increases for a "strong" salt, but does not when a "weak" salt is dissolved, as a rule. This is in agreement with the presence of undissociated molecules in the solution of a "weak" salt. Finally, molten salts are considered. Salts which are "strong" as regards solutions are also "strong" when molten. The same is true for "weak" salts. Thus, it should be expected that a "strong" salt is very nearly completely dissociated when melted. A. J. MEE.

Influence of neutral salts on the rotatory power of tartaric acid and the tartrates. E. DARMOIS (Ann. Physique, 1928, [x], **10**, 70—115).—Measurements of the rotatory power of mixed solutions of tartaric acid, calcium chloride, and hydrochloric acid of varying p_H value indicate that the degree of ionisation of the acid determines its specific rotation. For a given wave-length the specific rotation of the normal alkali tartrates varies regularly with the atomic weight of the metal. The curves obtained by plotting the specific rotation of the alkali tartrates against concentration form a pencil converging approximately at the value 42·5° for zero concentration. With increasing concentration the specific rotation of the lithium and sodium salts diminishes, whilst that of the potassium, rubidium, and cæsium salts increases. The effect of the addition of numerous salts on the rotatory power of the normal tartrates was investigated. The variation in specific rotation is attributed partly to the dehydration of the tartrate ion in the presence of the cations and partly to the deformation of the electronic orbits in the ion by the field of the cations. The rotatory power of the alkaline-earth and rare-earth tartrates was measured in solutions containing other salts of the respective metals and further evidence of deformation of the ion was then obtained. The extent of this increases with the charge on the ion for those cations which possess the electronic structure of the inert gases. The limits of increase of this deformation are determined by the formation of ionic complexes in the more concentrated solutions. F. G. TRYHORN.

Refractometric behaviour and the state in solution of ammonium salts and concentrated acids. K. FAJANS (Z. physikal. Chem., 1928, **137**, 361—382).—It is assumed that the far-reaching analogies between NH_4^+ and OH_3^+ and the rubidium ion, as regards the fields of force in the lattice, apply also to the deforming influence exerted on the anion in the molecule, and further, that the formation of OH_3Cl is accompanied by only a small change in the refraction. Observations of the volatility and ease of decomposition of ammonium chloride and OH_3Cl indicate that the deformation of NH_4^+ and OH_3^+ ions by an anion, together with the converse effect, depends on whether the anion is symmetrical or asymmetric. In the latter case there results a dis-

placement of the hydrogen nucleus in the NH_4^+ or OH_3^+ ion and an increased tendency to deformation by the cation. The large variations with concentration of the refraction of ammonium chloride, and the even greater variations in the case of hydrogen chloride, compared with that of rubidium chloride, are thus explicable. H. F. GILLBE.

Interferometric measurement of particles visible in the ultra-microscope. U. GERHARDT (Ann. Physik, 1928, [iv], **87**, 130—144).—The apparatus used for the determination is described, and the most important results of theory and experiment for both self-luminous and particularly for non-self-luminous particles are discussed. By the use of a sufficiently small azimuth-shutter both ends of the particle of which the diameter is to be measured can be seen as separate bright points. The influence of coherence is also investigated. A. J. MEE.

Preparation of gold sol. O. WUTH (Munch. med. Woch., 1928, **75**, 472—473; Chem. Zentr., 1928, i, 2192).—The optimal hydrogen-ion concentration is p_H 7·1—7·2 for preparation and 6·1—6·3 for the reaction. A. A. ELDRIDGE.

Preparation of negatively charged sols by means of tartaric acid. III. Adsorption of sodium tartrate and succinate by aluminium hydroxide. A. DUMANSKI and A. IAKOVLEV (Bull. Soc. chim., 1928, [iv], **43**, 969—977; cf. this vol., 584).—The adsorption of sodium tartrate by aluminium hydroxide in the form of hydrosol, newly-formed precipitate, and a four months' old precipitate can in each case be expressed by the ordinary adsorption isotherm $x/m=kc^{1/n}$. The value of k increases with increasing degree of dispersion, whereas $1/n$ remains constant. The adsorption of sodium succinate by aluminium hydroxide sol is much weaker than that of the tartrate; the presence of the hydroxyl groups in the acid has apparently a strong influence on the adsorbability. This is to be expected from the results previously obtained in the use of hydroxy-acids for the preparation of metallic hydroxide sols.

O. J. WALKER.

Preparation of negatively charged sols by means of tartaric acid. IV. Formation of lead hydroxide sols and gels from alkali tartrates. A. V. DUMANSKI and A. P. BUNTIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 933—949; cf. preceding abstract).—Solutions prepared by dissolving lead sulphate and lead hydroxide in alkali tartrate solutions in presence of excess of alkali or lead tartrate in alkalis contain the complex $C_4H_2O_6R_2Pb$, where R is K, Na, or NH_4. When the alkalinity of the solution is small, colloidal solutions of lead hydroxide may form, passing into vitreous, transparent gels if the solution contains more than 3% Pb. Lead alkali tartrates may be isolated by adding alcoholic alkali to solutions of lead tartrate. Solutions of this salt are alkaline and lævorotatory, and on dilution their conductivity changes considerably, indicating a high degree of hydrolysis. On dialysis, colloidal solutions of lead hydroxide are obtained. These sols are made up of negatively-charged particles, readily coagulable by electrolytes and of the composition expressed by $Na[C_4H_2O_6Pb,nPb(OH)_2]$. R. TRUSZKOWSKI.

Preparation of negatively charged sols by means of tartaric acid. V. Physico-chemical properties of tungstate-tartaric acid colloids. A. V. DUMANSKI and S. I. DIATSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 1053—1068).—The addition of sodium tungstate to d-tartaric acid solutions gives rise to the formation of a series of colloidal double salts, which undergo hydrolysis on dilution; the degree of dispersion increases with the tungsten content. These colloidal solutions exhibit mutarotation; on concentration they yield vitreous gels, which become blue on exposure to light. R. TRUSZKOWSKI.

Colloidal carbon solutions. H. LACHS and K. GESTEL (Z. physikal. Chem., 1928, **137**, 193—200).—Carbon hydrosols prepared by Sabbatini's method exist as definite systems containing probably carbohydrates and their decomposition products. The X-ray spectrograph yields no evidence of crystalline structure, nor is double refraction to be observed. Approximately 70% of the sol particles have a diameter of about 141 μμ, 15% 71 μμ, and 15% 4·4 μμ. Despite the large average particle size, the sols are very stable, probably on account of the high degree of hydration. Depolarisation measurements indicate that the sol particles are approximately spherical.

H. F. GILLBE.

Action of light on silver hydrosols containing particles of uniform magnitude. A. GAŁECKI and R. SPYCHALSKI (Rocz. Chem., 1928, **8**, 394—404).—The velocity of decolorisation of silver hydrosols subjected to ultra-violet illumination increases with diminution in the size of the silver particles. Such decolorised solutions possess greater conductivity and smaller viscosity than the original sols, pointing to the conversion of the colloidal silver particles into ions. If the illumination be continued after decolorisation the above effects are reversed, and a hydrosol is again obtained. R. TRUSZKOWSKI.

Dependence of the stability of carbon suspensions on the gas charge and the composition of the solution. N. BACH-NIKOLJEVA and A. FRUMKIN (Kolloid-Z., 1928, **46**, 89—90).—A preliminary communication in which the following results are recorded. Platinised carbon (prepared by mixing carbon with platinic chloride and heating in a stream of hydrogen) in hydrochloric acid gives the most stable suspension in air and the least stable in hydrogen; unplatinised carbon in air occupies an intermediate position. The suspension in potassium hydroxide is more stable in an atmosphere of hydrogen than in an atmosphere of air. The stability of suspensions saturated with air is much less in sulphuric acid than in hydrochloric acid.

E. S. HEDGES.

Dielectric properties and structure of the hydrophilic colloids. N. MARINESCO (Compt. rend., 1928, **187**, 718—720).—The fall in ε with increase in the concentration of the sol may be used to determine the water fixed by a hydrophilic colloid, the dipoles of the adsorbed water being subjected to the influence of an external field just as in the case of the solidification of a liquid. The amounts of water adsorbed by methæmoglobin, soluble starch, and gum arabic were determined, and indicate that the dispersing medium plays an important role in fixing the structure of

the micelles of which it constitutes the principal portion. J. GRANT.

Formation of gels. Vulcanised oils. B. C. J. G. KNIGHT and P. STAMBERGER (J.C.S., 1928, 2791—2798).—The products obtained by heating triolein with sulphur (B., 1928, 23) have been examined by means of *X*-rays; the diagrams obtained show only an amorphous circle of the same diameter for all the products. The behaviour of the products as thin films on a water surface has also been examined. All give unimolecular films. In the acetone-soluble product which is a viscous, sticky liquid, the mode of orientation of the molecules is not altered from that in triolein and the dimensions are only slightly affected. The benzene-soluble product, a more viscous fluid, gives a film of approximately the same thickness, but the area per molecule is twice that of the acetone-soluble product. When kept this product changes to an elastic, sticky solid which has a very high mol. wt., indicating that the molecule contains at least seven of vulcanised triolein. This product gives a slightly thicker film which is still unimolecular but much less expanded. A sulphurised oleic acid obtained from this solid by saponification had no elastic properties. It is suggested that sulphur first unites with triolein, the sulphur atoms forming a chain which connects the double linkings of the adjacent oleic acid chains. Double molecules are then formed by the linking together of two such molecules with the glyceryl groups combined by means of sulphur. The more highly polymerised elastic products are then formed by the linking of further molecules in the same manner. The significance of this polymerisation and orientation for the theory of gel structure (McBain, A., 1927, 1022) is briefly discussed. R. N. KERR.

Coagulation of strongly-solvated sols with organic substances and salts. II. B. JIRGENSONS (Kolloid-Z., 1928, **46**, 114—128; cf. this vol., 839).—The following results have been obtained in the coagulation of sols of casein, hæmoglobin, and albumin with organic substances and solutions of electrolytes. In small or medium concentrations, mixtures of organic compounds and inorganic salts coagulate the sol more rapidly than either constituent of the mixture alone. At higher concentrations (*e.g.*, 30—60 vol.-% of *n*-propyl alcohol and 0·3 mol. of calcium chloride per litre) stabilisation occurs in virtue of the capillary-active nature and small dielectric constant of the organic compound (*e.g.*, *n*- and *iso*-propyl alcohol, allyl alcohol, ethyl alcohol); this behaviour was observed with both positive and negative hæmoglobin and also with both acid and basic egg-albumin. At still higher concentrations of the capillary-active material (above 60 vol.-%), flocculation is again observed. Glycerol has a sensitising influence on the coagulation of a casein sol by magnesium chloride. The degree of adsorption of alcohols by both hæmoglobin and albumin particles is in the order *n*-propyl alcohol > ethyl alcohol > methyl alcohol, the adsorbability thus being parallel to the sensitising or stabilising effect. Colloids produce a greater increase in the viscosity of alcohol–water–salt mixtures than in pure water. Sensitisation is ascribed to the dehydrating effect of the organic compound and to the alteration of the dielectric properties of the medium. Stabilisation is due to the peptising effect of the salt through the formation of adsorption complexes of hydrated colloid particles and molecules of the salt and of the organic compounds. The rôle of the organic compound is to diminish the dielectric constant in the vicinity of the colloid particle, enabling easily adsorbable complexes of salt molecules to be formed. Thus, only those organic substances which have a low dielectric constant and can be strongly adsorbed by the colloid can have a stabilising effect. The flocculating effect observed at concentrations above 60 vol.-% is due to excessive dehydration of the complexes. Viscosity measurements support the view that the particles in the stabilised mixtures are more strongly solvated than particles of the sols in water. E. S. HEDGES.

General theory of rapid coagulation. Coagulation of rod-like and plate-like colloids; theory of general polydisperse systems and streaming coagulation. H. MÜLLER (Kolloidchem. Beihefte, 1928, **27**, 223—250).—Smoluchowski's theory of rapid coagulation is characterised by three conditions: (*a*) the spherical nature of the particles, (*b*) isodispersity of the colloid, and (*c*) neglect of sedimentation and other movements of the particles. The present paper is a general theoretical investigation of rapid coagulation where these conditions are not fulfilled. The theory involves three postulates: (1) for the coagulation of two micelles, contact of the surface is essential, (2) the frequency of collision of the particles is determined by the temperature movements and streaming of the particles, and (3) the coagulation of a given particle is determined only by the stationary distribution of particles. The application of these principles to isodisperse systems free from streaming has led to a theory of the coagulation of colloids with disc- and rod-like particles and shows that sols with disc-like particles are coagulated in a similar way to those with spherical particles, whereas sols with rod-like particles have a greater coagulation velocity. The influence of polydispersity of the sol is considered, and a relation between the initial tangents of the coagulation curve and the distribution curve of radii of the spherical particles of a sol has been derived. Approximately isodisperse systems must coagulate in accordance with Smoluchowski's rule within the limits of experimental error, but polydisperse systems coagulate more rapidly. The influence of sedimentation and of stirring is discussed, and it appears that these effects influence only the coagulation of the larger particles; a formula has been derived, expressing the minimal radius of particles where such an effect is observed. E. S. HEDGES.

Precipitation of mixtures of colloids of the same sign. M. A. BOUTARIC and (MLLE.) M. DUPIN (Bull. Soc. chim., 1928, [iv], **43**, 1059—1062).—The precipitating action of potassium, lithium, and barium chlorides on mixtures of sols of gamboge and arsenious sulphide has been studied by the spectrophotometric method. The minimum quantity of electrolyte required for precipitation of any mixture is less than that expected from the mixture rule. In

the case of mixtures of sols of mastic-resin and gamboge, the required quantity of electrolyte varies nearly linearly with the composition.

R. N. KERR.

Salting-out of gelatin into two liquid layers with sodium chloride and other salts. J. W. McBAIN and F. KELLOGG (J. Gen. Physiol., 1928, **12**, 1—15).—The concentrations of salt and of hydrogen ion necessary to bring about the separation of gelatin into two liquid layers have been studied in the case of sodium chloride, potassium chloride, sodium sulphate, ammonium sulphate, sodium nitrate, and potassium nitrate. The system gelatin–sodium chloride–hydrogen ion–water behaves as a true quaternary system.

E. A. LUNT.

Formation of Liesegang rings as a periodic coagulation phenomenon. E. S. HEDGES and (MISS) R. V. HENLEY (J.C.S., 1928, 2714—2726).—Experiments have been made to test the view that the occurrence of periodic bands is a secondary coagulation effect which takes place after the chemical change. The behaviour of silver dichromate and magnesium hydroxide in gelatin and of lead iodide in agar has been studied. When a concentrated solution of silver nitrate was superimposed on a colloidal solution of silver dichromate in gelatin which had been allowed to set, periodic rings exactly similar to those prepared in the normal way by chemical action were obtained. Bands were also obtained by diffusion of a concentrated ammonia solution into a gelatin gel of magnesium hydroxide. In the case of an agar gel of lead iodide diffusion of either reactant caused ring formation. Periodic structures were also obtained by the diffusion of an electrolyte other than one of the reactants. With sols of arsenious sulphide these were produced by ferric chloride and aluminium sulphate and with colloidal ferric hydroxide by sodium arsenite and ammonium carbonate. In both cases a decrease in the distance apart of successive rings throughout the diffusion was observed.

When gradually increasing concentrations of silver nitrate solution were added to colloidal silver dichromate, precipitation was not found to vary periodically with the concentration, but a critical concentration of silver nitrate was found necessary for coagulation.

The relative amounts of product in the bands and in the clear spaces (cf. Ostwald, A., 1925, ii, 530) were determined for a magnesium hydroxide gel by chemical analysis. The ratio of magnesium hydroxide in the band to that in the clear space was about 12 : 1, and the corresponding ratio for ammonium chloride (produced in the reaction) about 1 : 3.

Certain anomalous periodic structures are noted.

R. N. KERR.

Theory of the colloid reactions of cerebrospinal fluid. J. K. MAYR (Kolloidchem. Beihefte, 1928, **27**, 347—348).—Polemical against Schmitt (this vol., 477).

E. S. HEDGES.

Behaviour of caseinogen in partial solution in calcium hydroxide. V. PERTZOFF (J. Biol. Chem., 1928, **79**, 799—813).—Purified caseinogen was brought into equilibrium with calcium hydroxide in aqueous solution. The quantity of dissolved caseinogen can be expressed by $K_2/\{1/Ca(OH)_2-(K_1-K_2)/C\}$, where C is the total caseinogen in the system, K_1 is the equivalent combining weight of caseinogen, and K_2 the maximum base-binding power of caseinogen (A., 1927, 895). The solubility therefore depends on the total amount of caseinogen present as well as on the base added; a linear relationship was observed between the calcium hydroxide bound and the dissolved protein. Similar relationships hold for the solubility of caseinogen in large amounts of sodium hydroxide at 5°.

C. R. HARINGTON.

Titration curves of coagulated and uncoagulated egg-albumin. B. M. HENDRIX and V. WILSON (J. Biol. Chem., 1928, **79**, 389—403).—Comparison of the electrometric titration curves of coagulated and uncoagulated egg-albumin shows that the latter has a greater acid- and base-binding power, the difference being more marked if the coagulated protein has been dried before being brought into equilibrium with acid or alkali; the results are in accordance with the view that coagulation involves a decrease in the number of free amino- and carboxyl groups owing to internal condensation.

C. H. HARINGTON.

Filterability of hydatid "antigens." C. H. KELLAWAY, N. H. FAIRLEY, and F. E. WILLIAMS (Austral. J. Exp. Biol., 1928, **5**, 189—204).—When hydatid fluid is filtered through collodion membranes of various permeabilities the ultra-filtrates for the less permeable membranes do not act as an antigen towards serum from animals immunised to the parasite, although the ultra-filtrates for the more permeable membranes give a positive reaction when tested by intradermal injection into a sensitised animal, by the sensitised guinea-pig uterus, or, in some cases, by means of the complement fixation test. These ultra-filtrates remain active after boiling and fail to give most of the ordinary tests for protein.

W. O. KERMACK.

Cataphoresis and the electrical neutralisation of colloidal material. S. MATTSON (J. Physical Chem., 1928, **32**, 1532—1552; cf., A., 1922, i, 800).—An ultramicroscopic cell which permits the rapid determination of the cataphoretic movement of colloidal particles before and after flocculation and also of the isoelectric point is described. A study of the electrical neutralisation of electrodialysed clay suspensions by aluminium chloride alone and after treatment with acid and alkali shows the products of hydrolysis of the aluminium salt to be more active than the tervalent cations, and that the greatest efficiency is obtained at p_H 5·2. In the case of neutralisation of the clay by methylene-blue, the isoelectric ratio dye/clay is increased by the presence of anions and decreased by that of cations, the magnitude of the effect increasing with valency. The amount of methylene-blue required to neutralise the electronegative proteins in milk decreases with an increase in acidity of the latter, thus affording a means for determining its freshness.

Barium sulphate, by itself and in the presence of an excess of barium, is electropositive, whilst with an excess of sulphate ions it is electronegative. The conditions cause a decrease and an increase, respectively, in the p_H of the solution. An explanation based on a difference in solution tension of two ions for the former,

and one based on the assumption of adsorption of the hydroxyl and hydrogen ions of the water for the latter, are offered.

The behaviour of certain electrolytes, *e.g.*, sodium ferrocyanide, in forming a transient turbidity before dissolution has been studied. The crystalline chips which in water break away from the larger crystals carry a high electronegative charge.

It is pointed out that all electrolytes in water may give rise to a dissociation *P.D.* at the phase boundaries, the sign of the charge being determined by the solution tension and osmotic pressure of the respective ions, and that the electronegative charge of inert materials is due to an adsorbed layer of oriented water molecules. L. S. Theobald.

Influence of salts on the isoelectric behaviour of proteins. K. Kondo and T. Hayashi (Mem. Coll. Agric. Kyotō, 1928, No. 5, 1—29).—The optimum p_H value for the flocculation of rice glutelin is 5·38—5·08 in a 0·1*N*-sodium acetate solution which is 0·02—0·04*N* in acetic acid (cf. A., 1927, 269). The influence of the presence of a number of salts on such an apparent isoelectric solution had been studied. The presence of a chloride shifts the point of maximum precipitation to the acid side, and at the same time decreases the precipitability of rice glutelin up to a certain concentration of salt, which varies with the salt. The precipitability then increases until, at a still higher concentration, it again decreases. The first change of direction of the curve is explained by the formation of an insoluble complex compound of the protein molecule with the cations of the salt, and the second by the formation of a soluble complex compound. The higher the valency of the cation the more pronounced are the effects. The influence of the cations of the same valency decreases in the following order: $Li^{\cdot}>Na^{\cdot}>K^{\cdot}>Rb^{\cdot}$; $Cu^{\cdot\cdot}>Ni^{\cdot\cdot}>CO^{\cdot\cdot}>Mg^{\cdot\cdot}>Ca^{\cdot\cdot}>Ba^{\cdot\cdot}$; and $Fe^{\cdot\cdot\cdot}>Al^{\cdot\cdot\cdot}$. The poisoning action of cupric ions on the organism and the sterility of acid soil due to the presence of iron and alumina in the soil, may result from the inhibition of the living cell metabolism by the formation of a complex compound in which cupric, ferric, or aluminium ions combine with the protoplasmic protein. The effect of inorganic potassium salts, other than carbonate, is similar to that of the chloride, and the influence of the anion also is specific. The carbonate and the acetate, tartrate, and citrate, but not the oxalate, shift the apparent isoelectric point to the alkaline side, their influence being in the order of the dissociation constants of the acids. Potassium oxalate has no influence, owing to the relatively high dissociation constant of oxalic acid. They all decrease the precipitability of the salt. The effect of salts on the isoelectric point is said to be explainable in terms of the ionisation of the protein, each ion giving rise to a protein ion of opposite charge, and of the relative magnitudes of these ionising agencies. M. S. Burr.

Isoelectric point of glutenin. K. Kondo and T. Hayashi (Mem. Coll. Agric. Kyoto, 1928, No. 5, 31—47).—Glutenin free from gliadin, and containing 17·17% of Kjeldahl nitrogen, has been obtained by a method which is described. The apparent isoelectric point is p_H 5·15—5·39. This value is independent of the concentration of glutenin, but the proportion of glutenin flocculated increases with increasing concentration of the protein owing to the fact that the solubility of the protein at its maximum flocculation point is constant in a solution of fixed salt concentration. Dehydration of the glutenin with alcohol and ether has no effect on its isoelectric point, but addition of rubidium chloride to the buffer solution shifts the isoelectric point of the glutenin to the acid side and reduces the precipitability. The varying values obtained for glutenin from different flours by other investigators may possibly be explained by failure to remove completely the gliadin, which has an influence on the isoelectric point. M. S. Burr.

Equilibrium in the reaction $C_2H_6 \leftarrow C_2H_4+H_2$. R. N. Pease and E. S. Durgan (J. Amer. Chem. Soc., 1928, 50, 2715—2718).—Equilibrium may be approached from either side at 600°, 650°, and 700° (cf. Bone and Coward, J.C.S., 1908, 93, 1197; Sabatier and Senderens, A., 1905, i, 333), although the results are rendered uncertain by the methane formed in increasing quantities with rising temperature. When approximately equilibrium mixtures are heated, the equilibrium constants, K_p at the temperatures indicated are 0·0310, 0·082, and 0·20 respectively, and the heat of dissociation of 1 mol. of ethane is −31,244 g.-cal. H. E. F. Notton.

Equilibrium between hydrogen–carbon monoxide and methane–carbon dioxide in the corona discharge. G. L. Wendt and G. M. Evans (J. Amer. Chem. Soc., 1928, 50, 2610—2621).—The effect of corona discharge (10,000—20,000 volts) on the reaction $2H_2+2CO=CO_2+CH_4$ has been investigated, one of the electrodes being a wire along the axis of the discharge tube. After the initial "corona expansion" the volume (corrected for temperature influence) passes through a maximum when carbon dioxide and methane are the initial gases; otherwise an immediate contraction takes place. The equilibrium mixture always contains 13·3% CO_2, 37·1% CO, 8·7% CH_4, and 37·6% H_2, and is not influenced by the presence of phosphoric oxide. This equilibrium corresponds with that obtained at a temperature between 900° and 950°. The volume contraction, which continues beyond the equilibrium point, is due to a second reaction, as is evidenced by the deposition of carbon suboxide. A little aldehyde seems to be produced also. The end products are probably carbon and water. S. K. Tweedy.

New high-temperature fixation reactions of nitrogen. N. W. Krase and B. Mackey (J. Physical Chem., 1928, 32, 1488—1494).—Theoretical. A thermodynamic investigation of nitrogen fixation using the data of Lewis and Randall has been made. In the case of oxygen and nitrogen, only a small increase in the concentration of nitric oxide can be produced in the arc process, by the use of stoicheiometric proportions of these gases in place of air, but the reaction between nitrogen and carbon dioxide should double the concentration of nitric oxide. Nitrogen, hydrogen, and carbon should yield concentrations of hydrogen cyanide greater than 15% at the usual arc temperature, whilst nitrogen and acetylene should yield a product containing 70%

of hydrogen cyanide. The establishment of equilibrium in the reaction between nitrogen and methane at 2000° Abs. or above should result in a gas containing 40% of hydrogen cyanide and 60% of hydrogen.

L. S. THEOBALD.

Compound formation in ester–water systems. J. KENDAL and L. S. HARRISON (Trans. Faraday Soc., 1928, **24**, 588—596).—To determine the influence of the radicals R, R′ in esters of the type $R\cdot CO_2R'$ on compound formation in aqueous solutions, measurements have been made of the f.-p. depression and miscibility curves for systems of water and the following: methyl propionate, *n*-propyl formate, ethyl formate, methyl acetate, and methyl oxalate. An analysis of the results shows that the course of the miscibility curves depends primarily on the internal pressure of the ester. Esters with low internal pressures are only slightly soluble in water and exhibit retrograde solubility with rise of temperature. The solubilities of esters with higher internal pressures are either almost independent of, or increase with, temperature. Compound formation is extensive in all systems and increases with the strength of the acid radical of the ester. The nature of the alcohol radical appears to be of little influence in this respect.

F. G. TRYHORN.

Active volume. F. DOBRZYŃSKI (Rocz. Chem., 1928, **8**, 369—375).—The law of mass action is not applicable to esterification reactions; for these the relative volume and not the mass of the reacting substances is of importance. The expression $z=mf\pm c/V$ is derived, where z is the active volume, m the number of mols. of the given reagent, c the dilatation or contraction constant, and V the total volume of the system. The conception of active volumes explains the steady increase in the equilibrium constant as the relative concentration of alcohol to acid rises, and shows why a greater yield of ester is obtained when the relative concentrations of alcohol and acid are as $n:1$ than when they are as $1:n$. Finally, it explains why the esterification does not proceed to completion even when the concentration of alcohol is infinitely great.

R. TRUSZKOWSKI.

Equilibrium state for esterification reactions in the liquid phase. S. POZNAŃSKI (Rocz. Chem., 1928, **8**, 377—393).—The equilibrium constant for the reaction between acetic acid and ethyl alcohol varies from 2·45 in a mixture containing 3 mols. of acid to 1 mol. of alcohol to 4·73 when these proportions are reversed. The law of mass action does not therefore apply to the above reaction.

R. TRUSZKOWSKI.

Theory of acidity. L. P. HAMMETT (J. Amer. Chem. Soc., 1928, **50**, 2666—2673).—The influence of the solvent on the acidity of an acid is investigated mathematically, and the following conclusions are reached. Decreased basicity of the solvent means greater acidity and also less ionisation of the acid. The hydrogen-ion activity of a weakly ionised acid is independent of the dielectric constant of the solvent, but in the case of a highly ionised acid it is greater in solvents of low than in solvents of high dielectric constant. Decrease in the dielectric constant has little effect on salt formation when the ionisation is large, but decreases salt formation when the ionisation is small. For all except very highly ionised solutions the result of decreasing dielectric constant is a decrease in apparent acidity as measured by a basic indicator, but the latter change does not run parallel with the hydrogen-ion activity. The same scale of activities in all solvents is adopted throughout the discussion. The predictions of the theory are in agreement with the results of Hantzsch (A., 1927, 525) and of Hall and Conant (cf. this vol., 129) and of Hall and Werner (*ibid.*, 1188).

S. K. TWEEDY.

Partition of nitric acid between sodium and potassium hydroxides. V. I. NIKOLAIEV (J. Russ. Phys. Chem. Soc., 1928, **50**, 893—904).—A phase diagram for the quaternary system K_2O–Na_2O–N_2O_5–H_2O is described.

R. TRUSZKOWSKI.

Influence of neutral salts on acid–base equilibria. V. First and second dissociation constants of succinic, tartaric, and adipic acids, and the influence of neutral salts on the p_H of a mixture of the acid and its acid salt, and the acid salt and normal salt, respectively. VI. Dissociation constants of acetic, hexoic, and benzoic acids and the influence of neutral salts on the dissociation constants of weak acids. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1928, **47**, 861—872, 872—882; cf. this vol., 954).—V. The following values have been found from p_H measurements for the first and second dissociation constants of the three dibasic acids: succinic $6\cdot6\times10^{-5}$ and $2\cdot7\times10^{-6}$, adipic $4\cdot6\times10^{-5}$ and $3\cdot6\times10^{-6}$, tartaric $9\cdot6\times10^{-4}$ and $2\cdot8\times10^{-5}$. These results are extrapolated for infinite dilution. Neutral salts increase the activity of the undissociated acid; the dissociation constant of the acid is not increased. The Debye–Hückel equation does not completely represent the effect of neutral salts on the ratio of the activity coefficients of the uni- and bi-valent anions of the weak dibasic acid. A specific ionic interaction has to be taken into account.

VI. The dissociation constants of the three monobasic acids at 18° are found to be: acetic $1\cdot70\times10^{-5}$, hexoic $1\cdot44\times10^{-5}$, benzoic $7\cdot0\times10^{-5}$. In this case also, there is no evidence that neutral salts increase the dissociation constant of weak acids.

O. J. WALKER.

Electrochemical study of the action of acids on solutions of some zinc salts. J. GUÉRON (Compt. rend., 1928, **187**, 599—601).—The variation of p_H in solutions of zinc salts on addition of acid has been investigated in the cases of zinc acetate–acetic acid, zinc acetate–hydrochloric acid, and zinc sulphate–sulphuric acid.

C. W. GIBBY.

The equilibrium $2K_3Fe(CN)_6+2KI$ $2K_4Fe(CN)_6+I_2$ in aqueous potassium chloride solutions. V. K. LA MER and K. SANDVED (J. Amer. Chem. Soc., 1928, **50**, 2656—2665).—The system was investigated in water and in potassium chloride solutions (0—2 molar). The ionic strength is not an entirely satisfactory measure of the electric environment (cf. La Mer and Mason, A., 1927, 314). The data confirm the view that the law of mass action holds for ionic systems when sufficient neutral salt is present to maintain constant electrical environment, although this law fails completely in the absence of

excess of neutral salt. The acidity of the solution is without influence up to a p_H value of 3·5. Thermodynamic equilibrium constants for the ionic reaction, and the reaction in which I_3' is produced, are calculated with the aid of *E.M.F.* data. S. K. TWEEDY.

Effect of the position of substitution on the ionisation constants of some organic acids. D. A. MACINNES (J. Amer. Chem. Soc., 1928, **50**, 2587—2595).—If K is the dissociation constant of a substituted acid, and if d represents the position of the substituent (*i.e.*, $d=1$ for α position, 2 for β position, etc.), then, for many series of acids, $\log K=k_1+k_2/d$, where k_1, k_2 are constants. This relation holds even better for series of acids in which substitution is always on the final carbon atom of the chain. k_1 may be the logarithm of the ionisation constant of a hypothetical acid in which the chemical change of substitution has occurred, but in which the substituent is at an infinite distance from the carboxyl group. The term k_2/d is then a measure of the potential energy involved in bringing the two negative groups near to each other. Apparently d is the distance between the polar linking joining the carboxyl to the carbon chain and the polar linking joining the other substituent to the chain. The chlorobenzoic acids conform accurately to the equation if a "puckered" ring structure is assumed for benzene and if the "α-distance" in the fatty acid is equal to the "*ortho*-distance" in the aromatic acid. Evidence is adduced that the benzene ring is a stable system, whereas aliphatic chains are comparatively flexible. Bromine- and iodine-substituted aliphatic acids show small, systematic deviations from the equation with which, however, the corresponding aromatic acids agree closely. S. K. TWEEDY.

Effect of salts on weak electrolytes. II. Calculation of overlapping constants. H. S. SIMMS (J. Physical Chem., 1928, **32**, 1495—1515).—In continuation of a previous paper (this vol., 1093), the potentiometric titration data are given, and the method of calculating the titration indices of multivalent acids with overlapping constants is explained. L. S. THEOBALD.

Acid dissociation of aquo-ions. II. J. N. BRÖNSTED and K. VOLQVARTZ (Z. physikal. Chem., 1928, **134**, 97—124; cf. this vol., 18).—The acid dissociation constants at 15° have been found for the tervalent aquopentammino-, diaquotetrammino-, triaquotriammino-, and tetra-aquodiammino-cobalt ions, aquopentammino-rhodium ion, hexa-aquo-aluminium, -chromium, and -ferric ions by means of the determination of (i) the hydrogen-ion concentration by the diazoacetic ester method, (ii) the solubility of the salts in solutions of different acidities, and (iii) the hydrogen-ion concentration from the velocity of decomposition of the nitrato-aquotetrammino-cobalt salts. In the case of the first two ions, the values of the dissociation constant decrease with increase in the concentration, and the deviations from the theoretical values can be represented by an equation similar to that found for the hexa-aquochromic ion (*loc. cit.*). The extrapolated values of the acid dissociation constants at infinite dilution for the above ions are $2·04\times10^{-6}$, $6·2\times10^{-6}$, $2·0\times10^{-5}$, $4·0\times10^{-4}$, $1·38\times10^{-6}$, $1·3\times10^{-5}$, $1·26\times10^{-4}$, and $6·3\times10^{-3}$, respectively. The methods and results are discussed. L. S. THEOBALD.

Hydrolytic scission of succinimide. H. VON EULER and A. OLANDER (Z. physikal. Chem., 1928, **137**, 393—398).—Electrometric measurements of the hydrogen-ion concentration in acid solution of succinimide gave a value $K_a=2·6\times10^{-10}$ at 25° for the first ionisation constant. Efforts to determine the second ionisation were unsuccessful. Similar measurements with succinamic acid gave an acid ionisation constant of $2·72\times10^{-5}$ at 25°. Unsuccessful attempts were made to measure the basic ionisation constant, which is smaller than that of acetamide. Determinations were made in solutions of varying alkalinity of the velocity of hydrolysis of succinimide to succinamic acid. In the region p_{OH} 3 the rate of increase of the velocity coefficient becomes greater, but falls almost to zero at p_{OH} 2·5. Thence onwards the rate of increase becomes much greater, reaching 0·00418 at p_{OH} −0·083. No satisfactory theoretical explanation can be advanced for these irregularities.

The hydrolysis of succinimide is much slower in acid solutions at the ordinary temperature, but at 90° a mean value corresponding with $2·9\times10^{-4}$ H^+ was found in 0·118—0·05*N*-hydrochloric acid. F. G. TRYHORN.

Partial osmotic pressures and membrane equilibria, with special reference to the application of Dalton's law to hæmoglobin solutions in the presence of salts. G. S. ADAIR (Proc. Roy. Soc., 1928, **A**, **120**, 573—603; cf. A., 1926, 21).—By means of the method previously described (A., 1925, ii, 965), the osmotic pressures of hæmoglobin solutions in equilibrium with solutions of diffusible salts have been measured and correlated with determinations of the membrane potentials, and the distribution of diffusible ions. The relations between the activities of diffusible ions and the membrane potentials are in accordance with Donnan's theory, but his assumptions with regard to osmotic pressures do not appear to be applicable to protein solutions of finite concentration. Experiment shows that, even if the concentration of diffusible ions is only 0·01 equiv. per litre, the margin of uncertainty in the partial pressures of the diffusible ions is of the same order of magnitude as the observed osmotic pressures of the protein. The formula $p_p=p_{obs.}-p_i$, where p_p is the partial osmotic pressure of the protein ions and p_i the diffusible ion pressure difference, yields a provisional value for the partial osmotic pressure, which is approximately correct within a limited range of hydrogen-ion, salt, and protein concentrations. The application of Dalton's law to protein systems can be verified by determinations of the mol. wt. of a protein. Systematic experimental investigations of the partial pressures indicate that certain variations in the osmotic pressure, formerly attributed to actual changes in the aggregation of the protein, are really due to deviations from the ideal solution laws. In solutions of p_H 5·0—9·0, and with sodium chloride concentrations from 0·01 to 4·0 mols. per litre, and in solutions with different kinds of ions, including K, Na, NH_4, Mg, Cl, HCO_3, SO_4, H_2PO_4, HPO_4, the degree of aggregation of hæmoglobin appears to be constant. Methods are developed for determin-

ing the mol. wt. of proteins in non-ideal solutions containing salts, use being made of the formula $M_a = 170{,}330/k_m$, where k_m is an empirical constant. The value 67,000 obtained for hæmoglobin in physiological salt solutions agrees with that previously determined for hæmoglobin in distilled water.

L. L. BIRCUMSHAW.

Activity of univalent ions. H. MUELLER (Physical Rev., 1927, [ii], **29**, 216).—It is shown that Debye's theory is in accord with the experimental results for small ions without the assumption of partial association.

A. A. ELDRIDGE.

Application of the method of partition coefficients to the determination of the activity coefficients of the dissociated and undissociated fractions of salicylic acid in neutral salt solutions. B. VON SZYSZKOWSKI and A. VON SKAPSKI (Z. physikal. Chem., 1928, **137**, 238—262).—The partition coefficients of salicylic acid between benzene and aqueous solutions of sodium chloride, chlorate, nitrate, and sulphate, barium chloride, and magnesium sulphate over the concentration range 0·005—2·0M have been determined, and the activity coefficients of the undissociated and dissociated acid have been calculated. From thermodynamical considerations the equation $c'/c = 1 - \alpha/f_0 + \alpha/f$ has been derived, where c' is the solubility, c and α are the solubility and degree of ionisation in water, and f_0 and f the activity coefficients of the undissociated and dissociated molecules, respectively. The formula yields values of c' which are in close agreement with those determined experimentally, and accounts satisfactorily for the maxima which exist in all cases in the solubility curves.

H. F. GILLBE.

Activity coefficients of sodium and potassium hydroxides in their corresponding chloride solutions at high constant total molality. H. S. HARNED and J. McA. HARRIS, jun. (J. Amer. Chem. Soc., 1928, **50**, 2633—2637).—The *E.M.F.* at 25° of cells of the type $H_2|MOH(c_1),MCl(c_2)|M_xHg|MOH(c_0)|H_2$ are recorded, in which M=Na or K, and c_1+c_2 is kept constant (3, 3·5, or 5M) throughout a given series of measurements. The logarithms of the activity coefficients of the hydroxides in the chloride solutions, calculated from these results, are not a linear function of the concentration of the hydroxide, although the deviation is small.

S. K. TWEEDY.

Molecular statistical thermodynamics. E. SVENSEN (Ann. Physik, 1928, [iv], **87**, 424—460).—Mathematical.

W. E. DOWNEY.

Hydrodynamics and the kinetic theory of gases. Y. ROCARD (Ann. Physique, 1928, [x], **10**, 345—348).—A correction (cf. A., 1927, 826).

Second law of thermodynamics in general relativity. R. C. TOLMAN (Proc. Nat. Acad. Sci., 1928, **14**, 701—706).—Mathematical.

W. E. DOWNEY.

Thermodynamics of irreversible reactions. Evolution of physical and chemical systems in time. N. A. KOLOSOVSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 1079—1115).—The time factor is introduced as an independent variable into De Donder's thermodynamic theory of chemical reactions (Mem. Acad. Roy. Belg., 1927, **9**) and a series of expressions for velocity of reaction is derived from an exclusively thermodynamical point of view. Further equations are given expressing uncompensated heat of reaction in gaseous systems, which represent a generalisation of the ordinary conditions of equilibrium in such systems.

R. TRUSZKOWSKI.

[Polymorphism and solubility of] triglycerides. K. LOSKIT (Z. physikal. Chem., 1928, **134**, 135—155).—The polymorphism and the solubility of tristearin, tripalmitin, trimyristin, trilaurin, tricaprin, tricaprylin, tricaproin, tributyrin, and triacetin have been investigated. The velocity of crystallisation in all cases is small, the maximum speed (1·2 mm./min.) being shown by tristearin. The spontaneous crystallisation has also been studied. The first three glycerides mentioned above show three modifications, two unstable and one stable; the next three show two, one stable and one unstable, and the last three solidify to a glassy state. The unstable forms exist at the ordinary temperature, and change to the stable forms only at temperatures near the m. p. Solubility data for the triglycerides in benzene, ether, chloroform, and carbon disulphide are tabulated. In general, no depression of the m. p. of the solvent is to be observed, and the solubility curves for benzene as solvent consist of two parts and indicate the simultaneous existence of stable and unstable modifications. The results suggest that the triglycerides are polymerised and are colloidal in character and that a reversible equilibrium between the crystalline and colloidal states exists. Polymorphism is considered to be due to different degrees of polymerisation.

L. S. THEOBALD.

Polymorphism. K. LOSKIT (Z. physikal. Chem., 1928, **134**, 156—159).—The solubility curves for the systems resorcinol–water, benzophenone–benzene, phenyl salicylate–benzene have been determined by the method previously described (preceding abstract). A sharp break in the curves occurs at 41·6% of resorcinol, 48% of benzophenone, and 49·7% of phenyl salicylate, respectively. This is the case with many monotropic, polymorphous substances. The cause of polymorphism, it is considered, lies in polymerisation, and, contrary to the views of Smits (A., 1927, 1027), the modifications of a substance are not co-existent and do not form mixtures with each other. Polymerisation and depolymerisation are analogous to electrolytic dissociation.

L. S. THEOBALD.

Relation between deviations of the vapour-pressure curves of binary mixtures of normal substances from the linear law, and the heats of mixing in the liquid phase. J. J. VAN LAAR (Z. physikal. Chem., 1928, **137**, 421—446).—Theoretical. Expressions are deduced on a thermodynamical basis for the vapour pressure, heat of mixing, and for the volume changes of binary mixtures. The calculated values of the above quantities are compared with the experimental values of Schmidt (A., 1926, 787) for 21 binary mixtures.

F. G. TRYHORN.

Structure of copper–tin alloys. W. BRONIEWSKI and B. HACKIEWICZ (Compt. rend., 1928, **187**, 651—654).—Copper–tin alloys of varying composition were annealed for prolonged periods at temperatures between 200° and 620°, and measurements were

then made of (1) electrical conductivity at 0°, (2) temperature coefficient of resistance between 0° and 100°, (3) thermo-electric power against lead at 0°, and its variation between −78° and +100°, (4) solution potential, (5) coefficient of expansion at 0°, and its variation between −186° and +218°, (6) Brinell hardness. The results are given in abstract only, and indicate that the compound Cu_3Sn_2 dissolves about 1% of copper and 5% of tin. The compound Cu_3Sn dissolves about 1% of each constituent according to the curves for thermo-electric power, but the other curves are less clear. The component Cu_4Sn is of fixed composition. W. HUME-ROTHERY.

Equilibrium diagram of the copper–tin system. T. ISIHARA (Sci. Rep. Tohoku, 1928, **17**, 927—937).—A redetermination of the solubility of tin in copper by microscopical examination and electrical resistance measurements following very prolonged annealing shows that the saturated solid solution contains 14% Sn between 0° and 510° and 12% Sn at the triple point at 790°. The existence of a narrow range of solid solution between 68 and 70% Cu could not be confirmed. At the composition corresponding with the compound Cu_3Sn the solidus and liquidus lines do not coincide, but a freezing interval exists between them. A. R. POWELL.

Equilibrium diagram of the molybdenum–carbon system. T. TAKEI (Sci. Rep. Tohoku, 1928, **17**, 939—944).—The system contains one compound only, Mo_2C, m. p. 2307°. This forms a limited range of solid solutions with molybdenum containing 5·5—6% C and a eutectic with about 4% C (m. p. about 2300°). The solubility of carbon in molybdenum is about 0·3%. The carbide may be isolated as a greyish-white powder by electrolytic dissolution of an alloy containing 5% C in hydrochloric acid; it has a hexagonal close-packed lattice with the constants a—2·995 Å., c=4·723 Å. A. R. POWELL.

Equilibrium diagram of the iron–iron sulphide system. K. MIYAZAKI (Sci. Rep. Tohoku, 1928, **17**, 877—881).—The equilibrium diagram of the iron–ferrous sulphide system has been redetermined by thermal analysis and by measurements of the electrical resistance, the constituents being melted together in an electric furnace under a layer of calcium chloride. The eutectic contains 83% FeS and melts at 985°; no solid solutions are formed at either end of the system. Pure ferrous sulphide melts at about 1190° (extrapolated). A. R. POWELL.

Equilibrium diagram of the iron sulphide–manganese sulphide system. Z. SHIBATA (Tech. Rep. Tohoku, 1928, 7, 39—49).—The system iron sulphide–manganese sulphide has been investigated by thermal analysis and microscopically. The two components melt at 1163±2° and 1610±3°, respectively. $Fe_3Mn_2S_5$ does not exist (cf. Röhl, A., 1912, ii, 1059). Solid iron sulphide and manganese sulphide are partly miscible and give rise to a eutectic at 1164°. C. W. GIBBY.

System $LiCl–CoCl_2$. A. FERRARI (Atti R. Accad. Lincei, 1928, [vi], 7, 848—853).—The m.-p. curve for mixtures of lithium and cobalt chlorides shows a maximum corresponding with the formation of the double salt $2LiCl,CoCl_2$. R. W. LUNT.

F. p.–solubility relations of geometrical isomerides. I. β-Chlorocrotonic acids. E. L. SKAU and B. SAXTON (J. Amer. Chem. Soc., 1928, **50**, 2693—2701).—The f. p.–solubility diagram for the system β-chlorocrotonic acid–β-chloro*iso*crotonic acid was determined. The system is of the simple eutectic type. The molal heats of fusion of the separate acids are ΔH=20,300—94·15T+0·1426T^2 and ΔH(*iso*-)= 11,660—61·26T+0·1085T^2, which yield values at the m. p. differing somewhat from those calculated from the f.-p. measurements. The system is not entirely ideal; complex and mixed crystal formation are probably absent. The existence of a slight heat of mixing would account for the observed results.

In the region of the m. p. the molal heat of fusion of crotonic acid is ΔH=3695—13·56t+0·0736t^2 (t=°C.), or 3100 g.-cal. at the m. p., 71·4°, corresponding with a molal entropy of fusion of 0·9 g.-cal./1° at the m. p. S. K. TWEEDY.

Velocity of hydration of dehydrated gypsum. P. P. BUDNIKOV (Kolloid-Z., 1928, **46**, 95—97).—Hydration of natural and synthetic gypsum which has been dehydrated at 140° proceeds rapidly at first with formation of the hemihydrate, and then slowly with formation of a gel on the surface of gypsum nuclei; finally, the velocity increases once more as the dihydrate is formed. The first process lasts for 1 to 2 sec., the velocity of absorption of water depending on the time taken to dehydrate the original gypsum. E. S. HEDGES.

Velocity of dehydration of gypsum at various temperatures. P. P. BUDNIKOV (Kolloid-Z., 1928, **46**, 97—99).—At the beginning of the process, the velocity of dehydration of synthetic gypsum is less than that of natural gypsum, except at 160°, where they are equal. Subsequently, the curve for the synthetic form meets that of the natural form at some point depending on the temperature, and thereafter lies above it. At the point corresponding with the formation of the hemihydrate a retardation in the velocity of dehydration was observed at 100° and at 140°. E. S. HEDGES.

Pharmaceutical combinations and the formation of molecular compounds. P. PFEIFFER and R. SEYDEL (Z. physikal. Chem., 1928, **137**, 107—125).—Phase diagrams have been obtained for a number of binary mixtures of organic compounds which are often used medicinally. Orthoform (new) and antipyrine yield a molecular compound (1 : 1), m. p. 92°, sarcosine anhydride and orthoform (new) a (1 : 1) compound, m. p. 146°, sarcosine anhydride and methyl *p*-hydroxybenzoate a (1 : 2) compound, m. p. 99°, sarcosine anhydride and *o*-aminophenol a (1 : 1) compound, m. p. 101°, and sarcosine anhydride and methyl *m*-aminobenzoate a (1 : 2) compound, m. p. 64°. No evidence has been obtained of compound formation between orthoform (new) and pyramidone or acetamidoantipyrine; antipyrine and luminal, *o*-aminophenol, methyl *m*- or *p*-aminobenzoate, or methyl *p*-hydroxybenzoate; pyramidone and *o*-aminophenol, methyl *p*-hydroxybenzoate, or methyl *m*- or *p*-aminobenzoate. H. F. GILLBE.

System $KNO_3–HNO_3–H_2O$. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 844—846; cf. A., 1927,

628).—The earlier work at 25° has been extended to 40° and 60°. At neither temperature is there evidence of double salt formation. R. W. LUNT.

System KNO_3–$Al(NO_3)_3$–H_2O. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 846—848).—Data for this system at 0°, 40°, and 60° show, in agreement with earlier work at 25° (A., 1927, 518), that the solid phase consists of KNO_3 and $Al(NO_3)_3,9H_2O$. R. W. LUNT.

Ternary system ammonium chloride, ammonium succinate, and water. (MISS) J. C. LANZING (Rec. trav. chim., 1928, **47**, 901—903).—No compound is formed between the components of this system at 25·2°. O. J. WALKER.

Ternary systems. VII. Periodates of the alkali metals. A. E. HILL (J. Amer. Chem. Soc., 1928, **50**, 2678—2692; cf. A., 1927, 1142).—The influence of potassium hydroxide on aqueous potassium metaperiodate solution at 25° indicates that KIO_4 and $K_4I_2O_9,9H_2O$ (dimesoperiodate) are the only salts which can be obtained from the solution at this, or higher, temperature. There is no indication of the salts $K_3HI_2O_9$ and $K_3IO_5,4H_2O$. The solubility of potassium metaperiodate is recorded; it is 0·0238 mol./litre at 25°. The dimesoperiodate is very soluble and the temperature coefficient is large; it undergoes transition to the anhydrous form at about 78°. Similar experiments with sodium metaperiodate show that this is readily soluble (12·62% at 25°) and is converted into the slightly soluble (0·23% at 25°) paraperiodate (not hydrated dimesoperiodate), $Na_2H_3IO_6$, in presence of the smallest quantity of sodium hydroxide. The only other salt precipitated from the aqueous solution is $Na_3H_2IO_6$, and then only when excess of sodium hydroxide is present; this salt, which is a true salt of the para-series, cannot be crystallised from water without hydrolysis, which explains discrepancies previously observed in the preparation of sodium metaperiodate by oxidation of the iodate by chlorine. The transition $NaIO_4,3H_2O \quad NaIO_4+3H_2O$ occurs at 34·5°. The solid salt, Na_5IO_6, appears not to exist. The solubilities at 25° of the metaperiodates in periodic acid solutions do not disclose the formation of any acid periodates. The possible application of the results in the analytical separation of potassium and sodium is discussed. Lithium periodate could not be prepared pure and ammonium periodate could not be prepared at all by the oxidation by chlorine of the iodates in presence of the appropriate base. The solubility of the crystals $HIO_4,2H_2O$, *d* 2·3, is about 53% at the ordinary temperature. S. K. TWEEDY.

System $AlCl_3$–KCl–HCl–H_2O between 0° and 80°. G. MALQUORI (Gazzetta, 1928, 58, 562—568; cf. this vol., 956).—The only solids which can exist in contact with the saturated solutions are potassium chloride and the hydrate $AlCl_3,6H_2O$. Tetrahedral diagrams are given showing the composition of the aqueous phase at the various temperatures. From these a model is constructed which gives the proportions of potassium chloride, aluminium chloride, and hydrochloric acid in solutions saturated with respect to the two salts. O. J. WALKER.

Formation and decomposition of sodium salicylate. I. A. DAVIES (Z. physikal. Chem., 1928, **134**, 57—86).—The formation of sodium salicylate from sodium phenoxide and carbon dioxide and the thermal decomposition of sodium salicylate have been investigated by means of measurements of the *p*–time curves at various temperatures and of the *p*–temperature curves. Above 140°, sodium phenoxide and carbon dioxide result primarily from the thermal decomposition of sodium salicylate, and this is a case of "unilateral" equilibrium (cf. Baur and Orthner, A., 1916, ii, 232). Secondarily, disodium salicylate and phenol are formed by double decomposition from the phenoxide and salicylate. This equilibrium over the range 160—220° is completely reversible. The *p*–temperature curve shows a break at 190° and 4·15 atm., corresponding with a quintuple point in the three-component system with the phases sodium salicylate, disodium salicylate, the phenoxide, solution, and gas. Below this point the system salicylate–disodium salt–phenoxide–gas is stable, and above, the system salicylate–disodium salt–solution–gas. In the formation of sodium salicylate from sodium phenoxide and carbon dioxide, two definite intermediate products, "ester salt I and II," are formed. Both of these show a definite dissociation pressure, the first being metastable to the second, which in turn is metastable with regard to sodium salicylate. L. S. THEOBALD.

Sodium salicylate and salicylic acid and "unilateral equilibrium. E. BAUR (Z. physikal. Chem., 1928, **134**, 87—91).—The work of Davies (cf. preceding abstract) is discussed. Data on the thermal dissociation of salicylic acid show this to be another case of "unilateral" equilibrium. L. S. THEOBALD.

Establishment of equilibrium from one side or from both sides, as described in the literature. E. BAUR (Z. physikal. Chem., 1928, **137**, 63—71).—Discursive. H. F. GILLBE.

Heat of dilution of potassium chloride up to infinite dilution. E. LANGE and P. A. LEIGHTON (Z. Elektrochem., 1928, **34**, 566—571).—The integral heats of dilution of *N*/100, *N*/200, and *N*/300 (approx.) solutions of potassium chloride were measured at 12·5° and 25° in a slightly improved form of the apparatus previously described (Lange and Messner, this vol., 134). Below *N*/100 the heat of dilution is proportional to the square root of the salt concentration, as required by the Debye–Hückel theory. As far as can be inferred from the unsatisfactory and meagre results available the heats of dilution of uni-univalent salts are equally great in very dilute solution. S. K. TWEEDY.

Effect of certain corrections on the heat of combustion of organic compounds. W. SWIENTOSLAWSKI and H. STARCZEWSKA (Bull. Acad. Polonaise, 1928, **A**, 87—97).—See this vol., 845.

Accuracy of Stohmann's thermochemical data. W. SWIENTOSLAWSKI (Rec. trav. chim., 1928, **47**, 896—900).—Polemical. A reply to the criticism by Verkade and Coops (this vol., 712) of the author's correction of Stohmann's data. O. J. WALKER.

Electrical conductivity of hydrochloric, hydrobromic, and hydriodic acids, and the mobility of

the hydrogen ion. M. Hlasko and D. Wazewski (Bull. Acad. Polonaise, 1928, **A**, 181—190).—The equivalent conductivities of hydrochloric, hydrobromic, and hydriodic acids were determined by Kohlrausch's method, with a view to discover whether the strength of the acid increased as the atomic weight of the atom attached to the hydrogen atom increased. This increase in strength has been found in similar series of acids. It was found that hydriodic acid was a stronger acid than hydrobromic, and hydrobromic than hydrochloric, although the differences are small. The values of the equivalent conductivity obtained are greater than those usually accepted. In very concentrated solutions, however, the equivalent conductivity and degree of dissociation of hydrochloric acid are larger than those of hydrobromic acid, and the latter than those of hydriodic acid. This can be explained by the rule of Nernst and Thomson if the difference in dielectric constants of solutions of equivalent concentrations are taken into account. The viscosities and densities of the concentrated acid solutions were also determined. The viscosities diminish in the order hydrochloric, hydrobromic, hydriodic acid. The differences are, however, small. The mobility of the hydrogen ion at 25° was found to be 355·1. A. J. Mee.

Relaxation time of ionic layers in the irreversible passage of electricity in strong electrolytes. H. Falkenhagen and J. W. Williams (Z. physikal. Chem., 1928, **137**, 399—420; cf. this vol., 596, 957).—In amplification of previous work the significance of the ionic relaxation time is considered, and it is shown that it affords explanations of the dispersion effect in conductivity and of the field strength effect of Wien. The possibility thereby arises of eliminating experimentally the effect of the mutual coupling of ions, and of determining the actual degree of ionisation existing in a strong electrolyte solution. F. G. Tryhorn.

Electrical conductivity and diffusion in crystallised compounds. A. Smekal (Z. Elektrochem., 1928, **34**, 472—480).—A general account of work on this subject which has mostly been abstracted previously (cf. A., 1926, 564; 1927, 192). S. K. Tweedy.

Calculation of theoretical [electrode] potentials from thermal data. P. Drossbach (Z. Elektrochem., 1928, **34**, 715—716).—A reply to Devoto's criticism (this vol., 481) of the author's method of calculation of the theoretical potentials of sodium, potassium, and calcium (cf. this vol., 481). The method is shown to have a thermodynamic basis.

In a note added by Devoto, it is pointed out that his own values for the alkali metals agree with those calculated by Latimer by a different method (cf. A., 1927, 941). L. L. Bircumshaw.

Nature of gas-metal electrodes. S. J. French and L. Kahlenberg (Trans. Amer. Electrochem. Soc., Sept. 1928. Advance copy, 28 pp.).—The separate effects of the gases oxygen, hydrogen, and nitrogen on the single potentials of various metals half immersed in a potassium chloride solution have been examined. The gases were introduced under a bell-tube suspended over the metal electrode and escaped from an outlet at the top of this tube. With hydrogen and nitrogen the potentials of the metals became temporarily less negative but then notably more negative than the values in air and approached constant values which are specific for each metal and gas. On closing the gas outlet from the bell-tube and stopping the gas stream so that the metal remains half in the gas-saturated electrolyte and half in the gas atmosphere above, a sharp change of potential, usually towards more negative values, is generally observed, but on further keeping the potential tends to become less negative again, and eventually approaches the air potential. On passing oxygen the potential of a metal becomes somewhat more positive than the value in air, and, on stopping the gas stream when a constant value has been attained, a sharp change in potential is often observed, but the direction of the change depends on the metal employed. Most metals could readily be changed from hydrogen electrodes to oxygen electrodes, whereas the reverse change took a considerable time; with platinum and palladium the converse is true. If the solution was vigorously stirred when a metal base assumed its equilibrium potential in air, the potential immediately changed to a somewhat less negative value, but on passing hydrogen a more negative equilibrium value was attained than in an unstirred solution. Stopping the gas supply while stirring was continued caused no abrupt change of potential, but stopping stirring produced a sharp change of potential. It is suggested that the potentials of metals in the presence of gases arise, not only from absorption of the gas by the metal, but also from the formation of a condensed layer of the gas on the metal surface. Bubbling the gas through the electrolyte or stirring it vigorously prevents the formation of this condensed layer. Experiments with metals coated with collodion, gum mastic, or similar substances showed that the behaviour of a coated electrode in an unstirred solution was the same as that of an uncoated electrode in a stirred solution. Such coatings therefore prevent the formation of the condensed layer. Among other gases, carbon monoxide and methane alter the potentials of platinum and palladium materially, and helium has a very slight effect. H. J. T. Ellingham.

Oxidation–reduction potentials of the pentacyanoferroates. D. Davidson (J. Amer. Chem. Soc., 1928, **50**, 2621—2630).—The oxidation–reduction potentials of some complex iron cyanides were measured against the *N*-calomel electrode. Evidence was obtained for the existence of the compound $2Na_3Fe(CN)_5,H_2O,3Na_2Fe(CN)_5,H_2O$. S. K. Tweedy.

Oxidation–reduction systems of biological significance. I. Reduction potential of cysteine. L. Michaelis and L. B. Flexner (J. Biol. Chem., 1928, **79**, 689—722).—A definite negative potential, which is a logarithmic function of the concentration of cysteine and of hydrogen ions, is slowly established at a platinum electrode in a solution of cysteine in the complete absence of oxygen. Bubbling hydrogen through the solution, after attainment of equilibrium, causes the potential to become more negative. The presence of small amounts of oxygen accelerates the establishment of a definite potential and makes this

potential more positive. Gold-plated platinum electrodes behave similarly, save that the establishment of the final potential is slower, and its magnitude is less affected by hydrogen. With solid gold electrodes equilibrium is attained more rapidly, but the potential reached varies with each electrode. Mercury electrodes give the same final potential as platinum, but equilibrium is reached much more quickly and is less affected by oxygen. In accordance with the results of Dixon and Quastel (J.C.S., 1923, **123**, 2943), cystine is without effect on the cysteine potential; ferrous sulphate and potassium cyanide were also without effect. The explanation of Dixon (A., 1927, 209) of the behaviour of cysteine is rejected on the ground that, on his hypothesis, saturation of a cysteine solution with hydrogen, by suppressing diffusion of the latter from the metal, should lead to establishment of the hydrogen potential, which is, experimentally, not the case; it is considered that no satisfactory explanation of the phenomenon can yet be offered. It is pointed out that the anaerobic potential of cysteine is sufficiently negative to account for the reduction of indicator dyes by tissues under anaerobic conditions.

C. R. HARINGTON.

Pyrochemical Daniell cells. R. LORENZ and F. MICHAEL (Z. physikal. Chem., 1928, **137**, 1—17).—The following *E.M.F.* (millivolts) have been determined: $Sn|SnCl_2|Tl_2Cl_2|Tl$, $403+0{\cdot}45(T-500)$ for $T>427°$, and $370+0{\cdot}18(T-427)$ for $T<427°$; $Pb|PbCl_2|TlCl|Tl$, $365+0{\cdot}39(T-500)$; $Zn|ZnCl_2|SnCl_2|Sn$ $306-0{\cdot}1(T-500)$; $Zn|ZnCl_2|CdCl_2|Cd$, $148-0{\cdot}13(T-575)$: $Zn|ZnCl_2|PbCl_2|Pb$, $276-0{\cdot}095(T-500)$; $Zn|ZnCl_2|TlCl|Tl$, $110+0{\cdot}48(T-500)$; $Mg|MgCl_2|PbCl_2|Pb$, $1078+1{\cdot}075(T-720)$; $Mg|MgCl_2|CdCl_2|Cd$, $974+1{\cdot}07(T-720)$; $Mg|MgCl_2|TlCl|Tl$, $530-0{\cdot}43(T-720)$; $Mg|MgCl_2|ZnCl_2|Zn$, $759-0{\cdot}73\times(T-720)$.

H. F. GILLBE.

Characteristics of alkali cells and their significance for photo-electric methods of measurement. R. FLEISCHER and H. GOLDSCHMIDT (Physikal. Z., 1928, **29**, 691—698).—The discharge method of measuring light intensity is discussed theoretically. Experimental work on alkali cells constructed in different ways shows that the inclination of the current–voltage characteristic to the abscissa depends largely on the frequency of the incident light. The angle, starting from the red end of the spectrum, at first increases with increasing frequency, reaches a maximum, and then decreases. The position of the maximum varies with different types of cells. Without a knowledge of the cell characteristic, comparable and trustworthy data cannot be secured especially when corrections due to insulation defects are necessary. The best results are obtained when the current–voltage curves run parallel to the voltage axis, a condition obtained only with highly evacuated cells.

R. A. MORTON.

Gaseous explosion rates at constant pressure. F. W. STEVENS (Ind. Eng. Chem., 1928, **20**, 1018—1026).—Constant pressure conditions were adopted, as hydrodynamic disturbances are then less profound than at constant volume. Various mixtures of carbon monoxide and methane with oxygen were enclosed in a soap bubble and exploded from the centre, the soap bubble acting as a constant-pressure bomb. The rate of propagation of the zone of explosive reaction, determined by photographing the explosion on a film moving at a known speed, was uniform for each individual mixture and proportional to the product of the concentrations of the reacting gases. The effect on the rate of propagation of adding various percentages of inert gases, viz., helium, argon, nitrogen, and carbon dioxide, was similar for small additions, but for large additions depended on the physical characteristics of the gas added. Mixtures of methane, carbon monoxide, and oxygen followed the same laws as the simpler mixtures of two gases, and it was found possible to predict the velocity of propagation in any such mixture if its composition and the coefficients governing the explosions between (*a*) carbon monoxide and oxygen and (*b*) methane and oxygen are known. The maximum velocities for methane–oxygen and carbon monoxide–oxygen mixtures were 625 cm. per sec. and 100 cm. per sec., respectively, those for the ternary mixtures lying between these limits.

F. J. DENT.

"Normal" propagation of flame in gaseous mixtures. W. PAYMAN (Ind. Eng. Chem., 1928, **20**, 1026—1032).—A correlation of the available data on flame speeds in mixtures of air with hydrogen, carbon monoxide, methane (and other paraffin hydrocarbons), ethylene, and acetylene ignited under different conditions, *e.g.*, in tubes of varying diameter, in closed cylinders, etc. A comparison of the speed–percentage curves reveals relationships which it is hoped to extend as a result of work now in progress, a preliminary description of which is given. The determination of absolute values of flame speed is discussed, and the utility of the law of flame speeds in calculating speed–percentage curves for complex inflammable gases is indicated.

A. WILSON.

Gaseous explosions. VI. Flame and pressure propagation. J. V. HUNN and G. G. BROWN (Ind. Eng. Chem., 1928, **20**, 1032—1040; cf. B., 1925, 487; 1927, 243, 322).—Previous investigators of gaseous explosions have noted the rise in pressure at one point of the explosion chamber. Apparatus is now described whereby pressure records at several points are obtained. A cylindrical steel bomb, provided with a narrow longitudinal plate-glass window, was fitted with six equally-spaced pressure elements of the diaphragm type, placed above the flame window. Flame travel and time pressure charts were obtained photographically, the latter from the deflexion of a pencil of light from a concave mirror, mounted on the pressure elements and focussed on a revolving drum. Carbon disulphide and oxygen were used in the bomb. Examination of these charts showed that during the propagation of the flame through the explosive mixture a pressure wave behind, but travelling at a greater velocity than, the flame front was set up in the burning mixture. The maximum pressure of this wave was greater than that of the flame front or the unignited mixture. This pressure wave, overtaking the flame front, causes the latter to halt and recede. Maximum pressure in mixtures promoting after-burning was developed some time after total inflammation of the charge.

C. B. MARSON.

Influence of steam and of hydrogen on the burning of carbon monoxide. H. B. Dixon (Nature, 1928, **122**, 805).—The effect of hydrogen and of steam on the ignition temperature of carbon monoxide in air depends on the atmospheric pressure and differs in the two cases. Carbon monoxide containing 1% of hydrogen may ignite in dry air either above or below the temperature at which carbon monoxide ignites in air containing 1% of steam. A. A. Eldridge.

Flame speed of hydrogen sulphide. D. S. Chamberlin and D. R. Clarke (Ind. Eng. Chem., 1928, **20**, 1016—1018).—Apparatus and a method for determining the flame speed of hydrogen sulphide in air are described, the gas being burnt in a horizontal glass tube (1 m.×2·5 cm. diam.) and flame records made by the photographic method, using a moving film. The flame speed curve of hydrogen sulphide–air mixtures resembles those of other combustible gases except for deviations due to formation of sulphur and selective oxidation of hydrogen under certain conditions. A mixture containing 10·8% of hydrogen sulphide gave the maximum flame speed of 49·5 cm. per sec. The production of sulphur trioxide by burning hydrogen sulphide in an internal-combustion engine is suggested. C. B. Marson.

Explosibility of anæsthetics. A. P. Horner and C. B. Gardenier (Anæsth. and Analg., 1928, **7**, 69—72).—The following percentage limits of explosibility were determined: ethylene 4—14·5, air 96—85·5; ethylene 5—70, oxygen 95—30; ethylene 5—35, nitrous oxide 95—65; ethylene 5—47, nitrous oxide 85—43 (oxygen 10); ethylene 5—20, nitrogen 85—70 (oxygen 10); ethylene 5—55, oxygen 95—40 (carbon dioxide 5); ether 5—14·5, air 95—85·5; ether 5—65, oxygen 95—35; ether 5—30, nitrous oxide 85—60 (oxygen 10); ether 5—60, oxygen 90—35 (carbon dioxide 5). Chemical Abstracts.

Chemical interactions corresponding with the constant of mass action being a function of the volume and masses of the constituents as well as of the temperature, and catalytic action. R. D. Kleeman (Phil. Mag., 1928, [vii], **6**, 648—659; cf. this vol., 937).—Further applications of the author's earlier thermodynamic deductions are made. It is deduced that a solid substance which condenses a gaseous substance on to its surface has a catalytic effect on the constant of mass action involving the gaseous substance. An extension of the principles to ionisation in solution indicates that when an electrolyte dissociates easily into ions the constant of mass action (dissociation constant) is a function of the volume of the solution as well as of the temperature. This is interpreted as signifying that either the chance of a molecule dissociating into ions depends on its previous encounters with other molecules, or that the chance of two ions of opposite sign combining on collision depends on previous encounters with other ions and molecules, or that both effects occur. Values of the dissociation constant of potassium chloride, in aqueous solution, calculated from the theory are in fair agreement with those usually accepted. A. E. Mitchell.

Oxidation of sulphur vapour at low pressures. N. Semenov and G. Rjabinin (Z. physikal. Chem., 1928, **B**, **1**, 192—204).—As in the case of phosphorus vapour (this vol., 483; cf. Chariton and Walta, A., 1927, 122), sulphur vapour can burn in oxygen only between definite limits of pressure. This pressure interval increases with rise of temperature which fixes the pressure of sulphur vapour. The velocity of ignition, which may be very great, is independent of the oxygen pressure, and probably depends on the velocity of volatilisation of sulphur. It is supposed that, outside these limits of pressure, the number of active centres which, from the conditions of the experiments, may be either ozone molecules or oxygen atoms, does not reach the necessary value for ignition. The values of the limiting partial pressures of oxygen are not altered, as in the case of phosphorus vapour, by the presence of foreign gases. Even in the region of effective pressures spontaneous ignition takes place only when a very small quantity of ozone is introduced by some means. These results are regarded as confirmation of the theory of chain reactions and might probably form a basis for the theoretical treatment of some of the phenomena of homogeneous catalysis, *e.g.*, the part played by traces of moisture. M. S. Burr.

Action of iodine on phosphorous acid and sodium phosphite. A. Berthoud and W. E. Berger (J. Chim. phys., 1928, **25**, 568—580).—Reaction velocity measurements have been made for the action of iodine on (*a*) phosphorous acid and (*b*) sodium phosphite in aqueous solution (cf. Steele, J.C.S., 1908, **93**, 2203). In reaction (*a*) the velocity is proportional to the concentration of iodine and to the concentration of undissociated phosphorous acid, increases slightly with the hydrogen-ion concentration, and is independent of the iodide concentration. In all the experiments phosphorous acid or phosphite and potassium iodide were present in excess from the beginning of the reaction. In reaction (*b*) the velocity is also proportional to the iodine concentration, but increases slightly more rapidly than the phosphite concentration. Increase in concentration of hydrogen ion or of iodide decreases the velocity. The temperature coefficients of the unimolecular velocity coefficients are for (*a*) about 3·8 between 25° and 45° and for (*b*) 4·81—4·01 between 0° and 30°. The different mechanisms of the two reactions are discussed. In neither case is the reaction sensitive to light. O. J. Walker.

Neutral salt action in ionic reactions. II. Concentrated salt solutions. A. von Kiss (Z. physikal. Chem., 1928, **134**, 26—32; cf. A., 1927, 632, 1150).—The reaction between persulphate and iodine ions in the presence of various salts has been investigated. With solutions of magnesium sulphate as solvent, the effect of the concentration of the reacting components on the velocity coefficient disappears almost completely in concentrated salt solutions. The reaction is accelerated markedly and to widely varying extents by the presence of the sulphates of magnesium and sodium, the nitrates of magnesium, potassium, and ammonium, and the chlorides of lithium, sodium, and potassium. The data show

that in concentrated salt solutions neutral salt action follows the law of Grube and Schmid (A., 1926, 474) that the value of log k is linearly proportional to the salt concentration. L. S. THEOBALD.

Alkaline hydrolysis of edestin. I. S. JAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 929—932).—Sodium hydroxide solutions hydrolyse edestin three to four times as rapidly as acids of the same concentration. R. TRUSZKOWSKI.

Velocity coefficients of hydrolysis of nitroacetanilide and of the secondary reaction of hydrolysis of *p*-nitroaniline with elimination of ammonia. A. A. KUROTSCHKIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 1147—1150).—The velocity coefficient for the hydrolysis with 4% sodium hydroxide solution of *p*-nitroacetanilide at 100° is 0·0025, and that of formation of *p*-nitrophenol from *p*-nitroaniline is 0·0005. R. TRUSZKOWSKI.

Velocity of esterification of anisic and gallic acids in ethylene glycol and glycerol. A. KAILAN and A. BRABBÉE (Monatsh., 1928, **50**, 149—180; cf. this vol., 961, 962).—The velocity of esterification of anisic and gallic acids at 25° in anhydrous and moist ethylene glycol and glycerol in presence of hydrogen chloride as catalyst has been measured, and the unimolecular velocity coefficients have been expressed as a function of the concentration of water (w) and of hydrogen chloride (c) in intrapolation formulæ. The velocity coefficients, even at small water concentrations, increase more rapidly than the concentrations of hydrogen chloride. The ratios of the velocity coefficients in ethyl alcohol (k_a) (cf. Kailan, A., 1907, ii, 242), in glycerol (k_g), and in ethylene glycol (k_y), are, for anisic acid at c=0·166 mol./litre, k_a/k_g=1·53, k_y/k_g=0·87, and, at c=1·35, 0·34 and 1·64. The corresponding figures for gallic acid are 1·90, 1·06, 0·41, and 1·25. Thus gallic acid, like most of the acids already investigated, is more rapidly esterified in ethylene glycol than in glycerol, but this is the case with anisic acid only at high concentrations of water. In ethylene glycol and glycerol, as in alcohol, the effect of methylation of a *p*-hydroxyl group is small. In the case of gallic acid, as of all disubstituted benzoic acids so far investigated, the velocity coefficient of the esterification catalysed by hydrogen chloride is less than that calculated on the assumption that the effect of substituents is simply additive. At 183° the uncatalysed esterification of anisic acid in glycerol, similarly to previously investigated acids, follows the equation for a "sesquimolecular" reaction. The coefficients in glycerol when w=1 are about 20% less than in anhydrous glycerol. Increase of w to 2 causes no further decrease. In the uncatalysed esterification at 183° the back-reaction cannot be neglected as in the catalysed reactions at 25°. R. K. CALLOW.

Rate of reaction of liquid and gaseous zinc with carbon monoxide. R. W. MILLAR (J. Amer. Chem. Soc., 1928, **50**, 2707—2709).—The above reaction is extremely slow at 600—700° in the absence of a catalyst, such as iron. It is possibly slower than the reaction $2CO=CO_2+C$ under the same conditions. Zinc reduces carbon dioxide rapidly at these temperatures. S. K. TWEEDY.

Action of aqueous sodium polysulphide solutions on metallic copper. K. FISCHBECK and E. ELBEN (Z. Elektrochem., 1928, **34**, 642—645).—The times taken by sulphide solutions of various concentrations to form cuprous sulphide layers on metallic copper of a standard colour were measured. With solutions containing virtually sodium pentasulphide the velocity of thickening of the layer is proportional to the polysulphide content of the solution and inversely proportional to the thickness of the layer. An analogous result is obtained with sulphur vapour. The method of observation previously used (A., 1926, 692) cannot be applied to the interaction of sulphur and copper. Some observations are made on sulphide solutions; the pentasulphide ion is probably more highly coloured than the tetrasulphide ion. S. K. TWEEDY.

Metallic corrosion in the light of quantitative measurements. II. G. D. BENGOUGH, J. M. STUART, and A. R. LEE (Proc. Roy. Soc., 1928, **A, 121**, 88—121; cf. this vol., 250).—Corrosion–time curves have been obtained for annealed zinc in conductivity water and in dilute potassium chloride solution (N—0·00005N) under 1 atm. of oxygen pressure at 25°. The curves usually have a short branch, concave upwards, extending from zero time to 2—3 days, during which period a negative electrode potential is probably being built up at certain isolated positions on the metal surface. As far as the oxygen type of corrosion is concerned, the initial branches pass into second branches which may be either exponential or linear in form. The exponential type is reached when there is an ample supply of oxygen and the main controlling factor is the rate of withdrawal of chlorine ions from the solution. These conditions are satisfied only in solutions weaker than 0·001N, even in large vessels. The straight-line type is realised in solution stronger than 0·001N in medium-sized vessels, when oxygen is the controlling factor. The final branches of the curves are approximately straight lines, slightly inclined to the horizontal. With conductivity water and potassium chloride solutions of 0·00005N or less, no evolution of hydrogen is observed, but with solutions from 0·00001N and upwards, hydrogen is always evolved, except when very highly purified zinc is used. The cause of the hydrogen evolution from neutral salt solutions is discussed. Gas evolution–time curves have been obtained under various conditions, and their form is explained on the assumption that overvoltage as affected by metallic impurities is the determining factor. The proportion of total corrosion due to hydrogen varies between about 5 and 14% for solutions between 0·00001N and 0·1N. Curves for total corrosion are not exponential in form, probably because part of the corrosion is being carried on by some secondary process independent of chlorine ions, especially as regards hydrogen evolution and during the later period of the experiments. It is suggested that the relative maintenance of hydrogen-evolution type of corrosion may be due to the accumulation of potassium hydroxide towards the end of the experiments. The total amount of corrosion obtained for standard specimens in water of about 0·055 mho

conductivity is only about 1 mg. of zinc after 50 days. This is probably partly due to traces of non-metallic impurity (*e.g.*, dust particles). The total amount of corrosion that has occurred when the corrosion–time curves of potassium chloride have become nearly horizontal is independent of the oxygen supply, but dependent on the concentration of the solution, and the rate of withdrawal of chlorine ions from current-carrying capacity. The effect of precipitated corrosion products on the rate and amount of corrosion is found to be very small, even after 100 days from the start of the experiment. Extreme purification of the zinc has only a slight effect on the total corrosion in 0·0001*N*-potassium chloride, the effect being due to the suppression of the gas-evolution type of corrosion. In potassium chloride solution, the total corrosion is greatly affected by the nature of the metallic surface. Highly-worked surfaces give more variable, and usually lower, results than annealed surfaces. Annealing the specimens for a week at 250—260° gives fairly concordant results. The most satisfactory methods for determining relative corrodibility are discussed. L. L. Bircumshaw.

Double carbonate of copper and sodium. F. de Carli and P. Agostini (Atti R. Accad. Lincei, 1928, [vi], 7, 921—925).—The rate of dehydration of the double carbonate of sodium and copper, $CuCO_3,Na_2CO_3,3H_2O$, has been examined at 80° and 120°. At the lower temperature 1 mol. of water of crystallisation is lost and at the higher temperature the anhydrous salt is formed. The decomposition of the anhydrous salt is reversible according to the reaction $Na_2CO_3,CuCO_3 \rightleftharpoons Na_2CO_3+CuO+CO_2$; from the variation of the partial pressure with temperature the heat of formation of copper carbonate per mol. is found to be 138,300 g.-cal. R. W. Lunt.

Velocity of acid hydrolysis of cotton cellulose by hydrochloric acid, alone, and in the presence of alkali chloride. E. Hunter (J.C.S., 1928, 2643—2648).—An attempt has been made to determine whether the principles of activity can be extended to the consideration of the catalysis by hydrogen ions of a heterogeneous reaction such as the hydrolysis of cotton cellulose in solutions of hydrochloric acid both alone and in the presence of potassium, sodium, or lithium chlorides. With dilute acid solutions the ultimate product of hydrolysis is hydrocellulose, and under such conditions there exists a linear relationship between the rate of hydrolysis and the hydrogen-ion activity of the solution. For strongly acid solutions the results of the velocity measurements are untrustworthy owing to the tendency of the hydrocellulose to undergo further hydrolysis.

The linear relationship between hydrogen-ion activity and rate of hydrolysis does not hold for acid–salt solutions. Over the range of concentrations examined, of two solutions having the same hydrogen-ion activity, that with neutral salt present gives a higher reaction velocity than that with acid alone. It is suggested that these results may be explained by assuming that the added salt lowers the activity coefficient of the "critical complex" [(cellulose) $H^{\cdot}$, H_2O]. F. J. Wilkins.

Photographic study of detonation in solid explosives. I. Measurement of rate of detonation. E. Jones.—See B., 1928, 875.

Sixth report of committee on contact catalysis. R. E. Burk (J. Physical Chem., 1928, 32, 1601—1645).

Thermodynamic theory of catalysis. R. Dubrisay (J. Chim. phys., 1928, 25, 581—586).—The various definitions of the term "catalyst" are reviewed. A catalyst is defined theoretically as a substance which modifies the velocity of a chemical reaction whilst obeying the following two conditions: (*a*) it can be introduced into or removed from the system without any accompanying energy change, and (*b*) it is itself unchanged at the end of the reaction. These conditions are not obeyed ideally, but are fulfilled sufficiently exactly by many catalysts, since the amount of catalyst is small compared with the amounts of the reactants and of the products. The thermodynamic treatment of catalysis starting from this definition is not opposed to the kinetic explanation of catalytic phenomena by means of the Arrhenius theory, which makes use of activated molecules. O. J. Walker.

Problems in homogeneous catalysis. T. M. Lowry (Trans. Faraday Soc., 1928, 24, 545—551).—A paper introductory to a general discussion on homogeneous catalysis. F. G. Tryhorn.

Homogeneous catalysis. C. N. Hinshelwood (Trans. Faraday Soc., 1928, 24, 552—559).—A review of studies of the mechanisms of homogeneous reactions and of the influence on them of traces of foreign substances and of solvents and inert gases, and of the theories of the energy transfer phenomena characteristic of such reactions. F. G. Tryhorn.

Influence of nitrogen peroxide on the union of hydrogen and oxygen. A problem of "trace catalysis." C. H. Gibson and C. N. Hinshelwood (Trans. Faraday Soc., 1928, 24, 559—562).—The union of hydrogen and oxygen is accelerated and the explosion temperature lowered by 200° by the presence of traces of nitrogen peroxide. There occurs, however, no transition region as the percentage of nitrogen peroxide in the mixture is increased. The catalysed reaction occurs abruptly when a certain lower limit in the amount of nitrogen peroxide is reached, and ceases as abruptly when the peroxide is present in amounts greater than a fixed upper limit. At 371° these limits are 0·22 mm. and 0·83 mm., respectively, for a mixture of hydrogen and oxygen in stoicheiometric proportions and of a total pressure of 600 mm. The lower limit of effectiveness of the nitrogen peroxide was practically constant between 371° and 421°, but the upper limit increased from 0·83 to $>$3·3 mm. over the same temperature range. It is suggested that the explosion of the hydrogen and oxygen is initiated by ordinary ignition by the heat liberated in some independent reaction of the nitrogen peroxide. F. G. Tryhorn.

Catalytic phenomena in the tautomerism of certain α-diketones. H. Moureu (Trans. Faraday Soc., 1928, 24, 562—565).—A study has been made of the catalytic interconversion of the tautomeric forms of benzylmethylglyoxal and phenylbenzylglyoxal. If

the ketonic form (*B*) of lower m. p. is treated in the super-cooled state with a trace of an alkaline catalyst (benzylamine, diethylaniline, quinoline, pyridine, diethylamine, piperidine, or potassium hydroxide) there follows a change, more or less rapid (from a few seconds up to three days in duration) according to the nature and concentration of the catalysts, into the enolic (*A*) form of higher m. p. If the temperature is below that at which equilibrium exists between the two forms in a saturated solution of isomeride *A* in isomeride *B*, isomeride *A* crystallises out and the conversion into this form is complete. The change is also complete if the reaction occurs at the b. p. of the form *B* owing to the removal of this form by reason of its greater volatility. At intermediate temperatures an equilibrium mixture of *A* and *B* is formed of which the composition is dependent on temperature. Investigation of the effect of temperature on the composition of the equilibrium mixture showed that rise of temperature favoured the formation of the ketonic form, and that the conversion of the ketonic form into the enolic is exothermal. Evidence is adduced indicating that an intermediate compound is formed with the catalyst during the conversion. Glass acts as a catalyst for this change, but the *B* isomeride may be preserved unchanged in quartz vessels. F. G. TRYHORN.

Ionisation in chemical change. N. R. DHAR (Trans. Faraday Soc., 1928, **24**, 565—567).—A summary of the types of reaction of which the mechanism can be explained by assuming the generation of ions in exothermal chemical changes, followed by the adsorption by the reactants of the ions and electrons thus generated. F. G. TRYHORN.

Negative catalysis in slow and induced oxidations. N. R. DHAR (Trans. Faraday Soc., 1928, **24**, 567—570).—A discussion of negative catalytic effects in slow and induced reactions from the point of view of the author's theory of the generation of ions in exothermal chemical changes, in which it is shown that the conception of the occurrence of chain reactions in thermal oxidations is unnecessary.

F. G. TRYHORN.

Inhibition in chemical reactions. E. K. RIDEAL (Trans. Faraday Soc., 1928, **24**, 571—574).—A summary of the theories suggested to explain inhibition effects in chemical reactions. F. G. TRYHORN.

Phosphorescence and autocatalysis during slow combustion. F. GILL, E. W. J. MARDLES, and H. C. TETT (Trans. Faraday Soc., 1928, **24**, 574—587).—Measurements have been made of the temperatures at which fog, phosphorescence, and slow combustion occur when air charged with the vapours of carbon disulphide, ethyl ether, acetaldehyde, amylene, or *n*-hexane is passed through a heated glass tube. The action of a number of inhibitory substances on the phosphorescence of these vapours was studied. With an air-carbon disulphide vapour mixture containing 19% by weight of carbon disulphide fog occurred at 100°, phosphorescence at 150°, and rapid combustion at 195°. Carbon disulphide–air mixtures are anomalous inasmuch as the richer mixtures appear to be the more stable towards oxidation. The phosphorescence of these mixtures was inhibited by benzene, bromine, amyl nitrite, ethyl nitrate, iodine, pentane, acetaldehyde, ethyl acetate, ethylene dibromide, pyridine, acetone, chloroform, methyl alcohol, ethyl alcohol, lead tetraethyl, iron carbonyl, and by the gases acetylene, ethylene, hydrogen sulphide, and coal gas. The initial temperature of slow combustion was reduced in the presence of a number of metals. Carbon monoxide was alone found to promote phosphorescence. It is suggested that an unstable peroxide CS_2O_2 is formed and acts as a catalyst of combustion. This catalyst is reduced by inhibiting agents and is destroyed also by an excess of carbon disulphide, $CS_2+CS_2O_2=CS_2+SO_2+CS$. Results of a similar type were found for the mixtures of air with the other vapours used. The results suggest that peroxidation, occurring at the interfaces of nuclear particles, is directly responsible for phosphorescence, autocatalysis, and detonation in the internal-combustion engine. Inhibitory agents, by reacting with the primarily formed peroxides, remove from them their active oxygen and energy, thus destroying the positive catalyst of combustion and the cause of phosphorescence, and detonation. Evidence is adduced that the glow of hexane is due, not to the intermediate formation of aldehydes, but specifically to the formation of primary peroxides of hexane. In experiments carried out by inserting various metals in the combustion tube the glow seemed usually to be confined to the metal surface, which remained unaltered during the process, and the intermediate combustion products were diminished in amount and self-ignition was delayed. This inhibitory action of metals is in accord with the view that organometallic compounds, such as lead tetraethyl, owe their efficacy to the colloidal metal formed by thermal decomposition at the surface of nuclear particles.

F. G. TRYHORN.

Theory of chain reactions. J. A. CHRISTIANSEN (Trans. Faraday Soc., 1928, **24**, 596—601).—A review.

Mechanism of inhibition in autoxidation reactions. H. L. J. BACKSTROM (Trans. Faraday Soc., 1928, **24**, 601—605).—To investigate the relation between inhibition and induced reactions the velocity of oxidation of sodium sulphite solutions has been measured in the presence of *iso*butyl, *sec.*-butyl, and benzyl alcohols. The results are in agreement with the chain theory of the above reaction (A., 1927, 737, 1151), the inhibitory action of the alcohols arising from the breaking of the reaction chains through the preferential oxidation of the alcohol molecules to acetone, methyl ethyl ketone, and benzaldehyde, respectively. When two alcohols are present in the solution at the same time, the theory requires that they should be oxidised in proportion to their concentrations and relative inhibitory powers, but that the total number of molecules oxidised in a given time should remain constant. This was verified for an equimolecular mixture of benzyl and *iso*propyl alcohols. Photochemical experiments with *iso*propyl alcohol as an inhibitor showed that in a solution of a given composition the chain-length is the same whether the chains are started thermally or photochemically. The chain-length (58 mols.) deduced from data for the thermal reaction with benzyl alcohol

as an inhibitor agrees well with that obtained (64 mols.) from previous quantum efficiency measurements. Values obtained from the copper-catalysed sulphite oxidation reaction show that copper salts accelerate the total reaction without changing the ratio of sulphite oxidised to alcohol oxidised, and therefore without altering the chain-length.

F. G. TRYHORN.

Inhibition of chain reactions by bromine. M. PÓLANYI (Trans. Faraday Soc., 1928, **24**, 606—611).—An account of investigations by the author and co-workers (cf. this vol., 373). F. G. TRYHORN.

Theory of acid and basic catalysis. J. N. BRONSTED (Trans. Faraday Soc., 1928, **24**, 630—640).—A summary.

Catalytic effects of acids and bases and the influence of inert salts. H. M. DAWSON (Trans. Faraday Soc., 1928, **24**, 640—651).—A derivation and summary of the dual theory of catalysis.

F. G. TRYHORN.

Compounds between catalysts and substrates. H. VON EULER (Trans. Faraday Soc., 1928, **24**, 651—662).—A review of the author's theory so far as it applies to catalytic hydrolysis by acids and bases.

F. G. TRYHORN.

Salt action in homogeneous catalysis. H. S. HARNED and G. ÅKERLOF (Trans. Faraday Soc., 1928, **24**, 666—678).—A summary.

Kinetics of acid and basic catalysis. A. SKRABAL (Trans. Faraday Soc., 1928, **24**, 687—696).—A theoretical discussion of earlier work in which an explanation of acid and basic catalysis has been sought in the theories which have been advanced from the point of view of chemical kinetics. In these theories two types of intermediate compounds are postulated, the Arrhenius type, which is in equilibrium with the initial materials, and the van 't Hoff type, which is independent of this equilibrium and is less stable than the former. Lowry's electrolytic theory of catalysis accords best with experimental facts, and the intermediate compounds postulated by this theory are of the van 't Hoff type. F. G. TRYHORN.

Kinetics of the reaction between iodine and potassium nitrite in light and darkness. A. BERTHOUD and W. E. BERGER (J. Chim. phys., 1928, **25**, 542—561).—See this vol., 484.

Oxidation of potassium nitrite by iodine induced by sodium thiosulphate. A. BERTHOUD and W. E. BERGER (J. Chim. phys., 1928, **25**, 562—567).—See this vol., 486.

Definition of "area" in contact catalysis. F. P. BOWDEN (Nature, 1928, **122**, 647—648).—In studying the catalytic properties of a surface for a particular reaction the significant area is not the arbitrarily defined maximum area (Constable, this vol., 1101), but the area of the catalyst which can be reached by the reactants concerned. In a method for the measurement of the areas of metallic surfaces by the electrolytic deposition of hydrogen from solution, the quantity measured is the amount of hydrogen added to the surface in order to cause a given change in the electrode potential (Bowden and Rideal, this vol., 1088); it does not follow that the hydrogen is sparsely distributed over the plate. The catalytic activity of a surface probably depends mainly on the first few atomic layers. The applicability of the electrolytic and interference methods in studying the "area" and properties of the surface atoms is considered; the former method is preferred.

A. A. ELDRIDGE.

Catalytic oxidation of carbon monoxide. IV. Pore volume of the catalysts manganese dioxide, copper oxide, and mixtures of these oxides. H. D. DRAPER (J. Amer. Chem. Soc., 1928, **50**, 2637—2653; cf. Bray and Doss, A., 1926, 917).—Determinations of the densities of many samples of the porous, granular oxide catalysts previously used (copper oxide, manganese oxide, MnO_x, where $x<2$, and mixtures of these) indicate that the granules contain few very small micro-capillaries, or else they offer small resistance to filling by the immersion liquid. The pure oxides are less porous than mixtures containing them, which is explained by colloidal phenomena; the oxides do not combine on mixing. A theoretical discussion of absorption curves (liquid–solid) is given; an expression is deduced relating the volume of sorbed liquid with the curvature of the liquid surface corresponding with the equilibrium pressure of the liquid vapour, the number, and the radii and average length of the capillaries in the solid. This criterion indicates that the poorest of the above catalysts have the finest grained structure and the best catalysts have high porosity with a few fine pores and many large cavities. No explanation can be given for the effect on the catalytic activity of mixing the oxides, beyond the consequent difference in accessibility of the surfaces of the oxides. In spite of the enormous difference in pore size, practically all the catalysts have approximately equal surface exposure per unit pore volume, an anomaly for which no explanation is forthcoming. S. K. TWEEDY.

Poisoning effects of certain substances on the iron catalyst in the decomposition of carbon monoxide. T. WATANABE (Bull. Inst. Phys. Chem. Res. Japan, 1928, **7**, 1078—1087).—Permanent poisoning of the catalyst occurred after the addition of thiophen or hydrogen sulphide. Poisoning caused by naphthalene persisted for only a short time after the addition of the latter had ceased. Nitrogen, methane, and benzene had no effect, whilst acetylene was partly decomposed into carbon and hydrogen; water vapour formed carbon dioxide, hydrogen, and methane, and hydrogen was partly converted into methane.

F. S. HAWKINS.

Fission of carbon monoxide by nickel. N. A. BAHR and T. BAHR (Ber., 1928, **61**, [*B*], 2177—2183).—Metallic nickel and its oxide cannot continuously catalyse the reaction $2CO=C+CO_2+38\cdot9$ kg.-cal. Fission of carbon monoxide is due to the carbide Ni_3C at temperatures from about 270°. Catalysis by metallic nickel is only apparent; below 270° decomposition of carbon monoxide is effected with decreasing rapidity only until the metal is completely converted into the carbide. Above 270° to about 380—420° the action is catalytic, but the free metal is not present. The amount of carbon corresponding with the composition Ni_3C is invariably united with the metal, whereas

any excess of carbon is uncombined. Above 380—420° free metal is again present in the catalyst, since the carbide decomposes at this temperature. Combined carbon is readily converted by molecular hydrogen into methane at 180—380° (preferably 250—270°), whereas free carbon remains unchanged under these conditions. The carbide Ni_3C is thermostable below about 380—420°. Since it accelerates the decomposition of carbon monoxide above 270°, a higher carbide, Ni_3C_x, must be formed as a labile, intermediate product which immediately decomposes into Ni_3C and free carbon; the higher carbide probably has the composition Ni_3C_2. The carbide Ni_3C, formed from carbon and molten nickel, is considered identical with that derived from the metal and carbon monoxide at 270°. H. WREN.

Influence of acids and bases on the inhibitory effect of gelatin on the catalytic decomposition of hydrogen peroxide by colloidal platinum. H. V. TARTAR and N. K. SCHAFFER (J. Amer. Chem. Soc., 1928, 50, 2604—2610).—Acetic, sulphuric, and phosphoric acids, and potassium, sodium, and barium hydroxides were used over a very wide p_H range. In the case of the acids, for which the reproducibility of the results was only fair, the inhibition depends both on the nature of the acid and on the hydrogen-ion concentration, whereas in alkaline solutions the hydroxyl-ion concentration is the chief factor. The catalysis itself seems to be influenced by the acids and alkalis, and at any p_H value the inhibition depends on the concentration of the hydrogen peroxide and of the platinum. S. K. TWEEDY.

Catalytic decomposition of gaseous acetaldehyde at surface of various metals. P. C. ALLEN and C. N. HINSHELWOOD (Proc. Roy. Soc., 1928, A, 121, 141—155).—The decomposition of acetaldehyde has been shown to be bimolecular as a homogeneous gas reaction, and the present work is a study of the catalytic decomposition of the vapour at the surface of heated wires of platinum, platinum-rhodium alloy, gold, and tungsten. The apparatus used has been previously described (Hinshelwood and Prichard, J.C.S., 1925, 127, 327). The decomposition products are primarily methane and carbon monoxide, but with prolonged heating the former is to some extent decomposed. The reaction has been studied between 685° and 975° and at a number of initial pressures. The times required for 25, 50, and 75% change (denoted by t_{25}, t_{50}, and t_{75}, respectively) are constant above 150 mm., but below this pressure they increase rapidly as the pressure falls. The products of the reaction exert a retarding influence. For small pressures of carbon monoxide, the first additions have less effect than subsequent amounts, and at a pressure greater than 100 mm. this gas has no further effect, but the reaction rate is not reduced to zero. The actual reaction rate is proportional to the surface area of the wire and inversely proportional to the volume of the vessel. The reduced rates (in mm. per min.) at 1000° and 300 mm. initial pressure for platinum, platinum-rhodium, tungsten, and gold (two samples) are 9·6, 5·5, 5·0, 10·5, and 9·6, respectively. From a consideration of the variation of t_{25} and t_{50} with the initial pressure it is concluded that the reaction is bimolecular, but it is necessary to show why the apparent order approaches unity at high pressures. A number of possibilities are discussed, and it is suggested that the mechanism involves the reaction of a molecule in the gas phase with an activated molecule adsorbed on the wire. In support of this, it is found that the number of molecules striking the wire is always proportional to the pressure, whilst the number on the wire is at low pressures proportional to the pressure and at high pressures constant. A remarkable similarity is found between the different metals in respect of the relation between the reaction rate and pressure, the heat of activation, and the absolute rate of reaction. Examination of the molecular statistics of the reaction indicates that collisions between molecules from the gas and adsorbed molecules are inelastic, with a duration of 10^{-6}—10^{-8} sec. L. L. BIRCUMSHAW.

Ceria-thoria catalysts. A. B. GOGGS (J.C.S., 1928, 2667—2669; cf. Swan, A., 1924, ii, 400).—The influence of mixed ceria-thoria catalysts on the combustion of carbon monoxide has been studied. The rate of formation of carbon dioxide attains a maximum with mixtures containing 0·96% of ceria. The catalyst which Swan had found to be the most efficient for the oxidation of hydrogen is, therefore, also the most efficient for the oxidation of carbon monoxide.

F. J. WILKINS.

High-voltage arcing and alternating-current electrolysis. J. W. SHIPLEY and C. F. GOODEVE (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 87—102; cf. B., 1927, 633).—The rate of decomposition of boiling alkaline solutions by voltages of 110—2100 volts, applied to steel wire electrodes, depends chiefly on the rate of consumption of electrical energy and is independent of Faraday's law and the law of alternating-current electrolysis. It increases with the diameter of the electrodes. Arcing does not occur with low currents, and at high voltages commences at a definite current varying inversely as the potential between the electrodes. At constant voltage arcing commences at a current density which falls with increase in the electrode diameter. The principal factor is the potential gradient near the electrodes. Up to 220 volts, arcing which occurs at atmospheric pressure can be suppressed by raising the pressure. The high temperature reached in the arc is mainly responsible for the decomposition. C. W. GIBBY.

Preparation of potassium ferricyanide without the use of a diaphragm ; effect of superimposed alternating current. H. PAWECK and P. HIRSCH (Z. Elektrochem., 1928, 34, 684—696).—Attempts were made to prevent cathodic reduction in the electrolytic preparation of potassium ferricyanide by reducing the current density and using a cathodic diaphragm. A large number of substances were employed as diaphragms, but in no case was any permanent effect observed. The results indicate that ammonium tungstate could be used successfully in other oxidation processes. Cathodic reduction may be largely prevented by means of a diaphragm formed mechanically on the cathode—*e.g.*, a layer of cement or gypsum—and similar results are obtained by the use of a superimposed alternating current. The

influence on the current efficiency of the cathode material, the cathodic current density, the ratio of direct to alternating current, and the frequency has been studied in detail, and the results are tabulated. Solid potassium ferricyanide may be obtained by the electrolysis, without a diaphragm, of saturated ferricyanide solution saturated with potassium ferrocyanide, using direct current and a high current density. The use of a superimposed alternating current or of a cathode envelope (*e.g.*, a tile casing) results in a higher yield. L. L. BIRCUMSHAW.

Electrolytic oxidation of formaldehyde in alkaline solution. E. MÜLLER and S. TAKEGAMI (Z. Elektrochem., 1928, **34**, 704—713).—A study has been made of the relations between anode potential and current density in the electrolysis of a 24% formaldehyde solution mixed with an equal volume of 2*N*- or 4*N*-sodium hydroxide solution, using as anode material smooth or spongy platinum, palladium, rhodium, gold, and silver. The current–potential curves are all similar in form. They exhibit first a current rise at a low potential, a few tenths of a volt above the hydrogen potential, terminating at a definite current strength. The polarising potential being kept constant, the anode rises more or less rapidly to a higher potential with simultaneous decrease of the current strength, and on increasing the polarising potential, a second current rise occurs in the high potential region. Quantitatively, three differences are shown: (1) the current density at which the jump takes place is different for different smooth metals; (2) the first rise is steeper and leads to higher current densities for spongy electrodes than for smooth; (3) on the first rise a marked evolution of hydrogen occurs with gold and silver, a slight evolution with rhodium and palladium, and no evolution with platinum. Experiment showed that, in the high potential region, the products of electrolysis were both formic and carbonic acids, but that in the low potential region, no carbon dioxide was formed with any of the metal anodes. The following reactions evidently occur in the low potential region: (i) $H{\cdot}CHO+H_2O+2$ faradays$=H{\cdot}CO_2H+2H^{\cdot}$; and (ii) $2H{\cdot}CHO+2H_2O+2$ faradays$=H_2+2H{\cdot}CO_2H+2H^{\cdot}$. With gold and silver anodes, mainly (ii) takes place, with palladium and rhodium mainly (i), and with platinum (i) only. Process (i) is favoured by a rise in the current density, and at constant potential the ratio (ii)/(i) decreases with time. The significance of these results is discussed, with special consideration of the catalytic action of finely-divided metals on the decomposition of formaldehyde. A theory is developed to explain the observed phenomena, based on the supposed adsorption of glycol ions on the electrode surface (cf. Müller and Hindemith, this vol., 377). L. L. BIRCUMSHAW.

Co-deposition of copper and graphite. C. G. FINK and J. D. PRINCE.—See B., 1928, 822.

Electro-deposition of aluminium. D. B. KEYES, S. SWANN, jun., W. KLABUNDE, and S. T. SCHICKTANZ.—See B., 1928, 862.

Porosity of electro-deposited chromium. E. M. BAKER and A. M. RENTE.—See B., 1928, 819.

Steel anodes for chromium plating. E. M. BAKER and E. E. PETTIBONE.—See B., 1928, 823.

Causes and prevention of pitting in electrodeposited nickel. D. J. MACNAUGHTAN and A. W. HOTHERSALL.—See B., 1928, 823.

Velocity of photochemical reactions. J. PERRIN and (MLLE.) CHOUCROUN (Compt. rend., 1928, **187**, 697—698).—The authors' method (A., 1926, 884, 885) is used to show that the law of mass action holds only for those photochemical reactions in which feebly or non-fluorescent reagents are involved (*e.g.*, the atmospheric oxidation of indigo-carmine in ammonium oxalate by violet light, and the oxidation of helianthin in oxalic acid and ammonium oxalate). This is explained by the dependence on the concentration of the mean life in the activated state of a molecule of a fluorescent substance. J. GRANT.

Sensitised photolysis. E. BAUR (Z. Elektrochem., 1928, **34**, 595—598).—A summary of the results previously obtained by the author and his co-workers in this field. S. K. TWEEDY.

Photochemical ozonisation and its relation to the polymerisation of oxygen. O. R. WULF (J. Amer. Chem. Soc., 1928, **50**, 2596—2604; cf. this vol., 720).—Evidence is given that O_4 is the absorbing molecule in the photochemical ozonisation of oxygen at 2530 Å. and 2070 Å. From Warburg's absorption data (A., 1916, ii, 526), and assuming the absorption to be proportional to the number of O_4 molecules present, the equilibrium constant $p_{O_2}{}^2/p_{O_4}$ is calculated to be 1·2 g./c.c., in tolerable agreement with Lewis' computations from magnetic data (A., 1924, ii, 811). The molal absorption coefficient of O_4 for the above wave-length band is estimated to be $1{\cdot}1\times10^4$ cm.²/mol. S. K. TWEEDY.

Reaction between bromine and hydrogen in light of different wave-lengths. W. JOST (Z. physikal. Chem., 1928, **134**, 92—96).—Preliminary experiments on the reaction between hydrogen and bromine illuminated by light of wave-length corresponding with the region of the bromine spectrum showing absorption bands and with that corresponding with the continuous spectrum show that the velocity coefficient is of the same order of magnitude in the two cases. L. S. THEOBALD.

Light reaction between ferric chloride and oxalic acid. (FRL.) G. KORNFELD [with E. MENCKE] (Z. Elektrochem., 1928, **34**, 598—601).—The velocity is proportional to the square root of the intensity of the light in the blue, green, and violet and, within limits, is independent of the concentration of the reagents. The velocity varies with time and converges rapidly towards zero. Addition of ferrous sulphate retards the reaction at a rate proportional to the concentration of the added salt. The equation $x=k_1(1-e^{-k_2t})\sqrt{I}/k_2$ holds, where x is the concentration of ferrous ion formed and I the intensity of the light. Mechanisms are suggested for the reaction. S. K. TWEEDY.

Highly attenuated flames. I. H. BEUTLER and M. PÓLANYI (Z. physikal. Chem., 1928, **B**, **1**, 3—20).—See this vol., 491.

Highly attenuated flames. II. Nozzle flames. Increase of light emission with increasing partial pressure of sodium vapour. S. von Bogdandy and M. Pólanyi (Z. physikal. Chem., 1928, B, 1, 21—29; cf. this vol., 491).—If the apparatus previously employed is altered in such a way that the halogen or halide vapour streams through a nozzle into the tube through which an excess of sodium vapour is passing, the amount of light emitted due to chemiluminescence is found to increase with increasing pressure of sodium vapour through the range $0{\cdot}5\times10^{-3}$ to 1×10^{-2} mm. For chlorine it increases from 0·5 to 30% of the theoretical, for bromine from 2 to 18%, and for mercuric chloride from 1 to 7%. The mercuric chloride curve showing increase of light emission with partial pressure of sodium appears to reach a maximum at a pressure of about 3×10^{-3} mm., but no such maximum is obtained with the halogens, although, at a certain point, the curve becomes less steep. The following reactions are supposed to take place: (1) In the alkali metal vapour and halogen the primary reaction is $Na+Cl_2=NaCl+Cl$, followed by the reaction $Na+Cl=NaCl$, taking place on the walls of the tube, and the reaction $Na_2+Cl=NaCl+Na$ which produces light, in the gaseous phase. (2) In the alkali metal vapour and volatile halogen salt, *e.g.*, mercuric chloride, the primary reaction is $Na+HgCl_2=NaCl+HgCl$ and the secondary one $Na+HgCl=NaCl+Hg$. On the assumption that light is excited when a sodium atom strikes a freshly-formed sodium chloride molecule rich in energy, the light thus emitted should increase proportionately to the pressure of sodium vapour, as long as the mean free path between sodium chloride molecules and sodium atoms is greater than the dimensions of the tube. When the reverse conditions are reached the light emission approaches a limiting value as in the case of mercuric chloride. The continued rise at a slower rate in the case of the halogen curve is due to the increase in the molecular concentration, Na_2, of the sodium vapour with increasing pressure, since the light-exciting reaction in the gas, $Na_2+Cl=NaCl+Na$, is increasingly favoured in contrast to the reaction taking place on the walls of the tube without light emission. M. S. Burr.

Highly attenuated flames. III. Sodium–chlorine flame. Evidence for and analysis of the reaction and luminosity mechanism. Both reaction types. Survey of the whole work. M. Pólányi and G. Schay. **IV. Sodium–iodine flame. V. Sodium–mercuric chloride flame.** H. Ootuka and G. Schay (Z. physikal. Chem., 1928, B, 1, 30—61, 62—67, 68—73; cf. preceding abstract).—III. The suggested difference in mechanism between the two types of reaction, sodium with halogen and sodium with halide (*loc. cit.*), is confirmed by certain experimental observations. In type 1 the curve of distribution of light emission along the tube, when the flame burns at the nozzle, is much broader than the precipitation curve of solid halide; superheating of the reaction zone reduces the light to a small fraction; the increase of light emission is relatively more rapid than the increase in partial pressure of sodium vapour; and in presence of hydrogen hydrogen chloride is formed. In type 2, on the other hand, the light curve for the nozzle approximates more closely to the precipitation curve; superheating of the reaction zone has no effect; increase of light emission is relatively slower than increase in partial pressure of sodium vapour; and in presence of hydrogen no hydrogen chloride is formed. The presence of nitrogen has an extinguishing action on the excited light in the sodium–chlorine flame. The reduction of light by superheating follows an exponential law. The effect is due to the dissociation of the sodium molecule. From the data the heat of dissociation is calculated to be 18 ± 2 kg.-cal., and the dissociation constant at 600° Abs. approximately 3×10^3 at a pressure of 1 bar. The "true light emission," which gives the probability c that a sodium chloride molecule formed by the elementary process $Na_2+Cl=NaCl+Na$ emits light by collision with a sodium atom, is 0·7—1, which indicates that a considerable portion of the chemical energy is transformed into vibrational energy. The velocity coefficient for the reaction $Na_2+Cl=NaCl+Na$, when $c=0{\cdot}7$, is calculated to be 4×10^{-7}.

IV. When iodine is substituted for chlorine similar results are obtained. The "true light emission" of the elementary process $Na_2+I=NaI+Na$ in sodium vapour is 0·3—0·5. The velocity coefficient of this reaction is 5×10^{-8}. The heat of dissociation of the sodium molecule, calculated from the suppression of light by superheating, is of the same order as calculated from the data of the sodium–chlorine flame.

V. For the sodium–mercuric chloride flame without nozzle the velocity coefficient of the primary reaction $Na+HgCl_2=NaCl+HgCl$ is approximately $1{\cdot}5\times10^{-6}$ and for the secondary reaction $Na+HgCl=NaCl+Hg$, deduced from the nozzle flame, it is 1×10^{-7}. In the flame without nozzle the position of the light maximum relatively to the precipitate maximum can be calculated from the dependence of light emission on the pressure of sodium vapour. For mercuric chloride c is 0·11. M. S. Burr.

Photolysis of medium-free silver bromide. Determination of silver. H. Kieser (Z. wiss. Phot., 1928, 26, 1—45).—Darkened silver halide consists of colloidal silver in a medium of silver halide. To determine the elementary silver, the photographic layer is washed into a flask and shaken with alkaline thiosulphate for 20 min. in the dark, when the halide dissolves. The precipitate is then collected and ignited wet. This method, however, may be in error up to 50% unless the proper conditions, which are here investigated, are observed.

The silver bromide used was prepared by slowly adding 13·25 c.c. (*i.e.*, a very slight excess) of $2N$-silver nitrate solution (cold) to 400 c.c. of $0{\cdot}0667N$-potassium bromide solution at 83°; 10 c.c. of water were added, the liquid was stirred until the supernatant layer cleared, and the whole heated at the b. p. for 15 min. with constant stirring. Finally it was filtered, the precipitate washed with 400 c.c. of cold water, and spread out into a thin layer. By this method the presence of excess of silver or bromine ions in the bromide was avoided. The analysis of the darkened bromide must be carried out immediately after exposure; otherwise the silver partly redissolves as silver halide under the

joint action of the halogen ions and the atmospheric oxygen present, this recombination being accelerated by the presence of potassium bromide. A positive error occurs owing to the formation of silver sulphide and a negative one owing to incomplete coagulation of the colloidal silver in the thiosulphate solution; the sulphide error is the larger, however, and by subtracting 10% from the weight of the total precipitate after ignition the correct silver value is obtained. The quantity of silver sulphide in the precipitate (before ignition) was determined by washing with dilute nitric acid (33 vol.-%) for 1 hr., when the silver was selectively dissolved. The proportion of sulphide decreases as the amount of photolytically-formed silver increases; it increases with the time of fixing and also with the amount of thiosulphate solution, which must therefore be kept at the minimum which will effect dissolution. For very small precipitates the method fails, as the proportion of sulphide is so large. The entrance of carbon dioxide (*e.g.*, during shaking) into the thiosulphate solution accelerates the formation of sulphide only very slowly. The peptisation of the silver is increased by gelatin and decreased by electrolytes, *e.g.*, ammonium acetate.

The formation of silver sulphide is due to the adsorption of the sodium silver thiosulphate on the silver sol, which accelerates the decomposition of the thiosulphate; where, however, the sol concentration is large (*i.e.*, small volume of thiosulphate), the colloidal particles are so close that the adsorption forces bring about coagulation.

The quantum efficiency for blue light (500—400 μμ) was determined for different times of exposure to light of 436 μμ, the absorption being calculated from reflexion measurements owing to the thickness of the layer. For short exposures the quantum efficiency is approximately unity for silver bromide in sodium nitrite as acceptor, and $\frac{1}{1}$— in water. For green and red light with unexposed silver bromide the absorption values are independent of the presence of sodium nitrite, which must therefore be a true acceptor. For longer exposures the fall of quantum efficiency and the yield of silver decrease to an extent depending on the form of the precipitate and thus on its preparation. S. J. Gregg.

Photochemistry of silver halides. III. Relation between the gravimetrically determined silver and the lowering of sensitivity caused by dichromate–sulphuric acid reagent with subsequent chemical and primary and secondary physical development. H. H. Schmidt (Z. wiss. Phot., 1928, **26**, 86—95).—According to Lüppo-Cramer (cf. "Grundl. d. Negativerfahren, 3rd ed., 9) highly sensitive emulsions contain more "silver nuclei" or sensitivity centres, which might be thought to be connected with the gravimetrically determined excess of silver ions which always exists in the emulsion layer after decomposition with nitric acid.

To test this, the sensitivity changes of a control plate washed in conductivity water and of a plate washed in a dilute solution of sulphuric acid and potassium dichromate, respectively (both plates unsensitised), were compared, the plates being dried, exposed, and developed under identical conditions.

The sensitivity of the dichromate plate was reduced with chemical and primary physical development to an extent independent of the gravimetrically determined silver values, but bearing a direct relationship to the sensitivity. This must be a development phenomenon, for with secondary physical development (*i.e.*, development after fixing) the dichromate treatment produces no reduction of sensitivity, which disproves the view that the dichromate destroys the sensitivity centres.

No accurate method is yet available for the determination of the excess of silver in sensitised plates. Treatment with dichromate has the same effect on plates sensitised with acid dyes as on unsensitised plates of high sensitivity, but with plates sensitised with basic dyes, the dichromate causes great reduction in sensitivity for all three forms of development. This is due to the decomposition of the complex compounds of the silver halide with the basic dye which are much less stable towards dichromate than the silver compounds of the acid dye.

S. J. Gregg.

Formation of the photographic latent image. S. E. Sheppard.—See B., 1928, 837.

Photochemical studies. I. J. Houben and W. Fischer (Arb. biol. Reichsanst. Land- u. Forstwirtsch., 1928, **15**, 601—608; Chem. Zentr., 1928, i, 2486).—Photochemical decomposition of water into hydrogen and hydrogen peroxide, or synthesis of formaldehyde from carbon dioxide and water, could not be detected. Formaldehyde in ultra-violet light affords strongly reducing substances (pentoses); methyl alcohol and potassium nitrite produce formhydroxamic acid, which is rapidly decomposed by formaldehyde in light. Neither purine substances nor α-amino-acids were detected. Instead of alkaloids, which Baly claims to have isolated, alkylamines giving the usual alkaloid reactions were obtained. A. A. Eldridge.

Action of light on acetylene. H. Reinicke (Z. angew. Chem., 1928, **41**, 1144—1146).—An apparatus is described for the study of the action of light on acetylene. Hempel's apparatus cannot be used. Carefully dried and purified acetylene was unchanged in sunlight or in daylight either in glass or quartz vessels. Polymerisation occurs if the gas is exposed to the light from a mercury lamp, but only radiation of wave-length less than 300 μμ is active. Polymerisation occurs easily at atmospheric pressure as well as at higher pressures, and also at the ordinary temperature. Oxygen and moisture hinder the process, in the latter case aldehyde being formed. A. J. Mee.

Action of X-rays on chloroform and analogous compounds. P. Günther, H. D. von der Horst, and G. Cronheim (Z. Elektrochem., 1928, **34**, 616—625).—Chloroform produces hydrogen chloride in yields proportional to the radiated energy; in the presence of moisture hypochlorous acid is also produced. From dry carbon tetrachloride small yields of chlorine are obtained, acids being produced also if water is present. Very small yields of acids are obtained from mixtures of carbon tetrachloride or chloroform with petroleum and hexahydrobenzene; a reaction appears to occur between petroleum and

carbon tetrachloride. Hard rays are the most active. Other liquids were also used and numerous experiments are described in which iodoform in various solvents was exposed to *X*-rays (cf. Baumeister and Glocker, A., 1921, ii, 367). S. K. TWEEDY.

Influence of light on coloured [cotton] fabric. (MISS) E. HIBBERT.—See B., 1928, 854.

Syntheses with radiant energy. II. Photosynthesis of αββ-triphenyl-lactic acid. R. DE FAZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1287—1292; Chem. Zentr., 1928, i, 2174).—Phenylacetic acid (26 g.), benzophenone (30 g.), and anhydrous benzene (30 g.) were irradiated for 112 days in a tube attached to a U-tube containing calcium oxide. Crystals (0·5—2·5 g.) of αββ-triphenyl-lactic acid were deposited from the solution which had become orange-yellow, and also contained a small quantity of oil, b. p. 318—322°, and a viscous oil, phenylacetic acid (21·5, 24·5 g.) and benzophenone (26, 28 g.). Irradiation of the above mixture in a silica tube with a mercury lamp for 100 hrs. gave no triphenyl-lactic acid and only traces of carbon dioxide; irradiation with a 2000 c. p. Osram lamp, however, produced abundant quantities of these substances. Exposure of phenylacetic acid alone in anhydrous benzene to sunlight (6 months) gave little carbon dioxide (more in presence of uranium acetate) and a little yellow oil: exposure at 25 cm. distance to a 2000 c. p. Osram lamp resulted in the evolution in 24 hrs. of detectable quantities of carbon dioxide, in 280 hrs. of fairly large quantities, and crystals, m. p. 51—52°, probably *s*-diphenylethane.
A. A. ELDRIDGE.

Action of light on celluloid stained with malachite-green. (LORD) RAYLEIGH (Nature, 1928, **127**, 645—646).—The conversion of celluloid stained with malachite-green into a material transmitting only deep red and infra-red rays by exposure to sunlight can be effected also by heating. The change is due to a specific reaction of the cellulose nitrate constituent. A. A. ELDRIDGE.

Activation of hydrogen in silent discharge. I. G. M. SCHWAB and F. SEUFERLING (Z. Elektrochem., 1928, **34**, 654—657).—Experiments are described which indicate that in the silent discharge hydrogen at 50 mm. forms one form or other of active hydrogen. When sulphur is absent, the active hydrogen contains only one tenth of the amount of hydrogen sulphide which is formed when sulphur is present. An accurate micrometric method of determining the amount of hydrogen sulphide in the hydrogen, by collecting the gas in a capillary U-tube, is described.
S. K. TWEEDY.

Purification of helium. J. W. COOK (Physical Rev., 1927, [ii], **29**, 920).—Up to its saturation capacity, activated coconut charcoal completely removed air at −78° A. A. ELDRIDGE.

Helium. II. Employment of sensitive helium tests in questions of the transformation of the elements. F. PANETH and K. PETERS [with H. GEHLEN and P. L. GÜNTHER] (Z. physikal. Chem., 1928, **B**, **1**, 170—191).—A method previously described for the detection and measurement of quantities of helium of the order of 10^{-10} c.c. (this vol., 858) has been used to test the possibility of the formation of helium artificially, from other elements, under various conditions such as bombardment of potassium salts by cathode rays, passage of an electric discharge, with or without electrodes, through hydrogen or compounds of hydrogen, and action of β- and γ-rays on water and mercury. When precautions are taken to exclude the possibility of the entry of air, or the diffusion of helium from the air through hot glass, or the escape of helium occluded in glass, no helium in quantity larger than 10^{-10} c.c. is obtained by these methods. Experiments on the spontaneous production of helium in potassium and beryllium salts have not definitely excluded the possibility that this may take place. M. S. BURR.

Complex lithium, iron, and nitrogen compound. W. FRANKENBURGER, L. ANDRUSSOV, and F. DÜRR (Z. Elektrochem., 1928, **34**, 632—637).—Nitrogen is reversibly absorbed by a heated mixture of iron and lithium nitride with the formation of a greyish-black crystalline *compound*, Li_3N,FeN, or $Li_3[Fe^{III}N_2]$. An *X*-ray powder photograph of the compound is given. The compound, which decomposes in water to black micro-crystalline iron oxide and ammonia, has a heat of formation of 22,600 ± 2300 g.-cal./mol. Magnetic observations are also recorded. Absorption of nitrogen occurs when the iron is replaced by nickel or cobalt, but not when replaced by osmium. The contradictory results obtained in the previous investigations of the absorption of nitrogen by iron are explained on the basis of the varying surface structure of the latter.
S. K. TWEEDY.

Composition of precipitate obtained by the action of potassium ferrocyanide on calcium salts in presence of acetic acid. I. TANANAEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 905—908).—See this vol., 852. R. TRUSZKOWSKI.

Reduction of barium carbonate by aluminium. E. F. LINHORST and H. SCHLUNDT.—See B., 1928, 813.

Basic carbonates of zinc and cadmium. T. NISHIMURA and T. YAMAMOTO (Bull. Inst. Phys. Chem. Res., Japan, 1928, **7**, 985—995).—Normal zinc carbonate when prepared at a low temperature and in presence of carbon dioxide is stable when exposed to the air, but if air be bubbled through its aqueous suspension a basic carbonate of composition $ZnO,0{\cdot}421CO_2,nH_2O$, believed to be different from $5ZnO,2CO_2,3H_2O$, is formed. If zinc hydroxide is allowed to absorb carbon dioxide from the air, another compound, $ZnO,0{\cdot}363CO_2,mH_2O$, is obtained.

Cadmium carbonate is stable when dry or wet, unless it is prepared at a low temperature, when a temporary decomposition is caused by bubbling air through its aqueous suspension. Cadmium hydroxide absorbs atmospheric carbon dioxide rapidly up to 0·78 mol. CO_2 to 1 mol. CdO, and then the absorption suddenly slackens. No basic cadmium carbonate can be isolated. F. S. HAWKINS.

Separation on iron of carbon from carbon monoxide and light petroleum. II. Crystalline carbon with high adsorptive power. U. HOFMANN

(Ber., 1928, **61**, [*B*], 2183—2194; cf. this vol., 853).—The isolation of crystalline carbon capable of activation (*loc. cit.*) appears contrary to the observations of Ruff (A., 1925, ii, 192), who considers this property to be confined to amorphous carbon. The presence of amorphous particles in the author's specimens is regarded as impossible, since carbon, deposited on iron at 400° or 520°, does not show any discontinuity in rate of oxidation or adsorptive power when treated with carbon dioxide until two thirds of the material has disappeared, and its action towards boiling sulphuric acid and mercury sulphate is precisely similar to that of the undoubtedly homogeneous graphite, retort graphite, and lustre carbon. On the other hand, non-homogeneous carbons, such as sugar and ash charcoal, are very irregularly oxidised. The adsorptive power of crystalline carbon must be ascribed to its loose texture, as is shown by the observation of slight activity in lustre carbon deposited from a mixture unusually rich in light petroleum and in carbon obtained from iron pentacarbonyl and light petroleum at 900°. Activation does not depend on sundry amorphous and therefore unoriented carbon atoms, but on the surface of crystallites composing the regular, graphite lattice. With large crystallites the active surface becomes so small in relation to the mass of carbon that adsorptive power is not manifested measurably. This is the case with carbon deposited on iron at 900°, and particularly with graphite; the limiting length of the edge of crystallite is estimated to be 10^{-4} cm. Below this limit, the relative extent of the active surface is so considerable that an active product is obtained if the carbon can be so loosely deposited that the surfaces of the crystallites are free for the greater part; this is not usually the case with retort graphite and lustre carbon. Activation, for example, by carbon dioxide depends on the removal of foreign matter already adsorbed and on the roughening of the complete surface. The chemical resistance of carbon, also, depends solely on the surface which can be reached by the reagent and is therefore governed by the size of the crystallites and the closeness of packing. The hardness of the individual crystallites is not involved.

H. Wren.

Reduction of carbonic acid. H. Kautsky (Naturwiss., 1928, **16**, 204; Chem. Zentr., 1928, i, 2236).—Carbamidosiloxen, from carbon dioxide and aminosiloxen, when in contact with small quantities of oxygen yields hydrogen cyanide, the oxygen being taken up by the silicon compound.

A. A. Eldridge.

Reaction between nitrous acid and hydrogen sulphide. L. S. Bagster (J.C.S., 1928, 2631—2643; cf. Divers, *ibid.*, 1887, **51**, 48).—The products of the reaction between nitrous acid solution and hydrogen sulphide are mainly nitric and nitrous oxides with the former in excess and ammonia and hydroxylamine with the latter in excess. Only when the hydrogen sulphide concentration is very small does the relative proportion of sulphur trioxide become comparable with the free sulphur. It is suggested that the primary reaction occurs between nitrous acid and a sulphide ion to form hyponitrous acid when there is little hydrogen sulphide present, and hydroxylamine and ammonia when the concentration of nitrous acid is small.

Hydrogen sulphide reduces ammonium nitrite very slowly to ammonia. The reaction rate is diminished by addition of ammonium sulphide and increased by the addition of polysulphide. It is suggested that the former acts by decreasing the hydrogen-ion concentration and therefore the concentration of nitrous acid molecules, whilst the latter, owing to the greater acidity of the polysulphide ion, increases the concentration of free sulphide ions. F. J. Wilkins.

Allotropic modifications of phosphorus obtained at high temperatures and pressures. V. Ipatiev and V. Nikolaiev (J. Russ. Phys. Chem. Soc., 1928, **60**, 885—892).—Crystalline, white phosphorus, m. p. 44·5°, *d* 1·82, is obtained by heating yellow phosphorus with benzene at below 200° at 70—80 atm. in an inert atmosphere. Purple phosphorus, ignition point 210—240°, *d* 1·93—2·05, is obtained in crystalline aggregates by heating ordinary phosphorus with water in a silver tube at 260—290° under 30—60 atm. pressure. Crystalline, ruby-violet phosphorus, ignition point 346°, d_1^{16} 2·11, is obtained by heating phosphorus with lead in a glass tube filled with nitrogen at 335° and 165 atm. Crystalline, black phosphorus, ignition point 485—490°, d_1^{16} 2·61—2·70, is prepared by heating yellow phosphorus in nitrogen for 4—5 days at 300—350° and 90—250 atm. At higher temperatures all the above allotropes pass into the white modification.

R. Truszkowski.

Allotropic modifications and solid solutions of phosphorus. V. J. Nikolaiev (J. Russ. Phys. Chem. Soc., 1928, **60**, 1045—1051).—Four allotropes of phosphorus exist, viz., white phosphorus, d_{16}^{16} 1·82, ignition point 55°; purple, d_1^{16} 1·90, i. p. 200°; ruby-red, d_{16}^{16} 2·11, i. p. 346°; and black, d_{16}^{1} 2·70, i. p. about 490°. At *d* intermediate to the above a continuous series of solid solutions exists, in which the colours are also intermediate. Red phosphorus is a solid solution of the ruby-red and the purple forms, whilst violet phosphorus consists of ruby-red and black phosphorus. R. Truszkowski.

Preparation of phosphorus thiochloride. R. de Fazi (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1293—1294; Chem. Zentr., 1928, i, 2240).—Anhydrous carbon tetrachloride (220 g.) and phosphorus pentasulphide (250 g.), when heated for 2 hrs. in a sealed tube at 180—200°, yield the compound $PSCl_3$ (150 g.). A. A. Eldridge.

Action of an electric discharge on the gaseous mixture SO_2+O_2. J. Maisin (Bull. Soc. chim. Belg., 1928, **37**, 326—333).—Berthelot's experiments on the action of an electric discharge on a mixture of equivalent quantities of sulphur dioxide and oxygen have been repeated. The pressure in the apparatus rapidly falls and an oil, or more frequently an opaque solid, is formed on the walls of the discharge tube. The product is insoluble in sulphuric acid, contrary to the statement of Berthelot, but dissolves in water without any violent reaction, forming a strongly oxidising solution. The substance does not fume in moist air and is relatively stable. The residual gases in the tube give the reactions of

the sulphate ion. The product is not S_2O_7, as suggested by Berthelot, nor is its behaviour in agreement with Meyer's view (A., 1922, ii, 843) that it is a mixture of the anhydrides of sulphuric acid and Caro's acid, SO_3 and SO_4, but it appears to be a definite compound, S_3O_{11}, which might be regarded as a mixed anhydride of persulphuric acid, $H_2S_2O_8$, and Caro's acid, $H_2S_2O_5$. M. S. BURR.

Sulphur nitride. II. S. A. VOZNESENSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 1037—1044).—The colour reactions given by sulphur nitride, N_4S_4, and by thiotrithiazyl chloride, N_3S_4Cl, in various solvents and in acid and alkaline solutions are contrasted. The latter substance reacts with hydrochloric acid according to the equation: $2N_3S_4Cl+12H_2O+4HCl=2H_2S_3O_6+6NH_4Cl+2S$; with water: $2N_3S_4Cl+H_2O \longrightarrow 2(NH_4)_2S_3O_6+2NH_4Cl+2S$, and with 2% sodium hydroxide solution: $3N_3S_4Cl-nNaOH+mH_2O \longrightarrow 2H_2S_2O_3+H_2SO_3$.

R. TRUSZKOWSKI.

Constitution of some polythionates. J. A. CHRISTIANSEN (Z. Elektrochem., 1928, **34**, 638—640).—*p*-Toluoyl tri-, tetra-, penta-, and hexathionates were prepared (cf. Troeger and Hornung, A., 1899, i, 905), and their *X*-ray spectra (*K* radiation), electric moments, and mol. wts. (b.-p. method) investigated. Only the trithionate had the accepted m. p.; the pentathionate exists in two modifications, m. p. 183° and 160°, respectively. The m. p. of the latter form rises to 180° on keeping; the compound is precipitated, together with sulphur, by heating the hexathionate with acetic acid in presence of platinum. The m. p. of the hexathionate (90°) and the tetrathionate (114°) indicate that these compounds may be mixtures of different forms. This isomerism, and also the electric moment data, do not support the classic formulæ of Blomstrand and Mendeléev. The data do not suffice to determine whether the compounds contain polysulphide or thiosulphate linkings. The absence of colour does not support the former constitution. The compounds are associated in benzene solution (cf. Aoyama, Kimura, and Nishina, A., 1927, 999).

S. K. TWEEDY.

Co-ordination compounds of quinquevalent molybdenum: complex thiocyanates. R. G. JAMES and W. WARDLAW (J.C.S., 1928, 2726—2739; cf. A., 1927, 1044).—By the interaction of aqueous solutions of the compound $(NH_4)_2[MoOCl_5]$ and ammonium thiocyanate, *dihydrogen molybdenum dioxytrithiocyanate* has been prepared. Similarly by the interaction of the corresponding salts of the type $R_2[MoOCl_5]$ the *thallous*, *quinolinium*, and *pyridinium* salts have been isolated. Further, *salts* of the empirical formula $R_4[Mo_2O_3(CNS)_8]$ (where R—$NHMe_3$ or NMe_4) were prepared by treating $(NHMe_3)_2MoOCl_5$ and $(NMe_4)_2MoOCl_5$ with ammonium thiocyanate. They are given the configuration

$$R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}\text{——O——}\\CNS\quad CNS\end{matrix}Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right].$$

Both the tri- and octa-thiocyanates yield *salts* of the type $R_2[MoO(CNS)_5]$ ($R=C_5H_5N$, C_9H_8N, $NHMe_3$, NMe_4) with aqueous thiocyanic acid and a *sulphato*-compound, $(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$, with 5*N*-sulphuric acid. The relationship between the complex chlorides and thiocyanates of quinquevalent molybdenum has been demonstrated. *Ditetramethylammonium molybdenyl pentachloride* has been isolated.

The co-ordination number of oxygen in these compounds is discussed and evidence is brought forward to show that it may occupy two positions in the co-ordination sphere. F. J. WILKINS.

Additive compounds of hydrogen halides and salts of heavy metals. III. F. EPHRAIM and A. SCHARER (Ber., 1928, **61**, [*B*], 2161—2173; cf. A., 1926, 36, 587).—Addition of hydrogen chloride is not confined to the sulphates of copper, silver, zinc, cadmium, mercury, thallium, tin, lead, antimony, and bismuth, but extends to the dry phosphates, phosphites, and hypophosphites, which yield pulverulent adducts, but not to arsenates, selenates, and benzoates, which are immediately or rapidly decomposed. Hydrogen bromide and iodide give similar, but less stable, additive products. The following changes are possible: $XSO_4+2HBr \rightleftharpoons XSO_4,2HBr$; $XSO_4+2HBr \quad XBr_2+H_2SO_4$; $XSO_4+2HBr \quad XSO_3+H_2O+Br_2$. The additive products do not show any trace of free acid and their colour is identical with or similar to that of the metallic halide. Since the number of mols. of added halogen acid is invariably equal to the number of metallic valencies available, the structure

$$X\begin{matrix}\cdot\text{Hal—H}\cdot\\\text{————————}\\\cdot\text{Hal—H}\cdot\end{matrix}O_4S$$

is ascribed to the compounds.

Hydrogen bromide is conveniently prepared by the gradual addition of bromine to a mixture of technical resorcinol and sand. With anhydrous cadmium sulphate it gives the *compound* $CdSO_4,2HBr$, which slowly decomposes at the atmospheric temperature into cadmium bromide and sulphur dioxide. Copper sulphate immediately blackens, giving finally copper bromide, bromine, and sulphur dioxide. The *substances* $Ag_2SO_4,2HBr$ and $PbSO_4,2HBr$ are described. Zinc sulphate adds hydrogen bromide with difficulty. With thallous sulphate a thalloso-thallic derivative is formed. Mercuric bromide gives the *compound* $HgSO_4,HBr$ at 100°; at 120°, mercuric bromide sublimes, and absorption of 2 mols. of the acid, which occurs slowly at 120—140°, is accompanied by double decomposition into mercuric bromide and sulphuric acid. Mercurous sulphate and hydrogen chloride when cold give the *product* $Hg_2SO_4,2HCl$, quantitatively converted in a current of hydrogen chloride at 150° into mercuric chloride, sulphur dioxide, and water. Silver phosphate gives the *compound* $Ag_3PO_4,3HCl$; the *substance* $Pb_3(PO_4)_2,6HCl$ decomposes above 400° with separation of lead chloride. Mercuric phosphate absorbs hydrogen chloride, possibly with double decomposition; with zinc phosphate the results are ill-defined, whereas aluminium phosphate does not react. Ferric phosphate absorbs nearly 6 mols. of hydrogen chloride. Anhydrous nickel phosphate does not absorb hydrogen chloride, but the dihydrate unites with 7 mols. of the halide, giving a *compound* which loses water at 100° and passes at 200° into the *substance*

$Ni_3(PO_4)_2,6HCl$. The *compound* $Ag_3PO_4,3HBr$ is converted at 400° into silver bromide and phosphoric acid, whereas the analogous *lead* salt decomposes when strongly heated with evolution of phosphine. When cold, mercuric phosphate appears to yield the *compound* $Hg_3(PO_4)_2,3HBr$, which undergoes double decomposition when heated; the latter change occurs exclusively when cooling is not adopted. Anhydrous nickel phosphate does not react, whereas the dihydrate gives the substance $Ni_3(PO_4)_2,7HBr,2H_2O$. Anhydrous cadmium phosphite, conveniently prepared from solid cadmium carbonate and phosphorous acid, absorbs rather more than 2 mols. of hydrogen chloride or bromide. Lead phosphite yields the *compounds* $PbHPO_3,2HCl$ and (?) $PbHPO_3,2HBr$, the preparation of the latter being accompanied by evolution of bromine. Calcium phosphite does not add either hydrogen halide. Cadmium hypophosphite appears to combine with 2 mols. of hydrogen chloride or bromide. Arsenates and selenates react with hydrogen halides with reduction of the acid radical, benzoates with double decomposition. Silver, cupric, and mercuric sulphates and ferric phosphate are immediately decomposed by hydrogen iodide, with separation of iodine and production of hydrogen sulphide from the sulphates. Additive *compounds* of lead phosphate or phosphite with hydrogen iodide possibly exist. Hydrogen cyanide and methyl chloride do not exhibit additive power. Hydrogen chloride effects the removal of ammonia only from those ammonates which have appreciable ammonia tension; it does not react with the lower ammonates.

H. WREN.

Formation of iodates from iodides. R. LYDÉN (Finska Kemistsamfundets Medd., 1927, **36**, 126—141; Chem. Zentr., 1928, i, 2494).—Interaction of potassium chlorate and iodide (preferably 1 : 1·5 mol.) commences at 350—400° and proceeds vigorously with marked evolution of oxygen: $KClO_3+6KI \longrightarrow KCl+3K_2O+3I_2$; $5KClO_3+3I_2 \longrightarrow 5KCl+3I_2O_5$; $K_2O+I_2O_5 \longrightarrow 2KIO_3$. With perchlorate (1·5 : 1 mol.), $3KClO_4+4KI \longrightarrow 4KIO_3+3KCl$; with bromate (1·5 : 1 mol.), $KBrO_3+KI \longrightarrow KBr+KIO_3$.

A. A. ELDRIDGE.

Rhenium. W. NODDACK (Z. Elektrochem., 1928, **34**, 627—629).—Rhenium obtained by reducing the sulphide in hydrogen is a heavy, grey powder, unaltered at 2000° in a vacuum; it inflames at 300° in oxygen with formation of a volatile white *oxide*, Re_2O_7, m. p. 26—30°, sparingly soluble in water and acids. Yellow drops of the *oxide* ReO_3 also condense; they form hygroscopic crystals, m. p. 160°, b. p. 450°, which, on boiling, give the vapour of the white oxide. The latter becomes yellow at 150°. Reduction of these oxides by carbon monoxide or sulphur dioxide produces green, blue, and violet *oxides*, which, however, on prolonged heating are converted into the yellow or white oxide. The aqueous solution of the yellow oxide, which is acidic, is uninfluenced by hydrochloric, nitric, and sulphuric acids, by potassium and sodium hydroxides, by ammonia, and by oxidising agents. With barium hydroxide and silver nitrate it forms white precipitates, possibly $BaReO_4$ and Ag_2ReO_4, soluble in dilute nitric acid. The silver precipitate darkens at 100°. Hydrogen sulphide is oxidised by the yellow oxide solution to sulphur; in presence of acids a grey sulphide is quantitatively precipitated (together with sulphur), and this precipitation is not hindered by oxalic, tartaric, or phosphoric acids (distinction from tungsten). By heating the precipitate in carbon dioxide at 400—600° unstable black *sulphides*, Re_2S_7 and ReS_3, appear to be formed. Above 600° the stable black *sulphide*, ReS_2, is produced. The acidified yellow oxide solution will not react with ammonium phosphate or potassium ferrocyanide, nor will it give a colour with potassium xanthate. This behaviour serves to distinguish the element from molybdenum, as also does the behaviour of the solution towards potassium thiocyanate and the greater volatility of rhenium oxide as compared with molybdenum oxide. Absence of reaction with potassium iodide distinguishes the element from osmium. By heating rhenium in chlorine two volatile *chlorides* are formed, viz., $ReCl_6$, brown needles, subl. 150°, hydrolysed by water, and (?)$ReCl_7$, green, more volatile than the lower chloride. With iodine and bromine vapour, respectively, dark volatile compounds are formed. The above properties place rhenium between tungsten and osmium.

S. K. TWEEDY.

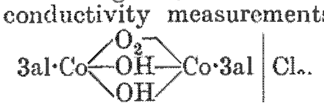
Iron crystals. L. W. MCKEEHAN (Physical Rev., 1927, [ii], **29**, 920).—Long crystals of iron are obtained by causing an electrically heated portion to move along a wire. The temperature of the hottest portion should be 1400°. Irregular tension and torsional stresses result in twinning. A. A. ELDRIDGE.

Univalent iron, cobalt, and nickel. W. MANCHOT (Gazzetta, 1928, **58**, 560—562; cf. this vol., 35).—A reply to Cambi's criticism (this vol., 258) of the author's previous work. O. J. WALKER.

Action of mercury salts on iron pentacarbonyl. H. HOCK and H. STUHLMANN (Ber., 1928, **61**, [B], 2097—2101).—Iron pentacarbonyl is converted by mercuric chloride (2 mols.) in aqueous solution into carbon dioxide, hydrogen chloride, and the *compound* $Fe(CO)_4,Hg_2Cl_2$, which darkens at 100°, evolves carbon monoxide at 140°, and is completely decomposed at 300°, leaving iron and mercurous chloride. It is almost completely stable towards air and very sparingly soluble in the usual media. In well-cooled acetone the reactants give the unstable additive *compound*, $Fe(CO)_5,HgCl_2$, which gradually passes into the tetracarbonyl derivative if mercuric chloride is in excess; if this is not the case, the tetracarbonyl compound is formed, but the excess of pentacarbonyl is decomposed with separation of ferrous chloride. In ethyl-alcoholic solution, the compound $Fe(CO)_4,Hg_2Cl_2$ is produced. The reaction appears suitable for the determination of iron pentacarbonyl. Mercuric bromide and iodide do not appear to react similarly. The pentacarbonyl reacts immediately with mercuric acetate in water or acetone. With mercuric nitrate the primary reaction appears to be followed by the immediate oxidation of the carbonyl groups by nitrate. The action of mercurous nitrate causes brisk evolution of gas and precipitation of mercury. With aqueous mercuric sulphate a yellow precipitate is formed. H. WREN.

Oxidation of cobalt in a solution of cobaltous nitrate by sodium bismuthate. S. KITASHIMA (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 1035—1040).—Cobaltous nitrate dissolved in concentrated nitric acid turns blue when shaken with sodium bismuthate owing to oxidation of the cobalt. The degree of oxidation depends on the time of shaking and the amount of sodium bismuthate present. If the salt is dissolved in very dilute nitric acid, it retains its red colour when shaken with sodium bismuthate, but a study of the absorption spectrum shows the presence of cobaltic salts. The degree of oxidation is almost independent of the time of shaking, and in each case the cobaltic salt is considerably reduced after 2 hrs. F. S. HAWKINS.

Cobalt allylamines: a supposed co-ordination number of eight for cobalt. W. R. BUCKNALL and W. WARDLAW (J.C.S., 1928, 2648—2654).—The composition of the compound obtained by the atmospheric oxidation of an alcoholic solution of cobaltous chloride containing allylamine has been re-investigated, and from analysis, mol. wt., and conductivity measurements ascribed the formula



In this formula cobalt has a co-valency of six, in agreement with Sidgwick's rule. The formula of Pieroni (cf. A., 1921, i, 315), which ascribes a co-ordination number of eight for cobalt, is shown to be erroneous. F. J. WILKINS.

[Chlorides of ruthenium.] H. REMY (Ber., 1928, **61**, [*B*], 2109—2110; cf. this vol., 722).—A reply to Gall and Lehmann (this vol., 975). Owing to an error in calculation, the results obtained by the manganate titration have been interpreted as establishing the exclusive tervalency of ruthenium in Gall and Lehmann's material, whereas they show the presence of 45% of the quadrivalent metal. H. WREN.

[Chlorides of ruthenium.] E. ZINTL and P. ZAIMIS (Ber., 1928, **61**, [*B*], 2110—2111; cf. A., 1927, 533).—A reply to Gall and Lehmann (this vol., 975) with regard to the potentiometric titration of ruthenium salts. H. WREN.

Methods for the calculation of analyses. II. O. LIESCHE (Z. angew. Chem., 1928, **41**, 1156—1159).—Indirect methods for the analysis of difficultly separable elements are discussed. Tables are prepared showing the essential calculations involved in the determination of mixed sodium and potassium salts, barium and strontium salts, halides, sulphides of antimony, and the constituents of fluorspar. Emphasis is laid on the importance of selecting analytical methods such that small differences in experimental figures do not lead to disproportionately large changes in the calculated results. A. G. POLLARD.

Potentiometric quantitative analysis. B. KAMIEŃSKI (Bull. Acad. Polonaise, 1928, **A**, 33—60).—The method uses two electrodes, one placed directly in the solution, the other placed inside a tube of insulating material in the solution. The solution is rapidly stirred so that it passes first of all the first electrode, and then, immediately afterwards, the electrode in the tube. The theory of the method is explained. If the liquid to be added to the solution is dropped in continuously from a burette, there will be a maximum *P.D.* between the electrodes when the end-point is reached, if the velocity of reaction is large enough. The method is successful only if the stirring is sufficiently rapid. Experiments were carried out with oxidation and reduction reactions, *e.g.*, $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$, $Fe(CN)_6^{\cdot\cdot\cdot\cdot} \rightleftharpoons Fe(CN)_6^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}+Cr^{\cdot\cdot} \rightleftharpoons Cr^{\cdot\cdot\cdot}+Fe^{\cdot\cdot}$, $Sn^{\cdot\cdot} \rightleftharpoons Sn^{\cdot\cdot\cdot\cdot}$. In each case platinum electrodes were used, with potassium permanganate as oxidation agent and a chromous solution as reducing agent. Precipitation reactions were also investigated, but it was found that these could not be suitably treated. The sharpness of the titrations is satisfactory. A. J. MEE.

Use of Emich filter-tubes for potentiometric analysis. T. HECZKO (Z. anal. Chem., 1928, **75**, 183—190).—Continuing his attempts (this vol., 726, 980) to simplify the apparatus used for potentiometric titrations, the author describes a simple arrangement in which an Emich filter-tube carrying a wire of an appropriate metal and containing a solution of suitable electrolytes serves as a comparison electrode in actual contact with the titrated solution. A column of a dilute solution of copper sulphate in a capillary serves as a suitable resistance. J. S. CARTER.

New iodoso- (iodoso-iodyl-)benzene electrode and its application to the determination of p_{OH} or p_H. F. GROSSMAN (Bull. Soc. chim., 1928, [iv], **43**, 1063—1072).—See this vol., 607.

4-Methylumbelliferone as a fluorescent indicator. C. BULOW and W. DICK (Z. anal. Chem., 1928, **75**, 81—86).—In acid solution 4-methylumbelliferone is colourless, whereas in alkaline solution it shows a blue fluorescence, the change-point occurring at p_H 6—7. It is a suitable indicator for the titration of strong acids and bases and its action is not masked by the presence of yellow, red, or blue compounds in the solution. A. R. POWELL.

Use of methyl-orange for the detection of free chlorine and chloroamines. BESEMANN (Chem.-Ztg., 1928, **52**, 826).—Methyl-orange is decolorised by chlorine in concentrations as low as 0·5 mg./litre, whereas chloroamines do not affect the indicator, but in acid solution they liberate iodine from potassium iodide. These tests therefore provide a means of distinguishing between free chlorine and chloroamines. A. R. POWELL.

Preparation of *o*-tolidine reagent for free chlorine [in water]. C. S. BORUFF, S. J. VELLENGA, and R. H. PHELPS.—See B., 1928, 838.

[Use of dimethyl-*p*-phenylenediamine hydrochloride as] indicator for chlorine [in water]. K. ALFTHAN.—See B., 1928, 838.

Electrometric titration of hypochlorite and hypochlorite–carbonate mixtures. A. RIUS and V. ARNAL.—See B., 1928, 813.

Volumetric determination of sulphuric acid. G. TESTONI (Annali Chim. Appl., 1928, **18**, 408—414).—When benzidine acetate is added gradually to a solution containing either free or combined sulphuric

acid, the separation of the benzidine sulphate is instantaneous and the end of the titration may be detected by placing a drop of the clear liquid on a strip of filter-paper previously soaked in a thin suspension of lead peroxide and dried, this giving a blue coloration with the benzidine. Greater accuracy may then be attained if, when the end of the titration is approached, a portion of the liquid is filtered off and treated with lead peroxide or potassium persulphate. When, of two volumes of the benzidine solution differing by 0·1 c.c., one does and the other does not give the blue colour in this way, the mean of the two volumes is taken as correct.

The reagent is prepared by dissolving 10 g. of benzidine in 100 c.c. of glacial acetic acid, making up to a litre, leaving for a day, and filtering; the exact titre is determined by means of 0·1*N*-sulphuric acid. In applying the method it is advisable to use always the same volume of liquid and concentrations not widely different. Test determinations on sulphates alone and on mixtures containing also chlorides and nitrates yield satisfactory results. T. H. Pope.

Determination of nitrogen by Dumas' method. I. Marek [with M. Krajcinovic and G. Zaljesov] (Arhiv Hemiju, 1928, **2**, 169—174).—The combustion tube contains a small boat in which is placed the substance intimately mixed with copper oxide, a roll of oxidised copper gauze some 10 cm. in length, and, at the exit end, a similar roll of bright gauze. The usual packing of copper oxide is omitted. The portions of the tube occupied by the boat and the rolls of gauze are heated electrically. The rolls of gauze are surrounded by an asbestos coating so that the tube is tightly packed and gases pass through the interstices of the gauze. The position of the boat may be altered at will without interrupting the determination. The gauze may be oxidised or reduced by passing a stream of oxygen or hydrogen through the tube and heating the desired portion. Carbon dioxide is generated in a special apparatus and absorbed in a 50% solution of potassium hydroxide. J. S. Carter.

Koch and McMeekin's method for the determination of nitrogen. H. A. Davenport (J. Lab. Clin. Med., 1926, **12**, 286—287).—Ordinary 3% hydrogen peroxide is added, a correction of 0 002 mg. N per drop being made for the acetanilide. Chemical Abstracts.

Detection of nitrous acid. W. Vaubel (Chem.-Ztg., 1928, **52**, 842).—The solution to be tested for nitrous acid is added to a solution of an alkali naphthionate which has been acidified with hydrochloric acid. On adding sodium hydroxide or ammonia solution a red colour is obtained in the presence of nitric acid due to the coupling of a second molecule of naphthionic acid with the diazo-compound formed in acid solution. A. R. Powell.

Acidimetric determination of phosphate. M. Hegedus (Z. anal. Chem., 1928, **75**, 111—120).—For the acidimetric determination of phosphate in alkali phosphates free from heavy metals or alkaline earths 0·1—0·2 g. of the salt is dissolved in dilute nitric acid and the solution boiled to expel carbon dioxide. After cooling, one drop of methyl-orange, followed by carbonate-free, 0·1*N*-sodium hydroxide solution, is added until the colour matches that of a standard solution containing 0·1 g. of potassium dihydrogen phosphate and one drop of methyl-orange. The neutralised solution is then treated with a large excess of a saturated solution of silver acetate and the coagulated silver phosphate precipitate is separated after 10—15 min. The filtrate is treated with 2—3 g. of sodium chloride and titrated, without filtration, with 0·1*N*-sodium hydroxide solution, free from carbonate, using phenolphthalein as indicator. Chlorides, nitrates, and sulphates do not interfere, but ammonium salts must first be destroyed by boiling with sodium hydroxide. A. R. Powell.

Determination of phosphate as magnesium pyrophosphate. N. Krilenko (Arhiv Hemiju, 1928, **2**, 197—205).—After the addition of 1 c.c. of concentrated sulphuric acid, 20 c.c. of solution containing not more than 0·2 g. of phosphorus pentoxide are evaporated to fuming; 2 c.c. of sulphuric acid and 4—5 c.c. of a cold, saturated solution of magnesium sulphate are added, and the whole is stirred with a glass rod until the solution becomes clear. The solution is made faintly alkaline (phenolphthalein) with ammonia. If aluminium, iron, or calcium is present, 3—5 c.c. of a saturated solution of ammonium citrate are added before precipitation with ammonia. After 30 min. 25 c.c. of a warm solution containing equal parts of 10% solutions of ammonia and ammonium chloride are added. The precipitate is washed by decantation with the ammonia–ammonium chloride solution until complete settling does not occur within 10 min., when the whole is transferred to the Gooch crucible and washed with a 2·5% solution of ammonia. The crucible is dried and heated at 900°. J. S. Carter.

Sensitive reagent for the phosphate ion. Distinction between antimony and tin. T. Gaspar y Arnal (Anal. Fís. Quím., 1928, **26**, 181—183, and Chim. et Ind., 1928, **20**, 631—632).—The solution obtained by adding a solution of antimony trichloride to one of sodium molybdate furnishes an exceedingly sensitive reagent for the phosphate ion. H. F. Gillbe.

Sodium arsenite solution. W. Meyer (Süddeut. Apoth.-Ztg., 1928, **68**, 226—227; Chem. Zentr., 1928, i, 2524).—The method for the analysis of the solution of sodium arsenite and hydroxide of the German pharmacopœia (6th ed.) is criticised. A. A. Eldridge.

Determination of small quantities of carbon monoxide and methane in mixtures of nitrogen and hydrogen. K. Keller and W. Klempt.—See B., 1928, 813.

Determination of traces of carbonate. J. Rae.—See B., 1928, 856.

Determination of small quantities of carbonate in presence of excess of sulphide and chloride, with particular reference to the analysis of metallic corrosion products. W. H. J. Vernon and L. Whitby.—See B., 1928, 856.

Thymolphthalein as indicator for titrimetric determination of carbon dioxide. C. J. Schollen-

BERGER (Ind. Eng. Chem., 1928, **20**, 1101).—Thymolphthalein is preferable to phenolphthalein in the titration of excess of barium hydroxide in which carbon dioxide has been absorbed. Barium carbonate is sufficiently soluble to colour the latter. As the end-point with thymolphthalein is at p_H 10·0 a blank titration should be made. C. IRWIN.

Reagent for ammonium, rubidium, and cæsium ions. Sensitive reagent for the potassium ion. T. GASPAR Y ARNAL (Anal. Fís. Quím., 1928, **26**, 184—185).—A 5% uranium nitrate solution produces no precipitate with sodium or ammonium chromate solution, but with potassium chromate solution a yellow precipitate is formed which is soluble in concentrated solutions of sodium chloride and uranium nitrate and in acids. A solution of equimolecular quantities of sodium chromate and uranyl nitrate forms a sensitive reagent for potassium, rubidium, and chromium ions, the solubility of the precipitate decreasing in the order given; ammonium salts also yield a precipitate. H. F. GILLBE.

Use of gelatin–oleate mixtures for the demonstration of small amounts of calcium. S. AMBERG, J. LANDSBURY, and F. SAWYER (J. Amer. Chem. Soc., 1928, **50**, 2630—2632).—Dilute gelatin solutions containing an oleate may be used to obtain ring reactions with solutions containing 0·0005 mg. of calcium in 1 c.c., but the reaction is not specific for this metal. S. K. TWEEDY.

Oxalate method for separating calcium and magnesium. W. T. HALL (J. Amer. Chem. Soc., 1928, **50**, 2704—2707).—The precipitation of calcium oxalate in presence of magnesium ions requires excess of ammonium oxalate; if too much of the latter is added, however, the subsequent precipitation of magnesium ammonium phosphate or of the 8-hydroxyquinoline compound of magnesium (Hahn and Vieweg, A., 1927, 639) is incomplete. Seventy-five c.c. of 0·5N-ammonium oxalate solution suffice for the precipitation of 0·3 g. of calcium ions in 500 c.c., or of 0·02 g. of calcium ions in presence of five or six times this quantity of magnesium ions.
S. K. TWEEDY.

Determination of traces of lead. P. SCHMIDT (Deut. med. Woch., 1928, **54**, 520; Chem. Zentr., 1928, i, 2190).—The material is ashed at a dull red heat in presence of sulphuric acid, the lead dissolved in nitric acid, recovered as sulphide, and precipitated electrolytically as dioxide from an acid solution; it is finally determined colorimetrically. Determination of 0·02 mg. is possible. A. A. ELDRIDGE.

Volumetric determination of copper and zinc. S. L. ROBERTSON (J. Roy. Tech. Coll. Met. Club, Glasgow, 1927—1928, (6), 37—40).—An account of the separation of copper from iron by thiosulphate precipitation, the determination of copper by titration with cyanide, and the determination of zinc by titration with ferrocyanide using a ferrous salt as internal indicator. A. R. POWELL.

Detection of copper in presence of iron. L. SZEBELLÉDY (Z. anal. Chem., 1928, **75**, 167—168).—To 5 c.c. of solution are added 1 g. of ammonium fluoride and 10 drops of a 1% solution of potassium ferrocyanide. If the amount of iron, which should be present in the ferric state, does not exceed 0·1 g. there is no interference and quantities of copper of the order 0·02 mg. are readily detected. J. S. CARTER.

Macro- and micro-iodometric determination of copper in copper salts of organic acids and enols. M. I. USCHAKOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 1151—1158, and Z. anal. Chem., 1928, **75**, 228—235).—The presence in solution of enols, aliphatic acids or oxy-acids, aliphatic-aromatic acids, aromatic oxy-, amino- or amino-sulpho-acids, aliphatic or aromatic–aliphatic acids with one ethylenic linking, and of aromatic nitro-acids does not appear to interfere with the iodometric macro- or micro-determination of copper. This method cannot, however, be applied in the presence of sulphinic acids, which react with iodine. R. TRUSZKOWSKI.

Determination and separation of rare metals from other metals. XI. Quantitative analysis of gallium. I. L. MOSER and A. BRUKL (Monatsh., 1928, **50**, 181—192).—Previous methods for the separation of gallium are critically reviewed. Precipitation of gallium hydroxide by ammonia solution is not a suitable method for determination, on account of its solubility in solutions containing ammonia and ammonium salts. The solubility of freshly-precipitated gallium hydroxide at 20° is 0·0010 g./litre in water, 0·0322 g./litre in 4·64% ammonia solution, and 0·574 g./litre in a solution containing $M/109$ ammonia and $M/31$ ammonium sulphate. Hydrolytic methods of precipitation are also unsatisfactory. Precipitation by the basic acetate method is incomplete, and although precipitation with chloride–bromate mixture in presence of sulphate is complete, the precipitate is too finely divided. A satisfactory method is precipitation with tannin in dilute acetic acid solution, and in this way gallium may be quantitatively separated from zinc, cadmium, cobalt, nickel, manganese, beryllium, and thallium. The solution, containing about 1% of acetic acid, is treated with 2% of ammonium nitrate, and 10% tannin solution (10 parts of tannin to 1 part of gallium hydroxide) are added to the boiling solution. The precipitate is washed with water containing ammonium nitrate and a trace of acetic acid, dissolved and reprecipitated, and finally ignited. A platinum crucible may not be used, as partial reduction of the gallium oxide occurs. Ignited gallium oxide is hygroscopic. If a large amount of gallium is present, it is convenient to remove the bulk of it by the basic acetate method before complete separation by the method described above. R. K. CALLOW.

Determination of iron in silicates. A. E. J. VICKERS.—See B., 1928, 816.

Determination of iron carbonyl. R. H. GRIFFITH and G. C. HOLLIDAY.—See B., 1928, 856.

Prussian-blue and Turnbull's-blue reactions [in presence of fluoride]. L. SZEBELLÉDY (Z. anal. Chem., 1928, **75**, 165—167).—In presence of increasing amounts of ammonium fluoride the colour of the precipitate obtained on addition of 1 drop of a N-solution of potassium ferrocyanide to 5 c.c. of a 0·02N-solution of ferric salt changes in the direction

blue→violet→pink→white. The corresponding colour change with solutions of potassium ferricyanide and ferrous salt is blue→grey→yellow→white. When ammonium fluoride is added after the precipitation, the ferrous ferricyanide colour is discharged, but the ferric ferrocyanide colour remains unchanged. In presence of excess of potassium ferricyanide or of mineral acid the disturbing effect of fluoride is considerably repressed. J. S. CARTER.

Analysis of potassium ferrocyanide. P. P. BUDNIKOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 1159—1164).—Gravimetric methods for the analysis of potassium ferrocyanide are too slow to be of any practical value; precipitation methods using zinc or silver salts are rejected owing to their indefinite end-point, iodometric methods give variable results, whilst good results are obtained by titration with $0 \cdot 05N$-potassium permanganate. R. TRUSZKOWSKI.

Electrometric determination of chromic acid in the presence of vanadic acid by the use of induction and catalysis. E. ZINTL and P. ZAIMIS (Z. Elektrochem., 1928, **34**, 714—715).—The criticisms of Lang and Zwerina (*ibid.*, 364) of the authors' method for the simultaneous determination of chromic and vanadic acids are refuted. The method may be used in the presence of large or small quantities of vanadium, an increase in the amount of catalyst (manganese salt) being necessary with larger quantities. The fact that Lang and Zwerina observed no potential change after the chromate reduction is probably due to their having used a hydrochloric acid solution. L. L. BIRCUMSHAW.

Determination of vanadium in steel. F. IBBOTSON.—See B., 1928, 861.

Determination of bismuth in substances used in the treatment of syphilis. BOUILLENNE and M. DUMONT (Compt. rend. Soc. Biol., 1928, **98**, 879—880; Chem. Zentr., 1928, i, 2636).—A micro-method, depending on the colour reaction of bismuth salts in presence of potassium iodide, is described. A. A. ELDRIDGE.

Tungsten and zirconium oxide furnace. W. M. COHN (Z. tech. Physik, 1928, **9**, 110—115; Chem. Zentr., 1928, i, 2521).—For furnaces employed below 1500° tungsten wire is used as resistance material. A furnace of tungsten and zirconium oxide employed for temperatures above 2000° is described. A. A. ELDRIDGE.

High-frequency induction furnace for chemical preparations above 1000°. C. N. SCHUETTE and C. G. MAIER.—See B., 1928, 822.

Thermostat. V. ČUPR (Z. Elektrochem., 1928, **34**, 679—682).—Details are given of a thermostat which can be used over a wide range of temperatures with a constancy of $\pm 0 \cdot 02°$. The apparatus consists essentially of two vessels, one (A) the thermostat proper, the other (B) a glass tube surrounded either by a freezing mixture or a heating coil. In order to maintain a constant temperature, liquid is automatically drawn from A to B, as required, where it is either heated or cooled and returned to A. The whole arrangement is simple, and is specially advantageous for use from $-40°$ to $+20°$. L. L. BIRCUMSHAW.

Thermostat for polarimetric work. L. RAMBERG and J. F. HEUBERGER (Svensk Kem. Tidskr., 1928, **40**, 227—229).—This thermostat is constant to within 0·01° and permits of rapid changing of the polarimeter tube. It consists of a brass trough with two small observation windows of plane glass let into opposite sides; heating is effected electrically by a wire resistance net mounted on the wooden stand which carries the bath, the regulator being a modification of Ramberg's earlier model (*ibid.*, 1926, **38**, 94). The polarimeter tube is carried on supports in the bath, which can be levelled bodily by three set screws attached to the wooden stand. The stirrer bearing is carried by the cover of the bath, which is hung from a support in the ceiling, hence vibration due to motor and transmission is isolated from the polarimeter tube. The thermostat liquid is optically inactive petroleum. S. J. GREGG.

Ebullioscopic method of mol. wt. determination. H. SHIBA and T. IMASE (Bull. Inst. Phys. Chem. Res., Japan, 1928, **7**, 996—998).—Cottrell's apparatus was improved by constructing the funnel-shaped part with a double wall which always contained the vapour phase, and so facilitated the boiling. Accurate determinations were made with 2·5 c.c. of solution. F. S. HAWKINS.

[Simple, automatic cryostat.] A. SIMON [with O. FISCHER, R. GLAUNER, and L. EHLING] (Ber., 1928, **61**, [*B*], 2173—2174; cf. A., 1927, 335).—A simplified method of adjusting the pressure to the required value is described. H. WREN.

Measurement of low pressures. H. TEICHMANN (Z. tech. Phys., 1928, **9**, 22—26; Chem. Zentr., 1928, i, 2273).

Hot centrifuge. C. HÜTTER.—See B., 1928, 801.

[Plate to prevent back-firing of] explosive gas mixtures. P. H. PRAUSNITZ.—See B., 1928, 803.

[Preparation of] nickel mirrors by the nickel carbonyl method. C. G. FINK and W. G. KING, jun.—See B., 1928, 819.

Voltaic hydrogen generator. W. C. GARDINER and G. A. HULETT.—See B., 1928, 822.

Oils, greases, and high vacua. C. R. BURCH (Nature, 1928, **122**, 729).—Vapour-pressure experiments indicate the possibility and advantage of using oil instead of mercury as working fluid in condensation pumps. A. A. ELDRIDGE.

Laboratory agitator. C. B. CARPENTER and W. A. MANUEL (Ind. Eng. Chem., 1928, **20**, 1072).—A pair of wooden wheels is mounted on a shaft with central bearing and driven from a motor connected to one wheel. On each wheel near its circumference are a number of coach screws which are the seats for universal clamps. In these the samples to be mixed are placed. Any type of motion can be given. C. IRWIN.

Apparatus for examining the solubility of gases or vapours in water and various body fluids. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1927, **97**, 1561—1563; Chem. Zentr., 1928, i, 2231).

Ballistic galvanometer method of potentiometric measurement for high resistance cells. H. T. BEANS and G. H. WALDEN, jun. (J. Amer. Chem. Soc., 1928, **50**, 2673—2678).—The method, which may be used with cell resistances as high as 50 megohms with an extreme deviation of $+0·5$ millivolt, is very similar to that of Jones and Kaplan (this vol., 954). S. K. TWEEDY.

Hydrogen electrode vessel useful for solutions of high resistance. R. J. BEST (Austral. J. Exp. Biol., 1928, **5**, 233—236).—The vessel is described and figured. A saturated potassium chloride–3% agar bridge dips into the solution of low conductivity, the p_H of which is to be measured, and by means of it connexion is effected with a standard cell. W. O. KERMACK.

Conductivity vessels. A. LOTTERMOSER and E. BUCHHOLZ (Z. angew. Chem., 1928, **41**, 1181—1182).—A vessel for carrying out conductivity measurements over long periods comprises a tube with a cylindrical bulb at its lower end; the bulb has two side tubes sealed in the lower half at opposite ends of a diameter, and from these are suspended two platinum wires 20 mm. in length and 0·3 mm. in diam. The whole is made of Jena high-resistance glass and, after filling at the temperature of the experiment, is sealed up. A modified platinum wire dipping electrode for series measurements at 25° is also illustrated and briefly described. A. R. POWELL.

Apparatus for electrolysis with high current densities. E. DUHME and H. GERDIEN.—See B., 1928, 863.

Geochemistry.

Natural gas. K. STOCKFISH (Z. angew. Chem., 1928, **41**, 472—475).—Methods of classifying natural gases are considered. Analyses of such gases are given, and are collected in a table giving the locality of the source, and the quantity of gas evolved in a definite time. A. J. MEE.

Composition of mineral springs in Berg-Cannstatt. I. F. EGGER and K. F. SCHMITT (Jahr. Ver. vaterl. Naturkunde Württemberg, 1927, **83**, 8 pp.; Chem. Zentr., 1928, i, 2593).

Helium. V. Helium content and the age of meteorites. F. PANETH [with H. GEHLEN and P. L. GÜNTHER] (Z. Elektrochem., 1928, **34**, 645—652; cf. this vol., 858, 1341).—The apparatus previously described for measuring minute quantities of helium is modified so that small portions of iron meteorites can be dissolved and small portions of stone meteorites can be fused with a suitable flux in complete absence of air. The ages of some meteorites are calculated from the helium and "radium" contents; a discussion of the results is given. Measurement of the helium content, which varies between very wide limits (*e.g.*, 2×10^{-10} to 2×10^{-5} c.c./g.), reveals differences between meteorites which cannot be detected from the results of other analyses. S. K. TWEEDY.

Florence meteorite of Williamson Co., Texas. J. T. LONSDALE (Amer. Min., 1927, **12**, 398—404).—The meteorite (Jan. 21, 1922), 3640 g., is a breccia-like chondrite, and consists mainly of olivine, enstatite, iron, and ferrous sulphide; metal 17·62, troilite 5·01, rock 77·37%. The metallic portion contains Fe 91·277, Ni 8·270, Co 0·426, Cu 0·009, P 0·018%. CHEMICAL ABSTRACTS.

Hydrothermal paragenesis of quartz and arsenic minerals in altered quartz porphyry from Saubach i. V.; properties of pharmakosiderite and symplesite. F. HEIDE (Z. Krist., 1928, **67**, 33—90; Chem. Zentr., 1928, i, 2591).

Radioactive pyromorphite from Sardinia. P. MISCIATTELLI (Atti R. Accad. Lincei, 1928, [vi], **7**, 929—932).—The feebly radioactive mineral contained: PbO 80·243, P_2O_5 14·640, Cl 2·4, SiO_2 1·06%, As_2O_5 trace. Spectroscopic examination showed the presence of traces of neodymium. R. W. LUNT.

Marmatite and christophite. W. F. DE JONG (Z. Krist., 1928, **66**, 515; Chem. Zentr., 1928, i, 2170).—*X*-Ray examination indicates that these substances are not individuals, but mixed crystals. Christophite, $Zn_{0·66}Fe_{0·34}(+Mn)S$, has a 5·420±0·005 Å.; marmatite, $Zn_{0·73}Fe_{0·27}(+Mn)S$ has a 5·414±0·005 Å.; sphalerite, ZnS, has a 5·395±0·005 Å. A. A. ELDRIDGE.

Structure and constitution of felspars. F. MACHATSCHKI (Zentr. Min. Geol., 1928, **A**, 97—104; Chem. Zentr., 1928, i, 2243—2244).—A discussion. A. A. ELDRIDGE.

Composition of some alkali rocks from the Eastern Arabian desert. E. SCHURMANN (Zentr. Min. Geol., 1928, **A**, 121—124; Chem. Zentr., 1928, i, 2244).

Larsenite and calcium-larsenite, from Franklin, N.J. C. PALACHE, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, **13**, 142—144).—Larsenite, $PbZnSiO_4$, orthorhombic, white, has d 5·90, optically negative, $2V$ about 80°, $\rho>v$ perceptible; α 1·92, β 1·95, γ 1·96, and contains SiO_2 16·87, PbO 56·66, ZnO 22·74, FeO 0·10, MnO 0·14, CaO 2·42, MgO 0·20, H_2O 0·76%. Calcium-larsenite, white, lemon-yellow fluorescence in ultra-violet light, has d 4·421, optically negative, $2V=5°$; α 1·760, β 1·770, γ 1·774, and contains SiO_2 24·10, FeO 0·48, MnO 0·57, CaO 16·36, ZnO 30·61, PbO 27·63, MgO 0·23, H_2O 0·12%. CHEMICAL ABSTRACTS.

Kernite. W. T. SCHALLER (Amer. Min., 1927, **12**, 24—25).—Kernite, $Na_2B_4O_7,4H_2O$, from Kern Co., California, is orthorhombic, H 3, d 1·953, $2V$ nearly 90°, α 1·454, β 1·472, γ 1·488. Analyses of kernite and ulexite are recorded. CHEMICAL ABSTRACTS.

Ammoniojarosite. E. V. SHANNON (Amer. Min., 1927, **12**, 424—426).—Ammoniojarosite, probably uniaxial, negative, ω 1·800, ε 1·750, contained Al_2O_3 0·02, Fe_2O_3 49·30, CaO 0·05, MgO 0·13, Na_2O 0·22,

K_2O 1·56 $(NH_4)_2O$ 4·23, SO_3 34·49, H_2O 9·86, insol. 0·76%. CHEMICAL ABSTRACTS.

Holdenite from Franklin, N.J. C. PALACHE and E. V. SHANNON (Amer. Min., 1927, **12**, 144—148).—Holdenite, $8MnO_2,4ZnO,As_2O_5,5H_2O$, orthorhombic, has $a:b:c=0·3802:1:0·2755$, H 4, d 4·07, optically positive, $2V=30°\ 20'$, α 1·769, β 1·770, γ 1·785. CHEMICAL ABSTRACTS.

Megovernite from Sterling Hill, N.J. C. PALACHE and L. H. BAUER (Amer. Min., 1927, **12**, 373—374).—Megovernite, uniaxial positive, ω 1·754, d 3·719, contained SiO_2 8·92, MnO 42·72, FeO 1·53, MgO 11·27, ZnO 10·22, As_2O_3 4·45, As_2O_5 12·48, H_2O 8·49%. CHEMICAL ABSTRACTS.

Cahnite from Franklin, N. J. C. PALACHE and L. H. BAUER (Amer. Min., 1927, **12**, 149—153).—Cahnite, $4CaO,B_2O_3As_2O_5,4H_2O$, has axial ratio 1 : 0·615, H 3, d 3·156, optically positive, ω 1·662, ε 1·663. The mineral exhibits abnormal interference colours. CHEMICAL ABSTRACTS.

Lyndochite. H. V. ELLSWORTH (Amer. Min., 1927, **12**, 212—218).—Lyndochite, a new mineral of the euxenite–polycrase group from Lyndoch Township, Renfrew Co., Ont., has d 4·909, H 6·5, and contains uranium, thorium, cerium, lanthanum, didymium, yttrium, erbium, zirconium, tantalum, and niobium. The age is computed to be 1100×10^6 years. CHEMICAL ABSTRACTS.

Maberly (Ont.) euxenite. H. V. ELLSWORTH (Amer. Min., 1927, **12**, 365—367).—The mineral contains PbO 1·01, UO_2 7·25, UO_3 1·51, ThO_2 2·64, $(Ce,La,Di)_2O_3$ 0·87, $(Yt,Er)_2O_3$ 24·95, TiO_2 25·04, Ta_2O_5 5·32, Nb_2O_5 22·28%, with smaller amounts of commoner elements. The age is computed to be 870×10^6 years. CHEMICAL ABSTRACTS.

Sphalerite from Mantov, near Cholesov. F. ULRICH and V. VESELY (Vestn. stat. geol. ust. Československ., 1927, **3**, 5 pp.; Chem. Zentr., 1928, i, 2798).—A new analysis does not include fluorine, but corresponds with the formula 9ZnS,FeS. The mineral has d^{18} 4·03. A. A. ELDRIDGE.

Pelargosite from Trementi, Adriatic Sea. E. ONORATO (Bull. Soc. Geol. Ital., 1926, **44**, 17; Chem. Zentr., 1928, i, 2797—2798).—Pelargosite, d 2·834, H 4, n_D 1·529, contained $CaCO_3$ 79·47, $MgCO_3$ 3·13, $SrCO_3$ 2·27, $CaSO_4$ 3·94, Fe_2O_3 0·23, Al_2O_3 0·57, NaCl 3·66, KCl 1·63, SiO_2 0·47, H_2O 2·44, organic material 2·10%. A. A. ELDRIDGE.

Sarkinite from Långban. G. FLINK (Geol. For. Forh., 1924, **46**, 661—670; Chem. Zentr., 1928, i, 2170).—Sarkinite, pink to blood-red, has d 4·173, H 4—5, n' 1·8085, n'' 1·8065, n''' 1·7930, and contains (analysis by ALMSTRÖM) As_2O_5 42·55, MnO 50·60, FeO 0·15, CaO 1·09, MgO 0·29, Na_2O 1·30, H_2O 3·44, Al_2O_3 0·10, insol. 0·14%. A. A. ELDRIDGE.

Weslienite from Långban. G. FLINK (Geol. For. Förh., 1923, **45**, 557—573; Chem. Zentr., 1928, i, 2170).—The mineral has d 4·967, H 6—7, and contains Sb_2O_5 67·37, As_2O_5 trace, FeO 6·56, MnO trace, CaO 17·96, MgO 1·24, K_2O 0·62, Na_2O 5·40, loss on ignition 1·03%. A. A. ELDRIDGE.

Lavas of the volcano Sumaco, Eastern Ecuador, S. America. R. J. COLONY and J. H. SINCLAIR (Amer. J. Sci., 1928, [v], **16**, 299—312).—Analyses and petrographic descriptions are recorded of specimens of lavas of the volcano Sumaco. C. W. GIBBY.

Ajkaite, a Hungarian fossil resin. L. ZECHMEISTER (Mat. term. Ertesito, 1926, **43**, 332—341; Chem. Zentr., 1928, i, 2799).—Ajkaite has d 1·05—1·06, H 2·5, n_D 1·5412. The light yellow and dark brown forms contain, respectively, C 80·38, 79·01; H 11·00, 9·89; O 7·20, 9·61; S 1·42, 1·99%. When heated, the material evolves hydrogen sulphide and then a pungent oil containing oxygen and a small amount of sulphur. A. A. ELDRIDGE.

Organic Chemistry.

Preparation of pure methane and ethane. W. M. KEMULA (Przemysł Chem., 1928, **12**, 411—412).—Methane prepared from aluminium carbide contains hydrogen, unsaturated hydrocarbons, oxygen, nitrogen, ammonia, and hydrogen sulphide, which may be removed by passing the gas through an ignition tube, packed with copper oxide and copper gauze, at the rate of 2 litres per hr. at 360°, and then through potassium hydroxide solution. Ethane produced by the electrolysis of potassium acetate is purified similarly. R. TRUSZKOWSKI.

Oxidation of *n*-hexane. M. BRUNNER and E. K. RIDEAL (J.C.S., 1928, 2824—2825).—Investigation of the rate of oxygen consumption of *n*-hexane–air mixtures in a closed bulb maintained at 210° has shown that the rate of oxygen uptake during the initial period of no pressure change (this vol., 731) is quite rapid, and hence it is considered that the predominating reactions involved in the initial stages of the combustion at low temperatures are (*a*) $C_6H_{14}+O_2\longrightarrow C_6H_{14}O_2$ (active moloxide), (*b*) $C_6H_{14}O_2\longrightarrow 2C_6H_{12}+2H_2O$, (*c*) $C_6H_{12}+O_2\longrightarrow C_6H_{12}O_2\longrightarrow$ decomposition. A. I. VOGEL.

Additive reactions of the ethylenic linking with formation of ethane compounds containing two asymmetric carbon atoms formed during the additive process and the influence of the velocity of reaction on its course. E. OTT [with R. SCHROTER and A. BEHR (Ber., 1928, **61**, [*B*], 2124—2142).—The hydrogenation of the dimethylfumaric and dimethylmaleic acids as sodium salts in aqueous solution and of the stereoisomeric $\beta\gamma$-diphenyl-Δ^β-butenes in various solvents has been examined. The results, compared with those obtained by the addition of halogen or hydroxyl to the ethylenic linking, show an undoubted analogy in the course of all additive reactions, but the process is most obvious in the case of reduction owing to the absence of side reactions. A homogeneous addition is not the rule, but merely the exception which can be attained only by using a rate of reaction defined by the "reaction stage

rule" (cf. A., 1927, 441). In the cases of the acids and the dimethylstilbenes, the *cis*-forms, which are more reactive, have lower m. p., and hence are presumably richer in energy, are much more readily and therefore more speedily hydrogenated than the corresponding *trans*-varieties. Hydrogenation of the *cis*-forms in both cases therefore leads exclusively or predominatingly to the *meso*-forms, which, in each case, are richer in energy.

With the *trans*-compounds it is possible, by suitable choice of conditions of reaction under which addition occurs at a sufficiently slow rate, to convert dimethylfumaric acid exclusively into the racemic form of its additive product and to transform the butene almost entirely into *trans*-dimethylstilbene. With both compounds such an increase in the rate of reaction can be obtained by modifying the experimental conditions that the proportion of *meso*-form of the additive product far exceeds that of the racemic form. It has not been possible to make the *meso*-additive compound the sole product from the *trans*-derivative. The favoured *cis*-addition of hydrogen must doubtless be regarded as a stereochemical regularity, but its existence is merely a consequence of definite energy relationships. The course of the additive process in the case of the ethylenic linking is dependent on the differences in energy of the additive products and of those of the *cis*- and *trans*-initial materials and on the rate of reaction of the additive process. As in the case of the acetylenic linking, the processes are explained solely by considerations of energy, but the explanation is simpler with the triple linking, since a single initial material yields two products with differing energy content.

The preparation of dimethylmaleic anhydride is described in detail. It is isomerised to an equilibrium mixture of sodium dimethyl-maleate and -fumarate in neutral aqueous solution; the change is readily effected in a steel flask at 180° and the established equilibrium is nearly maintained if the flask is cooled rapidly in water. Reduction of sodium dimethylmaleate in the presence of palladised charcoal or nickel, of sodium dimethylfumarate in presence of palladium under varied conditions or nickelised charcoal, and of dimethylfumaric acid by zinc dust and acetic acid is described. *s-l*-Dimethylsuccinic acid forms rhombic crystals, $a:b:c=0{\cdot}5332:1:0{\cdot}4784$.

cis-$\beta\gamma$-*Diphenyl*-Δ^{β}-*butene*, m. p. 66°, is isolated from the products of the action of sulphuric and glacial acetic acids on ββ-diphenylbutan-γ-ol; its reduction in the presence of ether and palladised or nickelised charcoal is described. *trans*-βγ-Diphenyl-Δ^{β}-butene is reduced under very varied conditions. The racemic nature of the liquid variety of diphenylbutane is established by the preparation of the liquid hydrocarbon in its optically active form. For this purpose, phenylmethylcarbinol is resolved by the phthalic acid method and the active modification is transformed into the chloride by thionyl chloride (cf. McKenzie and Clough, J.C.S., 1913, **103**, 687).

α-Chloroethylbenzene is converted by magnesium in absolutely anhydrous ether almost exclusively into the Grignard compound, whereas the action proceeds nearly completely in the direction of hydrocarbon synthesis if a little moist ether is added; the liquid diphenylbutane is mainly produced. If active α-chloroethylbenzene is used, complete racemisation occurs. Treatment of the active chloride with sodium in presence of ether gave an active *diphenylbutane* of opposite sign, the optical homogeneity of which is not established.

The following heats of combustion are recorded: *l*-dimethylsuccinic acid, 4599·2 and 4599·7 g.-cal./g., whereas the values for the corresponding *r*- and *meso*-acids are 4597·5 and 4607·7; *r*-βγ-diphenylbutane 10106 and 10098 g.-cal./g. and *meso*-βγ-diphenylbutane 10098 g.-cal./g. (as liquid). H. Wren.

Relative rates of bromination of the olefines. H. S. Davis (J. Amer. Chem. Soc., 1928, **50**, 2769—2780).—The addition of bromine to olefines in carbon tetrachloride has been followed by colorimetric and titrimetric measurements. In solutions dried with phosphoric oxide, ethylene and bromine react very slowly in the dark. The bimolecular reaction coefficient, K, is not altered by the presence of oxygen or hydrogen bromide, but it may be increased 100—1000 times by adding traces of water or by exposure to sunlight. In the dark, K is increased 20—130 times by cooling the mixture from 25° to 0°. This probably indicates that bromination is effected mainly by a bromine hydrate, the formation of which is favoured by a fall in temperature. The rate of bromination of propylene is also increased by cooling from 25° to 0°, but those of trimethylethylene and di*iso*butylene are not appreciably changed. The following are comparative minimum values of K at 25° for bromination in the dark in carbon tetrachloride dried with phosphoric oxide: ethylene, 0·006; propylene, 0·2; Δ^{α}-butylene, 2·0; Δ^{β}- and *iso*-butylenes, 60·0: trimethylethylene, 250·0; di*iso*butylene, 20·0. Exposure to light increases the rate of bromination in each case, but decreases the differences between the relative rates of bromination. H. E. F. Notton.

Relative rates of absorption of gaseous butylenes into sulphuric acid. H. S. Davis (J. Amer. Chem. Soc., 1928, **50**, 2780—2782).—Calculations based on the work of Michael and Brunel (A., 1909, i, 197) show that the rate of dissolution of a butylene, whether pure or diluted with an inert gas, in sulphuric acid is proportional to the amount remaining undissolved. The following relative rates of dissolution at 28—30° are calculated from the absorption coefficients: Δ^{α}-butylene, 1; Δ^{β}-butylene, 2; *iso*butylene, 280—390. H. E. F. Notton.

Oxidation of hexadecylene. S. Landa (Bull. Soc. chim., 1928, [iv], **43**, 1086—1088).—Hexadecylene, b. p. 152—154°/13 mm., d^{15} 0·7850, $n^{9.9}$ 1·44327, is readily oxidised to pentadecoic acid, b. p. 193—195°/13 mm., m. p. 52—52·5° (ethyl ester, b. p. 172—174°/15 mm.), by agitation with 2 parts of potassium permanganate in warm 1% solution. R. Brightman.

Action of light on acetylene. H. Reinicke.—See this vol., 1340.

Semi-hydrogenation of the acetylenic linking and dependence of the geometrical configuration of the ethylenic compound so formed on the rate of reaction. E. Ott (Ber., 1928, **61**, [*B*], 2119—2123; cf. Ott and Schroeter, A., 1927, 441; Salkind, *ibid.*, 643).—The occurrence of the irregular course of

reaction is regarded as a direct measure of the increase in velocity of reaction. In the hydrogenation of tetramethylbutinenediol, the catalysts may be arranged in the following order of efficiency. The irregular course is observed with palladised charcoal which has not come into contact with oxygen after precipitation of the metal on the carrier, but is not observed after contact with oxygen. Colloidal palladium and nickelised charcoal do not cause irregular hydrogenation even when shielded from oxygen. With spongy platinum the irregularity is particularly marked.

The following heats of combustion are recorded: diphenyldiacetylene, 9769±2 g.-cal./g.; *trans-trans*-diphenylbutadiene, 9841±3; *cis-cis*-diphenylbutadiene, m. p. 70°, 9864±2, *cis-cis*-diphenylbutadiene (liquid), 9970±4. Determination of the heat of combustion of *iso*stilbene prepared by various methods indicates a lack of homogeneity which is not disclosed by chemical analysis or examination of absorption spectrum or refractive index.

[With F. Schurmann.]—*ωω'-Tetramethyl*-p-*xylylene glycol*, m. p. 140°, from magnesium methyl bromide and *p*-diacetylbenzene, and -*tetramethyl*-o-*xylylene glycol*, m. p. 166°, from methyl phthalate and magnesium methyl bromide, are described. H. Wren.

Action of X-rays on chloroform and analogous substances. P. Günther, H. D. von der Horst, and G. Cronheim.—See this vol., 1340.

Production of isomerides in the formation of the double linking by dehydration of substituted alcohols. W. Chalmers (Trans. Roy. Soc. Canada, 1928, [iii], **22**, III, 69—78).—A study of the known cases of dehydration of the secondary alcohols, $CH_2R\cdot CH(OH)\cdot CH_2R'$, shows that the unsaturated compound, $CH_2R\cdot CH:CHR'$ (I), is produced when R=Me, Et, Pr^{β} and R'=$\cdot CH_2Ac$, $\cdot CH_2\cdot CHO$, $\cdot CH_2\cdot OEt$, $\cdot CHMe\cdot CO_2H$, $\cdot CHMe\cdot CHO$. When R=Me or $\cdot CH_2Cl$ and R'=$\cdot CH_2\cdot CO_2H$ or $\cdot CH_2\cdot CN$, the dehydration product is I, but if R=Et, Pr^{β}, Bu^{β}, a mixture of I and $CHR:CH\cdot CH_2R'$ is obtained. From these and other examples it is deduced that in a series of substituted alcohols a hydrogen atom will separate most easily from the following groups in the order given: $\cdot CH_2\cdot CO_2H$ ($\cdot CH_2OEt$, $\cdot CH_2Ac$, $\cdot CH_2\cdot CHO$, $\cdot CH_2\cdot CO_2Me$), [CH_2Cl], Pr^{β}, Bu^{β}, Et, Me. The chloromethyl group appears to be anomalous: in the majority of examples of dehydration of chlorohydrins it occupies the position given. Saytzeff's rule (A., 1876, i, 541) is incapable of foretelling the isomeride produced.

Dehydration of α-chloro-β-methylbutan-β-ol by distillation over anhydrous oxalic acid gives a mixture of α-chloro-β-methyl-Δ^{β}-butene (44%), b. p. 96—97°, d_4^{20} 0·9170, *trans*-β-chloromethyl-Δ^{β}-butene (15%) (II), and 41% of *cis*-β-chloromethyl-Δ^{β}-butene and β-chloromethyl-Δ^{α}-butene. A similar mixture of chloroamylenes and αβ-dichloro-β-methylbutane, b. p. 133—135°, d_4^{20} 1·0785, is produced by the action of phosphorus pentachloride on *as*-methylethylethylene oxide (cf. Sever and Chalmers, A., 1927, 442). Dehydration of *α-chloro-βγ-dimethylbutan-β-ol*, b. p. 162—164°, d_4^{20} 1·049, affords α-chloro-βγ-dimethyl-Δ^{α}-butene (48%), γ-methyl-β-chloromethyl-Δ^{α}-butene (20%), and γ-methyl-α-chloromethyl-Δ^{β}-butene (32%) (III). The proportions of the isomerides in the above mixtures are found by determining the active (chloromethyl) halogen with alcoholic potassium hydroxide solution. When a 15% solution of sodium iodide in acetone is used (cf. Finkelstein, A., 1910, i, 453), II and III do not react, presumably because of some steric hindrance factor.

as-Methyl*iso*propylethylene oxide has b. p. 100—101°, d_4^{20} 1·049. H. Burton.

Preparation of nitro- and chloronitro-olefines. E. Schmidt and G. Rutz (Ber., 1928, **61**, [*B*], 2142—2148).—The preparation of nitro- and chloronitro-olefines is effected by protracted heating of ethereal solutions of the acetyl derivatives of the corresponding chloro- or chloronitro-alcohols with potassium hydrogen carbonate: $R\cdot CH(OAc)\cdot CH_2\cdot NO_2=$ $R\cdot CH:CH\cdot NO_2+AcOH$ and $R\cdot CH(OAc)\cdot CHCl\cdot NO_2=$ $R\cdot CH:CCl\cdot NO_2+AcOH$. With increasing length of the hydrocarbon chain, the tendency of the nitro-olefines towards polymerisation diminishes rapidly and appears less pronounced when the chlorine atom is also present. The presence of the double linking in the αβ-position follows from the difference in properties between nitropropylene and nitroallyl and from the physical properties of the compounds.

The following substances are described (cf. this vol., 504, and previous abstracts): *α-nitro-β-propyl acetate*, b. p. 94—95°/8 mm., d_4^{20} 1·1568, n_D^{20} 1·4242; *α-chloro-α-nitro-β-propyl acetate*, b. p. 90—91°/9 mm., d_4^{20} 1·2773, n_D^{20} 1·4391; *α-nitro-β-butyl acetate*, b. p. 105—106°/11 mm., d_4^{20} 1·1224, n_D^{20} 1·4285; *α-chloro-α-nitrobutan-β-ol*, b. p. 97—98°/9 mm., d_4^{20} 1·2827, n_D^{20} 1·4548, and its *acetate*, b. p. 98—99°/12 mm., d_4^{20} 1·2376, n_D^{20} 1·4429; *α-nitro-β-amyl acetate*, b. p. 111—113°/10 mm., d_4^{20} 1·0898, n_D^{20} 1·4339; *α-nitro-β-octyl acetate*; *α-chloro-α-nitro-octan-β-ol*, b. p. 140°/9 mm., d_4^{20} 1·1174, n_D^{20} 1·4570, and its *acetate*; *α-nitro-Δ^{α}-propene*, b. p. 37°/10 mm., d_4^{20} 1·0661, n_D^{20} 1·4527, and its *polymeride*; *αβ-dibromo-α-nitropropane*, b. p. 97—99°/15 mm., d_4^{20} 2·0303, n_D^{20} 1·5228; *α-chloro-α-nitro-Δ^{α}-propene*, b. p. 51—52°/13 mm., d_4^{20} 1·2840, n_D^{20} 1·4759; *α-nitro-Δ^{α}-butene*, b. p. 55°/12 mm., d_4^{20} 1·0251, n_D^{20} 1·4532; *αβ-dibromo-β-nitrobutane*, b. p. 99—100°/12 mm., d_4^{20} 1·8857, n_D^{20} 1·5181; *α-chloro-α-nitro-Δ^{α}-butene*, b. p. 57—58°/10 mm., d_4^{20} 1·2143, n_D^{20} 1·4728; *α-nitro-Δ^{α}-pentene*, b. p. 69—70°/12 mm., d_4^{20} 0·9952, n_D^{20} 1·4550; *α-nitro-Δ^{α}-octene*, b. p. 112°/9 mm., d_4^{20} 0·9476, n_D^{20} 1·4596; *α-chloro-α-nitro-Δ^{α}-octene*, b. p. 110—111°/9 mm., d_4^{20} 1·0685, n_D^{20} 1·4700. H. Wren.

Nitroso-compounds. J. C. Earl, F. C. Ellsworth, E. C. S. Jones, and J. Kenner (J.C.S., 1928, 2697—2703).—The marked tendency for a nitroso-group to undergo isomerisation to the oximino-form is demonstrated by a review of the literature. In appropriate cases the necessary hydrogen atom can be supplied by a hydroxymethyl group, with elimination of formaldehyde, as in the glycerol synthesis of Piloty and Ruff (A., 1897, i, 453). The authors have extended the work of Schmidt and Wilkendorf (A., 1919, i, 249) and of Wilkendorf and Trénel (A., 1923, i, 288) on α-nitrobutane-βγδ-triol by showing that the sodium salt of β-nitropropane-αγ-diol interacts with

nitrous acid, giving formaldehyde and β-*hydroxyethylnitrolic acid*, m. p. 76—77° (corr. decomp.), identical with the substance formed from β-nitroethyl alcohol. Similarly, ethylnitrolic acid has been prepared from the *sodium* salt of β-nitropropanol and nitrous acid.

Compounds containing one carbonyl group in place of the nitroso-group do not undergo loss of formaldehyde, although the authors consider that the oxidation of pentaerythritol by dilute nitric acid (Rave and Tollens, A., 1893, i, 617) proceeds by such a mechanism. R. J. W. LE FEVRE.

Electrolytic oxidation of alcohols. IV. Propyl alcohol in alkaline solution. S. KOIDZUMI (Mem. Coll. Sci. Kyōtō, 1928, [*A*], **11**, 391—400).—Electrolytic oxidation of methyl alcohol in sodium hydroxide solution at 15—17° at a platinum anode gives a mixture of hydrogen (79—84·5%), oxygen (13·8—19·5%), and carbon monoxide (1·0—2·6%) (cf. Müller, A., 1921, i, 218). After about 27 hrs. the proportion of hydrogen decreases rapidly, carbon monoxide increases, and carbon dioxide is formed also, presumably by oxidation of the aldehyde and acid produced. *n*-Propyl alcohol in aqueous methyl-alcoholic sodium hydroxide solution gives, in addition to hydrogen, ethylene and ethane, an increased amount of the hydrocarbons being obtained at lower temperatures. The production of ethylene is explained $CH_2Me{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow CH_2O+CH_2Me{\cdot} \longrightarrow CH_2{:}CH_2+H^{\cdot}$, and an analogous mechanism is suggested for the production of ethylene during the electrolysis of propionates. H. BURTON.

Configurational relationships of hexan-β-ol and of α-hydroxy-*n*-hexoic acid to lactic acid; relationship of chemical structure to optical activity. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1928, **79**, 475—488).—l-α-*Hydroxy*-n-*hexoic acid*, $[\alpha]_D$ −1·9° (*sodium* salt, $[\alpha]_D^{20}$ +11·8°), gave *ethyl* d-α-*hydroxy*-n-*hexoate*, b. p. 91—93°/17 mm., $[\alpha]_D$ +11·0°, which was reduced to n-*hexane*-αβ-*diol*, $[\alpha]_D$ +10·8° in alcohol (*di*-α-*naphthylcarbamate*, m. p. 155—160°, $[\alpha]_D$ −5·7° in acetic acid). The same glycol, b. p. 110—113°/6 mm., $[\alpha]_D^{22}$ +15·2°, was obtained in larger amount by yeast fermentation of *n*-hexan-α-ol-β-one (prepared through α-*chlorohexan*-β-*ol*, b. p. 74—77°/12 mm., and α-chlorohexan-β-one, b. p. 70°/15 mm.), and was converted into d-α-*bromo*-n-*hexan*-β-*ol*, b. p. 93—95°/17 mm., $[\alpha]_D^{22}$ +2·85°, which was reduced to d-n-*hexan*-β-*ol*, b. p. 135—140°, $[\alpha]_D$ +15·0° in ether (α-*naphthylcarbamate*, m. p. 61—65°, $[\alpha]_D$ +6·3° in alcohol). Δ^{ϵ}-*Hexen*-β-*ol*, b. p. 138—140°, was obtained by the reduction of allylacetone and was resolved through the hydrogen phthalate, thus yielding d-Δ^{ϵ}-*hexen*-β-*ol*, $[\alpha]_D^{25}$ +18·2° in ether (*hydrogen phthalate*, $[\alpha]_D^{25}$ +43·75° in ether). l-Δ^{ϵ}-Hexen-β-ol, $[\alpha]_D$ −14·1° in ether, on reduction with hydrogen and palladium, gave l-n-*hexan*-β-*ol*, b. p. 138—139°, $[\alpha]_D$ −10·8° in ether (α-*naphthylcarbamate*, m. p. 78—81°, $[\alpha]_D$ −10·4° in alcohol); *d*-Δ^{ϵ}-hexen-β-ol, $[\alpha]_D$ +18·2° in ether, when treated with ozone, gave d-γ-*hydroxyvaleric acid*, $[\alpha]_D^{24}$ +10·5° (*barium* salt, $[\alpha]_D$ +3·5°). It follows that *d*-*n*-hexan-β-ol and *l*-α-hydroxy-*n*-hexoic acid are configuratively related to *d*-γ-hydroxyvaleric acid and hence to *d*-lactic acid (A., 1926, 1024). Up to the present this research indicates that in the carbinols the direction of rotation is determined by the distribution of masses around the asymmetric carbon atom (cf. Guye, A., 1890, 722), but that in the hydroxy-acids the effect of polarity outweighs that of mass as a determining factor. C. R. HARINGTON.

Catalytic hydrogenation under reduced pressure. I. Reduction of the methylheptenols. R. ESCOURROU (Bull. Soc. chim., 1928, [iv], **43**, 1101—1115).—A recapitulation of earlier work (A., 1923, i, 740). Under diminished pressure, and preferably in presence of pumice impregnated with platinum oxide (A., 1922, ii, 558), the methylalkylheptenols afford the corresponding heptanols already described. Hydrogenation under ordinary pressure at 180—200° in presence of nickel affords the corresponding saturated hydrocarbons. The following are described: βζ-dimethylheptane, b. p. 133—134°/740 mm., d^{11} 0·7209, n_D^{5} 1·40672; βξ-dimethyloctane, b. p. 158—159°/750 mm., d^{11} 0·7410, n_D^{11} 1·41611; βξη-*trimethyloctane*, b. p. 173—176°/752 mm., $d^{10\cdot7}$ 0·7637, $n_D^{10\cdot7}$ 1·4270; βξ-*dimethylnonane*, b. p. 173—176°/745 mm., n_D^{1} 1·4214, d^{11} 0·7506; βξ-*dimethyldecane*, b. p. 193—196°/752 mm., $d^{10\cdot5}$ 0·7642, $n_D^{10\cdot5}$ 1·42821; βξι-*trimethyldecane*, b. p. 206—208°/745 mm., d^{11} 0·7756, n_D^{11} 1·43362, and the *acetate* of βζ-dimethyloctan-ξ-ol, b. p. 98—100°/15 mm., d^{12} 0·861, n_D^{12} 1·42971. Poisoning of the catalyst may be occasioned by selective absorption of reaction products, particularly in the hydrogenation of nitriles. Reactivation may be effected by extraction with ether and combustion of the remaining impurities in a current of oxygen at 300°. Under diminished pressure the activity of catalyst is reduced and removal of the reaction products from the heated zone facilitated, thus favouring selective hydrogenation. R. BRIGHTMAN.

Preparation of chaulmoogryl alcohol. M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 33—35).—Chaulmoogryl alcohol (40 g.), m. p. 36°, [α] +58·5° in chloroform, iodine value 95·1, was obtained from ethyl chaulmoograte (100 g.) by Prins' method (A., 1923, i, 1172).

CHEMICAL ABSTRACTS.

Catalytic influence of hydrogen ions on the internal dehydration of a *cis*-ethylenic γ-glycol in the presence of water. BOURGUEL and RAMBAUD (Compt. rend., 1928, **187**, 663—666).—The velocity of the dehydration of βε-dimethyl-Δ^{γ}-hexene-βε-diol in acidic media at the ordinary temperature is shown to be a unimolecular reaction approximately proportional to the concentration of hydrogen ions. The reaction is slightly retarded on increasing the concentration of the glycol owing possibly to a weak basic action of the hydroxyl groups. The glycol is stable to alkaline media even at 100°.

G. A. C. GOUGH.

[Synthesis of the diastereoisometric trisubstituted α-glycols.] J. PASCAL (Anal. Fís. Quím., 1928, **26**, 219—221).—Polemical against Tiffeneau and Lévy (A., 1924, i, 825). H. F. GILLBE.

History of ethyl ether. E. DARMSTAEDTER (J. pr. Chem., 1928, [ii], **120**, 74—88).

***iso*Propyl βγ-dibromopropyl ether.** V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1928, **16**, 53—55).—Propyl and *iso*propyl allyl ethers were prepared by boiling the sodium derivatives of the alcohols with allyl iodide. Bromination of *iso*propyl allyl ether in carbon disulphide yielded iso*propyl βγ-dibromopropyl ether*, b. p. 205—207°. R. K. CALLOW.

***n*-Butyl ether as solvent for the Grignard reagent.** C. S. MARVEL, A. T. BLOMQUIST, and L. E. VAUGHN (J. Amer. Chem. Soc., 1928, **50**, 2810—2812).—Under standard conditions of preparation (cf. Gilman, A., 1923, i, 193; ii, 272; 1927, 865) the yields of Grignard reagents in *n*-butyl ether are nearly equal to those obtained in ethyl ether. The resulting solutions are especially useful for reactions which require an elevated temperature for their completion. Thus, *cyclo*hexylcarbinol (60% of the theoretical) is prepared from magnesium *cyclo*hexyl bromide and paraformaldehyde in *n*-butyl ether at 100—110°. H. E. F. NOTTON.

Preparation of neutral sulphuric esters. R. LEVAILLANT (Compt. rend., 1928, **187**, 730—732; cf. this vol., 990).—The action of *n*-propyl alcohol on sulphuryl chloride cooled in a freezing mixture produces a 70% yield of n-*propyl chlorosulphonate*, b. p. 71—72°/22 mm., 44°/4 mm., 1·4214, $d^{19.5}$ 1·2855, which is stable at 0°, but slowly decomposes at the ordinary temperature, and is converted by the slow addition of a slight excess of *n*-propyl nitrite at 70—80° into *n*-propyl sulphate (yield 30—40%). Similarly from glycol monochlorohydrin is obtained β-*chloroethyl chlorosulphonate*, b. p. 101°/23 mm., $n_D^{18.3}$ 1·4587, $d^{18.3}$ 1·555 (yield 70%), which with β-chloroethyl nitrite, b. p. 89·5—90°, $n_D^{20.25}$ 1·4125, 1·212 (with a freshly-prepared sample; the value changes on keeping the sample), yields β-*chloroethyl sulphate*, b. p. 130°/3·5 mm., n_D^{20} 1·4620, d^{20} 1·481 (yield 40%). J. W. BAKER.

Stereochemical studies. XVII. Optical separation and configuration. B. HOLMBERG (Z. physikal. Chem., 1928, **137**, 18—28).—Winther's hypothesis, that two acids derived from the same base must possess analogous configuration, has been investigated by separation of 22 racemic acids by active phenylethylamine. Although certain related groups of acids exhibit definite regularities, the anomalies render the hypothesis a doubtful method of determining configurations. The pairs $d(-)$-lactic acid, $(-)$-α-iodopropionic acid, $l(-)$-malic acid, $(+)$-monochlorosuccinic acid, and $d(+)$-tartaric acid, $(-)$ dichlorosuccinic acid afford evidence for the inclusion, previously suggested by the authors on purely chemical grounds, of the $(-)$-halogeno-propionic and -succinic acids in the α series of the hydroxy-acids. H. F. GILLBE.

Formation of allyl alcohol. Preparation of glycerol formins. R. DELABY and P. DUBOIS (Compt. rend., 1928, **187**, 767—769).—From the product of reaction of glycerol and formic acid under the conditions described by Koehler (A., 1914, i, 133) there were isolated by fractional distillation a glycerol monoformin, b. p. 154—157°/10 mm., d_0^0 1·3052, $n_D^{12.5}$ 1·4614, and a diformin, b. p. 148—149°/15 mm., 1·3209, $n_D^{23.4}$ 1·4492 (cf. Wahl, A., 1925, i, 880). No triformin was separated. By the reaction of sodium formate with glycerol α-chlorohydrin, αγ-dichlorohydrin, and αβ-dibromohydrin, respectively, were prepared the α-monoformin, decomp. 150° in a vacuum (cf. van Romburgh, A., 1882, 378), the αγ-diformin, b. p. 144—146°/11 mm., d_0^0 1·3218, $n_D^{18.3}$ 1·4486, and the αβ-diformin, b. p. 151—153°/17 mm., d_0^0 1·3252, n_D^{14} 1·4503. R. K. CALLOW.

Interaction of bromine with acetic anhydride. IV. Bromination and chlorination compared. H. B. WATSON and E. H. ROBERTS (J.C.S., 1928, 2779—2786; cf. A., 1927, 1168; this vol., 153).—Measurements of the velocity of chlorination of acetic anhydride, acetyl chloride, and acetic acid have been made. The chlorination of acetic anhydride proceeds by two routes involving (*a*) the halogenation of the acid chloride and (*b*) the preliminary enolisation of the anhydride, but the velocity is slower than for bromination. Quinoline, pyridine, and sodium acetate, which inhibit the bromination of acetic anhydride, have little effect on chlorination and a theoretical interpretation of the difference is given. Chlorination of acetyl chloride proceeds more slowly than bromination, but is complicated by side reactions which are rendered imperceptible by the addition of a small quantity of iodine. Chlorination of acetic acid at 100° proceeds similarly to bromination but is slower; the reaction is accelerated by acetyl chloride or hydrogen chloride, but is almost unaffected by sulphuric acid or ferric chloride. A. I. VOGEL.

Polymerisation and condensation. IV. Glycidol acetate. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1928, **79**, 363—376).—Glycidol acetate was heated for 5 days at 132—145° and the product distilled. The fraction 101—125°/0·05 mm. was a mixture of crystals of bimolecular glycidol acetate with a liquid which was chiefly a mixture of acetins, with possibly a higher polymerisation product of glycidol acetate. The fraction 120—130°/0·05 mm. was a viscous liquid again consisting chiefly of a mixture of acetins. The vapours escaping from the main (water-cooled) receiver were condensed in a chilled tube, and yielded a partly crystalline product; it comprised for the most part a polymeride of glycidol acetate together with a small amount of a condensation product. Acetol acetate, after similar treatment, was recovered almost entirely unchanged. C. R. HARINGTON.

Esters of αβ-dibromopropionic acid. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1928, **16**, 49—52).—Methyl, propyl, and iso*propyl* αβ-dibromopropionates were prepared by heating the acid with the appropriate alcohol and sulphuric acid. The iso*propyl* ester has b. p. 212—215°. R. K. CALLOW.

Glycerides of aliphatic acids. A. HEIDUSCHKA and H. SCHUSTER (J. pr. Chem., 1928, [ii], **120**, 145—159).—Triglycerides containing 1, 2, or 3 different aliphatic acid residues have been synthesised by methods which define their constitutions. Mono- and di-glycerides are prepared from the appropriate sodium salts and halogenohydrins (Guth, Z. Biol., 1902, **44**, 83), and the diglycerides converted into triglycerides by interaction with the requisite acid chloride in dry chloroform–pyridine solution, or with

the anhydride; when using unsaturated acid chlorides or anhydrides, the reaction should be carried out in dry carbon dioxide.

Thionyl chloride reacts only with primary alcoholic groups present in the glyceride, and thus serves to differentiate between αβ- and αα′-diglycerides. The wandering of an acyl group (cf. Fischer, A., 1920, i, 808) has been investigated by this means, and under the conditions of reaction αβ-distearin is converted into the αα′-isomeride to the extent of 20%. Thionyl chloride, followed by the appropriate sodium salt, may be used to introduce an acid residue into the α-position in the glyceride molecule, and by suitable combination of this with the above method any triglyceride may be obtained. The m. p. of glycerides are subject to alteration on keeping.

αα′-Dipalmitin, m. p. 72°, prepared from αα′-dichlorohydrin and sodium palmitate, when treated with lauryl chloride in chloroform–pyridine solution for 8—10 hrs. at 45—50° yields *glyceryl β-laurate αα′-dipalmitate*, m. p. 54·6°. From αβ-dipalmitin, m. p. 66·5°, by the action of thionyl chloride *αβ-dipalmitin-α′-chlorohydrin*, m. p. 48·6°, is prepared, which, when heated for 8 hrs. at 150° with sodium palmitate, gives a 65% yield of *glyceryl αβ-dipalmitate α′-laurate*, m. p. 53·5°. αα′-Dimyristin, m. p. 60·5°, heated with excess of palmitic anhydride for 8—10 hrs. at 75—80°/20—25 mm., in an atmosphere of carbon dioxide, yields *glyceryl β-palmitate αα′-dimyristate*, m. p. 49·5°. From αβ-dimyristin, m. p. 58·1°, by treatment with palmityl chloride at 50° for 8 hrs. in chloroform–pyridine solution, *glyceryl α′-palmitate αβ-dimyristate*, m. p. 47·8°, is prepared in 60% yield.

α-Myristin is converted by octoyl chloride, in chloroform–pyridine solution at 50—60° for several hours, into *glyceryl α-octoate α′-myristate* (an oil), which with lauric anhydride ($1\frac{1}{2}$ mols.) at 70—80° for 9 hrs. in carbon dioxide yields *glyceryl α′-octoate β-laurate α-myristate*, m. p. 17·7°, f. p. 3°. α-Chloro-α′-myristin is converted by octoyl chloride under the same conditions into *α-chloro-β-octoyl-α′-myristin*, which when heated for 8 hrs. at 150° with sodium laurate yields *glyceryl β-octoate α-laurate α-myristate*, m. p. 18·8°, f. p. 4·55°. α-Laurin, by successive treatment with octoyl chloride and myristyl chloride in chloroform–pyridine solution, gives a 54% yield of *glyceryl α-octoate α′-laurate β-myristate*, m. p. 14·1°, which closely resembles the product isolated from coconut oil (Bomer, B., 1914, 756). Similarly, α-octoin, by treatment with oleyl chloride in a carbon dioxide atmosphere, followed by myristic anhydride, gives a 60% yield of *glyceryl α-octoate β-myristate α′-oleate*, m. p. 10·5°, f. p. −1°; the isomeric *glyceryl α-octoate α′-myristate β-oleate*, m. p. 15·8°, f. p. 3·5°, is obtained in 35% yield from α-myristin by successive treatment with octoyl chloride and oleyl chloride. α-Chloro-α′-myristin, by treatment with sodium oleate for 8 hrs. at 150° in carbon dioxide, yields 80% of *glyceryl α′-myristate α-oleate*, m. p. 20—23°, which is converted by octoyl chloride in chloroform–pyridine solution into glyceryl β-octoate α′-myristate α-oleate, m. p. 14·8°, f. p. 6·7°, in 67% yield; the glyceride appears to be identical with that isolated from palm-kernel oil (Bomer, B., 1923, 1232). Improved methods for the preparation of α-stearin and αα′-distearin, m. p. 83·5° and 78·5°, respectively, are given. C. W. SHOPPEE.

Synthesis of behenolic acid. R. BHATTACHARYA, S. R. SALETORE, and J. L. SIMONSEN (J.C.S., 1928, 2678—2681; cf. A., 1927, 339).—Methyl decane-ακ-dicarboxylate, b. p. 170°/10 mm., was converted in poor yield into the *hydrogen* ester, m. p. 51°, by partial hydrolysis with cold alkali or by Grün and Wirth's method (A., 1922, i, 805), the potassium salt reduced with sodium and alcohol, and the resulting *hydroxy-acid*, m. p. 78—79° (*magnesium* salt), converted into *methyl λ-bromododecoate*, m. p. about 50°, with hydrogen bromide and methyl alcohol. Decinene, prepared from octyl iodide and sodium acetylide at 180° (cf. Picon, A., 1919, i, 429), b. p. 175—180°/685 mm., 0·799, n_D^{20} 1·44, when condensed in the form of its sodio-derivative with methyl γ-bromododecoate in xylene solution at 160°, resulted in the formation of an oily ester which, when hydrolysed with methyl-alcoholic potassium hydroxide, gave an acid, m. p. 57°, identical in all respects with behenolic acid prepared from erucic acid. A. I. VOGEL.

Synthesis of iododihydrochaulmoogric acid and its ethyl ester. A. L. DEAN, R. WRENSHALL, and G. FUJIMOTO (U.S. Pub. Health Service Bull., 1927, No. 168, 28—30).—*Iododihydrochaulmoogric acid*, m. p. 68—69°, $[\alpha]^{25\cdot5}$ +6·24° in chloroform, acid value 139·8, saponif. value 274·8 (*ethyl* ester, m. p. 35—36°), obtained from chaulmoogric and hydriodic acids, is probably μ-(2- or 3-iodo*cyclo*pentyl)tridecoic acid. CHEMICAL ABSTRACTS.

Condensation of hydroxy-acids by catalysts in the presence of hydrogen at high pressures. V. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 909—912).—α-Hydroxybutyric and α-hydroxy*iso*valeric acids were treated with hydrogen at about 70 atm., in the presence of nickel oxide and alumina as catalysts. With α-hydroxybutyric acid, heating for 7 days at 280—290° gave a 10% yield of methylethylsuccinic, 25% of *n*-butyric, and small amounts of the higher fatty acids. The residual gas contained 35% of methane. α-Hydroxy*iso*valeric acid did not condense under the above conditions. The carboxyl group was eliminated to a great extent since formic acid and carbon dioxide were freely formed as well as considerable quantities of propyl alcohol. M. ZVEGINTZOV.

Condensation of hydroxy- and ketonic acids: β-, γ-, and *tert*.-hydroxy-acids. G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1928, **60**, 913—916).—β-Hydroxybutyric, lævulic, and α-hydroxy*iso*butyric acids were treated with hydrogen by Ipatiev's method (cf. preceding abstract). No dibasic condensation products were obtained. β-Hydroxybutyric acid gives a 33% yield of *n*-butyric acid, together with a number of degradation products—formic and acetic acids and carbon dioxide and a pleasant-smelling oil with a wide boiling range. Lævulic acid is reduced with greater difficulty, owing to the lower temperature (230°) which must be employed. The keto-group is first reduced to the hydroxyl, and the resulting γ-hydroxyvaleric acid is then further reduced to *n*-valeric acid (20% yield). Decomposition

products are also formed. Above 250° the acid is decomposed with evolution of carbon dioxide and methane and the formation of a tarry residue. α-Hydroxy*iso*butyric acid is easily reduced, giving a 60% yield of *iso*butyric acid, together with formic acid, carbon dioxide, and methane.

M. ZVEGINTZOV.

Complex oxalates of quinquevalent molybdenum. H. M. SPITTLE and W. WARDLAW (J.C.S., 1928, 2742—2756).—The three crystalline complex oxalates of quinquevalent molybdenum, $Mo_2O_2(OH)_6(C_2O_4)_2H_2Ba,H_2O$, $Mo_2O_3(OH)_4C_2O_3(OH)_2R_2,2H_2O$ (R=K or NH_4), described by Bailhache (A., 1903, i, 66), are members of a series, $R[MoO_2(C_2O_4),xH_2O]$, where R=K, NH_4, 0·5Ba, etc., and x=1, 1·5, 2·5, or 3·5. When concentrated solutions of the pyridinium and quinolinium derivatives of the series $R_2[MoOCl_5]$ (A., 1927, 1044) are treated with oxalic acid, complex oxalates are obtained. Thus $(C_9H_8N)_2[MoOCl_5],H_2O$ gave *quinolinium molybdenum dioxyoxalate*, $[C_9H_8N)_2[MoO_2(C_2O_4),H_2O]$ (yellowish-brown); $(C_5H_6N)_2[MoOCl_5]$ gave a complex *pyridinium molybdenum oxyoxalate*, $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$ (orange-yellow) which with pyridine passed into $(C_5H_6N)[MoO_2(C_2O_4),C_5H_5N]$; barium chloride and $(NH_4)_2[MoOCl_5]$ gave *barium molybdenum dioxyoxalate*, $Ba[MoO_2(C_2O_4)]_2,5H_2O$ (red), which with (*a*) potassium sulphate yielded the following *potassium molybdenum dioxyoxalates*, $K[MoO_2(C_2O_4),3·5H_2O]$ (yellow crystals), $K[MoO_2(C_2O_4),2·5H_2O]$ (red), $K[MoO_2(C_2O_4),1·5H_2O]$ (yellow powder) and $K[MoO_2(C_2O_4),H_2O]$ (red), or (*b*) ammonium sulphate yielded *ammonium molybdenum dioxyoxalates*, $(NH_4)[MoO_2(C_2O_4),2·5H_2O]$ (orange), $NH_4[MoO_2(C_2O_4),1·5H_2O]$ (yellow powder), $NH_4[MoO_2(C_2O_4),H_2O]$ (red crust), or (*c*) quinolinium sulphate gave *quinolinium molybdenum dioxyoxalate* $(C_9H_8N)[MoO_2(C_2O_4),H_2O]$ (yellowish-brown), or (*d*) pyridinium sulphate gave a normal *pyridinium molybdenum oxyoxalate*, $(C_5H_6N)[MoO_2(C_2O_4),H_2O]$ (chrome-yellow), which on steam distillation in an atmosphere of nitrogen was transformed into the acid *salt*, $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$ (orange-yellow), or (*e*) with dilute sulphuric acid in an atmosphere of nitrogen a pale yellow *oxyoxalate* of quinquevalent molybdenum $[HMoO_2(C_2O_4),1·5H_2O]$ was produced, regarded as the parent acid of the series. Determinations of mol. wts. and molecular conductivities are described and these are in accord with the co-ordination formulæ in dilute solutions, but polymerisation is indicated in concentrated solutions.

A. I. VOGEL.

Oxidation of αβγδ-tetrahydroxyhexoic acids by nitrous acid, and the reduction products of δ-ketorhamnolactone. E. VOTOČEK and L. BENES (Chem. Listy, 1928, **22**, 362—364, 385—391).—δ-Ketorhamnolactone (*p*-nitrophenylhydrazone, m. p. 176°), δ-ketorhodeolactone, and δ-ketofucolactone are prepared by adding a cold aqueous solution of nitrous acid (1 mol.) to the corresponding lactone. δ-Ketorhamnolactone yields on reduction with sodium amalgam a mixture of tetrahydroxyhexoic acids, chiefly *l*-rhamnonic, isolated as lactones. A highly lævorotatory rhamnolactone, $[\alpha]_D$ −99°, previously described by Kiliani (A., 1922, i, 1111) as a lactone of guleonic acid, a supposed stereoisomeride of rhamnonic acid, is found in this mixture, and shown to be a different lactone of the same acid. The phenylhydrazones of the above reaction mixture are separated into rhamnonic phenylhydrazone, m. p. 195—196°, and *gulomethylonic phenylhydrazone*, m. p. 153°, yielding on warming with barium hydroxide *gulomethylolactone*, distinguished from rhamnolactone by its initial and final $[\alpha]_D$, −58·3° and −38·3°, respectively, its indefinite m. p, 103—153°, and by the solubility of its phenylhydrazone in 96% alcohol. This new lactone on reduction yields d-*gulomethylose* (annexed formula), $[\alpha]_D$ −17·1° (*phenylosazone*, m. p. 140—142°).

CHO
HC·OH
HC·OH
OH·CH
HC·OH
CH_3

R. TRUSZKOWSKI.

Water of crystallisation of calcium citrate. F. PERCIABOSCO (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1368; Chem. Zentr., 1928, i, 2171).—Calcium citrate tetrahydrate loses 5·5% of its water at 100° and becomes anhydrous at 138—140°.

A. A. ELDRIDGE.

Nitrile esters of dicarboxyglutaconic acid. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, **3**, 219—226; cf. this vol., 49).—Condensation of ethyl ethoxymethylenecyanoacetate with methyl sodiocyanoacetate in ethyl alcohol yields diethyl αα′-dicyanoglutaconate hemihydrate, but in methyl alcohol the product is *methyl ethyl αα′-dicyanoglutaconate hemihydrate*, m. p. 197° (corr.). This product is also obtained by the condensation of methyl ethoxymethylenecyanoacetate with ethyl sodiocyanoacetate in ethyl alcohol, but when this condensation is carried out in methyl alcohol the product is dimethyl αα′-dicyanoglutaconate hemihydrate. Interchange of alkyl groups must occur when the cyanoacetic ester reacts with the sodium alkoxide, since no such interchange takes place when dimethyl sodiocyanoglutaconate is boiled with ethyl alcohol for 1 hr. By similar replacement condensation, methyl malonate with ethyl ethoxymethylenemalonate in ethyl alcohol yields *methyl triethyl dicarboxyglutaconate*, whilst in methyl alcohol the product is the *dimethyl diethyl* ester. By examination of various free nitrile esters of dicarboxyglutaconic acid and their sodium derivatives of known constitution it is shown that these give a colour with ferric chloride only when the sodium is attached to carbon bearing two carbethoxyl groups, and hence the constitution of the sodium derivative obtained by the action of ethyl ethoxymethylenemalonate on sodiomalononitrile, or of ethoxymethylenemalononitrile on ethyl sodiomalonate, is $C(CN)_2{:}CH·CNa(CO_2Et)_2$, from which the oily, unstable *ethyl γγ-dicyano-Δ^β-propylene-αα-dicarboxylate* is liberated by dilute acids. The alcoholic solution of this ester on keeping yields crystals of ethyl γ-cyano-γ-carbamyl-Δ^β-propylene-αα-dicarboxylate. Similar arguments lead to the structure $C(CN)(CO_2Et){:}CH·CNa(CO_2Et)_2$ for ethyl sodiocyanocarbethoxyglutaconate. Since previous work (this vol., 1216) has shown that the α and γ positions in glutaconic esters are not identical, the formation of the same sodio-derivative by the condensation of methyl (or ethyl) ethoxyethylidenecyanoacetate with ethyl (or methyl) sodiocyanoacetate, respectively, is

explained by the following scheme: $CXY{:}CH{\cdot}OEt+CH_2X'Y'$ (or $CX'Y'{:}CH{\cdot}OEt+CH_2XY$) $\longrightarrow$ $CHXY{\cdot}CH(OEt){\cdot}CHX'Y' \xrightarrow{NaOEt} CXY{:}CH{\cdot}CNaX'Y'$ or $CXY'{:}CH{\cdot}CNaXY$, the hydrogen on the carbon with the smallest number of attached cyano-groups being substituted by sodium, and that on the carbon atom with the larger number of cyano-groups being eliminated with the ethoxy-group as alcohol.

J. W. Baker.

Photochemical studies. I. J. Houben and W. Fischer.—See this vol., 1340.

Oxidation reactions of aldehydes. J. B. Conant and J. G. Aston (J. Amer. Chem. Soc., 1928, 50, 2783—2798; cf. A., 1927, 116).—When $0{\cdot}14M$-aqueous *iso*butaldehyde is oxidised with potassium ferricyanide in slightly alkaline solution at 80° 2 : 2 : 5 : 5-*tetramethyldihydropyrazine* (27·5% of the theoretical), m. p. 83—84°, b. p. 160° (*dinitroso*-derivative, m. p. 208—210°), is formed. In $0{\cdot}28M$-solution, the aldehyde yields, in addition, 3 : 6-*di-cyano*-2 : 2 : 5 : 5-*tetramethylpiperazine*, m. p. 193—194·5° (*dinitroso*-derivative, decomp. 178°), which is also formed from the above dihydropyrazine and aqueous hydrogen cyanide. Quantitative experiments in borate or phosphate buffer solutions show that the nitrogen in these products is derived from part of the ferricyanide, 65% of which is recovered as ferrocyanide and the remainder as ferric hydroxide and formic acid. No *iso*butyric acid is obtained. Methyl *iso*propyl ketone is similarly oxidised to hexamethyl-2 : 5-dihydropyrazine (33% yield) (Gabriel, A., 1911, i, 212), but acetaldehyde yields only indefinite products. Similar reactions, involving oxidation of the β-carbon atom, occur with acid oxidising agents and are favoured by increasing dilution. Thus, *iso*butaldehyde gives with potassium dichromate in $2N$-sulphuric acid at 80° *iso*butyric acid and 20—40% of acetone. *n*-Butaldehyde undergoes β-oxidation under these conditions to a similar extent, liberating carbon dioxide. With ceric sulphate in $2N$-sulphuric acid at 80°, *iso*butaldehyde yields acetone, β-hydroxy-*iso*butaldehyde, carbon dioxide, a trace of a substance, m. p. 166—169°, and 20% of the theoretical of *iso*butyric acid. The same products are obtained in acid solution with permanganate or cobaltic sulphate. Chloranil and palladium-black yield β-hydroxy*iso*butaldehyde but no acetone. Acetaldehyde, when kept in excess, is oxidised by very dilute permanganate at 80° to carbon dioxide (20%) as well as acetic acid. These reactions probably do not involve oxidation of the enolic forms of the aldehydes (cf. Evans and Adkins, A., 1919, i, 572).

H. E. F. Notton

Determination of trioxymethylene. M. E. Alessandrini (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1356—1367; Chem. Zentr., 1928, i, 2191).—The decomposition of the liberated formaldehyde by sodium hydroxide in Orlov's method is avoided by adding exactly the required amount of alkali to the Nessler reagent. Romijn's method can be carried out in a 2% alcoholic potassium hydroxide solution or in a $0{\cdot}1N$-potassium cyanide solution. Romeo's method gives too high results.

A. A. Eldridge.

Polymerides of aliphatic chloroaldehydes. F. D. Chattaway and E. G. Kellett (J.C.S., 1928, 2709—2714).—The interaction of chloral and a large excess of concentrated sulphuric acid at 15—20° gives metachloral as the main product together with about 2% of chloralide (trichloroethylidene trichlorolactate) and about 1% of α-*parachloral*, m. p. 116°, b. p. 223°/760 mm. (capillary tube), and β-*parachloral*, m. p. 152°, b. p. 250° (capillary tube), which are separated by fractional crystallisation from alcohol. The polymerides are trimeric in benzene, not interconvertible, odourless, stable to boiling aqueous alkalis, do not react with phenylhydrazine or potassium cyanide, and dissociate into chloral on distillation under ordinary pressures, but distil unchanged at 15 mm. The isomerism is probably of the *cis–trans* type corresponding with the two possibilities in the paraldehyde ring, one having all the three trichloromethyl residues on the same side of the plane of the ring and the other having two on one side and one on the other (cf. Hantzsch and Oechslin, A., 1907, i, 1009). Paradichloroacetaldehyde does not appear to exist in isomeric forms. Butylchloral hydrate on treatment with not less than 6 parts by weight of concentrated sulphuric acid gave an 80% yield of the two α- and β-*parabutylchlorals*, which were separated by crystallisation from acetic acid. α-*Parabutylchloral* has m. p. 180°, b. p. 235°/760 mm. (capillary tube), and β-*parabutylchloral* has m. p. 157°, b. p. 233°/760 mm. (capillary tube); they are trimeric in benzene and resemble the parachlorals in properties. Butylchloral appears not to form a polymeride of the meta-type; it is unaffected by hydrogen chloride and is converted into a mixture of the two parabutylchlorals by pyridine. Anhydrous butylchloral is best prepared by distillation of the hydrate with about half its weight of acetic anhydride in the absence of moisture or by distillation of the dry polymeride under ordinary pressure (quantitative yield).

A. I. Vogel.

Action of ketones on mercuric iodide in presence of alkali. E. Montignie (Bull. Soc. chim., 1928, [iv], 43, 1115—1117).—When boiled with mercuric iodide and aqueous potassium hydroxide acetone gives a yellow precipitate of a *compound*, $COMe{\cdot}CHMg_3I_2$, decomp. at 180°, insoluble in all solvents and very slowly attacked by warm 30% potassium hydroxide. It is readily decomposed by cold dilute acids, but not by dry hydrogen chloride. Potassium iodide removes mercuric iodide. The following ketones give a similar reaction: methyl ethyl ketone, methylheptenone, acetophenone, benzylacetone, methyl benzyl ketone, *cyclo*hexanone, essence of rue (mixture of methyl heptyl ketone and methyl nonyl ketone), antipyrine, and, in alcoholic solution, benzophenone and benzylideneacetone and in aqueous alcohol, camphor. The reaction is not given by quinones, and it can be utilised for the determination of acetone in urine by adding 0·5 c.c. of phosphoric acid to 100 c.c. of the urine, distilling, and using 25 c.c. of the distillate for the test.

R. Brightman.

Determination of constitution by means of ozone. R. Escourrou (Bull. Soc. chim., 1928, [iv], 43, 1088—1100).—Methylheptenone, obtained by hydrolysis of citral, yields a colourless ozonide which, on decomposition with ice-water, affords acetone and

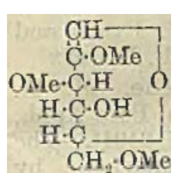
lævulaldehyde (cf. Harries, 1903, i, 605) with a little lævulic acid and probably a polymeride of high b. p. This methylheptenone accordingly has the β-structure, $CMe_2:CH\cdot CH_2\cdot COMe$, only traces of the α-isomeride being present. When similarly treated the methylheptenone obtained as a by-product in the preparation of ψ-ionone gives much formaldehyde, which may be due to the presence of dipentene in the methylheptenone. Proof of the presence of the α-isomeride in this product is afforded by the formation of formaldehyde from the ozonide of the benzylmethylheptenol, b. p. 146—147°/7 mm., obtained from it by means of magnesium benzyl chloride. The presence of impurities containing a terminal $:CH_2$ group vitiates the direct ozonisation of methylheptenone, b. p. 60—61°/10 mm., d^{10} 0·8531, n_D^{11} 1·46195, α_D −45·33°, obtained by fractionation of essence of lemon-grass, but decomposition of the ozonide of inactive *methyl*iso*amylheptenone*, b. p. 120—122°/13 mm., d^{10} 0·8565, n_D^{11} 1·45947, prepared from it affords formaldehyde and a considerable amount of acetone, indicating that the original methylheptenone consists of both α- and β-forms with the latter predominating. The dimethyldecadiene obtained by dehydration of methylbutylheptenol is similarly shown to consist almost entirely of βξ-dimethyl-$\Delta^{\beta\xi}$-decadiene, since its ozonide affords on decomposition acetone, butaldehyde, and lævulaldehyde with only traces of formaldehyde, possibly from βξ-dimethyl-$\Delta^{\alpha\xi}$-decadiene. Quantitative experiments in aqueous acetic acid as solvent confirm the results obtained previously with Java geraniol and citronellol (A., 1925, i, 772). Similarly, limonene, b. p. 175—176°, d^{14} 0·847, n_D^{25} 1·4717, $[\alpha]_D^{17}$ +116·1, is shown to contain about 80% of the limonenic and 12% of the terpinolenic form, the remaining 8% being probably α-terpene. Decomposition of the ozonide gives a small quantity of an insoluble waxy substance, m. p. 88—90°. Analysis of methyl*iso*amylheptenol shows that this product contains 10—11% of the α-form. R. BRIGHTMAN.

Action of alkali and carbon disulphide on xylan. E. HEUSER and G. SCHORSCH (Cellulosechem., 1928, **9**, 109—119; cf. this vol., 1219).—The trustworthiness of two methods for the determination of carbon, (1) oxidation with chromic and phosphoric acids and direct measurement of the volume of carbon dioxide evolved (Berl and Innes, A., 1909, ii, 520), (2) oxidation with an excess of potassium dichromate and sulphuric acid and determination of excess of dichromate by titration, was tested on pure sodium oxalate. In this case the former method gave the better results, but with xylan the results obtained by this method varied by as much as 10% from the theoretical value. Better results (2% error) are obtained, in the case of xylan, by the titration method when the following conditions are fulfilled. The xylan is oxidised with 33·3—66·6% excess of potassium dichromate solution (90 g./litre) in a solution containing 20—25 vol.-% of concentrated sulphuric acid with addition of several drops of mercury, by heating for 3—5 min. After cooling, an excess of ferrous ammonium sulphate solution is added and the excess titrated with 0·1*N*-potassium permanganate solution. J. W. BAKER.

Gasometric determination of reducing sugars. D. D. VAN SLYKE and J. A. HAWKINS (J. Biol. Chem., 1928, **79**, 739—767).—The solution containing sugar is heated with a known amount of potassium ferricyanide in presence of alkali; the excess of ferricyanide remaining is determined by measurement of the nitrogen evolved when it is caused to react with excess of hydrazine in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to blood (0·2 c.c. and upwards), after removal of proteins with tungstic acid, and may be applied directly to diluted urine. In the case of blood from anæsthetised patients, care must be taken to remove all ether by boiling before carrying out the gasometric analysis. C. R. HARINGTON.

Determination of reducing sugars, especially dextrose, in presence of hydrocyanic acid, with alkaline copper solutions. M. HERISSEY and A. CHALMETA (J. Pharm. Chim., 1928, [viii], 8, 393—406).—The presence of hydrocyanic acid in the sugar solution causes a diminution in the weight of copper oxide formed. The losses of copper oxide have been found to be due to (*a*) reaction of the hydrocyanic acid with dextrose according to the Kiliani reaction, (*b*) the formation of small quantities of copper cyanide, (*c*) the formation of soluble sodium copper cyanide. Satisfactory results can be obtained by preliminary removal of the hydrocyanic acid by heat, by a current of air, or by precipitation and removal as silver cyanide, the small excess of silver nitrate necessary for the precipitation being removed with sodium chloride. The end-point in the titration of a sugar solution in presence of hydrocyanic acid with an alkaline copper solution is very indistinct. E. H. SHARPLES.

Oxygen bridges in sugars. IV. Anhydrides of 2 : 3 : 6-trimethylglucose. K. HESS and F. MICHEEL (Annalen, 1928, **466**, 100—114; cf. A., 1927, 1056).—Repetition of the preparation of 2 : 3 : 6-trimethylanhydroglucose previously described (*loc. cit.*) yielded the same product, b. p. 111—113°/0·2 mm., $[\alpha]_D^{18}$ +70·6° in chloroform, contrary to the statement of Freudenberg and Braun (this vol., 399), but the behaviour of the product with pyridine and acetic anhydride and the action of bromine indicate that instead of being a mixture of the strained and unstrained forms of trimethylanhydroglucose in the proportions 75% and 25%, respectively (not 25% and 75% as previously misprinted), it contains the unstrained form and an unsaturated compound, probably (I), which gives an oily *acetyl* derivative, $[\alpha]_D^{18}$ +45·5° in chloroform.



(I.)

An attempt was made to complete an analogous series of reactions with derivatives of 2 : 3 : 6-trimethylglucose containing a butylene oxide ring. 2 : 3 : 6-Trimethylglucose, conveniently prepared in quantity by hydrolysis of trimethylcellulose with methyl-alcoholic sulphuric acid, was converted into a mixture of the α- and β-forms of butylene-oxidic 2 : 3 : 6-trimethylmethylglucoside (cf. Schlubach and Bomhard, A., 1926, 600). The action of benzoyl chloride in pyridine yielded the 5-*benzoyl* derivative, $[\alpha]^{20}$ −35° to −43° in methyl alcohol,

which was converted by hydrogen chloride into butylene-oxidic 1-*chloro*-5-*benzoyl*-2 : 3 : 6-*trimethylglucose*, m. p. 122—123°, $[\alpha]^{19}$ −114·5° in chloroform. Reaction with trimethylamine yielded butylene-oxidic 5-*benzoyl*-2 : 3 : 6-*trimethylglucosidotrimethylammonium chloride*, m. p. 146—149° (decomp.), $[\alpha]_D^{17}$ −60·2° in water (additive *compound* with pyridine hydrochloride, m. p. 102—194°, $[\alpha]_D^{20}$ −48·4° in water). Attempts to prepare an anhydride by the action of alkali yielded only butylene-oxidic 2 : 3 : 6-*trimethylglucosidotrimethylammonium hydroxide*, m. p. 187—188°, $[\alpha]_D^{15}$ −68·3° in water (*chloride*, m. p. 165° $[\alpha]_D^{17}$ −68·4 in water), and decomposition occurred on more vigorous treatment. The unbenzoylated base began to decompose at 180° when heated in a vacuum, without any sign of anhydride formation. Butylene-oxidic 5-*acetyl*-2 : 3 : 6-*trimethylglucosidotrimethylammonium chloride*, $[\alpha]_D^{19}$ −33·9° in water, prepared from the base, could not be converted into an anhydride. Following the conclusion that only one anhydride was formed in the reaction previously described (*loc. cit.*), and assuming that the configuration of the ammonium salt must be favourable to anhydride formation, it follows that the α-configuration must be assigned to both the present compounds and those previously described, but this is in conflict with the evidence of relative rotatory powers. R. K. CALLOW.

Oxygen bridges in sugars. V. Method of determining α- or β-configuration of disaccharides. K. HESS, F. MICHEEL, and O. LITTMANN (Annalen, 1928, **466**, 115—130).—If a disaccharide is hydrolysed by methyl-alcoholic hydrogen chloride, the proportions of α- and β-methylhexosides derived from the hexose present as hexoside may be expected to vary according to the nature of the linking in the original disaccharide, and an excess of one form as compared with the proportion present in the equilibrium mixture may be taken as evidence that the hexoside linking in the disaccharide is of that configuration, assuming that no inversion takes place. In the application of this method to the determination of the configurations of lactose and cellobiose, the fully methylated sugars were used, in order to avoid shifting of the oxygen bridge, and the hydrolysis was performed at 0°, with the addition of sufficient methyl chloride to keep the concentration of acid sensibly constant. The tetramethylmethylhexoside mixture was separated from the mixed sugars after benzoylation by extraction with water and distillation. The equilibrium mixtures were obtained by keeping the tetramethylmethylhexosides under the conditions used in the hydrolysis and working up in a similar way. Both lactose and cellobiose yielded tetramethylmethylhexoside mixtures containing the β-form in larger proportion than the equilibrium mixture, as determined by observations of the rotatory powers of the mixtures and the pure components, and the β-configuration deduced by fermentation methods was thus confirmed.

α-Methylgalactoside, $[\alpha]_D^{20}$ +175·6° in water (as hydrate) (cf. Fischer, A., 1895, i, 437), prepared by passing hydrogen chloride into a solution of galactose in methyl alcohol and keeping, was converted by acetic anhydride in pyridine into 2 : 3 : 4 : 6-*tetra-acetyl-α-methylgalactoside*, m. p. 86—87°, $[\alpha]_D^{20}$ +132·5° in chloroform, which yielded the unchanged α-methylgalactoside on hydrolysis. Methylation of the acetate by methyl sulphate and alkali yielded 2 : 3 : 4 : 6-tetramethyl-α-methylgalactoside, b. p. 80—84°/0·05 mm., $[\alpha]_D$ +188·5° in water (Irvine and Cameron, J.C.S., 1904, **85**, 1078, give +143·4°), and +148·0° in alcohol. *Octamethylcellobiose*, m. p. 86°, $[\alpha]_D^{19.5}$ −15·70° in water, −14·63° in chloroform, was prepared by repeated treatment of hepta-acetylmethylcellobioside with methyl sulphate and sodium hydroxide. The other substances were prepared by known methods.

R. K. CALLOW.

Reactivity of methylated sugars. III. Action of dilute alkali on tetramethyl-*d*-mannose. R. D. GREENE and W. L. LEWIS (J. Amer. Chem. Soc., 1928, **50**, 2813—2825).—Mainly a more accurate repetition of previous work (cf. A., 1927, 751; this vol., 509). The equilibrium solution obtained from mannose in presence of dilute alkali contains mannose (71·7%), dextrose (8·9%), and lævulose (16·9%). At the same alkali concentration, pure tetramethylmannose, m. p. 50·5—51·5°, $[\alpha]_D^{19}$ +23·0° in chloroform (crystallographic data), undergoes 50% conversion into tetramethylglucose. The sugars have been isolated almost quantitatively from the product by fractional crystallisation of their anilides from aniline. Tetramethylmannoseanilide has a variable initial rotation changing to $[\alpha]^{20}$ −8·5° in ethyl alcohol containing a trace of hydrochloric acid, and tetramethylglucose-anilide has $[\alpha]_D^{20}$ +230° changing to +59°.

H. E. F. NOTTON.

Acetylmonosaccharides. V. Rates of hydrolysis of tetra-acetylmethylmannosides and of triacetylmethyl-lyxosides. P. A. LEVENE and M. L. WOLFROM (J. Biol. Chem., 1928, **79**, 471—474).—The α- and β-forms of methylmannoside tetra-acetate and the α-form of methyl-lyxoside triacetate hydrolyse at the same (slow) rate, whilst the γ-forms in both cases hydrolyse rapidly, these three forms corresponding with those described by Fischer and others (A., 1921, i, 96) in the case of the methylrhamnoside triacetates. C. H. HARINGTON.

Periplocymarin and periplogenin. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1928, **79**, 519—530).—Periplocin (cf. Lehmann, A., 1897, i, 626), or extracts of the stems and branches of *Periploca græca*, on treatment with strophanthobiase (cf. A., 1926, 982) yielded a chloroform-soluble glucoside *periplocymarin*, $C_{30}H_{46}O_8$ (also +MeOH), m. p. 148°, $[\alpha]_D^{27}$ +29° in 95% alcohol; when hydrolysed with dilute hydrochloric acid this gave *periplogenin*, $C_{23}H_{34}O_5$, m. p. variable, $[\alpha]_D^{27}$ +31·5° in alcohol (*benzoate*, m. p. 235°); periplogenin is an unsaturated lactone, since on boiling with alkali it neutralises one equivalent, and with hydrogen and palladium it gives the *dihydro*-derivative, m. p. 204°. When treated with methyl-alcoholic sodium hydroxide, periplogenin gave iso*periplogenin*, m. p. 258°, which, with sodium hypobromite, yielded iso*periplogenic acid*, m. p. 215° (with water of crystallisation; *methyl* ester, m. p. 252°), which still contained a lactone group. The chemical behaviour of periplogenin is therefore closely analogous to that of strophanthidin and digitoxigenin.

C. R. HARINGTON.

Polysaccharides. II. Acetylation and methylation of starch. W. N. HAWORTH, E. L. HIRST, and J. I. WEBB (J.C.S., 1928, 2681—2690).—Potato starch, precipitated from its aqueous solution by alcohol, when acetylated in presence of traces of sulphur dioxide and chlorine as catalysts gives triacetylstarch, $[\alpha]_D$ +170° in chloroform, in 96% yield, which is similar to Bergmann and Knehe's triacetylamylose (A., 1927, 342). The regenerated starch produced by deacetylation appears to be identical with amylose. The relationship between amylose and amylopectin is discussed and the views of Samec and Meyer (A., 1921, i, 707) are supported. Methylation of triacetylstarch in acetone solution with methyl sulphate and dilute alkali gave after six methylations an 89% yield of trimethylstarch (44% OMe), m. p. 148°, $[\alpha]_D$ +208° in chloroform, probably identical with Irvine and Macdonald's material (A., 1926, 823) derived from rice and potato starch. Hydrolysis with methyl-alcoholic hydrogen chloride gave an 80% yield of trimethyl-methylglucoside, which on further hydrolysis with 5% aqueous hydrochloric acid gave only βγζ-trimethylglucose (yield 85%). Methylation of triacetylstarch in aqueous solution gave an 80% yield of "dimethylstarch" (OMe 31·8%), $[\alpha]_D$ +143° in chloroform, which is not homogeneous (cf. Irvine and Macdonald), since when hydrolysed it gave a mixture of trimethyl-, dimethyl-, and monomethyl-glucose. A. I. VOGEL.

Polysaccharides. III. Molecular complexity of inulin. H. D. K. DREW and W. N. HAWORTH (J.C.S., 1928, 2690—2697).—Determinations of the mol. wt. of inulin in water by the b.-p. method show a continuous diminution over a period of time, the initial value being about 4000, which fell to about 900. It is considered that the initial mol. wt. of inulin in boiling water is not less than 3200 or 3600 and hence that the polysaccharide is composed of fructofuranose units linked together in chains containing 20—24 such units. The results of Pringsheim, Aronowsky, and Lassmann (A., 1921, i, 545; 1922, i, 634) by the cryoscopic and ebullioscopic methods are criticised. Inulin when treated in aqueous solution by carbon dioxide or when the solid is exposed to ethyl chloroformate vapour, is transformed into a product, termed "inulin lævulin," which is readily soluble in cold water to a clear solution and has a greater specific rotation and greater reducing action towards hot Fehling's solution than inulin itself. This represents the intermediate stage in the hydrolysis of inulin to lævulose. A. I. VOGEL.

Cellulose. XXXII. Characterisation of cellulose preparations by the rotation method. K. HESS and N. LJUBITSCH (Annalen, 1928, **466**, 1—18).—The identity of the rotatory power of cuprammonium solutions of cellulose from different sources and of the course of variation of rotatory power with concentration (cf. A., 1925, i, 1246) is reaffirmed, contrary to the observations of Hägglund and Klingstedt (B., 1928, 119). The exact experimental procedure is now described in greater detail. Repetition of the measurements recorded by Hägglund and Klingstedt, using samples of the same material, showed that when appropriate precautions were taken, including preparation of solutions in absence of air and complete removal of foreign materials from the crude cellulose material, the figures for cotton and pine-wood cellulose agreed closely with those for "standard cellulose" (*loc. cit.*).

In view of the suggestion that foreign materials might influence the values of the rotatory power, the behaviour of mannan and xylan from pine wood (cf. this vol., 1361) was examined. The mannan is completely precipitated as a copper–alkali complex under the standard conditions of the determinations and therefore has only an indirect influence on the figures obtained if it is not removed. In absence of alkali the rotatory power is much less than that of cellulose, but the rotatory power–concentration curve is of the same type. The xylan has a slightly greater rotatory power than cellulose, and the curve is again of the same type. Rotatory powers, but not the course of the curve, may, therefore, be affected by these impurities, and an estimate of their amount may be obtained by measurement of the rotatory power of the crude material. R. K. CALLOW.

Cellulose. XXXIII. Detection of a foreign substance in cellulose fibres. II. K. HESS, F. MICHEEL, and W. REICH (Annalen, 1928, **466**, 73—79; cf. A., 1927, 44).—Further investigation of the nitrogenous, ash-containing, foreign substance in cotton fibres showed that it was destroyed completely by hydrolysis with concentrated hydrochloric acid, partly destroyed by acetolysis with acetic acid and hydrogen bromide, or, to a smaller degree, with acetic anhydride and sulphuric acid. The last process yields an ash-free substance. A similar foreign substance can be isolated from ramie fibres. The substance can be obtained practically free from ash by precipitation of the calcium in aqueous solution by oxalic acid. Treatment of the ash-free substance with calcium hydroxide yields a substance containing 33% of ash. R. K. CALLOW.

Cellulose. XXXIV. Trimethylcellulose. K. HESS, C. TROGUS, and H. FRIESE (Annalen, 1928, **466**, 80—94).—There is no real discrepancy between the results of methylation of cellulose by Hess and Pichlmayr (A., 1927, 44) and by Urban (B., 1926, 531) and Freudenberg and Braun (this vol., 399). A sample of the product obtained by the last-named could be partly dissolved in water with suitable mechanical treatment (shaking with glass beads in water, or keeping in water for several weeks), or after swelling and dissolving in indifferent solvents. The water-soluble fractions in each case had the same rotatory power and *X*-ray diagrams. Such difference as appears to exist at first sight is caused by preservation of the non-cellulosic coating of the fibre due to incomplete purification in the case of the cotton from which "insoluble" trimethylcellulose is prepared. There are, therefore, no grounds for assuming either that an insoluble trimethylcellulose exists or that soluble trimethylcellulose is a disintegration product.

[With H. PICHLMAYR.]—Further details are given of the preparation of crystalline trimethylcellulose. R. K. CALLOW.

Cellulose. XXXV. Crystalline triethylcellulose. II. K. HESS and A. MÜLLER (Annalen, 1928,

466, 94—99; cf. A., 1927, 861).—Triethylcellulose was prepared in 70% yield by repeated treatment of purified cotton with ethyl sulphate and sodium hydroxide, and had the same properties as the material from other sources (*loc. cit.*). Hydrolysis by ethyl-alcoholic hydrogen chloride furnished *triethyl-ethyl-glucoside*, b. p. 120—123°/0·2 mm., $[\alpha]_D^{18}$ +63·37° in water, in 94% yield. Further hydrolysis of the latter yielded triethylglucose. R. K. CALLOW.

Substances accompanying cellulose. III. Isolation of mannan and xylan from pine sulphite pulp. K. HESS and M. LUDTKE (Annalen, 1928, 466, 18—26; cf. this vol., 1360).—Extraction of pine sulphite pulp with 2*N*-sodium hydroxide and addition of acetic acid to the extract yielded a precipitate containing mannan, cellulose, and xylan. The mannan was isolated by precipitating the copper–alkali complex from cuprammonium solution by the addition of sodium hydroxide to a concentration of 0·2*N*. From the solution of the complex in water, made faintly acid with acetic acid, methyl alcohol precipitated crude mannan. After redissolving in cuprammonium solution and two repetitions of the above process, pure mannan was separated, the rotatory power of which was unchanged by further purification, and showed identical properties with mannan *A* from ivory nut (A., 1927, 960). The alkaline cuprammonium solution from which the mannan had been precipitated yielded on neutralisation a precipitate of cellulose. Crude xylan was precipitated from the filtrate by methyl alcohol and purified by precipitation from cuprammonium and aqueous solution. The *xylan* thus obtained differed from that from bamboo (cf. following abstract); it gave no reaction with zinc chloride–iodine, was soluble in water only when freshly precipitated, and had $[\alpha]^{20}$ −87·44° in 2*N*-sodium hydroxide, and $\alpha^{20}_{435\cdot8}$ −4·55° in cuprammonium solution under standard conditions. Xylose, characterised by the osazone and the cadmium bromide compound of xylonic acid, was the only product of hydrolysis. R. K. CALLOW.

Substances accompanying cellulose. IV. Cell membrane of plants. K. HESS and M. LUDTKE (Annalen, 1928, 466, 27—58; cf. this vol., 559).—Bamboo stalks, after disintegration by treatment with chlorine dioxide and sodium sulphite, yielded a fibre containing 70% of cellulose. By extraction of the fibres with sodium hydroxide, precipitation of the extract by methyl alcohol, and purification by precipitation from cuprammonium solution with acetic acid, a *xylan* was isolated, $\alpha^{20}_{435\cdot8}$ −4·85° in cuprammonium solution under standard conditions, coloured violet by zinc chloride–iodine, and yielding only xylose on hydrolysis. Further fractionation from cuprammonium solution gave no evidence of separation. The pentosan content of the fibre was 22·5%, but after removal of long fibres by sieving this rose to 39%, and it is concluded that the xylan is essentially a constituent of the parenchyma. This is confirmed by microscopical observation of corrosion of the fibres by sodium hydroxide and by 12% hydrochloric acid. Cutin was detected in residual epidermal cells after treatment of the fibre with cold 75% sulphuric acid.

A further account is given of the detection of a substance of "furfuroid" nature, not a carbohydrate, present in the primary layer of the bamboo fibre (cf. *loc. cit.*), characterised by a reddish-violet coloration with phloroglucinol and alcoholic hydrochloric acid which appears after 1—2 days. Bamboo fibres swollen in cuprammonium solution assume the appearance of a string of beads. This phenomenon appears to be due to an outer skin on the fibre and crosswise subdivision of the fibre at intervals of 10—30 μ by layers of the above substance. Microscopical observation of the swelling also indicates that the fibre is constructed of concentric layers, probably separated by a substance similar to that which forms the skin, and a lengthwise striation is also visible. It is suggested that the sections of fibre formed in this way yield the "cell-wall units" isolated by Hess and Schultze from the bast-fibres of ramie (A., 1927, 861). Further subdivisions of the cell-wall may exist in the form of actual or potential fibrillæ. The investigations of bamboo fibres confirm the previous conclusion (*loc. cit.*) that lignin is not chemically combined with the cellulose. R. K. CALLOW.

Substances accompanying cellulose. V. Cellulose from young shoots and old heart wood. K. HESS, M. LUDTKE, and H. REIN (Annalen, 1928, 466, 58—72).—The fibre obtained from 14-day-old beech shoots by treatment with chlorine dioxide and sodium sulphite was repeatedly extracted with sodium hydroxide of increasing concentrations. The residue was pure cellulose. The extracts contained no cellulose, but only a xylan and a small amount of a new glucosan. Similar treatment of 385-year-old wood of *Sequoia gigantea* yielded cellulose indistinguishable from the first in rotatory power or viscosity in cuprammonium solution.

[With C. TROGUS.]—The separation of the cellulose from each of the raw materials was followed by observation of the *X*-ray diagrams. In each case the characteristic cellulose interference rings, at first faint, are intensified as the interference by foreign substances decreases. The crystallites appear to be less uniformly oriented in the young shoot. R. K. CALLOW.

True lignin. II. Action of bromine on acetylated pine wood. W. FUCHS and O. HORN (Ber., 1928, 61, [*B*], 2197—2202; cf. this vol., 743).—Dry, acetylated wood is uniformly converted by bromine in carbon tetrachloride in presence of iodine as catalyst with small loss of acetyl groups and slight evolution of hydrogen bromide into *perbromoacetylated wood* I, containing about 6% Br. This somewhat unstable material loses two thirds of its bromine as hydrogen bromide when treated with a solution of alkali acetate, giving *bromoacetylated wood* I, which retains the structure of wood and, after restoration of the removed acetyl, contains 2% Br, 38—39% OAc, and 17% of lignin. Hydrolysis of perbromo- and bromoacetylated wood I with acid gives a lignin preparation having about 11% Br, so that the firmly-bound portion of the halogen, at any rate, must be contained almost exclusively in the lignin component. Bromoacetylated wood I is transformed by bromine into *perbromoacetylated wood* II, which loses three fifths of its bromine as hydrogen bromide under the influence

of alkali acetate, giving *bromoacetylated wood* II containing, after restoration of any removed acetyl, 3·5% Br, 18% of lignin, and 37% OAc. Hydrolysis transforms these products into *bromolignin* II, containing about 18% Br. Bromoacetylated wood II does not absorb bromine. On the basis of the bromine content of the various preparations, the minimum mol. wt. of the lignin present in acetylated wood is calculated to be 690±40.

The simplest explanation of the bromination phenomena is found in the assumption of the presence of a double linking in a tetrahydrobenzene ring which, by a process of exhaustive bromination, passed into a derivative of bromobenzene. H. WREN.

Methoxyl content in the degradation of the lignin and cellulose of wood. R. FALCK and W. COORDT (Ber., 1928, **61**, [*B*], 2101—2106; cf. B., 1927, 213).—Great variations are observed in the methoxyl content of wood, before and after extraction with a mixture of alcohol and benzene and after " corrosion and destruction " in varying degree. The methoxyl content of lignin isolated by Urban's process is about 6% lower than in extracted wood. As " destruction " proceeds the difference sinks to about 3 %, so that, according to methoxyl content, three types of lignin may be distinguished: (1) that in sound, corroded, and feebly destroyed wood, (2) that in greatly destroyed wood, and (3) Urban's lignin. The isolated lignin preparations have suffered change during chemical treatment leading to a minimal loss of about 6% OMe. On the other hand, the lignin obtained by biological degradation of wood by corrosion or the early stages of destruction is primarily unchanged in methoxyl content. When, however, the cellulose is mostly consumed by destruction, the lignin content is lowered but not so strongly as in the isolation of the pure material by chemical means. As far as the methoxyl content is concerned, lignin obtained by the bacterial destruction process is less changed than that prepared by chemical methods. H. WREN.

Nitrogen trichloride and unsaturated hydrocarbons. II. G. H. COLEMAN, G. M. MULLINS, and E. PICKERING (J. Amer. Chem. Soc., 1928, **50**, 2739—2741; cf. A., 1924, i, 131).—Ethylene and nitrogen trichloride in carbon tetrachloride at 20—25° for 2 weeks yield β-chloroethyldichloroamine, which is converted by concentrated hydrochloric acid into β-chloroethylamine (*hydrochloride*, m. p. 104—105°; *benzoyl* derivative). Propylene at −10° gives α-chloro-β-dichloroaminopropane, isolated as *α-chloro-β-propylamine* (*hydrochloride*, m. p. 74—75°; *benzoyl* derivative), which is reduced by sodium amalgam and acid to *iso*propylamine. *iso*Butylene reacts readily, even at −50°, giving *α-chloro-β-amino-β-methylpropane* (*hydrochloride*, m. p. 83—84°; *benzoyl* derivative); Δ^{β}-pentene at 0—10° gives β-(or γ-)*chloro-γ-*(or β-)*amylamine* (*hydrochloride*, m. p. 106—107°; p-*nitrobenzoyl* derivative); and *cyclo*hexene at −19° gives 1-*chloro*-2-cyclo*hexylamine* (*hydrochloride*, m. p. 162—163°; *benzoyl* derivative). The yields of chloroamine are 10—23% of the theoretical.

H. E. F. NOTTON.

Nitrogen trichloride and unsaturated hydrocarbons. III. Nitrogen chloride and diphenylketen. G. H. COLEMAN and A. W. CAMPBELL (J. Amer. Chem. Soc., 1928, **50**, 2754—2757).—Styrene and nitrogen trichloride in carbon tetrachloride at −10° yield nitrogen, ammonium chloride, and a solution which, when treated with hydrogen chloride, gives β-chloro-α-phenylethylamine hydrochloride (benzoyl derivative, m. p. 133—134°; cf. Gabriel and Colman, A., 1914, i, 828). Stilbene is similarly converted into β-chloro-αβ-diphenylethylamine. αα-Diphenyl-, triphenyl-, and tetraphenyl-ethylenes and αα-diphenyl-Δ^{α}-propylene do not give amines under these conditions, nearly all the nitrogen being evolved as such. Diphenylketen reacts rapidly at −10°, probably forming diphenylchloroacetdichloroamide, which is converted by hydrogen chloride into benzophenoneimide hydrochloride. H. E. F. NOTTON.

Cobalt allylamines. W. R. BUCKNALL and W. WARDLAW.—See this vol., 1345.

Attempted resolution of triethylenediaminenickel chloride. W. R. BUCKNALL and W. WARDLAW (J.C.S., 1928, 2739—2742).—*X*-Ray evidence indicates that in salts such as $[Ni,6NH_3]Cl_2$, the units are octahedrally distributed round the nickel atom (Wyckoff, A., 1922, ii, 573), but attempts to confirm this by resolution of *triethylenediaminenickel chloride*, $[Ni\,(en)_3]Cl_2,2H_2O$, prepared from crystallised nickel chloride and ethylenediamine hydrate, by means of tartaric acid and *d*-camphorsulphonic acid (*triethylenediaminenickel tartrate*, $[Ni\,(en)_3](C_4H_4O_6),3H_2O$; *triethylenediaminenickel* d-*camphorsulphonate*, $[Ni\,(en)_3](C_{10}H_{15}O_4S)_2,H_2O$) were unsuccessful.

A. I. VOGEL.

αββ-Trialkylhydroxylamines. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1928, **50**, 2742—2747).—αβ-Dimethylhydroxylamine (this vol., 744) is converted by methyl iodide in ether into its *hydriodide*, m. p. 134°, and *αββ-trimethylhydroxylamine*, b. p. 30° [*hydrochloride*, m. p. 123°; *chloroplatinate*, m. p. 159° (decomp.)], which shows no tendency to isomerise to trimethylamine oxide, and is hydrolysed by hydrochloric acid at 190° to methyl chloride and the decomposition products of ββ-dimethylhydroxylamine, formaldehyde and methylamine. Formaldehyde and dimethylamine cannot be the primary reaction products, since the latter remains unchanged under these conditions. αβ-Diethylhydroxylamine does not react with ethyl iodide, but with methyl iodide it gives *β-methyl-αβ-diethylhydroxylamine*, b. p. 79° (oily *hydrochloride*; *chloroplatinate*, m. p. 158°). Attempts to prepare αββ-triethylhydroxylamine from αβ-diethylhydroxylamine hydrochloride, acetaldehyde, and *iso*propyl alcohol yielded only acetone and ethylamine hydrochloride.

Trimethylhydroxylamine and methyl iodide yield methoxytrimethylammonium iodide, identical with that prepared from trimethylamine oxide (Meisenheimer, A., 1913, i, 595). H. E. F. NOTTON.

Neutral salt additive compounds of *N*-methylated glycines: their formulation and that of their hydrates. W. K. ANSLOW and H. KING (Biochem. J., 1928, **22**, 1253—1263).—The following compounds have been prepared. *Trisarcosine calcium bromide* (anhyd.), *disarcosine calcium iodide trihydrate*, *disarcosine barium iodide dihydrate*, *sarcosine strontium*

chloride tetrahydrate, *sarcosine strontium bromide tetrahydrate*, *sarcosine strontium iodide tetrahydrate*, *trisarcosine potassium chloride pentahydrate*, *N*-dimethylaminoacetic acid hydrochloride and its *chloroaurate*, m. p. 96—98°. the *hydrobromide*, m. p. 158—160°, the *monohydriodide*, m. p. 149°, and the *hemihydriodide* $(C_4H_9O_2N)_2,HI,H_2O$, m. p. 157°, the *calcium chloride tetrahydrate*, *di-(N-dimethylaminoacetic acid) calcium bromide hexahydrate*, $(C_4H_9O_2N)_2,CaBr_2,6H_2O$, *N-dimethylaminoacetic acid calcium iodide*, the *barium chloride tetrahydrate*, the *barium bromide tetrahydrate*, *di-(N-dimethylaminoacetic acid) barium iodide tetrahydrate*, *N-dimethylaminoacetic acid strontium chloride tetrahydrate*, the *strontium bromide tetrahydrate*, *di-(N-dimethylaminoacetic acid) strontium iodide trihydrate*, *N-dimethylaminoacetic acid lithium chloride dihydrate*, the *lithium bromide monohydrate* and *di-(N-dimethylaminoacetic acid) lithium bromide*, the *lithium iodide hexahydrate*, *di-(N-dimethylaminoacetic acid) sodium chloride dihydrate*, *N-dimethylaminoacetic acid sodium bromide monohydrate* and *di-(N-dimethylaminoacetic acid) sodium bromide sesquihydrate*, *N-dimethylaminoacetic sodium iodide trihydrate*, the *potassium iodide sesquihydrate*, *pentabetaine di(calcium iodide) undecahydrate*, $(C_5H_{11}O_2N)_5(CaI_2)_2,11H_2O$, *betaine barium iodide tetrahydrate*, the *strontium chloride tetrahydrate* the *strontium bromide pentahydrate*, the *lithium bromide hydrate*, *dibetaine strontium iodide tetrahydrate*, $(C_5H_{11}O_2N_2)_2,SrI_2,4H_2O$, the *lithium iodide monohydrate*, the *lithium chloride*, *betaine sodium chloride sesquihydrate*, *dibetaine sodium bromide sesquihydrate*, *betaine sodium iodide trihydrate* and the *ammonium iodide dihydrate*. The constitution of the above compounds is discussed from the point of view of electron sharing. S. S. ZILVA.

Hydroxyamino-compounds which show the biuret reaction. IV. Anhydride formation of γ-amino-β-hydroxybutyric acid. M. TOMITA and T. FUKAGAWA (Z. physiol. Chem., 1928, **178**, 302—305).—In an attempt to prepare the free ester of γ-amino-β-hydroxybutyric acid from the ester hydrochloride by the action of the theoretical amount of sodium in methyl alcohol, γ-hydroxy-α-pyrrolidone was obtained. The original acid was regenerated on heating with barium hydroxide.

J. H. BIRKINSHAW.

Solubility of cystine under various conditions. Preparation of cystine. L. OKABE (J. Biochem. Japan, 1928, **8**, 441—457).—The solubility of cystine in salt solutions varies with the concentration and nature of the salt and the hydrogen-ion concentration. The solubility is increased by ammonium sulphate, or sodium chloride or sulphate, decreased by ethyl alcohol, and unaffected by ammonium chloride or acetate.

Dry, washed hair, or fat-free wool (100 g.), is boiled with 20% hydrochloric acid (300—500 c.c.) under reflux for 7—10 hrs., then for 0·5 hr. after stirring with animal charcoal (10—20 g.). The decolorised solution is filtered, evaporated in a vacuum to a thick syrup, dissolved in water (100 c.c.), 90% alcohol (50 c.c.) is added, and sufficient 10% ammonia solution to produce a bluish colour (p_H 4·8). The hydrolysate is cooled for 2 hrs. at 0° and the crystals obtained are filtered by suction. The cystine is purified by decolorising a solution in 10% ammonia with charcoal and adjusting the reaction to p_H 4·8 with 36% acetic acid. CHEMICAL ABSTRACTS.

Zinc chloride–nitroprusside reaction of cysteine. Y. OKUDA and Y. NISHIJIMA (Bul. Sci. Fak. Terkult. Kjusu, 1928, **2**, 209—212).—The addition of zinc chloride in the nitroprusside test for cysteine renders the colour more stable and the reaction more sensitive, the colouring matter being adsorbed on the white precipitate of zinc hydroxide.

CHEMICAL ABSTRACTS.

Aminofibroin. A. MOREL and P. SISLEY (Bull. Soc. chim., 1928, [iv], **43**, 1132—1133).—Diazotised fibroin when reduced with sodium hyposulphite in the dark gives a product containing the same percentage of nitrogen as the original fibroin. This "aminofibroin" (cf. A., 1927, 1212) can also be obtained from Vignon and Sisley's nitrated silk (A., 1891, 1111), and when diazotised gives the same colorations on coupling with phenols and amines as are obtained by the direct diazotisation of fibroin. The affinity of aminofibroin is greater for basic dyes but towards acid and substantive dyes its affinity is unchanged.

R. BRIGHTMAN.

αβ-Unsaturated dinitriles. B. B. CORSON and R. W. STOUGHTON (J. Amer. Chem. Soc., 1928, **50**, 2825—2837).—These have been prepared from aldehydes and malononitrile in presence of piperidine or dilute aqueous alkali (cf. Heuck, A., 1895, i, 651). Some, *e.g.*, ββ-dicyanostyrene and its *m*-nitro- and *o*-chloro-derivatives, have an irritant physiological action. They resemble αβ-unsaturated aldehydes and ketones in that (*a*) with equimolecular proportions of sodium hydrogen sulphite they form sulphonic acids from which they are not regenerated by acids or bases; (*b*) they are readily oxidised to acids by permanganate in acetone; thus, ββ-dicyanostyrene yields benzoic acid; (*c*) they are reconverted into aldehyde and nitrile by acids or alkalis, and (*d*) they combine with hydrogen cyanide to derivatives of αββ-tricyanoethane. These act as weak acids, forming potassium, sodium, and silver salts which are mixtures containing between 1 and 2 equivalents of base. The trinitriles are hydrolysed by boiling acids to succinic acids. The following derivatives of ββ-dicyanostyrene are described: o-*methoxy*-, m. p. 84—84·5°; p-*hydroxy*-, m. p. 188·5—189·5°; m-*nitro*-, m. p. 104·5—105°; 3 : 4-*methylenedioxy*-, m. p. 199—200°; o-*chloro*-, m. p. 95—96°, and 4-*hydroxy*-3-*methoxy*-, m. p. 133·5—134·5°; also cyclo*hexylidenemalononitrile*, m. p. 173·5—174·5°, and the following derivatives of αββ-tricyanoethane: α-*phenyl*-, m. p. 124·5—125°; α-p-*methoxyphenyl*-, m. p. 122—122·5° (*potassium* and *silver* salts); α-o-*methoxyphenyl*-, m. p. 140·5—141°, and 3 : 4-*methylenedioxyphenyl*-, m. p. 153—153·5°. The *potassio*-derivative of αββ-tricyano-α-phenylethane, which may be obtained directly from ββ-dicyanostyrene and potassium cyanide, is converted by methyl iodide into *αββ-tricyano-α-phenylpropane*, m. p. 83—84°, identified by its hydrolysis to α-phenyl-β-methylsuccinic acid (I), m. p. 182—183°. Methyl α-cyanocinnamate is converted by potassium cyanide and acid into *methyl αβ-dicyano-β-phenyl-*

propionate, m. p. 100—101°, the sodio-derivative of which yields with methyl iodide *methyl αβ-dicyano-β-phenyl*iso*butyrate*, m. p. 87—88°. This is hydrolysed by hydrochloric acid to an acid identical with I. *Methyl* p-*methoxyphenylsuccinate*, m. p. 93—94°, is obtained from αββ-tricyano-α-*p*-methoxyphenylethane and alcoholic sulphuric acid. o-*Methoxyphenylsuccinic acid* has m. p. 184—185° (rapid heating).

H. E. F. NOTTON.

Preparation of aliphatic compounds of selenium, tellurium, and arsenic. G. NATTA (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1326—1331; Chem. Zentr., 1928, i, 2245).—Interaction between aluminium or magnesium selenide etc. with alcohols or ethers is employed: $Al_2M_3+3R{\cdot}OH$ (or $3R_2O$)$=Al_2O_3+3MHR$(or $3MR_2$); $2AlM+3R{\cdot}OH=Al_2O_3+MHR_2+MH_2R$; $2AlM+3R_2O=Al_2O_3+2MR_3$; further: $2MHR=MR_2+MH_2$ $MHR_2+2MH_2R=MR_3+MH_3$. Aluminium selenide and telluride react preferably at 250—300° with alcohols, and at 300—350° with ethers; aluminium arsenide reacts with difficulty above 300°, magnesium arsenide more readily. The presence of water in the alcohols and ethers only slightly affects the purity of the products. The following compounds were prepared: diethyl selenide, b. p. about 110°; diethyl diselenide, orange-yellow, b. p. 137°, m. p. −90° to −98°; ethyl hydrogen selenide; di*iso*propyl selenide; *iso*propyl hydrogen selenide, b. p. 70—75°; di*iso*propyl diselenide; dimethyl telluride; ethyl hydrogen telluride; trimethylarsine, b. p. 68—73°; dimethylarsine; black substances, $(CH_3As)_x$ and $(C_2H_5As)_8$; mono-, di-, and tri-ethylarsine. Amines and phosphines were also prepared.

A. A. ELDRIDGE.

Organic arsenic derivatives. Action of alkalis on diethylchloroarsine. E. GRYSZKIEWICZ-TROCHIMOWSKI, M. BUCZWIŃSKI, and J. KWAPISZEWSKI (Rocz. Chem., 1928, 8, 423—431).—Sodium carbonate, hydrogen carbonate, and hydroxide react with diethylchloroarsine to yield a mixture of *diethylarsine oxide*, b. p. 225—230°, *d* 1·2986, triethylarsine (*mercurichloride*, m. p. 163—164°), and ethylarsine oxide.

R. TRUSZKOWSKI.

Compounds from α-glycols with arsenic acid and arsenoacetic acid. B. ENGLUND (J. pr. Chem., 1928, [ii], **120**, 179—184; cf. A., 1927, i, 121).—Arsenic acid and arsenoacetic acid combine with aliphatic dihydroxy-compounds to yield products which are regarded as esters of type I. They are hydrolysed with extreme ease by water, and can be titrated with sodium hydroxide as arsenic acid or arsenoacetic acid, respectively.

$$\left(\begin{matrix}CR_2{\cdot}O\\ |\quad\\ CR_2{\cdot}O\end{matrix}\!>\right)_2 As{\cdot}X \qquad \left|\left(\begin{matrix}CH_2{\cdot}O\\ |\quad\\ CH_2{\cdot}O\end{matrix}\!>\right)_2 As{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CH_2\right|_2$$

(I.) (II.)

By dissolving arsenic acid (1 mol.) in warm ethylene glycol (2 mols.) is obtained *di-ethylene glycol arsenic acid*, [(I); R=H, X=OH], m. p. 120°, bimolecular in bromoform solution; the *pyridine* and *brucine* salts are described. A mixture of di- and tri-ethylene glycol arsenic acids is obtained when 3 mols. of glycol are used, but the triethylene glycol arsenic acid could be isolated only as the *aniline*, *pyridine*, and *brucine* salts. *Di-ethylene glycol arsenoacetic acid* [(I); R=H, $X=CH_2{\cdot}CO_2H$], m. p. 142° (*brucine* salt), is obtained in 60% yield by dissolving arsenoacetic acid in warm ethylene glycol; it is bimolecular in bromoform solution. If the solution of arsenoacetic acid in ethylene glycol be heated for a short time at 100°, only small quantities of *ethylene glycol bis(di-ethylene glycolarseno)acetate* (II), m. p. 130° (decomp.), are obtained, which is not hydrolysed to free arsenoacetic acid by water. The same solution heated at 130° evolves carbon dioxide, and yields *di-ethylene glycol methylarsinic acid* [(I); R=H, X=Me], b. p. 135—136°/15 mm.; at 140° the same product, isolated as the monohydrated *lead* salt of methylarsinic acid by hydrolysis with water and precipitation with lead acetate solution, is produced in 70% yield.

Dipinacolarsenic acid [(I); R=Me, X=OH], m. p. 131° (*pyridine* salt), and *dipinacolarsenoacetic acid* [(I); R=Me, $X=CH_2{\cdot}CO_2H$], m. p. 188° (decomp.), are similarly obtained from pinacol and the appropriate acid in acetone and ethyl-alcoholic solution, respectively. *d*-Tartaric acid, but not *meso*-tartaric acid, heated with arsenoacetic acid for a few minutes in boiling glacial acetic acid solution yields the *substance* $\begin{matrix}CO_2H{\cdot}CH{\cdot}O\\ CO_2H{\cdot}CH{\cdot}O\end{matrix}\!>AsO{\cdot}CH_2{\cdot}CO_2H$, decomp. above 250°.

C. W. SHOPPEE.

Action of fuming sulphuric acid on *cyclo*hexane. V. MENSCHUTKIN and M. WOLF (Neft. Choz., 1927, **13**, 340—342).—By the action of fuming sulphuric acid (25% SO_3; 27 parts) on *cyclo*hexane (1 part), sulphur dioxide and benzenesulphonic acids (up to 70%) are formed, together with some pitch.

CHEMICAL ABSTRACTS.

Conversion of hydroaromatic into aromatic compounds. III. 3 : 5-Dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene and its behaviour with chlorine. L. E. HINKEL and D. H. HEY (J.C.S., 1928, 2786—2791; cf. this vol., 760).—Phenyldihydroresorcinol is converted by phosphorus pentachloride in the presence of dry chloroform into 3 : 5-*dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene*, b. p. 156°/10 mm. (main product) (I), and a small quantity of 3 : 5-dichlorodiphenyl, b. p. 166°/10 mm., m. p. 36°. Chlorination of I at the ordinary temperature affords 3 : 5-dichlorodiphenyl, m. p. 36°, whilst at a higher temperature 2 : 3 : 5-*trichlorodiphenyl*, m. p. 41°, is also formed (the constitution of the latter was confirmed by its synthesis from 3 : 5-dichloro-2-aminodiphenyl), the two chlorodiphenyls being separated by regulated oxidation with chromic acid or through their nitro-derivatives. Nitration of 3 : 5-dichlorodiphenyl gave chiefly 3 : 5-*dichloro*-4′-*nitrodiphenyl*, m. p. 146° (corresponding *amino*-compound, m. p. 124°, and its *acetyl* derivative, m. p. 188°; 3 : 5 : 4′-*trichlorodiphenyl*, m. p. 88°), together with a small quantity of 3 : 5-*dichloro*-2′-*nitrodiphenyl*, m. p. 75° (corresponding *amino*-compound, m. p. 74°, and its *acetyl* derivative, m. p. 163°; 3 : 5 : 2′-*trichlorodiphenyl*, m. p. 58°). Nitration of 2 : 3 : 5-trichlorodiphenyl gave a mono-nitro-compound, regarded as 2 : 3 : 5-*trichloro*-4′-*nitrodiphenyl*.

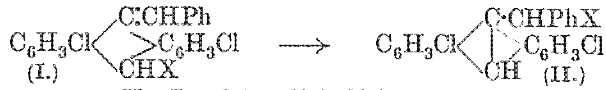
A. I. VOGEL.

Action of silver on diphenyl*tert*.-butylethinylmethyl bromide. P. L. SALZBERG and C. S. MARVEL (J. Amer. Chem. Soc., 1928, **50**, 2840—2844; cf this vol., 988).—*Diphenyl*tert.*-butylethinylcarbinol*, $CMe_3{\cdot}C{:}C{\cdot}CPh_2{\cdot}OH$, m. p. 66·5—67·5°, obtained by the successive addition of magnesium ethyl bromide and benzophenone to *tert*.-butylacetylene, is converted by phosphorus tribromide in light petroleum into the corresponding *bromide*, m. p. 58·5—60·5° (corr.). This is debrominated in an inert atmosphere by "molecular" silver in ether, giving a solution which absorbs only a trace of oxygen and contains a *hydrocarbon*, $C_{38}H_{38}$, m. p. 153·5—155° (corr.), which is stable in alcoholic solution at 100°. In an atmosphere of oxygen, however, the reaction proceeds with vigorous oxidation and a large excess over the amount necessary for the formation of a peroxide is absorbed. Only indefinite products are obtained. The hydrocarbon does not react with 1% sodium amalgam, but with 40% amalgam or with sodium–potassium alloy it gives a coloured metallic derivative, which does not yield the expected acid on treatment with carbon dioxide. It is probably not tetraphenyldi*tert*.-butylethinylethane, but an isomeride formed by its dissociation to diphenyl*tert*.-butylethinylmethyl, and subsequent rearrangement. H. E. F. NOTTON.

Structure of benzene and the alicyclic hydrocarbons. F. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1928, **60**, 871—883).—The structure of benzene, *cyclo*hexane, *cyclo*hexadiene, heptamethylene, *cyclo*octane, and *cyclo*octatetraene is discussed from the point of view of the various structural formulæ proposed. The factors which are supposed to determine the configurations are taken to be (1) equal distances between the atoms constituting the ring, (2) equal angles between all the valency linkings, (3) the tendency of the angles to approach the "normal" angle, 109·5°. The conclusions reached are, that in systems of 5 carbon atoms or less Baeyer's theory holds; with more carbon atoms, several configurations are possible, which form a consecutive series. For C_6H_6, C_6H_8, C_6N_{10}, and C_6H_{12} there exist analogous series of configurations, of which, for benzene, V. Henri's formula is the most stable. C_6H_{12} has the octahedral structure, to which the structures of C_7H_{14} and C_8H_{16} are analogous. C_8H_{12} and C_8H_8 are both hexahedral. The properties of the various compounds are explained from the point of view of the structural formulæ assigned to them. M. ZVEGINTZOV.

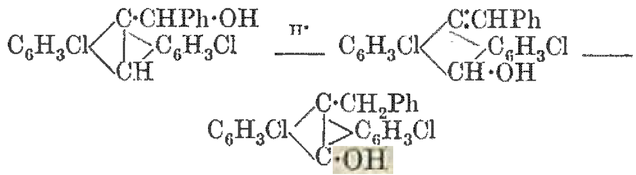
Chlorination of naphthalene in benzene solution. J. TRAUBENBERG and E. WASSERMAN (J. pr. Chem., 1928, [ii], **120**, 177—178; cf. this vol., 627).—α-Chloronaphthalene is obtained in 85% yield by chlorination of naphthalene in cold benzene suspension in the presence of iron. Some naphthalene can be recovered, and if allowance for this be made, the yield is 90%. The benzene is almost entirely unaffected under the above conditions. C. W. SHOPPEE.

Transannular anionotropic migrations. J. W. COOK (J.C.S., 1928, 2798—2810).—Experimental evidence is described which favours structures of type I rather than a bridged formula for the colourless forms of derivatives of 1 : 5-dichloro-9-benzylanthracene, the coloured forms being of type II.



[X=Br, OAc, OH, OMe, OEt.]

The change I ⟶ II is evidently a case of mobile anion tautomerism, since (*a*) the order of mobility of anions (Br>OAc>OH or OR) is identical with that found by Burton and Ingold (this vol., 904) for another system and (*b*) prototropic and anionotropic changes can be effected by the action of hydroxyl and hydrogen ions, respectively :



Thus 1 : 5-dichloro-10-hydroxy-9-benzylidene-9 : 10-dihydroanthracene is converted by boiling with alcoholic sodium hydroxide into 1 : 5-dichloro-9-benzylanthrone. The conversion of a new geometrical (?) isomeride of 1 : 5-dichloro-10-ethoxy-9-benzylidene-9 : 10-dihydroanthracene (cf. Barnett and others, this vol., 52) (from 1 : 5-dichloroethoxyanthrone and magnesium benzyl chloride followed by dehydration of the resulting dihydroanthranol) into the ω-ethoxy-compound by alcoholic hydrogen chloride was slow and incomplete (cf. stereoisomeric hexatrienes, Farmer and others, this vol., 151). Replacement of ethoxyl by bromine gave a monobromo-derivative identical with the monobromination product of 1 : 5-dichloro-9-benzylanthracene. This inversion of geometrical configuration is considered to pass through a form of type II.

Attempts to oxidise compounds of type I to the corresponding anthrones are described. The mobile hydrogen was fixed by replacement by phenyl; thus 1 : 5-dichloro-9-benzyl-10-phenylanthracene gave a reactive *monobromo*-derivative, m. p. 179—180°, but the *hydroxy*-, m. p. 189—191°, and *ethoxy*-, m. p. 173—174°, derivatives (obtained respectively by treatment with aqueous acetone and ethyl alcohol in the presence of calcium carbonate) were of the "yellow" type, which is therefore probably II. 1-*Chloro*-9-*benzylanthracene*, m. p. 119—120° (the corresponding 1-*chloro*-9-*hydroxy*-9-*benzyl*-9 : 10-*dihydroanthracene* has m. p. 126—127°), and 4-*chloro*-9-*benzylanthracene*, m. p. 120°, were prepared from the appropriate chloro-9-anthrones (obtained by reduction of chloroanthraquinones with aluminium and sulphuric acid). The former when brominated gave an unstable dibromide, which decomposed into a mixture of 30% of 1-*chloro*-10-*bromo*-9-*benzylanthracene* (type II), m. p. 160°, and 70% of *benzylidene* compound (IV, type I), m. p. 151—153°.

From IV compounds of types I and II were obtained (X=OH, OAc, or OR). Thus the action of aqueous acetone and calcium carbonate gave 1-*chloro*-10-

hydroxy-9-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 185°, acetylation of which gave 1-*chloro*-10-*acetoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 151—153°. Methyl alcohol in the presence of calcium carbonate gave 1-*chloro*-10-*methoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene*, m. p. 129—130°. The last compound undergoes isomerisation when treated with methyl-alcoholic hydrogen chloride, giving the "yellow" (type II) form, m. p. 135—135°. Similarly, the "yellow" form of the above *acetoxy*-derivative (prepared also by acetylation of the "colourless" hydroxy-compound) has m. p. 157—158°.

4-Chloro-9-benzylanthracene gives an unstable dibromo-derivative leading to (reactive) 4-*chloro*-ω-*bromo*-9-*benzylanthracene*, m. p. 165—166° (ω-*pyridinium bromide*, m. p. 220—225° [decomp.] after sintering at 215°), which passed into type II compounds with ease, aqueous acetone and calcium carbonate giving "yellow" 4-*chloro*-ω-*hydroxy*-9-*benzylanthracene*, m. p. 98—100°, acetylation of which gave 4-*chloro*-ω-*acetoxy*-9-*benzylanthracene*, m. p. 129—130°, whilst methyl and ethyl alcohols in the presence of calcium carbonate gave 4-*chloro*-ω-*methoxy*-9-*benzylanthracene*, m. p. 144° (also formed by methylation of the ω-hydroxy-compound with methyl-alcoholic hydrogen chloride), and 4-*chloro*-ω-*ethoxy*-9-*benzylanthracene*, m. p. 135—137°, respectively. The differences between the 1- and the 4-chloro-derivatives of 9-benzylanthracene are ascribed to steric effects of the α-chlorine atom. The ω-methoxy-compound gave an unstable dibromide which spontaneously decomposed into benzaldehyde and 4-chloro-9-bromoanthracene [identical with the substance, which is incidentally oriented by the present work, obtained by Barnett and Matthews (A., 1924, i, 752) from α-chloroanthracene dibromide]. 4-Chloro-9-bromoanthracene is stable in presence of excess of bromine. 1-Chloro-9-bromoanthracene was not isolated from the product of thermal decomposition of the dibromide of 1-chloro-ω-methoxy-9-benzylanthracene, only 1-chloro-9 : 10-dibromoanthracene being obtained. These results are attributed to the steric effect of the α-chlorine atom on the assumption that bromination is preceded by 9 : 10 addition of bromine.

Only 4-chloro-9-bromoanthracene was isolated from the action of excess of bromine on 1-chloro-10-bromo-9-benzylanthracene. R. J. W. Le Fèvre.

Reactions of stable azides. A. Berthó (J. pr. Chem., 1928, [ii], **120**, 89—118).—A summary of work already published (this vol., 1028, and previous papers), discussed in relation to results obtained by other workers. Organic azides fall into two groups on the ground of purely chemical behaviour: (*a*) containing all azides in which the carbazido-group, $\cdot CO\cdot N_3$, is directly attached to carbon; these are accessible by the Curtius reaction, and (*b*) containing the so-called stable azides, which include all alkyl and aryl azido- compounds, sulphonazides, and those carbazides of which the carbazido-group is attached to nitrogen or oxygen; with a few exceptions, the members of this group are not accessible by the Curtius reaction. The reactions of the stable azides towards aromatic hydrocarbons and bases, towards doubly and triply unsaturated aliphatic compounds (including reactive CH and CH_2 groups), and towards azo-compounds are considered. C. W. Shoppee.

Reduction of aromatic nitro-compounds with sodium alkoxides. C. M. Suter and F. B. Dains (J. Amer. Chem. Soc., 1928, **50**, 2733—2739).—The yields of amines and azoxy-derivatives from benzene suspensions of sodium alkoxides and aromatic nitro- and halogenonitro-derivatives in some 50 experiments are tabulated. The proportion of amine formed is increased by the presence of benzene and by using the higher aliphatic alcohols, which are oxidised mainly to formic acid with traces of acetic acid and acetone. With propyl, butyl, and *iso*amyl alcohols, the yields of amine and azoxy-derivative together total 50—90% of the theoretical. Sodium benzyloxide gives practically no amine, but high yields of azoxy-derivative, being oxidised to benzaldehyde and benzoic acid. Whilst the *m*- and *p*-halogenonitrobenzenes react normally, the *o*-derivatives give with alkoxides of the type $R\cdot CH_2\cdot CH_2\cdot ONa$ anilino-acids instead of azoxy-derivatives. Thus, sodium *n*-propoxide and *o*-chloronitrobenzene afford *o*-chloroaniline (40%) and α-*o*-*chloroanilinopropionic acid* (60%), m. p. 150°, which is also formed from *o*-chloroaniline and α-bromopropionic acid. α-*o*-*Chloroanilinobutyric acid*, m. p. 95°; α-*o*-*chloroanilinoisovaleric acid*, m. p. 75°; α-*o*-*bromoanilinopropionic acid*, m. p. 162—164°; α-*o*-*bromoanilinobutyric acid*, m. p. 83°; α-2 : 5-*dichloroanilinopropionic acid*, m. p. 163°; and α-*o*-*chloroanilinophenylacetic acid*, m. p. 160°, together with varying proportions of *o*-halogenoanilines, are obtained similarly. *o*-Iodonitrobenzene and sodium propoxide give a trace of α-*o*-*iodoanilinopropionic acid*, m. p. 157°, but *o*-nitroanisole gives only *o*-aminoanisole and tarry products. *o*-Chloroaniline and ethyl sulphate yield *o*-*chloro*-N-*ethylaniline*, b. p. 219°/726 mm., d_4^{20} 1·104 (*hydrochloride*, m. p. 138—139°; *phenylurethane*, m. p. 144°). H. E. F. Notton.

Reduction of aromatic mono- and poly-nitro-compounds. K. Brand and A. Modersohn (J. pr. Chem., 1928, [ii], **120**, 160—176).—The reduction of aromatic mono- and poly-nitro-compounds to β-arylhydroxylamines in so-called neutral solution has been investigated, and it is shown that, using aqueous-alcoholic calcium chloride solution and zinc dust, the solution becomes alkaline slowly at the ordinary temperature and more rapidly on heating. The role played by the calcium chloride is obscure, and a scheme is given for the reaction which does not include this substance, but zinc and water only. Zinc dust and ammonium chloride solution react in the absence of a nitro-compound to produce hydroxyl ions, but the concentration of the latter is much lower than that produced by zinc dust, calcium chloride, and a nitro-compound.

On the basis of the above facts it is possible to explain the results of Brand (A., 1906, i, 80), who showed that reduction of *m*-dinitrobenzene with zinc dust and calcium chloride gives, not *m*-nitro-β-phenylhydroxylamine, but *mm'*-dinitroazoxybenzene. Brand and Kowallek (unpublished observation) find that the velocity of combination of *m*-nitronitrosobenzene with *m*-nitro-β-phenylhydroxylamine to yield *mm'*-dinitroazoxybenzene in "neutral" solution is greater than

that of nitrosobenzene with β-phenylhydroxylamine to azoxybenzene, under the same conditions. This difference is due to the acceleration by small hydroxyl-ion concentrations of the velocity of the reactions : $NO_2·C_6H_4·NO+NH(OH)·C_6H_4·NO_2$ —— $NO_2·C_6H_4·NO{:}N·C_6H_4·NO_2$, and $3NO_2·C_6H_4·NH·OH \rightarrow NO_2·C_6H_4·NH_2+NO_2·C_6H_4·NO{:}N·C_6H_4·NO_2$. Since these small hydroxyl-ion concentrations prevail the velocity of formation of *mm'*-dinitroazoxybenzene increases and becomes greater than the reduction velocity of *m*-nitronitrosobenzene to *m*-nitro-β-phenylhydroxylamine and the formation of the azoxy-compound proceeds at the expense of the hydroxylamine. The velocity of formation of azoxybenzene is smaller than that of *mm'*-dinitroazoxybenzene, and although accelerated by increased hydroxyl-ion concentrations, does not overtake the velocity of reduction of nitrosobenzene to β-phenylhydroxylamine; consequently the latter is the main product. By adding traces of acids or acid salts (*e.g.*, potassium hydrogen sulphate) at the commencement of the reaction, the hydroxylamines may be intercepted and preserved, and the formation of azoxy-compounds checked.

Owing to the lower concentration of hydroxyl ions produced, the use of zinc dust and ammonium chloride is preferable to that of zinc and calcium chloride for the general preparation of β-arylhydroxylamines; by adding traces of acids (acetic acid is recommended) hydroxylamines sensitive to very small hydroxyl-ion concentrations are readily obtained. The preparation of the following is described : *m*-nitro-β-phenylhydroxylamine, m. p. 118° (yield 58%); 2-nitro-6-hydroxylaminotoluene, m. p. 120—121° (yield 68%); 2-nitro-4-hydroxylaminotoluene, m. p. 108—109° (cf. lit.) (yield 50%); 2-nitro-4-hydroxylaminoanisole, m. p. 129°; 2 : 6-dinitro-4-hydroxylaminotoluene, m. p. 143—144°. C. W. SHOPPEE.

Diphenyl series. VIII. Derivatives of 2- and 4-aminodiphenyl. F. BELL (J.C.S., 1928, 2770—2779).—2-p-*Toluenesulphonamidodiphenyl*, m. p. 99°, gives when nitrated successively 5-*nitro*-, m. p. 169°, and 3 : 5-*dinitro*-2-p-*toluenesulphonamidodiphenyl*, m. p. 186° (3 : 5-*dinitro*-2-*aminodiphenyl* has m. p. 182°), and on methylation 2-p-*toluenesulphonmethylamidodiphenyl*, m. p. 136°. Similarly, 4'-*nitro*-2-p-*toluenesulphonamidodiphenyl*, m. p. 163°, when gently nitrated gives 3 : 5 : 4'-*trinitro*-2-p-*toluenesulphonamidodiphenyl*, m. p. 190° (3 : 5 : 4'-*trinitro*-2-*aminodiphenyl* has m. p. 229°). 2-Acetamidodiphenyl with nitric and acetic acids gives mainly 5-*nitro*-2-*acetamidodiphenyl*, m. p. 133° (5-*nitro*-2-*aminodiphenyl*, m. p. 125°), which when further nitrated gives only 5 : 4'-dinitro-2-acetamidodiphenyl. 4-*p*-Toluenesulphonamidodiphenyl easily gives 3 : 5-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 189°, hydrolysed to 3 : 5-*dinitro*-4-*aminodiphenyl*, m. p. 177° (*acetyl* derivative, m. p. 146°; N-*methyl* derivative, m. p. 144°; 3 : 5-*dinitro*-4-*acetmethylamidodiphenyl*, m. p. 149°), different from the dinitro-base of Fichter and Sulzberger (A., 1904, i, 325). 2-*p*-Toluenesulphonmethylamidodiphenyl gives 5-*nitro*-2-p-*toluenesulphonmethylamidodiphenyl*, m. p. 152° (also formed by direct methylation of 5-nitro-2-*p*-toluenesulphonamidodiphenyl). Experimental details for the preparation of *p*-nitrobenzenesulphonyl chloride from *p*-chloronitrobenzene are given. The following *p*-nitrobenzenesulphonates are described : *ethyl*, m. p. 91°, *menthyl*, m. p. 72°, *phenyl*, m. p. 114°, m-*nitrophenyl*, m. p. 133°, p-*nitrophenyl*, m. p. 156°, p-*tolyl*, m. p. 106°, 3-*nitro*-p-*tolyl*, m. p. 136°, and 2-*nitro*-p-*tolyl*, m. p. 116°. *p*-Tolyl *p*-nitrobenzenesulphonate and p-*nitrobenzenesulphon*-p-*toluidide*, m. p. 179—180°, give when nitrated 2-nitro-*p*-tolyl *p*-nitrobenzenesulphonate and p-*nitrobenzenesulphon*-3 : 5-*dinitro*-p-*toluidide*, m. p. 185°, respectively. Phenyl *p*-nitrobenzenesulphonate gives *p*-nitrophenyl *p*-nitrobenzenesulphonate (above).

2-Aminodiphenyl readily gives 5-*acetoxymercuri*-2-*acetamidodiphenyl*, m. p. 200°, which yields 5-bromo-2-acetamidodiphenyl with bromine in acetic acid. 4-Aminodiphenyl gives a *monomercuri*-derivative, $C_6H_3Ph<^{NH}_{Hg}$ (?), m. p. 167°, which by warming with acetic acid forms 3-*acetoxymercuri*-4-*acetamidodiphenyl*, m. p. 205°. Treatment with bromine in acetic acid gives 3 : 4'-dibromo-4-acetamidodiphenyl. 3-Bromo-4-hydroxydiphenyl gives a *monomercuri*-derivative, m. p. 235°, which similarly yields 3 : 5 : 4'-tribromo-4-hydroxydiphenyl. The preparation of 3-*acetoxymercuriaceto*-p-*toluidide*, m. p. 178°, by direct mercuration and by acetylation of acetoxymercuri-*p*-toluidine is described (cf. Schrauth and Schoeller, A., 1910, i, 459).

Bromination of 4-*p*-toluenesulphonamidodiphenyl gives only poor yields of 3-*bromo*-4-p-*toluenesulphonamidodiphenyl*, m. p. 119°.

2-Aminodiphenyl when diazotised and treated with copper powder gives no diphenylene, only 2-chlorodiphenyl and 2-azodiphenyl being formed.

R. J. W. LE FÈVRE.

Absorption spectra and constitution of azoxy-compounds. L. SZEGO (Ber., 1928, 61, [B], 2087—2091).—The absorption spectra of the α- and β-forms of *p*-bromo-, *p*-nitro-, and *p'*-bromo-*p*-nitroazoxybenzene, *p*-hydroxyazoxybenzene and its methyl and ethyl ethers, and of 5-hydroxy-2-methylazoxybenzene have been investigated. All the compounds exhibit a fairly well-defined band with an absorption maximum between 3600 and 3250 Å. A similar band is shown by azoxybenzene. The absorption spectra of all the isomeric hydroxy-substituted compounds and of *p'*-bromo-*p*-nitroazoxybenzene are markedly different, whilst those of *p*-bromo- and *p*-nitro-azoxybenzene are almost identical, probably because the entry of a halogen as substituent into the benzene nucleus is generally without influence on the optical character of compounds. The relationships for the nitro-group are obviously similar. In general, the results are in harmony with the behaviour expected for the isomerides on the basis of Angeli's formulation. In addition to the band characteristic of all azoxy-derivatives, all the α-forms exhibit a second band in the neighbourhood of 2600—2500 Å., which is not shown by the β-varieties. α-5-Hydroxy-2-methylazoxybenzene has a third maximum which does not occur with the corresponding β-compound. In explanation, it is assumed that the oxygen atom of the azoxy-group is attached by residual valencies to the neighbouring nucleus. H. WREN.

Azopicric acid [2 : 4 : 6 : 2′ : 4′ : 6′-Hexanitro-5 : 5′-dihydroxyazobenzene]. K. Elbs and O. H. Schaaf (J. pr. Chem., 1928, [ii], **120**, 1—35; cf. A., 1924, i, 255).—The methyl and ethyl ethers of azopicric acid could not be obtained from it directly, but only by nitration of the corresponding ethers of *m*-azophenol. When recrystallised they become deep red, possibly owing to a change into the *aci*-nitro-form. Reduction of azopicric acid to an analogue of picramic acid does not occur, a phenylbenztriazole derivative being formed. Azopicric acid is decomposed by alkalis, sodium and potassium carbonates yielding nitrohydroxylaminophloroglucinol derivatives. The absorption of light by azopicric acid and related compounds was investigated.

Azopicric acid and its ethers are most readily prepared from *m*-nitroaniline, which is diazotised and converted into *m*-nitrophenol. This could not be directly reduced to azophenol, but reduction of the methyl ether by zinc dust and aqueous-alcoholic sodium hydroxide in two stages yielded successively 3 : 3′-dimethoxyazoxybenzene, m. p. 49°, and 3 : 3′-*dimethoxyazobenzene*, m. p. 76—77°, and from the ethyl ether were obtained 3 : 3′-*diethoxyazoxybenzene*, m. p. 75—76°, and 3 : 3′-diethoxyazobenzene, m. p. 90° (*hydrazo*-compound, m. p. 78—80°). Nitration of the azo-compounds in sulphuric acid containing potassium nitrate, to which fuming sulphuric acid was added, yielded, on pouring into water, yellow products, which gave on recrystallisation 2 : 4 : 6 : 2′ : 4′ : 6′-*hexanitro*-5 : 5′-*dimethoxy*-, red, m. p. 127°, and -5 : 5′-*diethoxy-azobenzene*, m. p. 138—139°, respectively. These compounds gave no evidence of formation of additive compounds with aromatic hydrocarbons. They were hydrolysed to azopicric acid by boiling with water or 25% aqueous alcohol containing a trace of hydrochloric acid.

Reduction of azopicric acid by sodium hydrogen sulphide in amount corresponding with 4 mols. of hydrogen yielded 5 : 7 : 2′ : 4′ : 6′-*pentanitro*-4 : 3′-*dihydroxy*-2-*phenylbenztriazole*, m. p. 176—180° (decomp.). Excess of reducing agent yielded amorphous materials which appeared to contain amino-derivatives of the benztriazole.

The action of aqueous alkali hydroxides on azopicric acid yielded tarry products. Neutralisation of the warm aqueous solution by potassium carbonate solution yielded the potassium salt, and from the filtrate on further addition of potassium carbonate and acidification a *substance*, m. p. 110°, and trinitrophloroglucinol, m. p. 157—158°, were obtained. The action of more concentrated potassium carbonate solution at a higher temperature yielded, with evolution of nitrogen, a product, red in acid and yellow in alkaline solution, from which was separated (?)*mononitrodihydroxylaminophloroglucinol*, m. p. 166°, and (?)*dinitrohydroxylaminophloroglucinol*, m. p. 146—148°. The formation of these products is supposed to take place analogously to the formation of trinitrophloroglucinol from *s*-tribromotrinitrobenzene and sodium carbonate.

The absorption spectra and extinction curves of azopicric acid, *m*-azophenol, and picric acid are similar, apart from the considerable displacement of absorption towards the red shown by azopicric acid, and demonstrate their constitutional relationship. R. K. Callow.

Substantive dyes derived from 2 : 7-diaminofluorene. A. Novelli and C. Ruiz (Anal. Asoc. Quim. Argentina, 1928, **16**, 56—64).—Diazotised 2 : 7-diaminofluorene couples with α-naphthylamine-4-sulphonic acid to give the *disazo-dye*, analogous to Congo-red. The free acid is blue, and the *sodium* salt, m. p. above 300°, red, dyeing wool, cotton, and silk in red shades not fast to alkali. The constitution was confirmed by reduction. The analogous *disazo-dye* obtained by coupling with α-naphthol-4-sulphonic acid, violet, dyeing cotton violet, was not obtained pure. The existence of these dyes supports the analogy between fluorene and 2 : 2′-substituted diphenyl derivatives. R. K. Callow.

Manufacture of azo dyes [and new dichloro-*p*-xylidines]. I. G. Farbenind. A.-G.—See B., 1928, 849.

Interaction of chloral and 2 : 4 : 6-trihalogen-substituted phenylhydrazines. F. D. Chattaway and F. G. Daldy (J.C.S., 1928, 2756—2762).—Chloral condenses smoothly in glacial acetic acid with 2 : 4 : 6-trichlorophenylhydrazine, giving an unstable hydrazone which rapidly passes into *αα-dichloro-β*-2 : 4 : 6-*trichlorobenzeneazoethylene* (I), m. p. 54°, evidently by reversible loss of hydrogen chloride, since treatment of this product with hydrogen chloride and hot acetic anhydride gives *chloral-α-acetyl*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 144°. The compound I in acetic acid gives with chlorine in the cold *chloral-ω-chloro*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 104°, which when heated at the b. p. of the solvent gives *ααβ-trichloro-β*-2 : 4 : 6-*trichlorobenzeneazoethylene*, m. p. 75°. The analogous *αα-dichloro-α-bromo-β*-2 : 4 : 6-*trichlorobenzeneazoethylene* has m. p. 108·5°.

The compound I is converted by hot hydrogen chloride and acetic acid into *glyoxylic acid* 2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 167° (decomp.) (or by hot hydrogen chloride and ethyl alcohol into *ethyl glyoxylate* 2 : 4 : 6-*trichlorophenylhydrazone* [II], m. p. 97·5°), also prepared directly from glyoxylic acid and trichlorophenylhydrazine. The ester II gives (*a*) with hot acetic anhydride *ethyl glyoxylate α-acetyl*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 112·5°; (*b*) with chlorine in acetic acid *ethyl glyoxylate ω-chloro*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 73·5° (also formed by long boiling of ααβ-trichloro-β-2 : 4 : 6-trichlorobenzeneazoethylene in alcohol); (*c*) with bromine in acetic acid, *ethyl glyoxylate ω-bromo*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 75°. Chlorination of glyoxylic acid 2 : 4 : 6-trichlorophenylhydrazone in acetic acid gives *glyoxylic acid ω-chloro*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 151·5° (decomp.).

Diazotised 2 : 4 : 6-trichloroaniline and ethyl acetoacetate give *ethyl* 2 : 4 : 6-*trichlorobenzeneazoacetoacetate*, m. p. 94·5°, which by chlorination (bromination) in acetic acid gives ethyl glyoxylate ω-chloro-(bromo)-2 : 4 : 6-trichlorophenylhydrazone.

A similar series of reactions with 2 : 4 : 6-tribromophenylhydrazine gave rise to the following new compounds: *αα-dichloro-β*-2 : 4 : 6-*tribromobenzene-azoethylene*, m. p. 92°; *ααβ-trichloro-β*-2 : 4 : 6-*tri-*

bromobenzeneazoethylene, m. p. 105°; *αα-dichloro-β-bromo-β-2 : 4 : 6-tribromobenzeneazoethylene*, m. p. 115°; *glyoxylic acid 2 : 4 : 6-tribromophenylhydrazone*, m. p. 170·5° (decomp.); *ethyl glyoxylate 2 : 4 : 6-tribromophenylhydrazone*, m. p. 126°; *ethyl glyoxylate α-acetyl-2 : 4 : 6-tribromophenylhydrazone*, m. p. 133·5°; *ethyl glyoxylate ω-chloro-2 : 4 : 6-tribromophenylhydrazone*, m. p. 108·5°; *ethyl glyoxylate ω-bromo-2 : 4 : 6-tribromophenylhydrazone*, m. p. 102·5°; and *ethyl 2 : 4 : 6-tribromobenzeneazoacetoacetate*, m. p. 96·5°.

R. J. W. Le Fèvre.

Absorption spectra and constitution of diazotates. L. Cambi and L. Szego (Ber., 1928, 61, [*B*], 2081—2086; cf. A., 1927, 1063).—Observation of the absorption spectra of the compounds [PhN(O):N]K, [C_6H_4Cl·N(O):N]K, [C_6H_4Br·N(O):N]K, [PhN:N·O]K, [C_6H_4Cl·N:N·O]K, and [C_6H_4Br·N:N·O]K shows the absence of an ultra-violet absorption band in the spectrum of all normal salts (and in the normal diazotate of sulphanilic acid), whereas all the *iso*-compounds exhibit a distinct band. It follows therefore that the normal and *iso*diazotates cannot possibly be stereoisomerides. Examination of the curves of the compounds [PhN(:O):NO]Na, [C_6H_4Cl·N(:O):NO]Na, [C_6H_4Br·N(:O):NO]Na, [PhN:N(:O)·O]Na, [C_6H_4Cl·N:N(:O)·O]Na, and [C_6H_4Br·N:N(:O)·O]Na proves that the nitrosoarylhydroxylamines and nitroamines have a maximal absorption in the ultra-violet between 2900 and 2800 Å., whilst the latter compounds have small extinction coefficients. The compounds are distinct optically from the normal diazohydrates. From purely formal considerations, a similarity would be expected between the *iso*diazotates and the nitroamines which is actually observed, but a correspondence between the normal diazotates and nitrosohydroxylamines does not exist, probably because the anion of the normal diazotates has nothing in common with the nitrosoarylhydroxylamines. The *iso*diazohydrates, nitrosoarylhydroxylamines, and nitroamines have the chain $-C_6H_4$·N:N·O−, which may be regarded as responsible for the band. On the other hand, the structure of the normal diazohydrates, $-C_6H_4$·N(:N)·O− or $-C_6H_4$·N(:O):N−, in which the central nitrogen atom has the nitro-character is totally different. The optical behaviour of the normal diazohydrates is quite distinct from that of the diazonium compounds, all of which show a characteristic band in the ultra-violet. This is explained by the hypothesis that the central nitrogen atom has ammonium character in the diazonium compounds and nitro-properties in the normal diazotates.

H. Wren.

Nitration of phenol. K. Beaucourt and E. Hammerle (J. pr. Chem., 1928, [ii], 120, 185—192).—Nitration of phenol in water, ethyl alcohol, or glacial acetic acid (cf. Arnall, A., 1924, i, 636) with nitric acid of *d* 1·35 at 7—12° yields 77—82% of nitro-compounds, which consist of 40% of *o*-nitrophenol, 35—40% of *p*-nitrophenol, and 2·5% of 2 : 4-dinitrophenol (for details the original should be consulted). With nitric acid of *d* 1·42, a yield of 75% of mononitro-compounds is obtained, but the *o* : *p*-ratio is shifted in favour of the *p*-isomeride. Variation of temperature has only a small effect on the *o* : *p*-ratio, rise of temperature favouring the production of the *o*-isomeride and *vice versa*. The yield of *o*-nitrophenol is but little affected by employing excess of nitric acid, but the yield of the *p*-isomeride is largely depressed, whilst the production of 2 : 4-dinitrophenol is correspondingly increased; this is probably due to the greater solubility of *p*-nitrophenol in the residual nitric acid. This residual acid, containing dissolved *p*-nitrophenol, after restoration to the original nitric acid concentration by addition of nitric acid, may be used again.

C. W. Shoppee.

Directive action of the carbethoxyl group in phenols. E. Gebauer-Fulnegg and J. Smith-Reese (Monatsh., 1928, 50, 231—234).—The specific *p*-directive action of the carbethoxyl group in phenols noticed in the reaction with chlorosulphonic acid (Gebauer-Fülnegg and Schlesinger, this vol., 631) is also evident in nitration. This has been shown by parallel observations of the nitration of phenol, anisole, and carbethoxyphenol by acetyl nitrate (cf. Pictet, Ber., 1907, 40, 1163) and by benzoyl nitrate (cf. Francis, J.C.S., 1906, 89, 1; A., 1907, i, 53). The results of these authors were confirmed, and rough quantitative observations made of the preponderant formation of *p*-nitro-derivative in the case of carbethoxyphenol. Nitration of carbethoxyphenol by potassium nitrate and sulphuric acid was incomplete, but the *p*-derivative was again formed in largest amount.

R. K. Callow.

Derivatives of *p*-dichlorobenzene containing sulphur. E. Gebauer-Fulnegg and E. Neumann (Monatsh., 1928, 50, 235—236).—The 2 : 5-dichloronitrobenzenesulphonyl chloride obtained by Gebauer-Fülnegg and Figdor (this vol., 280) has m. p. 59—60°. When boiled with potassium hydroxide solution the *dipotassium* salt of *4-chloro-2-nitrophenol-6-sulphonic acid* (+H_2O) is formed, and separates on cooling. It is a derivative of the *aci*-form. The *monopotassium* salt (*acetyl* derivative) is also described. The mother-liquors of the dipotassium salt yield *potassium 2 : 5-dichloro-4-nitrobenzenesulphonate*.

The substance described as *p*-dichlorobenzene-2 : 5-disulphonyl chloride, m. p. 100°, by Quilico (this vol., 169) appears to be a mixture of the 2 : 5- and 2 : 6-disulphonyl chlorides, m. p. 182° and 114°, respectively, previously described (*loc. cit.*).

R. K. Callow.

Halogenoaminophenols. H. H. Hodgson and A. Kershaw (J.C.S., 1928, 2703—2705).—The preparation of the following 3-halogenoaminophenols from the corresponding nitro-compounds by reduction with alkaline sodium hyposulphite is described: *3-chloro-2-aminophenol*, m. p. 122° (*hydrochloride*); *3-bromo-2-aminophenol*, m. p. 138° (*hydrochloride*); *3-iodo-2-aminophenol*, m. p. 137° (decomp.) (*hydrochloride*); *3-chloro-4-aminophenol hydrochloride*; *3-bromo-4-aminophenol*, m. p. 151° (*hydrochloride*); *3-iodo-4-aminophenol*, m. p. 145·5° (*hydrochloride*); *3-chloro-6-aminophenol*, m. p. 154° (*hydrochloride*); *3-bromo-6-aminophenol*, m. p. 150° (*hydrochloride*); *3-iodo-6-aminophenol*, m. p. 141° (*hydrochloride*). These compounds are more stable than the unsubstituted aminophenols. The orders of rate of reduction of ammoniacal silver nitrate are: for the 3-halogeno-6-aminophenols, Cl>Br>I; the 3-halo-

geno-2-aminophenols, I>Br>Cl; the 3-halogeno-4-aminophenols, Cl>Br>I. The water-solubility of the 3-halogenoaminophenols decreases in the order Cl>Br>I. R. J. W. LE FÈVRE.

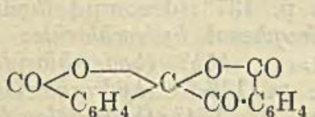
Mobility of some halogen atoms. A. ANGELI and R. POGGI (Atti R. Accad. Lincei, 1928, [vi], 7, 966—969).—*p*-Anisylmethyl chloride changes gradually on keeping from a mobile liquid to a red, glassy mass, with the evolution of hydrogen chloride and methyl chloride. The product has the empirical formula $C_{15}H_{14}O_2$ and exhibits the properties of an artificial resin. F. G. TRYHORN.

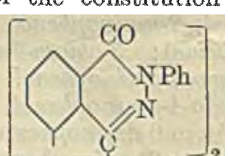
Condensation of chloroindane with phenols. C. COURTOT (Compt. rend., 1928, 187, 661—663).—1-Chloroindane condenses with phenol in benzene or ethereal solution or in the homogeneous state (cf. Courtot and Dondelinger, A., 1923, i, 1090) to give *p*-indanylphenol, b. p. 190—193°/8 mm., m. p. 92—93° (*benzoyl* derivative, m. p. 108°; m-*nitrobenzoyl* derivative, m. p. 96—97°). The constitution of this substance is indicated by the fact that the same p-*indanylanisole*, b. p. 201—202°/19 mm., m. p. 40°, is obtained by the direct methylation of indanylphenol or by the interaction of magnesium *p*-methoxyphenyl bromide and 1-chloroindane. In the first-named reaction small amounts of *indanoxybenzene*, b. p. 185—190°/9 mm., and a viscous *liquid*, b. p. 293°/8 mm. (probably containing two indane residues), are also formed. Chloroindane reacts with sodium phenoxide or with magnesium phenyl bromide to give the expected products. G. A. C. GOUGH.

New compounds from indene and phenols [3-hydroxyphenylhydrindenes]. I. G. FARBENIND. A.-G.—See B., 1928, 845.

Acid from oxidation of α-naphthol. O. DISCHENDORFER (Monatsh., 1928, 50, 97—104).—The acid obtained by Henriques (A., 1888, 843) in small quantity by the oxidation of α-naphthol with alkaline permanganate solution, to which he assigned the formula $C_{20}H_{14}O_8$, is identified as benzil-2 : 2′-dicarboxylic acid (Graebe and Juillard, A., 1888, 154) (*silver* and *barium* salts; diethyl ester, m. p. 154—155°). It is suggested that its formation from α-naphthol proceeds through the stages di-α-naphthol, di-β-naphthaquinone (cf. Korn, A., 1885, 392), a compound of *o*-carboxycinnamic acid type being a possible intermediate compound in the last stage.

Observations made by Henriques of the reactions of the acid were repeated and corrected. When heated for a few minutes above its m. p. the acid yields the anhydride, m. p. 164° (cf. Graebe and Juillard, *loc. cit.*), probably of the constitution I,


(I.)


(II.)

which decomposes on further heating with the formation of diphthalyl and phthalic anhydride. Heated with phenylhydrazine in alcohol, the acid yields the *bisphenylhydrazone*, decomp. 175°, and, when the heating is prolonged, the *bisphenyl-lactazam* (II), m. p. 305—306°. R. K. CALLOW.

Catalytic production of polynuclear compounds. I. G. R. CLEMO and R. SPENCE (J.C.S., 1928, 2811—2819).—The dinaphthol obtained by ferric chloride oxidation of β-naphthol (Dianin, A., 1874, 262; Julius, A., 1887, 56) has been synthesised and its identity thereby definitely established. 1-Bromo-2-naphthol gave, when heated in presence of copper, β-dinaphthol, 1 : 1′-dinaphthylene-2 : 5′ : 2′ : 8-dioxide and 1 : 1′-dinaphthylene-2 : 2′-oxide, the last being also formed by prolonged heating of β-dinaphthol with 4% of vanadium pentoxide.

β-Naphthol, when heated at 300° in contact with air with either tungsten or molybdenum trioxides, gave 2 : 2′-dinaphthyl ether. Similar treatment using vanadium pentoxide gave β-dinaphthol; at 340° 1 : 1′-dinaphthylene-2 : 2′-oxide was formed, but in the absence of air only 2 : 2′-dinaphthyl ether was obtained. Titanium dioxide gave mostly 2 : 2′-dinaphthyl ether and some 1 : 1′-dinaphthylene-2 : 2′-oxide.

Similar treatment of β-naphthol with alkaline-earth oxides gave an iso*oxide*, m. p. 158—159° (either 2 : 2′-dinaphthylene-3 : 3′-oxide or 1 : 2′-dinaphthylene-2 : 3′-oxide) (*dibromo*-derivative, m. p. 193°), identical with the compound of Merz and Weith (A., 1881, 605), accompanied by a second *compound*, m. p. 300° (cf. Niederhausen, A., 1882, 1211).

Both 1 : 1′-dinaphthylene-2 : 2′-oxide and the *iso*-oxide are stable to red-hot zinc dust or fused potassium hydroxide; with hydriodic acid they give hydrogenated naphthalenes, and by oxidation with sulphuric acid, phthalic acid is formed in both cases. Chromic acid destroys the first compound, but converts the *iso*oxide into an iso*dinaphthaquinone oxide* (I), m. p. 268°, which does not condense with *o*-phenylenediamine and is therefore probably 1 : 2′-dinaphthylene-1′ : 4′-quinone-2 : 3′-oxide. Distillation of I over zinc dust regenerates the *iso*oxide; by reduction with zinc and acetic anhydride *diacetoxy*iso*dinaphthylene oxide*, m. p. 245—246°, is formed. With alcoholic sodium hydroxide I undergoes ring scission, giving *dihydroxydinaphthaquinone*, m. p. 222° (*diacetyl* derivative, m. p. 167°), which loses water on heating, forming an isomeric (red) o-*dinaphthaquinone oxide*, m. p. 255—256°, which condenses with *o*-phenylenediamine to give a substituted *phenazine*, m. p. 240°.

Attempts are described to synthesise 2 : 2′-dinaphthylene-3 : 3′-oxide. The Ullmann reaction applied to 2-chloro-3-naphthoic acid gives only β-naphthoic acid. The chlorine atom in ethyl 2-chloro-3-naphthoate is stable to copper-bronze under the conditions employed.

2-*Methoxy*-3-*naphthylamine*, m. p. 109·5° (*acetyl* derivative, m. p. 124—125°), by the Hofmann reaction from 2-methoxy-3-naphthoamide, was converted into 3-*bromo*-2-*methoxynaphthalene*, m. p. 76°, b. p. 178—190°/16 mm., and 3-*iodo*-2-*methoxynaphthalene*, m. p. 65°. The former gives 3-*bromo*-β-*naphthol*, m. p. 80—81°, by heating with hydrobromic acid; when hydriodic acid was used only β-naphthol was isolated. Under the conditions of Ullmann's reaction the last three halogen compounds give β-methoxynaphthalene or β-naphthol.

Only dinaphthaxanthone (Strohbach, A., 1902, i, 171) was isolated from the action of tungsten trioxide or vanadium pentoxide on 2-hydroxy-3-naphthoic acid or its ethyl ester.

α-Naphthol is converted by vanadium pentoxide or calcium oxide into α-dinaphthylene oxide (Merz and Weith, *loc. cit.*), also formed by the dehydration of α-dinaphthol. R. J. W. Le Fevre.

Compounds of 2 : 3-dihydroxynaphthalene with tervalent iron and aluminium and with arsenic acid. R. Weinland and H. Seuffert (Arch. Pharm., 1928, **266**, 455—464).—Dihydroxynaphthalene, like pyrocatechol, forms co-ordination compounds with tervalent iron and aluminium and with arsenic acid. Two series of compounds, one red and the other violet, are formed with ferric iron. The red compounds, which are stable towards alkalis but not towards acids, are obtained as dark brownish-red powders from ferric acetate, dihydroxynaphthalene, and the corresponding alkali hydroxide in aqueous or dilute alcoholic solution. The iron has the co-ordination number 6, the compounds being formulated as $[Fe(O{\cdot}C_{10}H_6{\cdot}O)_3]M_3$. The following are described: *potassium* ($+2H_2O$), *ammonium* ($+2H_2O$), and *sodium* ($+H_2O$) *tri-(2 : 3-dihydroxynaphthalene)ferrates*. The corresponding *potassium*, *ammonium*, and *sodium* *tri(dihydroxynaphthalene)aluminates* are colourless and less well-defined.

The violet compounds in which iron has the co-ordination number 4, $[C_{10}H_6{<}^{O}_{O}{>}Fe{\cdot}O{\cdot}C_{10}H_6{\cdot}O{\cdot}]M$, are obtained from dihydroxynaphthalene, ferric acetate, and the corresponding alkali acetates in concentrated alcoholic solution. They are more stable towards acids than the red compounds. *Di-(2 : 3-dihydroxynaphthalene)ferric acid* ($2H_2O$), the *potassium* ($4H_2O$), *ammonium* ($4H_2O$), and *sodium* ($1H_2O$) salts are described.

Tri(dihydroxynaphthalene)arsenic acid ($5H_2O$) is obtained from dihydroxynaphthalene and arsenic acid in absolute-alcoholic solution. S. Coffey.

Bathochromic action of the methylthiol group in azo-dyes. I. E. Blumenstock-Halward and E. Jusa. **II.** E. Blumenstock-Halward and E. Riesz [with P. G. Bum] (Monatsh., 1928, **50**, 123—138, 139—143).—I. Advantage was taken of the bathochromic action of the methylthiol group observed by Brand (cf. A., 1925, i, 397) to prepare from 3 : 6 : 8-*trimethylthiol*-β-*naphthol* and diazotised *p*-nitroaniline a reddish-violet *azo-dye*, markedly deeper in shade than the other dyes of this class ("ice colours"). The shade deepens successively in the dyes derived from the trisulphonic acid, trithiol, and trimethylthiol derivatives, corresponding with the change from sexavalent to bivalent sulphur, and methylation, respectively. The poor yield of the trithiol derivative obtained makes technical application impossible in this case.

Potassium O-carbethoxy-β-naphthol-3 : 6 : 8-trisulphonate, when heated with phosphorus pentachloride, yielded the *trisulphonyl chloride*, m. p. 195°. The action of aniline caused partial hydrolysis of the carbethoxyl group, completed on recrystallisation, and yielded β-naphthol-3 : 6 : 8-trisulphonanilide (cf. Pollak, Gebauer-Fülnegg, and Blumenstock-Halward, this vol., 751). O-*Carbethoxy*-3 : 6 : 8-*trithiol*-β-*naphthol*, m. p. 80—86° (decomp.), which could not be obtained pure, was formed in 15—20% yield by the reduction of the trisulphonyl chloride by adding hydrochloric acid to the alcoholic solution containing zinc dust in suspension. It was readily oxidised to polysulphides, and yielded, with simultaneous hydrolysis of the carbethoxyl group, a dark red *azo-dye* with diazotised *p*-nitroaniline, slowly formed in neutral solution, rapidly in alkaline solution. The orange-red *lead* salt of the trithiol was obtained with alcoholic lead acetate. The action of ethyl chloroformate yielded O-*carbethoxy*-6 : 8-*dithiol*-3-*carbethoxythiol*-β-*naphthol*, m. p. 115—120° (decomp.). Hydrolysis with potassium hydroxide yielded 2 : 2′-*dihydroxy*-6 : 6′ : 8 : 8′-*tetrathioldinaphthalene* 3 : 3′-*disulphide* (*lead* salt), which yielded 3 : 6 : 8-*trithiol*-β-*naphthol* (isolated as the *lead* salt) on reduction. O-*Carbethoxy*-3 : 6 : 8-*trimethylthiol*-β-*naphthol*, resinous, no characteristic m. p., accompanied in certain circumstances by 2 : 2′-*di(carbethoxyoxy)tetramethylthioldinaphthalene disulphide*, was obtained by treatment of the trithiol derivative with methyl sulphate and sodium carbonate, and yielded 3 : 6 : 8-*trimethylthiol*-β-*naphthol*, m. p. 140°, on hydrolysis with alcoholic potassium hydroxide.

II. The *azo-dye* derived from 3 : 6-*dimethylthiol*-β-*naphthol* and diazotised *p*-nitroaniline had a similar dull reddish-violet colour to the 3 : 6 : 8-trimethylthiol derivative; the 8-methylthiol group thus appears to have no influence on the colour of the dye.

The following compounds were prepared, chiefly by the methods described above: O-*carbethoxy*-3 : 6-*dithiol*-β-*naphthol*, m. p. 117° [from the disulphonyl chloride (cf. Pollak and others, *loc. cit.*)], which yielded 3 : 6-*dithiol*-β-*naphthol*, m. p. 152°, when hydrolysed with dilute alkali; 3 : 6-*dimethylthiol*-β-*naphthol*, m. p. 125° (*methyl ether*, m. p. 93°); 1-*p*-*nitrobenzeneazo*-3 : 6-*dimethylthiol*-β-*naphthol*, m. p. 258°. Combined reduction and acetylation of *O*-carbethoxy-β-naphthol-3 : 6-disulphonyl chloride by treatment with acetic anhydride, acetic acid, zinc dust, and sodium acetate yielded O-*carbethoxy*-3 : 6-*diacetylthiol*-β-*naphthol*, m. p. 120°. R. K. Callow.

Action of phosphoric oxide on benzyl alcohol in benzene solution. S. S. Nametkin and D. A. Kursanov (J. Russ. Phys. Chem. Soc., 1928, **60**, 917—920).—The less volatile products of the action of phosphoric oxide on benzyl alcohol in benzene solution were investigated, to determine whether other compounds besides diphenylmethane are formed. The fraction of b. p. 218—220°/11 mm. gave on recrystallisation *p*-dibenzylbenzene, m. p. 87°, which must have been formed by the further action of benzyl alcohol on diphenylmethane, since it was obtained by heating these compounds with phosphoric oxide.

M. Zvegintzov.

Electrolytic oxidation of alcohols. III. Benzyl alcohol. S. Koidzumi (Mem. Coll. Sci. Kyōto, 1928, [*A*], **11**, 383—390).—Electrolytic oxidation of benzyl alcohol in acid or alkaline media gave, in most experiments made, a mixture of benzaldehyde and benzoic acid. The experiments were carried out

in a divided cell with a rotating cathode of iron plate, lead, or nickel gauze, and a cathode solution of either sulphuric acid, sodium hydroxide, or sodium carbonate solutions enclosed in a porous cylinder. In acid solution with lead peroxide as anode material and iron as cathode, the current density has no effect on the products formed, but the amount of aldehyde diminishes with current quantity. With platinum or gold anodes and a lead cathode, oxidation efficiency is low, but the product is almost free from benzoic acid. In sodium carbonate solution the maximum yield of benzaldehyde, free from benzoic acid, is about 71%.

H. BURTON.

Electrolytic reduction of aldehydes. III. *o*- and *p*-Hydroxybenzaldehydes. IV. Vanillin and piperonal. G. SHIMA (Mem. Coll. Sci. Kyoto, 1928, [*A*], **11**, 407—418, 419—427).—III. Electrolytic reduction of salicylaldehyde to salicyl alcohol is best carried out at 16—18°, using a mercury cathode, an almost neutral catholyte, and a current density of 4 amp./100 cm.^{2} The yield of alcohol is 85%. With an alkaline catholyte there are formed dihydroxyhydrobenzoin (cf. Law, J.C.S., 1906, **89**, 1512) and 9 : 10-dihydroxy-9 : 10-dihydrophenanthrene. *p*-Hydroxybenzaldehyde gives a 92% yield of *p*-hydroxybenzyl alcohol under the above conditions.

IV. Reduction of vanillin suspended in a slightly acid catholyte at 8—10° gives hydrovanilloin (10%) and 4-hydroxy-3-methoxybenzyl alcohol (82%; *dibenzoyl* derivative, m. p. 120°). At higher temperatures there is an increase in the amount of hydrovanilloin and other condensation products. In slightly alkaline suspension the yield of alcohol is 92%. Under similar conditions piperonal gives a 90% yield of 3 : 4-methylenedioxybenzyl alcohol, m. p. 56° (lit. 51°; *benzoate*, m. p. 66°).

H. BURTON.

Attempt to dehydrate benzhydrol by Tschugaev's xanthate method. D. N. KURSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 921—924; cf. A., 1926, 399).—When methyl benzhydryl xanthate was decomposed by heating at 190—260°, among the products tetraphenylethylene was obtained in a manner analogous to stilbene in the experiments of Nametkin and Kursanov (*loc. cit.*). These products indicate a new mechanism for Tschugaev's reaction.

M. ZVEGINTZOV.

Urethanes of nuclear-substituted benzyl alcohols. I. G. FARBENIND. A.-G.—See B., 1928, 873.

Amines of the hydroaromatic-aliphatic series [*cyclo*hexyl-β-aminoethyl alcohol etc.]. I. G. FARBENIND. A.-G.—See B., 1928, 846.

Oxidation of cholesterol by molecular oxygen. G. BLIX and G. LOWENHIELM (Biochem. J., 1928, **22**, 1313—1322).—Oxycholesterol is formed by the action of atmospheric oxygen when cholesterol is heated in the air at temperatures slightly above the m. p. or by aeration of cholesterol suspensions. Aqueous suspensions of pure cholesterol are very stable against atmospheric oxygen even at boiling temperature. The impurities which catalyse the formation of oxycholesterol adhere, however, very stubbornly to the cholesterol. Alkali soaps catalyse the oxidation, whilst other hydrophilic colloids, higher fatty acids, triglycerides, or heavy metal salts have no catalytic influence. The degree of dispersion is of great importance in the oxidation of cholesterol by molecular oxygen.

S. S. ZILVA.

Metacholesterol bromide. I. LIFSCHÜTZ (Arch. Pharm., 1928, **266**, 518; cf. A., 1922, i, 251, 541).—Metacholesterol bromide melts at 104—105° and shows the same behaviour on melting as cholesterol dibromide, m. p. 93—94°.

S. COFFEY.

Preparation of cholestenone. W. A. SEXTON (J.C.S., 1928, 2825—2826).—An 80% yield of cholestenone is obtained by the distillation of a mixture of cholesterol and copper-bronze under 2—3 mm. pressure.

A. I. VOGEL.

Ultra-violet irradiation of dehydroergosterol. A. WINDAUS and O. LINSERT (Annalen, 1928, **465**, 148—166).—During ultra-violet irradiation ergosterol loses its lævorotatory power and eventually becomes slightly dextrorotatory; there is at the same time a change in the ultra-violet absorption spectrum, and the activated ergosterol has greater solubility and is no longer precipitated by digitonin. Since the change occurs in absence or presence of air or solvents and the mol. wt. remains the same, it is probably due to isomerisation. The hydroxyl content, determined by Zerewitinov's method, is unchanged, and a ketonisation of the type ·CH(OH)·C̊H·CH:CH· ⟶ ·CO·CH·CH_2·CH_2· (cf. A., 1927, 557) is thus excluded. Cyclisation, with consequent loss of a double linking (cf. Sernagiotto, A., 1918, i, 444), is also improbable, since titration with perbenzoic acid gives similar figures before and after irradiation and the same amount of hydrogen (**3** mols.) is absorbed in presence of platinum sponge. The remaining possibilities are migration of double linkings or stereoisomerisation or both. Esters and other derivatives of ergosterol, and also dehydroergosterol, show the same isomerisation and activation by irradiation as ergosterol itself; dehydroergosterol compounds have the advantage of forming crystallisable products.

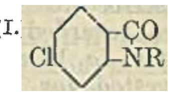
Dehydroergosterol, $C_{27}H_{40}O$, m. p. 146°, b. p. 230°/0·5 mm. almost without decomposition, $[\alpha]_D^{18}$ +149° (digitonin additive *product*; *acetate*, m. p. 146°, $[\alpha]_D^{18}$ +193°; *phenylurethane*, m. p. 161—162°, $[\alpha]_D^{19}$ +202°; *peroxide*, m. p. 158°), is prepared by distilling in high vacuum the trihydric *alcohol*, $C_{27}H_{44}O_2$, m. p. 227°, $[\alpha]_D^{21}$ −121·6°, obtained by reduction of ergosterol peroxide with zinc and alcoholic potassium hydroxide; it is more conveniently prepared by boiling ergosterol in alcohol with mercuric acetate. Air-dried dehydroergosterol contains $1H_2O$, removable with difficulty. Insolation of dehydroergosterol after boiling with eosin in alcohol yields *dehydroergopinacone*, $C_{54}H_{78}O_2,H_2O$, m. p. 196° (decomp.). Hydrogenation of the acetate leads, as with ergosterol, to γ-ergostanol (*allo*-α-ergostanol), with intermediate production of α-ergostenol (tetrahydroergosterol). By the action of ultra-violet light dehydroergosteryl acetate (0·1% solution in alcohol) is converted into two products, separable as acetates by fractional crystallisation and as alcohols after hydrolysis by precipitation with digitonin. The more soluble acetate gives on hydrolysis an *alcohol*,

$C_{27}H_{40}O$, m. p. 134°, $[\alpha]_D^{20}$ +119·5°, without antirachitic properties, which by acetylation yields an *acetate*, m. p. 126—127°, $[\alpha]_D^{18}$ +87·0° (hydrogenated to an *octahydro-acetate*). The less soluble *acetate*, m. p. 178°, is hydrolysed to an *alcohol*, m. p. 175°, precipitable with digitonin, which also has no antirachitic value. C. HOLLINS.

Reaction between the binary system, magnesium–magnesium iodide, and aromatic acids and acid derivatives. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1928, **50**, 2762—2769: cf. A., 1927, 245, 1190).—Although the aromatic acids in 5% ethereal solution react very slowly with magnesium, they are readily and quantitatively converted by the above binary system into iodomagnesium salts. The acid and magnesium iodide probably react reversibly, forming hydrogen iodide, which then attacks the magnesium or the ether. Hydrogen bromide also dissolves magnesium in ether, but hydrogen chloride acts only in presence of magnesium bromide, giving apparently homogeneous magnesium chlorobromide. The additive products of magnesium bromide with organic acids, $2R\cdot CO_2H,MgBr_2,2Et_2O$, are less soluble than those of magnesium iodide. The iodomagnesium salts separate as oily or crystalline etherates, mixed with normal magnesium salts formed by their decomposition. They are slowly reduced by the binary reagent in boiling ether to the bimolecular *derivatives*, $[\cdot CR(OMgI)_2]_2$ and $[:CR(OMgI)]_2$, which are hydrolysed by water to benzils and benzoins, respectively. The combined yields of the latter products are: from benzoic acid 43%; *p*-toluic acid, 30%; α-naphthoic acid, 30—35%; β-naphthoic acid, 75%, and from *p*-phenylbenzoic acid, 46% of the theoretical. Alkyl esters of aromatic acids are decomposed by magnesium iodide to alkyl iodides and iodomagnesium salts, both of which react with the binary system; thus benzyl benzoate yields dibenzyl and benzoin, and methyl benzoate yields a little benzoin. Phenyl benzoate is decomposed to iodomagnesium phenoxide and benzoyl iodide which gives resinous products. Benzoyl peroxide and magnesium iodide quantitatively yield iodine and iodomagnesium benzoate. H. E. F. NOTTON.

4-Chloroanthranilic acid. G. HELLER and L. HESSEL (J. pr. Chem., 1928, [ii], **120**, 64—73).—The tendency of 4-chloroanthranilic acid to yield condensation products containing four-, five-, and six-membered heterocyclic systems has been investigated and examples of each type have been obtained. The *methyl* ester of the acid, m. p. 68·5° (*ethyl* ester, m. p. 41°), with hydrazine hydrate yields 4-*chloro*-2-*aminobenzhydrazide*, m. p. 151°, which with acetic anhydride in ethyl acetate solution is converted into 4-*chloro*-2-*aminobenzdiacetylhydrazide*, m. p. 214°, which is easily soluble in dilute acids and therefore considered to bear both acetyl groups on the hydrazine residue (cf. Heller, A., 1925, i, 1322). When the hydrazide, m. p. 151°, is heated at 200° for 5 hrs., *bis*-(4-*chloro*-2-*aminobenz*)*hydrazide*, m. p. 272°, is obtained, which when treated with nitrous acid yields *bis*-4-*chlorobenzazimide*, m. p. 245°.

With benzoyl chloride in pyridine solution, 4-chloroanthranilic acid yields 4-*chloro*-N-*benzoylanthranil*, m. p. 198° [I : R=Bz], together with 4-*chloro*-2-*benzamidobenzoic acid*, m. p. 219°, which with concentrated sulphuric acid gives the preceding compound.

(I.)


This compound is converted by alcoholic hydrazine into 6-*chloro*-3-*hydrazino*-3-*phenyl*-3 : 4-*dihydro*-2 : 4-*benzoxazone*, m. p. 214°, which when heated in glacial acetic acid solution at 100° undergoes rearrangement with loss of 1 mol. of water to give 7-*chloro*-3-*amino*-2-*phenyl*-4-*quinazolone*, m. p. 198°. The acid when treated with hot acetic anhydride yields 4-*chloro*-N-*acetylanthranil*, m. p. 145° [(I) : R=Ac], slowly converted by water and more rapidly by alkali into 4-*chloro*-2-*acetamidobenzoic acid*, m. p. 213°, and giving with alcoholic hydrazine 7-*chloro*-3-*amino*-2-*methyl*-4-*quinazolone*.

4-*Chlorophenyl*-2-*glycine*-1-*carboxylic acid*, m. p. 228°, could not be obtained by condensation of 4-chloroanthranilic acid with chloroacetic acid, but was prepared by alkaline hydrolysis of 4-*chloro*-2-*cyanomethylaminobenzoic acid*, m. p. 215°, obtained by the action of formaldehyde and potassium cyanide on 4-chloroanthranilic acid in the presence of acetic acid. The *dimethyl* ester of 4-chlorophenyl-2-glycine-1-carboxylic acid has m. p. 189°, and could not be converted into chloroindoxylic ester by heating with sodium methoxide solution. By heating 4-chlorophenyl-2-glycine-1-carboxylic acid with acetic anhydride and sodium acetate, followed by treatment with sodium hydroxide, is obtained 2 : 2′-dichloroindigotin, identical with the synthetic product. C. W. SHOPPEE.

Metallic derivatives of hydroxy-esters. I. Copper and nickel derivatives of methyl salicylate. B. W. DOAK and J. PACKER (J.C.S., 1928, 2763—2769).—The preparations of *methyl cuprisalicylate dihydrate* (I*a*), decomp. 115°, *methyl nickelosalicylate dihydrate* (I*b*), and anhydrous *methyl nickelosalicylate* from methyl salicylate are described.

$$(CO_2Me\cdot C_6H_4\cdot O)_2X{<}{}^{OH_2}_{OH_2} \quad (Ia,\ X{=}Cu;\ Ib,\ X{=}Ni)$$

When boiled with water, methyl cuprisalicylate is hydrolysed to methyl salicylate and copper hydroxide, whereas methyl nickelosalicylate yields methyl salicylate and *methyl hydroxynickelosalicylate*, $CO_2Me\cdot C_6H_4\cdot O\cdot Ni\cdot OH$. Passage of wet air over I*a* at 100° gives *methyl hydroxycuprisalicylate*, which when heated at 100° in dry air gives a basic *compound* (II), $CO_2Me\cdot C_6H_4\cdot O\cdot Cu\cdot O\cdot Cu\cdot O\cdot C_6H_4\cdot CO_2Me$. The reaction $(CO_2Me\cdot C_6H_4\cdot O)_2Cu+H_2O$ $CO_2Me\cdot C_6H_4\cdot OH+CO_2Me\cdot C_6H_4\cdot O\cdot Cu\cdot OH$ is reversible and proceeds slowly (left to right) at the ordinary temperature.

I*a* and I*b* undergo reversible alcoholysis with methyl alcohol, yielding the respective methoxymetallosalicylates, $CO_2Me\cdot C_6H_4\cdot O\cdot X\cdot OMe$. With ethyl alcohol the alcoholysis occurs less readily, but with the copper compound is more complete, methyl salicylate and *cupric ethoxide* being formed. I*b* gives *methyl ethoxynickelosalicylate*. Methylation of sodium cuprisalicylate by methyl sulphate gave II in good yield. By the action of ammonia on alcoholic solutions of I*a* and I*b*, ammine *complexes* are formed, only *methyl diamminenickelosalicylate* (III),

$(CO_2Me\cdot C_6H_4\cdot O)_2Ni(NH_3)_2$, being isolated (two metastable and a stable octahedral form described).

The copper and nickel atoms are regarded as possessing the co-ordination number 4 in I*a*, I*b*, and III; a similar constitution is suggested for the aluminosalicylates of Burrows and Wark (this vol., 288). R. J. W. LE FÈVRE.

Derivatives of *p*-methoxycinnamic acid. P. A. FOOTE (J. Amer. Pharm. Assoc., 1928, 17, 958—962).—The following esters of *p*-methoxycinnamic acid have been prepared: *phenyl*, m. p. 76—77°; β-*naphthyl*, m. p. 130—131°; *thymyl*, m. p. 58—59°; *carvacryl*, m. p. 78—79°; *eugenyl*, m. p. 112—113°; *phenacyl*, m. p. 136° (*monoxime*, m. p. 116—117°); also the *gold*, *mercuric*, *zinc*, and *ammonium* salts. *Carvacryl cinnamate*, m. p. 65—66°, and eugenyl cinnamate, m. p. 90—91°, are described. The above esters have no toxic action on *B. typhosus* or *B. staphisaurius*. E. H. SHARPLES.

4-Bromophthalic acid. L. C. BAKER (J.C.S., 1928, 2829).—Details are given of the preparation of ethyl 4-bromophthalate (yield 66%) and 4-bromophthalic acid (yield 88%) from ethyl 4-aminophthalate by Sandmeyer's reaction and acid hydrolysis of the product, respectively. R. J. W. LE FEVRE.

Absorption spectra of phthaleins and sulphonphthaleins of phenol and *o*-cresol. R. C. GIBBS and C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, 50, 2798—2810; cf. A., 1922, ii, 806; 1924, ii, 346; this vol., 526, 1019).—The presence of a pair of bands between the frequency numbers 3500 and 3700 $mm.^{-1}$ in the absorption spectra of phenol-phthalein (I) and -tetrachlorophthalein and *o*-cresol-phthalein (II) and -tetrachlorophthalein in neutral absolute alcoholic solutions indicates that these substances have a benzenoid structure (cf. this vol., 570). The absorption spectra of phenolsulphonphthalein (III) in (*a*) water or 95% alcohol and (*b*) absolute alcohol are of different types, which confirms the suggestion (Orndorff and Sherwood, A., 1923, i, 340) that the former solution contains a quinonoid hydrate and the latter an internal complex salt. After long keeping in the dark, the latter solution acquires an absorption closely similar to that of the lactonoid phenolsulphonphthalein diethyl ether, which is probably present in equilibrium with a small quantity of a quinonoid form. The corresponding solutions of *o*-cresolsulphonphthalein (IV) have closely similar absorption curves to those of III, but the slow fading of the alcoholic solution is not, in this case, due simply to the formation of the diethyl ether. The absorption spectra of I, II, III, and IV in sulphuric acid or in a large excess of hydrochloric acid (cf. A., 1926, 884) are all very similar, but IV is slowly sulphonated by sulphuric acid. The absorption curves of the dibasic salts of III and IV are obtained in solutions containing 100 mol. proportions of alkali. With 2 mols. of alkali considerable hydrolysis to the free phthalein occurs in dilute solutions and the use of these derivatives for p_H comparisons is, therefore, possible only under closely similar conditions of concentration. Potassium hydroxide, 33%, converts III in a few days and IV in several months into the colourless tripotassium salts of the carbinolcarboxylic acids. The absorption spectra of the solutions mentioned are shown graphically and the frequency numbers of the heads of the bands are tabulated. H. E. F. NOTTON.

Enolisation of homophthalic anhydrides. T. S. STEVENS and J. L. WILSON (J.C.S., 1928, 2827—2828).—4 : 5-*Methylenedioxyhomophthalic anhydride*, m. p. 178—180° (obtained by boiling the parent acid with acetic anhydride), forms yellow alkali salts (cf. Davies and Poole, this vol., 885), the oxidation of which by alkaline permanganate give methylenedioxyphthalidecarboxylic acid, m. p. 213—215° (decomp.) (lit. 216° decomp.), and methylenedioxyphthalide. R. J. W. LE FEVRE.

Constitution of "β-resodicarboxylic acid." K. BRUNNER [with, in part, N. MADERSBACHER and E. GORITSCHAN] (Monatsh., 1928, 50, 216—224).—"β-Resodicarboxylic acid," first prepared from 3 : 5-dihydroxybenzoic acid by Senhofer and Brunner (A., 1881, 265), has now been prepared by an improved method and its constitution determined. From its method of formation, the non-formation of an anhydride or imide, and comparison of the *dimethyl ether* of the acid with 3 : 5-dimethoxyphthalic acid (Fritsch, A., 1897, i, 569), it is concluded that it is 3 : 5-dihydroxyterephthalic acid.

3 : 5-Disulphobenzoic acid was prepared from benzoic acid by treatment with fuming sulphuric acid containing 50% of anhydride and hydrogen chloride, or by heating with pure chlorosulphonic acid, and separated as the dipotassium salt ($+3H_2O$ and $+2H_2O$), which yielded 3 : 5-dihydroxybenzoic acid, subliming at 190—195°/14 mm., when fused with potassium hydroxide. 3 : 5-Dihydroxybenzoic acid, when heated with potassium hydrogen carbonate and glycerol in a stream of carbon dioxide, yielded 3 : 5-dihydroxyterephthalic acid, separated as the *ammonium hydrogen* salt ($+H_2O$). The *dimethyl* ester, m. p. 151·5—152°, by treatment with methyl iodide and potassium hydroxide gave *methyl* 3 : 5-*dimethoxyterephthalate*, m. p. 121·5—122°, which was hydrolysed to 3 : 5-*dimethoxyterephthalic acid*, m. p. 285°. R. K. CALLOW.

Ethyl 1 : 2 : 3 : 6-tetracarbethoxy-5-methoxy-$\Delta^{2:5}$-*cyclo*hexadiene-1-acetate, a derivative of triethyl aconitate. G. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 217—219).—When a mixture of ethyl aconitate (1 mol.), sodium ethoxide (1 mol.), and an excess of methyl iodide in alcohol solution is heated in a sealed tube at 115—120°, the product is *ethyl* 1 : 2 : 3 : 6-*tetracarbethoxy*-5-*methoxy*-$\Delta^{2:5}$-cyclo*hexadiene*-1-*acetate*, b. p. 225—230°/1 mm. The mechanism of its formation is probably similar to that involved in the condensation and methylation of ethyl glutaconate (Curtis and Kenner, J.C.S., 1914, 105, 282), the sodium derivative of ethyl 1 : 2 : 3 : 6-tetracarbethoxy-5-keto-Δ^2-*cyclo*hexene-1-acetate being first produced and then converted into the above *O*-methyl derivative. J. W. BAKER.

Condensation of heptaldehyde with aromatic aldehydes. I. B. N. RUTOVSKI and A. Y. KOROLEV (J. Russ. Phys. Chem. Soc., 1928, 60, 925—927).—Benzaldehyde and heptaldehyde in the presence of alkali hydroxides in aqueous alcohol give β-*phenyl*-

α-n-*amylacraldehyde*, a yellow liquid with an odour of jasmine, b. p. 174—175°/20 mm., d_{20}^{20} 0·97108, n_D^{20} 1·5381. The *oxime*, m. p. 72·5—73°, and *semicarbazone*, m. p. 117·5—118°, were prepared. By condensing the β-*phenyl*-α-n-*amylacraldehyde* with benzoylglycine, 2-*phenyl*-4-α-*benzylideneheptylidene*-ɒ-*oxazolone*, m. p. 97—98°, was obtained. M. ZVEGINTZOV.

Vinylene homologues of *p*-dimethylaminobenzaldehyde. W. KÖNIG, W. SCHRAMEK, and G. RÖSCH (Ber., 1928, **61**, [*B*], 2074—2080).—*p*-Dimethylaminobenzaldehyde condenses readily with paracetaldehyde in the presence of concentrated sulphuric acid, giving compounds, $NMe_2·C_6H_4·[CH:CH]_n·CHO$, in which *n* depends greatly on the duration of the change. Thus, after 3 hrs. the product when treated with 60% of the sodium hydroxide required for neutralisation of the sulphuric acid affords the trivinylene aldehyde (see later), the filtrate from which, after further neutralisation with sodium hydroxide, gives *p*-dimethylaminocinnamaldehyde, m. p. 141°, maximum absorption, 399 μμ (*phenylhydrazone*, m. p. 169°; *oxime*, m. p. 151°). If reaction is extended to 5—6 hrs., the main product is strepto*trivinylene*-p-*dimethylaminobenzaldehyde* (η-p-*dimethylaminophenyl*-$\Delta^{\beta\delta\zeta}$-*heptatrienal*), m. p. 184° or 176° from light petroleum or ethyl acetate, absorption maximum, 440 μμ (*phenylhydrazone*, m. p. 217°). On one occasion, the attempted purification of the trivinylene aldehyde by means of 60% sulphuric acid led to the isolation of strepto*pentavinylene*-p-*dimethylaminobenzaldehyde* (λ-p-*dimethylaminophenyl*-$\Delta^{\beta\delta\zeta\theta\kappa}$-*undecapentaenal*), m. p. 209°, in which the number of vinylene groups is confirmed by spectroscopic analysis (absorption maximum, 470 μμ). Aldehydes containing an even number of vinylene groups do not appear to be produced from paracetaldehyde or crotonaldehyde. strepto*Divinylene*-p-*dimethylaminobenzaldehyde* (ε-p-*dimethylaminophenyl*-$\Delta^{\beta\delta}$-*pentadienal*), m. p. about 155°, is identified spectroscopically as by-product of the condensation of *p*-dimethylaminocinnamaldehyde and pyruvic acid in presence of sulphuric acid; its absorption maximum is at 420 μμ. H. WREN.

Nitration of piperonal. J. B. EKELEY and M. S. KLEMME (J. Amer. Chem. Soc., 1928, **50**, 2711—2715).—Attempts to obtain the *isomeride*, m. p. 143°, present in commercial *o*-nitropiperonal (cf. A., 1922, i, 934) from piperonal and nitric acid alone or in presence of sulphuric acid, acetic acid, or catalysts, yielded only *o*-nitropiperonal, nitro- (m. p. 144°) and dinitro-methylenepyrocatechol, nitropiperonylic acid, and a new *nitromethylenepyrocatechol*, m. p. 70°, probably formed from the desired isomeride. Nitric acid (*d* 1·38) at 45° gives the best yield of *o*-nitropiperonal. H. E. F. NOTTON.

Derivatives of phenacyl sulphide. A. CHRZASZCZEWSKA and S. CHWALINSKI (Rocz. Chem., 1928, **8**, 432—444).—p-*Methylphenacyl sulphide*, $(C_6H_4Me·CO·CH_2)_2S$, m. p. 88·8—89·3° (*dioxime*, m. p. 158—159°), is obtained by adding aqueous sodium sulphide solution to a boiling alcoholic solution of *p*-tolyl chloromethyl ketone. p-*Bromophenacyl sulphide*, m. p. 142·2—143·1° (*dioxime*, m. p. 180—180·5°), and p-*chlorophenacyl sulphide dioxime*, m. p. 150—150·5°, and *diphenylhydrazone*, m. p. 127—128°, are prepared similarly. R. TRUSZKOWSKI.

Hydroxy-ω-aminoacetophenone derivatives [hydroxyphenacylamines and their ethers]. H. LEGERLOTZ.—See B., 1928, 837.

Organic compounds of sulphur. X. Action of air on thiobenzophenone. A. SCHONBERG, O. SCHUTZ, and S. NICKEL (Ber., 1928, **61**, [*B*], 2175—2177; cf. this vol., 897).—Thiobenzophenone is converted by exposure to air into a trisulphide, $C_{26}H_{20}S_3$ (cf. Staudinger and Freudenberger, this vol., 1246), regarded as $CPh_2<\overset{S·S}{\underset{S}{}}>CPh_2$, which is decomposed by heat into thiobenzophenone and sulphur.

[With J. PETER.]—*Dibenzhydryl sulphide*, m. p. 66·5°, prepared from benzhydryl mercaptan and diphenylbromomethane in dry benzene, yields thiobenzophenone at 275°. H. WREN.

Action of nitric acid on derivatives of ethylene. II. Nitration of styrene derivatives. J. VAN DER LEE (Rec. trav. chim., 1928, **47**, 920—933; cf. A., 1926, 1245).—Nitration of 4 : 4′- and 3 : 3′-dinitrodistyryl ketone, obtained by the action of potassium hydroxide solution on 3-nitrostyryl methyl ketone, with absolute nitric acid affords ω : 4- and ω : 3-dinitrostyrenes, respectively. The same dinitro-compounds are formed during the nitration of 4- and 3-nitrostyryl methyl ketones. 3-Nitrophenyl 3-nitrostyryl ketone is nitrated under various conditions, yielding 3-*nitrophenyl* α : 3-*dinitrostyryl ketone*, $NO_2·C_6H_4·CH:C(NO_2)·CO·C_6H_4·NO_2$, m. p. 152·5—154°, which is converted by methyl-alcoholic potassium hydroxide and bromine water into ββ-dibromo-β : 3-dinitro-α-methoxyethylbenzene. The trinitro-ketone is converted by methyl and ethyl alcohols into m-*nitrophenyl* β-(α : 3-*dinitro*-β-*methoxy*)*phenylethyl ketone*, m. p. 128·5°, and the corresponding *ethoxy*-derivative, m. p. 120·5—121°, respectively. These ketones are converted by aqueous potassium hydroxide and bromine water into ββ-dibromo-β : 3 dinitro-α-alkoxyethylbenzenes.

p-Nitrobenzaldehyde condensed with 3-nitroacetophenone in presence of alcohol and a small amount of sodium hydroxide solution yields 3-*nitrophenyl* 4-*nitrostyryl ketone*, m. p. 205·5°. Nitration of this gives 3-*nitrophenyl* α : 4-*dinitrostyryl ketone*, m. p. 135°, converted by methyl alcohol into m-*nitrophenyl* β-(α : 4-*dinitro*-β-*methoxy*)*phenylethyl ketone*, m. p. 122·5° (decomp.).

The action of potassium hydroxide solution on methyl β-hydroxy-β-*p*-nitrophenylethyl ketone is to form 4 : 4′-dinitrodistyryl ketone (cf. Baeyer and Becker, A., 1883, 1120). H. BURTON.

Pungent principles of ginger. V. Distillation of methylzingerol. H. NOMURA and K. IWAMOTO (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 973—984)—Distillation of methylzingerol (*oxime*, m. p. 85·5—86·5°) under ordinary pressure yields hexaldehyde (isolated as its oxime, and semicarbazone, m. p. 113·5—114°; lit. 106°) in the distillate, whilst the residue consists of methylzingerone and an unsaturated ketone which on reduction yields β-3 : 4-dimethoxyphenylethyl *n*-heptyl ketone and is therefore *methylshogoal* (cf. A., 1918, i, 446),

$C_6H_3(OMe)_2\cdot[CH_2]_2\cdot CO\cdot CH{:}CH\cdot[CH_2]_4\cdot Me$. No trace of *n*-heptaldehyde (semicarbazone, m. p. 111—112°; lit. 109°) was detected. Methylzingerol itself is probably $C_6H_3(OMe)_2\cdot[CH_2]_2\cdot CO\cdot CH_2\cdot CH(OH)\cdot[CH_2]_4\cdot Me$ (cf. Lapworth and others, J.C.S., 1917, **111**, 779). Methylzingerol distils at 194—200°/0·1—0·4 mm. with very little decomposition into methylzingerone, but at 3 mm. the distillate contains a much larger proportion of the latter. J. W. BAKER.

Perylene and its derivatives. XVIII. A. PONGRATZ (Monatsh., 1928, **50**, 87—96).—3 : 9-Dichloro-4 : 10-diacylperylenes containing aliphatic acyl groups yield, when boiled with cuprous cyanide in quinoline, vat-dyes having the constitutions I or II, of which I is supported by the absence of detectable alkylimino-groups, and II by the non-reactivity of benzaldehyde with the dyes from the propionyl and butyryl derivatives (R=Me, Et).

(I.)  (II.)

3 : 9-*Dichloro*-4 : 10-*dibutyrylperylene*, m. p. 258—259°, was prepared by a Friedel–Crafts reaction from 3 : 9-dichloroperylene and butyryl chloride. The *dyes* from 3 : 9-dichloro-4 : 10-diacetyl-, -dipropionyl-, and -dibutyryl-perylenes were coloured dark violet. They were purified by reduction to the vats (red), and reoxidation. The dye from the diacetyl derivative was also formed in pyridine at 200° under pressure. Oxidation of the dyes by potassium permanganate or chromic acid yielded perylene-3 : 4 : 9 : 10-tetracarboxylic acid. The dye from the diacetyl derivative yielded a *tetrabenzoyl* derivative, which did not form a vat, and reacted with benzaldehyde to yield a *benzylidene* derivative, which was reduced to the vat with difficulty. R. K. CALLOW.

Plumbagin. A. MADINAVEITIA and M. GALLEGO (Anal. Fís. Quím., 1928, **26**, 263—270).—The therapeutic action of plumbagin (cf. Greshoff, A., 1891, 334), the active principle of *Plumbago europea*, appears to be due to its antiseptic properties. It is best obtained by extraction of the plant with ether, the yield being 3% of the dry rhizomes. The substance thus obtained, recrystallised from alcohol, had the composition $C_{11}H_8O_3$, m. p. 76°. Its properties are typical of a hydroxyquinone, and it yields an *acetyl* derivative, m. p. 115°, and a *monoxime*, m. p. 210°. It resembles juglone in forming a *copper* derivative, $Cu(C_{11}H_7O_3)_2$, and a nickel derivative appears to be formed in solution. Distillation with zinc dust yielded an oily hydrocarbon. Oxidation with hydrogen peroxide gives an *acid*, probably a hydroxymethylphthalic acid, separated as the *monopotassium* salt, $C_9H_8O_4K$. Plumbagin is considered to be a methyljuglone (methyl-5-hydroxy-α-naphthaquinone). R. K. CALLOW.

7-Acylamino-α-naphthaquinones. I. G. FARBENIND. A.-G.—See B., 1928, 846.

Dihydroanthraquinone derivatives. I. G. FARBENIND. A.-G.—See B., 1928, 847.

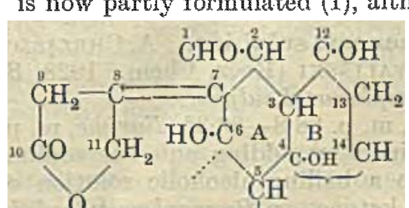
Condensation products of the benzanthrone series. I. G. FARBENIND. A.-G.—See B., 1928, 847.

New derivatives of anthanthrone. I. G. FARBENIND. A.-G.—See B., 1928, 848.

Digitalis glucosides. II. Gitoxigenin and *iso*gitoxigenin. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, **79**, 553—562).—*Gitoxigenin*, m. p. 231—232°, has the formula $C_{23}H_{34}O_5$ (cf. Windaus, Chem. Zentr., 1928, ii, 669), and is therefore isomeric with periplogenin (this vol., 1359); with chromic acid, it yielded *gitoxigenone*, $C_{23}H_{32}O_5,H_2O$, m. p. 206—207°, and, on hydrogenation, *dihydrogitoxigenin*, m. p. 249—250°. Difficulty was experienced with the isomerisation; on treatment of gitoxigenin in pyridine at 0° with methyl-alcoholic potassium hydroxide, there was, however, obtained, in 25% yield, iso*gitoxigenin*, m. p. 249—250°, which failed to give the nitroprusside reaction and could not be hydrogenated; with sodium hydroxide this gave iso*gitoxigeninic acid*, $C_{23}H_{36}O_6,1\cdot5H_2O$, m. p. 152—153°, *methyl* ester, m. p. 145°; the latter failed to react with semicarbazide, and, with chromic acid, yielded *methyl* iso*gitoxigenonate*, a neutral substance, $C_{24}H_{34\text{ or }36}O_6$, m. p. 170—172°. Treatment of *iso*gitoxigeninic acid with hypobromite gave an *acid*, $C_{21}H_{30}O_6$, m. p. 252—253° (*methyl* ester, m. p. 105° and 180°), possessing no lactone group, so that the oxidation probably involved the original lactone group of gitoxigenin. The difference in the behaviour of *iso*gitoxigenin from that of *iso*strophanthidin and of *iso*digitoxigenin may be due to the absence, in the former, of a carbinol group γ- or δ- to the γ-carbon atom of the lactone. C. R. HARINGTON.

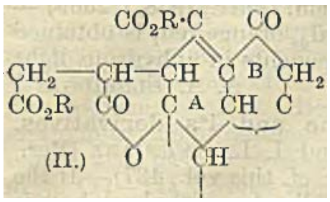
Strophanthin. XV. *Hispidus* strophanthin. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1928, **79**, 531—537).—The aqueous extract of the seeds of *Strophanthus hispidus* when extracted with chloroform yielded a small amount of cymarin. The chloroform-insoluble glucoside was hydrolysed by hydrochloric acid to strophanthidin; the action of strophanthobiase from *S. courmonti* gave a trace of dextrose, but no cyamarin; prolonged treatment with a similar enzyme preparation from *S. hispidus* gave dextrose with a little cymarin. *Hispidus* strophanthin, like *Kombe* strophanthin, is therefore a mixture of glucosides, but the structure of the latter is different in the two cases (cf. A., 1926, 982). C. R. HARINGTON.

Strophanthin. XVI. Degradation in the *iso*-strophanthidin series. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, **79**, 539—552).—As the result of previous work (A., 1927, 1194) strophanthidin is now partly formulated (I), although in view of the recent work (this vol., 1120) on digitoxigenin the attachment of the lactone group remains uncertain as between positions 7 and 5. Careful oxidation with permanganate of anhydro-α-*iso*strophanthonic dimethyl



(I.)

ester (A., 1927, 1194), for which formula II is preferred,



yields principally *undephanthontriacid dimethyl* ester, $H_{32}O_9$, m. p. 179—180°, which, with diazomethane, gave the *trimethyl* ester, m. p. 154·5—155·5°; the latter gave an *oxime*, m. p. 188—189° and 226—227°, and a *phenylhydrazone*, m. p. 196·5—197·5°, which when heated yielded a *phenyl-γ-lactazam*, m. p. 155—157° and 240—242°; it was therefore a β-ketonic ester. Partial hydrolysis gave the *monomethyl* ester, m. p. 237—238°, which could also be obtained by oxidation of anhydro-α-*iso*strophanthonic monomethyl ester. The trimethyl ester, on boiling with N-sodium hydroxide, neutralised 5 equivalents, corresponding with three ester groups, one lactone group, and ring cleavage at the ketonic group; the monomethyl ester, however, with 0·1N-sodium hydroxide, underwent ketonic decomposition, with the production of *duodephanthondiacid*, $C_{21}H_{28}O_7$, m. p. 266—268° (from acetone); this was a dibasic lactone acid and gave a *dimethyl* ester, m. p. 166—167°, and a *trimethyl ester oxime*, m. p. 187—189°. The formation of undephanthontriacid is therefore regarded as resulting from cleavage of ring B (formula II), with loss of carbon atom 12, carbon atoms 3 and 13 becoming carbonyl and carboxyl, respectively; duodephanthondiacid would thus be derived by loss of carbon atom 1.

In the oxidation of anhydro-α-*iso*strophanthonic acid dimethyl ester, there was further obtained a small amount of a *lactonetriacid dimethyl* ester, $C_{25}H_{32}O_{10}$, m. p. 188—190° (*trimethyl* ester, m. p. 236—237°; free *acid*, m. p. 187—189°); the trimethyl ester gave no ketonic reactions, and it could not be acylated, although the Grignard reagent indicated two active hydrogen atoms; it failed to give the Legal reaction; with methyl alcohol it formed a *compound*, $C_{26}H_{34}O_{10}$,MeOH, m. p. 193—195°.

C. R. HARINGTON.

Constitution of bixin. I. J. RINKES (Rec. trav. chim., 1928, **47**, 934).—The compounds isolated from the oxidation of methylbixin (Rinkes and van Hasselt, A., 1917, i, 660) do not support the constitution assigned to bixin by Kuhn and others (this vol., 644, 869).

H. BURTON.

Occurrence of *d*-β-pinene [*d*-nopinene]. B. N. RUTOVSKI and I. V. VINOGRADOVA (J. pr. Chem., 1928, [ii], **120**, 41—48).—The fruit of *Ferula Badra-Kema* (*F. galbaniflua*) yielded on steam-distillation 2·35% of essential oil, d_{20}^{20} 0·8736, α_D +16·16°, n^{20} 1·4765, acid value 1·2, ester value 6·65, ester value after acetylation 31·78, and 10·3% of wax and resin on extraction with light petroleum and alcohol. Fractionation of the essential oil showed the presence of 30% of *d*-nopinene, together with *dl*-α- and *d*-α-pinene (40%), *d*-limonene (1·5%), an unidentified alcohol (3%), a ketone (1%), and traces of acids. The *d*-nopinene was separated in a pure state after repeated fractionation, and had b. p. 162—163°, d_{20}^{20} 0·8662, α_D +20·75°, n^{20} 1·4745, $[R]_D$ 44·17. These properties, with the exception of α_D, correspond with those found by Halse and Dedichen (A., 1917, i, 398) and by Aschan (A., 1919, i, 336) for *d*-nopinene from other sources. The identification was confirmed by oxidation to *d*-nopinic acid, m. p. 126·5—127°, $[\alpha]_D$ +17·00° in alcohol, and further oxidation to l-*nopinone*, m. p. 0—1°, $[\alpha]_D$ −18·35° in ether (*semicarbazone*, m. p. 187—188°), and comparison with the optically isomeric derivatives from *l*-nopinene.

R. K. CALLOW.

Action of substituted aromatic amines on camphoric anhydride. Bromo- and iodo-camphoranilic acids and camphoro-bromo- and -iodo-phenylimides. M. SINGH, R. S. AHUJA, and K. LAL (J.C.S., 1928, 2410—2414).—When a substituted aniline is condensed with camphoric anhydride a camphoranilic acid and the corresponding imide are formed. The ratio of the acid to the imide decreases when the aniline is substituted by CO_2H, Me, Cl, I in that order, no imide being formed by the aminobenzoic acids. The position of the substituent in the aniline ring also affects the relative yields, the yield of imide decreasing in the order $p<m<o$. The relative effect of the substituents in diminishing the molecular rotatory power of these compounds when dissolved in acetone or in methyl ethyl ketone is in the same order as their effect in diminishing the optical activity of menthyl and *sec*-β-octyl esters of mono-substituted acetic and benzoic acids (cf. Rule, this vol., 221). When methyl or ethyl alcohol is the solvent the order of the substituents is displaced. The following are described: camphoro-*o*-bromophenylimide, m. p. 142°; *m*-bromo-derivative, m. p. 190° (lit. 139—140° and 184—185°, respectively); 2′-bromocamphoranilic acid, m. p. 168°, $[M]_D$ −61·1° in acetone (lit. m. p. 78°, $[M]_D$ −41·1°); 3′-bromocamphoranilic acid, m. p. 224° (lit. 215—217°); *4′-bromocamphoranilic acid*, m. p. 206—207°; *camphoro-*p*-bromophenylimide*, m. p. 182·5°; *2′-iodocamphoranilic acid*, m. p. 147—148°, and the corresponding 3′- and *4′-iodo-acids*, m. p. 226—227° and 221°, respectively; *camphoro-*m*- and -*p*-iodophenylimides*, m. p. 172° and 197°, respectively; 2-methoxycamphoranilic acid has $[M]_D$ −90·75° in methyl ethyl ketone. The rotations of these compounds in methyl and ethyl alcohols, acetone, and in methyl ethyl ketone are given.

M. CLARK.

Mono- and sesqui-terpene series. I. West Indian sandalwood oil. II. Nomenclature of the caryophyllene series. E. DEUSSEN (J. pr. Chem., 1928, [ii], **120**, 119—144).—I. Previous work by von Soden and Rojahn (A., 1900, i, 401, 677) and the author (A., 1900, ii, 579; 1902, i, 552) indicates that the oil contains a mixture of sesquiterpene hydrocarbons and alcohols. The hydrocarbon fraction consists of at least two isomerides, one being β-caryophyllene (A., 1912, i, 368); the other is now shown to be *d*-cadinene. By repeated fractionation in a vacuum over potassium, two fractions, b. p. 131—133·5°/10·5 mm. and 138—140°/13 mm., of almost pure *d*-cadinene were obtained, which when dehydrogenated with sulphur yielded cadalene, b. p. 159—163°/15 mm., identified as the picrate, m. p. 114·5°, and the styphnate, m. p. 138°; catalytic hydrogenation with platinum-black in 96% alcohol gives tetra-

hydrocadinene, b. p. 135—137°/14 mm., d^{16} 0·8874, n_D^{16} 1·48157 (cf. Semmler and Jonas, A., 1915, i, 63).

The sesquiterpene alcohol fraction appears to consist of two alcohols, $C_{15}H_{25}$·OH (termed amyrol by von Soden and Rojahn) and $C_{15}H_{23}$·OH, the former predominating, which can be only imperfectly separated by fractionation owing to the proximity of their b. p. After removal of the latter alcohol by oxidation, the resulting amyrol has been shown to consist of a mixture of two isomeric alcohols, $C_{15}H_{25}$·OH, called α- and β-amyrol. A fraction consisting mainly of amyrol, b. p. 160°/15 mm., d^{22} 0·972, on dehydrogenation with sulphur, yielded cadalene. Sodium did not react with amyrol in xylene solution, but potassium gave a *potassium* derivative which reacted with methyl iodide, yielding potassium iodide; no other product was isolated. On treatment with phenylcarbimide, 1 mol. of water was eliminated, yielding diphenylcarbamide and a sesquiterpene hydrocarbon, $C_{15}H_{24}$. Attempted benzoylation of amyrol using Einhorn's method led to the production of a sesquiterpene hydrocarbon, $C_{15}H_{24}$, b. p. 130—132°/12 mm.; by the Ruzicka–Stoll method a small quantity of an impure *benzoyl* derivative was obtained. Zinc dust at 100—160° under pressure had no effect, but at 220° loss of 1 mol. of water occurred, yielding cadinene. Similarly 85% formic acid with amyrol yields a sesquiterpene hydrocarbon, $C_{15}H_{24}$, b. p. 157—160°/31 mm., d^{15} 0·9192. By treatment of amyrol with powdered potassium permanganate in aqueous acetone at 0° and fractionation of the product were obtained *α-amyrol*, b. p. 137—138°/5 mm., $d^{17.5}$ 0·9814, $n_D^{17.5}$ 1·51147, hydrogenated in alcoholic solution in the presence of palladised calcium carbonate to *α-dihydroamyrol*, b. p. 134—136°/6 mm., d^{19} 0·9659, n_D 1·50068, and *β-amyrol* (contaminated with a little of the α-isomeride), b. p. 149·5—150·5°/10 mm., $d^{15.2}$ 0·9463, $n^{15.2}$ 1·50158 (cf. Ruzicka and Huyser, this vol., 425).

II. In reply to Chapman (this vol., 646), the author admits the identity of humulene and α- or inactive caryophyllene, but suggests that the latter name be retained for the hydrocarbon to avoid confusion.

The work of Henderson and his collaborators (A., 1926, 298, 841) in the caryophyllene series is criticised on the ground of nomenclature and the apparent non-acquaintance of these authors with the work of Deussen and Ober (A., 1923, i, 813) and of Asahina and Tsukamoto (A., 1922, i, 845). C. W. SHOPPEE.

Colouring matters of flowers. P. KARRER (Bull. Soc. chim., 1928, [iv], **43**, 1041—1058).—A lecture.

Nitro- and dinitro-thiophens. V. S. BABASINIAN (J. Amer. Chem. Soc., 1928, **50**, 2748—2753).—Cautious addition of thiophen in acetic anhydride to nitric acid in glacial acetic acid at 10° affords more than 80% of the theoretical yield of 2-nitrothiophen (cf. Steinkopf, A., 1914, i, 426). This with sulphuric and nitric acids readily yields a mixture, m. p. 52° (>80% yield), of isomeric dinitrothiophens, m. p. 54° and 78°, respectively. Contrary to the statement of Meyer and Stadler (A., 1885, 141), these are not interconvertible by distillation in steam, by heating at 140°, or by ultra-violet irradiation.

H. E. F. NOTTON.

Dipyridine iodostannate. A. G. DIMITRIOU (Praktika, 1927, **2**, 496; Chem. Zentr., 1928, i, 2369).—The compound $(C_5H_5N)_2SnI_4$, orange-red, is obtained by interaction of the components in anhydrous light petroleum. A. A. ELDRIDGE.

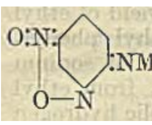
2-Methylaminopyridine and its derivatives. A. E. TSCHITSCHIBABIN and I. L. KNUNIANZ (Ber., 1928, **61**, [*B*], 2215—2217; cf. this vol., 427).—If the methylation of 2-aminopyridine by methyl sulphate is effected under conditions such that considerable proportions of the monomethyl compound are produced, its isolation is readily effected by exhaustive benzoylation of the mixture. Unchanged 2-aminopyridine is transformed thereby into the dibenzoyl derivative, which is insoluble in dilute acid, in which dimethylaminopyridine and methylbenzamidopyridine dissolve readily. The last two compounds are separated from one another by distillation under diminished pressure. 2-*Methylbenzamidopyridine*, b. p. 200°/11 mm., m. p. 61—62°, is hydrolysed by 20% hydrochloric acid to 2-*methylaminopyridine*, b. p. 90°/9 mm., m. p. 15°. It is readily converted into the corresponding *nitrosoamine*, b. p. 123—124°/30 mm. (*picrate*, m. p. 186—187°), which is not isomerised by warm sulphuric acid, but is reduced by zinc dust and 80% acetic acid to as-*methyl-2-pyridylhydrazine*, b. p. 105°/10 mm. (*benzylidene* compound, m. p. 67—68°). H. WREN.

Nitro-derivatives of the methylated α-aminopyridines. II. A. E. TSCHITSCHIBABIN and A. W. KIRSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 915—982).—The conclusions of Tschitschibabin and Konovalova (A., 1925, i, 1328) concerning the isomerisation mechanism in the nitro-derivatives of the methylated aminopyridines are found to be incorrect. Methyl iodide and 5-nitro-2-aminopyridine reacted at 120° to give a 90% yield of 5-nitro-2-methylaminopyridine, m. p. 181°. With 3-nitro-2-aminopyridine, 3-*nitro-2-methylaminopyridine*, m. p. 63—64°, b. p. 262—262·5°/740 mm., was obtained as golden-yellow crystals. By the action of sulphuric acid on methyl-2-pyridonenitroimine considerable quantities of the 5-nitro-2-methylaminopyridine, m. p. 181°, were formed, together with traces of the 3-compound. The nitration of 2-methylaminopyridine gave 2-*methylnitroaminopyridine*, m. p. 30—31°, which isomerised by sulphuric acid to a mixture of 3- and 5-nitro-2-methylaminopyridines, m. p. 181° and 63—64°.

When boiled with concentrated alkali hydroxide solutions the nitroaminopyridines are decomposed, whilst with dilute alkalis good yields of nitrohydroxypyridines are obtained. The 3- and 5-nitro-2-methylaminopyridines gave the corresponding 3- and 5-nitro-2-hydroxypyridines, m. p., 190—191° and 221—222°, whilst with nitrous acid the products were 3- and 5-*nitro-2-nitrosomethylaminopyridine*, both melting at 112—113°. Bromine in potassium bromide solution gave 5-*bromo-3-nitro-2-aminopyridine*, m. p. 163—164°, with the 3-nitro-compound, and 3-*bromo-5-nitro-2-aminopyridine*, m. p. 149—150°, with the 5-nitro-compound. The 5-nitro-compound had been nitrated by Tschitschibabin and Konovalova (*loc. cit.*), and the compound obtained, m. p. 59—60°, must now be assigned the structure of 5-nitro-2-methylnitroaminopyridine. The 3-nitro-compound, under the same

conditions, gave 3-*nitro-2-methylnitroaminopyridine*, m. p. 89°. On methylation of 3- and 5-nitro-2-nitroaminopyridine, the corresponding 3- and 5-nitro-2-methylnitroamino-compounds are obtained, together with small amounts of the 3- and 5-nitro-*N*-methyl-2-pyridonenitroimines. Both the 3- and 5-nitro-2-methylnitroaminopyridines when treated with sulphuric acid gave 3 : 5-*dinitro-2-methylaminopyridine*, m. p. 147—148°, whilst the 3-nitro-2-methylpyridinenitroimine under the same conditions yielded at high temperatures the dinitro-, and at low temperatures the mononitro-derivative. With 3-nitro-2-nitroaminopyridine, dinitroaminopyridine, m. p. 190—191°, was obtained.

The action of methyl iodide at 125° on 5-nitro-2-methylaminopyridine gave a bright yellow *solid*, m. p. 149·5—150·5°, identical with that obtained by nitrating methylpyridonemethylimine, for which formula I is suggested. The mother-liquor contained small quantities of 5-nitro-2-dimethylaminopyridine. On boiling the solid with water, 5-nitro-*N*-methyl-2-pyridone, m. p. 171—172°, was obtained. M. ZVEGINTZOV.



(I.)

Reactions of the bromo-substituted derivatives of 2-aminopyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 983—994; cf. preceding abstract).—The behaviour of methylated halogen derivatives of 2-aminopyridines and their nitration products was investigated, to discover whether reactions similar to those of the nitro-derivatives of the α-aminopyridines took place. 3 : 5-Dibromo-2-aminopyridine, m. p. 105°, gives with methyl iodide 3 : 5-*dibromo*-N-*methyl-2-pyridoneimine*, m. p. 99—100°. If the sodium derivative of the 3 : 5-dibromo-2-aminopyridine is methylated with methyl sulphate, 3 : 5-*dibromo-2-methylaminopyridine*, m. p. 56·5—57°, b. p. 137—138°/8 mm., and the corresponding dimethyl compound are obtained. Bromination of 2-methylaminopyridine gives both the dibromo-compound and 5-*bromo-2-methylaminopyridine*, m. p. 70—71°.

With nitrous acid, the dibromo-compound yields a colourless *nitroso*-derivative, m. p. 56—57°. 3 : 5-*Dibromo-2-methylnitroaminopyridine*, m. p. 100—101°, can be obtained by nitrating the dibromo-compound. If 3 : 5-dibromoaminopyridine is nitrated, some bromine is lost, and together with the 3 : 5-dibromo-2-nitroaminopyridine, m. p. 123°, some 3-bromo-5-nitro-2-aminopyridine, m. p. 216—217°, is formed. On methylating 3 : 5-dibromo-2-nitroaminopyridine, 3 : 5-dibromo-2-methylaminopyridine results, together with 3 : 5-*dibromo*-N-*methyl-2-pyridonenitroimine*, m. p. 186—187°, and 3 : 5-*dibromo*-N-*methyl-2-pyridone*, m. p. 182°. Of the last two, the former is also obtained by nitrating 3 : 5-dibromo-*N*-methyl-2-pyridoneimine, whilst the latter is obtained by the action of alkali hydroxides on the nitroimine, or of nitrous acid on the pyridoneimine. Sulphuric acid converts 3 : 5-dibromo-2-nitroaminopyridone into 3 : 5-dibromo-2-hydroxypyridine, m. p. 208°, together with dibromoaminopyridine, 3 : 5-dibromo-2-methylnitroaminopyridine, into the same product, together with 3 : 5-dibromo-2-methylnitrosoaminopyridine, m. p. 56—57°, and 3 : 5-dibromo-*N*-methyl-2-pyridonenitroimine into 3 : 5-dibromo-*N*-methyl-2-pyridoneimine. In the last case, if air is blown through the reaction mixture, some 3 : 5-dibromo-*N*-methyl-2-pyridone, m. p. 182°, is obtained, *i.e.*, there is no ejection of bromine by the nitro-group, or migration of the methyl radical. M. ZVEGINTZOV.

Action of thionyl chloride on pyridinemonocarboxylic acids. H. MEYER and R. GRAF (Ber., 1928, **61**, [*B*], 2202—2215; cf. A., 1901, i, 407).—The action of thionyl chloride on pyridinemonocarboxylic acids gives primarily the corresponding acid chlorides of low m. p. More extended or drastic treatment leads to chlorination in the nucleus. If the crude acid chlorides are preserved in a vacuum over potassium hydroxide, a product of high m. p. is obtained, identified as the acid chloride hydrochloride [instead of a polymeric acid chloride as assumed previously (*loc. cit.*)], which ultimately passes into the acid hydrochloride if a trace of moisture is present.

Picolinyl chloride, m. p. 46° (cf. Späth and Spitzer, A., 1926, 958), is converted by hydrogen chloride in benzene into *picolinyl chloride hydrochloride*, m. p. 118—122° (decomp.), the production of which does not occur in the complete absence of moisture. Nicotinyl acid hydrochloride is more stable than the corresponding picolinyl derivative, but is transformed into *nicotinyl chloride*, b. p. 85°/12 mm., m. p. 15—16°, by prolonged ebullition with thionyl chloride. It is also prepared from sodium nicotinate and thionyl chloride. Similar methods are employed in the preparation of iso*nicotinyl chloride*, m. p. 15—16°. Protracted treatment of picolinyl chloride with technical or homogeneous thionyl chloride yields 4-*chloropicolinyl chloride hydrochloride*, converted by water into 4-*chloropicolinic acid*, m. p. 182° (decomp.). The constitution of the acid is deduced by converting its ammonium salt by ammonia at 180° into 4-*aminopicolinic acid*, m. p. 260° (decomp.), which yields 4-aminopyridine, m. p. 157—158°, when heated above its m. p. 4-*Aminopicolinic acid hydrochloride*, $C_6H_6O_2N_2$,HCl, m. p. 240° (decomp.), and *methyl* 4-*aminopicolinate*, m. p. 129°, are described. 4-Aminopicolinic acid is converted in the usual manner into 4-hydroxypicolinic acid, m. p. 254—255° (decomp.), converted above its m. p. into 4-hydroxypyridine, m. p. 65—66°. 4-*Chloropicolinyl chloride*, m. p. 46°, *methyl* 4-*chloropicolinate*, m. p. 57—58°, *phenyl* 4-*chloropicolinate*, m. p. 68°, and 4-chloropicolinamide, m. p. 158°, are described. 4-Chloropicolinic acid is converted by boiling hydriodic acid and red phosphorus through the basic *iodohydrate* of 4-*iodopicolinic acid*, m. p. 185—190° (decomp.), into 4-*iodopicolinic acid*, m. p. 169° (decomp.) (*methyl* ester, m. p. 75—76°), in which the iodine atom is replaced by chlorine under the influence of thionyl chloride. Protracted treatment of 4-chloropicolinic acid with thionyl chloride at 180° affords 4 : 6-*dichloropicolinic acid*, m. p. 111—112° (*monohydrate*, m. p. 96—97°), in which the second chlorine atom must occupy the 6 position since the acid is converted by boiling hydriodic acid (*d* 1·7) and red phosphorus into the basic iodohydrate of 4-iodopicolinic acid (see above).

Methyl 4 : 6-*dichloropicolinate*, m. p. 73—74°, *phenyl* 4 : 6-*dichloropicolinate*, m. p. 90—91°, and 4 : 6-*dichloropicolinamide*, m. p. 172—174°, are described. 3(5) : 4 : 6-Trichloropicolinic acid (*methyl* ester, m. p. 122—123°) is obtained as by-product of the preparation of dichloropicolinic acid.

5-Chloronicotinic acid, m. p. 171°, is obtained in modest yield from nicotinic acid hydrochloride and thionyl chloride at 130°. 5-*Chloronicotinyl chloride*, b. p. 120°/12 mm., m. p. 53°, *methyl* 5-*chloronicotinate*, m. p. 88—89°, *phenyl* 5-*chloronicotinate*, m. p. 79°, and 5-*chloronicotinamide*, m. p. 205—206°, have been prepared. 5-Chloronicotinic acid is transformed by ammonia in presence of copper oxide at 180° into 5-aminonicotinic acid (*copper* salt), the *methyl* ester, m. p. 137°, of which is converted by diazotisation in concentrated hydrochloric acid into methyl 5-chloronicotinate. The acid passes above its m. p. into 3-aminopyridine. 5 : 6-Dichloronicotinic acid, m. p. 161—162° (monohydrate), is obtained from nicotinic acid hydrochloride and thionyl chloride at 150°. The corresponding *chloride* has m. p. 48—49°. *Methyl* 5 : 6-*dichloronicotinate*, m. p. 67—68°, *phenyl* 5 : 6-*dichloronicotinate*, m. p. 133°, and 5 : 6-*dichloronicotinamide*, m. p. 218—220°, are described. Cautious heating of 5 : 6-dichloronicotinic acid under diminished pressure at 150° affords 2 : 3-*dichloropyridine*, m. p. 46—47°; less cautious treatment leads to loss of hydrogen chloride and production of 5-chloro-6-hydroxynicotinic acid, m. p. 305° (incipient decomp.), more conveniently prepared by boiling 5 : 6-dichloronicotinic acid with excess of potassium hydroxide.

*iso*Nicotinic acid is converted by treatment with thionyl chloride at 180—220° into a mixture of 3-*chloro*iso*nicotinic acid*, m. p. (indef.) 235° (*methyl* ester, m. p. 32°; 3-*hydroxy*iso*nicotinic acid*, m. p. 312°), and 3 : 5-*dichloro*iso*nicotinic acid*, m. p. 217°. The last-named acid passes at 230° in a sealed tube into 3 : 5-*dichloropyridine*, m. p. 64—65°, also prepared by transforming 5-chloronicotinic acid into its *hydrazide*, m. p. 178°, and thence into the urethane and 5-chloro-3-aminopyridine, from which the dichloro-compound is derived in the usual manner. Methyl *iso*cinchomeronate is transformed into 2 : 5-diaminopyridine and thence by diazotisation in presence of cuprous chloride into 2 : 5-*dichloropyridine*, m. p. 60°.
H. WREN.

Syntheses by means of magnesylpyrroles. Series II. XII. Indolephthalein. B. ODDO (Gazzetta, 1928, **58**, 569—573).—The action of phthalyl chloride on magnesium 2-methylindyl bromide yields a phthalein (cf. A., 1925, i, 588; 1926, 1157); its action on magnesium indyl bromide is now found to give two products. One, soluble in water, is regarded as ω-[*indolidene-indolyl*]-o-*toluic acid*, m. p. 145°, of which some metallic *salts* and a *monohydrochloride* are described. The other, insoluble in ether or water, contains *indolephthalein*,

$$\left[NH{<}{\substack{C_6H_4\\CH}}{\gg}C^{\cdot}\right]_2{:}C{<}{\substack{O\\C_6H_4}}{>}CO,$$ m. p. 286·5°.
E. W. WIGNALL.

Manufacture of chloroiodo-compounds of the quinoline series. CHEM. FABR. AUF ACTIEN.—See B., 1928, 874.

Production of quinoline-4-carboxylic acids. A. HAUSSLER ETC.—See B., 1928, 837.

Condensation of rhodanic acids with 5-nitroisatin. 5′-Nitro-3-rhodanylidene-$\Delta^{5:3'}$-oxindoles. H. A. JONES and R. M. HANN (J. Amer. Chem. Soc., 1928, **50**, 2491—2493; cf. A., 1925, i, 987).—The following red 5′-*nitro*-3-*aryl-rhodanylidene*-$\Delta^{5:3'}$-*oxindoles* have been prepared by condensing 5-nitroisatin with arylrhodanic acids in boiling glacial acetic acid in presence of sodium acetate: -*phenyl*-, m. p. 260—267°; -o-*anisyl*-, m. p. 247°; -p-*anisyl*-, m. p. 370°; -ψ-*cumyl*-, m. p. 245°, and -β-*naphthyl*, m. p. 330°.
H. E. F. NOTTON.

Preparation of ethyl phenylmalonate and of 5-phenyl-5-β-hydroxyethylbarbituric acid. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1928, **50**, 2758—2762).—The maximum yield of ethyl phenylmalonate (I), d_4^{20} 1·095, from ethyl phenylacetate and ethyl carbonate in presence of sodium or sodamide is 20% of the theoretical; from ethyl phenylcyanoacetate and saturated alcoholic hydrogen chloride it is 78%. The latter is best obtained (70% yield) from phenylacetonitrile and ethyl carbonate in presence of sodamide in ether. Attempts to condense α-substituted phenylacetonitriles [*e.g.*, *phenylvinyloxyethylacetonitrile*, b. p. 147°/8 mm., d_4^{20} 1·029, prepared from phenylacetonitrile and β-chloroethyl vinyl ether by the method of Bodroux and Taboury (A., 1910, i, 557)] with ethyl carbonate were unsuccessful. The ester (I) was converted into ethyl phenylethylmalonate (61% yield), and this into 5-phenyl-5-ethylbarbituric acid (35% yield). Ethyl sodiophenylmalonate and β-chloroethyl vinyl ether in absence of solvent at 140—145° yield *ethyl phenylvinyloxyethylmalonate*, b. p. 196—197°/17 mm., d_4^{20} 1·098, which when condensed with carbamide and hydrolysed (cf. A., 1926, 180) yields 5-*phenyl*-5-β-*hydroxyethylbarbituric acid* ("hydroxyluminal"), m. p. 200°. 2-*Thio*-5-*phenyl*-5-β-*hydroxyethylbarbituric acid* has m. p. 167°.
H. E. F. NOTTON.

Oxidation reactions of aldehydes. J. B. CONANT and J. G. ASTON.—See this vol., 1357.

Effect of substituents on the colour and absorption spectrum of indigotin, thioindigotin, and indirubin. J. FORMANEK (Z. angew. Chem., 1928, **41**, 1133—1141).—By introducing chlorine or bromine into the benzene nucleus in indigotin the colour is changed from violet-blue to greenish-blue, the absorption spectrum showing a movement of the bands towards the red. Introduction of bromine causes displacement of the absorption bands proportionately more than introduction of chlorine; the position of the bands is dependent on the position of the halogen atom. If an alkyl group is introduced into one of the benzene nuclei, there is a negligible change in colour and absorption spectrum; if, however, it is substituted in the imino-group, the colour changes from violet-blue to green, and there is a marked displacement of the absorption bands. The indigotin derivatives dissolve in sulphuric acid with a green or bluish-green colour, and the solution gives no absorption bands. An essentially different effect on the colour and absorption spectrum of indigotin

is obtained by substituting halogen in the 6 : 6′-position. The colour changes to red and the absorption spectrum appears to be split up into bands. The same effect is obtained by introducing the amino-group into the 6 : 6′-position. By introducing halogen or alkyl groups into the benzene nucleus of thioindigotin, the absorption bands are moved in the same direction as for indigotin. Halogen, alkyl, and amino-groups substituted in the 6 : 6′-position give a change in colour from red to orange-yellow. The derivatives of thioindigotin dissolve in sulphuric acid with a green colour, the solutions giving either no absorption bands or only very weak ones. Similar derivatives are obtained with indirubin.

A. J. Mee.

Opening of the glyoxaline ring. II. B. Oddo and Q. Mingoia (Gazzetta, 1928, **58**, 573—584; cf. A., 1927, 260).—Benzoylglyoxaline (*loc. cit.*) forms a *dibromo*-derivative, m. p. 255°. E. W. Wignall.

Glyoxaline compounds. B. Oddo and Q. Mingoia (Gazzetta, 1928, **58**, 584—597).—The effect of reagents on magnesium glyoxalyl bromide is as follows. Water yields glyoxaline; methyl iodide, 1 : 2-*dimethylglyoxaline* (*picrate*, m. p. 179°); ethyl iodide, 1 : 2-*diethylglyoxaline*, m. p. 218—220°. Carbon dioxide, acetyl chloride, acetic anhydride, and ethyl acetate give negative results. Ethyl chloroformate furnishes *ethyl glyoxalinecarboxylate*, b. p. 135—138°/60 mm. (*picrate*, m. p. 182°); carbonyl chloride, *diglyoxalyl ketone* (*picrate*, m. p. 204°). Ethoxalyl chloride and carbethoxyacetyl chloride cause opening of the ring, furnishing respectively *diethyloxalyldiaminoethylene*, b. p. 115—117°/52 mm., and *di(carbethoxyacetyl)diaminoethylene*, b. p. 270°/101 mm., together with formic acid in each case.

E. W. Wignall.

Conversion of oximes of o-diketones into pyrazines. O. Wallach (Nachr. Ges. Wiss. Gottingen, 1927, 238—244; Chem. Zentr., 1928, i, 2177—2178).—The dioximes of *o*-diketones, on reduction, pass by way of the monoxime to the *o*-aminoketone, which by enolisation and condensation of two molecules affords a dihydropyrazine, readily oxidised in air to the pyrazine. Diacetyl-di- or -mon-oxime affords tetramethylpyrazine, $\begin{array}{c}\mathrm{CMe{\cdot}N{\cdot}CMe}\\ \| \quad | \quad \| \\ \mathrm{CMe{\cdot}N{\cdot}CMe}\end{array}$, m. p. 76—78°, after drying over calcium chloride, m. p. 86—87°, b. p. 189—190° (picrate, m. p. 192—195°; chloroplatinate; mercuric chloride and cyanide compounds). Reduction of *cyclo*hexane-1 : 2-dione dioxime affords dihydropyrazine, oxidised to pyrazine, m. p. 108° (hydrochloride; chloroplatinate; picrate; mercuric chloride compound. A. A. Eldridge.

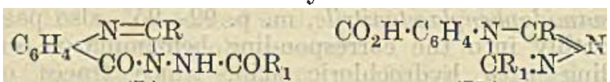
Formation of 2-substituted benziminazoles. M. A. Phillips (J.C.S., 1928, 2393—2399).—The reaction between boiling hydrochloric acid and mono- or di-acetyl-*o*-diamines or between acetic anhydride, hydrochloric acid, and *o*-phenylenediamine, whereby 2-methylbenziminazole is formed (this vol., 305), has been extended to the formation of 2-ethyl-, 2-hydroxymethyl-, 2-α-hydroxyethyl-, and 2-α-hydroxybenzylbenziminazoles by substitution of the appropriate organic acid for acetic anhydride. Benziminazole is produced by reduction of *o*-nitroformanilide or by the action of boiling hydrochloric acid on *o-phenylenediamine monoformate*, whilst 3-amino-4-formamidophenylacetonitrile, 3-amino-4-acetamidophenylacetonitrile, 3-amino-4-lactamidophenetole, and 3 : 4-*diformamidophenylacetonitrile*, m. p. 92—95°, also pass smoothly into the corresponding benziminazole on boiling with hydrochloric acid. Since traces of 4-nitro-*o*-phenylenediamine, which increase with diminution in the length of heating with hydrochloric acid, accompany 5-nitro-2-methylbenziminazole in the formation of the latter compound from 4-nitrodiacetyl-*o*-phenylenediamine, it is now considered that the diacetyl-*o*-diamines are completely hydrolysed to the diamines with subsequent formation of the iminazole ring (cf. *loc. cit.*). Oxalic acid and *o*-phenylenediamine condense in the presence of boiling hydrochloric acid to give 2 : 3-dihydroxyquinoxaline, m. p. above 350° (*sodium* salt). With malonic acid, the same reagents yield *o*-phenylenemalonamide (*monosodium* salt) and 2-*aminomalonanilic acid*, m. p. 175—176°. Succinic acid and *o*-phenylenediamine (I) in equimolecular proportions with hydrochloric acid yield 2 : 2′-diaminosuccinanilide (II) and benziminazole-2-propionic acid (III). When 2 mols. of the base are used, II and αβ-dibenziminazolylethane (IV) are formed. IV is also produced when a mixture of I and III or II alone is boiled with hydrochloric acid. Diacetylethylenediamine yields 2-methyl-4 : 5-dihydroglyoxaline when it is boiled with hydrochloric acid. M. Clark.

Relationship between ring closure and "specific affinity." Complex compounds of bivalent silver. W. Hieber and F. Mühlbauer (Ber., 1928, **61**, [*B*], 2149—2153; cf. this vol., 510, 511).—Addition of 2 mols. of *o*-phenanthroline (prepared from *o*-phenylenediamine, glycerol, arsenic and sulphuric acids) dissolved in water to a solution of silver nitrate gives a colourless, gelatinous precipitate which is quantitatively transformed by ammonium persulphate into the chocolate-brown, stable *di-o-phenanthroline silver persulphate*, $[Ag(C_{12}H_8N_2)]S_2O_8$. The salt is readily soluble without decomposition in 64% nitric acid, and addition of the requisite sodium salt to this solution leads to the formation of the corresponding *perchlorate*, $Ag(ClO_4)_2,2C_{12}H_8N_2$, *chlorate*, and *hydrogen sulphate*; with sodium phosphate, ammonium fluoride, and sodium dichromate mixed salts appear to be formed. The bivalency of silver in the salts is established by determination of the carbon dioxide evolved when the perchlorate reacts with oxalic acid in presence of sulphuric acid and of iodine liberated when it is mixed with potassium iodide. Similar examination of the persulphate appears to indicate the presence of the hydrogen sulphate. Further confirmation of the bivalency of silver is found in the existence of isomorphism between its salts and analogous cupric and cadmium compounds with which mixed crystals are produced.

H. Wren.

Transformation of quinazolones into triazole derivatives. G. Heller [with W. Köhler, S. Gottfried, H. Arnold, and H. Herrmann] (J. pr. Chem., 1928, [ii], **120**, 49—63).—Quinazolones of type I, obtained from diacyl-*o*-aminobenzhydrazides

(A., 1925, i, 1322), are transformed by dilute alkali into triazolecarboxylic acids of type II. The latter are extremely stable, being unaffected by hydrochloric acid at 200° and by chromic and acetic acids



(I.) (II.)

at 100°; they are also directly obtained under the same conditions, but less smoothly, from the diacyl-*o*-aminobenzhydrazides. 3-Benzamido-2-phenyl-4-quinazolone (*loc. cit.*) thus yields 2 : 5-*diphenyl*-1-o-*carboxyphenyl*-1 : 3 : 4-*triazole*, m. p. 310°, also obtained from dibenzoyl-*o*-aminobenzhydrazide (*loc. cit.*) Similarly, 3-acetamido-2-phenyl-4-quinazolone (*loc. cit.*) or 3-*diacetamido*-2-*phenyl*-4-*quinazolone*, m. p. 153°, prepared from 3-amino-2-phenyl-4-quinazolone by treatment with excess of acetic anhydride, yields 2-*phenyl*-1-o-*carboxyphenyl*-5-*methyl*-1 : 3 : 4-*triazole*, m. p. 241° (*hydrated form*, m. p. 140—145°; *anilide*, m. p. 253°; *methyl* ester, m. p. 156°; *ethyl* ester, m. p. 165°), nitrated in sulphuric acid to give a *dinitro*-compound, m. p. 273°, together with a yellow *substance*, and oxidised by potassium permanganate in concentrated nitric acid at 40° to an *acid*, $C_{10}H_9O_2N_3$, m. p. 259° (see below). o-*Benzamidobenz*-p-*chlorobenzoylhydrazide*, m. p. 175°, prepared from *o*-benzamidobenzhydrazide and *p*-chlorobenzoyl chloride in pyridine solution, is converted by dilute alkali into 2-*phenyl*-5-p-*chlorophenyl*-1-o-*carboxyphenyl*-1 : 3 : 4-*triazole*, m. p. 204°. Treatment of *o*-aminobenzhydrazide with *p*-chlorobenzoyl chloride in ethyl acetate solution yields o-4-*chlorobenzamidobenzhydrazide*, m. p. 225°, together with o-4-*chlorobenzamidobenz*-p-*chlorobenzoylhydrazide*, m. p. 227°; the former when benzoylated in pyridine solution yields o-4-*chlorobenzamidobenzbenzoylhydrazide*, m. p. 213°, converted by dilute alkali into 5-*phenyl*-2-p-*chlorophenyl*-1-o-*carboxyphenyl*-1 : 3 : 4-*triazole*, m. p. 212°, and the last with dilute alkali yields 2 : 5-*di*-p-*chlorophenyl*-1-o-*carboxyphenyl*-1 : 3 : 4-*triazole*, m. p. 345°.

To distinguish between the three formulæ proposed for the acid $C_{10}H_9O_2N_3$, m. p. 259°, attempts have been made to synthesise triazolecarboxylic acids, but without success. NN-*Diacetylbenzhydrazide*, m. p. 152°, is obtained in 90% yield by the action of boiling acetic anhydride on benzhydrazide (cf. A., 1895, i, 34); the corresponding monoacetyl compound heated with aniline and aniline hydrochloride at 100° yields benzoylbenzhydrazide (cf. A., 1912, i, 225) and at 140° benzanilide is also formed, but triazole formation does not occur; similarly with *p*-toluidine and its hydrochloride benzoylbenzhydrazide and benz-*p*-toluidide are obtained. Negative results were obtained by heating acetylbenzhydrazide with boiling aniline, but in the presence of phosphorus pentoxide triazole formation takes place to the extent of 10%; from acetylbenzhydrazide and aniline, *o*-toluidine, and *p*-toluidine, respectively, are produced 1 : 5-*diphenyl*-2-*methyl*-1 : 3 : 4-*triazole*, m. p. 161° (*picrate*, m. p. 182°), 5-*phenyl*-1-o-*tolyl*-2-*methyl*-1 : 3 : 4-*triazole*, m. p. 177·5° (*picrate*, m. p. 186°; *hydrochloride*, m. p. 210°), and 5-*phenyl*-1-p-*tolyl*-2-*methyl*-1 : 3 : 4-*triazole*, m. p. 162·5° (*picrate*, m. p. 160—162°; *hydrochloride*, m. p. 205—210°). Similarly, *formylacethydrazide*, m. p. 96°, obtained in 70% yield by treating formylhydrazide (cf. Schofer and Schwan, A., 1895, i, 263) with acetic anhydride at 0°, is converted by aniline and phosphorus pentoxide at 190—200° into a triazole, which is, however, 1-phenyl-2 : 5-dimethyl-1 : 3 : 4-triazole, m. p. 236° (cf. Pellizzari, A., 1901, i, 488), and not the expected 1-phenyl-2-methyl-1 : 3 : 4-triazole; if in the preparation of formylacethydrazide cooling is not efficient, *diformylhydrazide*, m. p. 158°, is produced. By heating benzhydrazide and acetamide at 230—260°, 2-*phenyl*-5-*methyl*-1 : 3 : 4-*triazole*, m. p. 164·5° (*picrate*, m. p. 158°; *hydrochloride*, m. p. 230°), is obtained in poor yield, together with some benzoylbenzhydrazide. Similarly, acethydrazide and formanilide heated together at 150—230° yield 1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 122° (*picrate*, m. p. 172°), and not the expected 1-phenyl-2-methyl-1 : 3 : 4-triazole prepared by Pellizzari (*loc. cit.*). The author concludes that the conditions necessary to produce triazole derivatives by the above methods render direct condensation of hydrazides with carboxylic acids to triazolecarboxylic acids impossible. Attempts to use compounds containing an amino-group, which could be converted into a carboxyl group after triazole formation, failed; thus with *o*-aminobenzhydrazide and acetamide at 200°, the latter acted as an acetylating agent, yielding 3-amino-2-methyl-4-quinazolone. An attempt to prepare dichlorohydrazides also failed, a tetrachloro-compound, probably *di*(*chloroacetyl*)*benzhydrazide dichloride*, m. p. 143°, being produced.

C. W. SHOPPEE.

Condensation of pyrrole with aliphatic ketones. T. SABALITSCHKA and H. HAASE (Arch. Pharm., 1928, **266**, 484—492).—A well-defined compound is obtained by the condensation of 4 mols. of pyrrole with 4 mols. of acetone in presence of acids. This reaction is quite general and has been applied to other aliphatic ketones. It takes place less readily and with diminished yield, however, as the series is ascended. *Compounds* derived from the following ketones are described: acetone (m. p. 296° decomp.), methyl ethyl ketone (m. p. 149°), diethyl ketone (m. p. 208°), methyl propyl ketone (m. p. 226°), ethyl propyl ketone (m. p. 219°), methyl butyl ketone (m. p. 193—194°), ethyl *iso*butyl ketone (m. p. 199°), ethyl butyl ketone (m. p. 205—206°), methyl hexyl ketone (m. p. 178°). The compound from methyl ethyl ketone affords maleimide on oxidation with chromic acid, whilst the acetone compound furnishes α-iso-*propylpyrrole*, b. p. 175°, when distilled with zinc dust. The compounds give a blood-red coloration when treated with warm nitric acid or ferric chloride solution and a deep bluish-red coloration with glacial acetic acid. The structure of these compounds and their possible connexion with the porphyrins are discussed.

S. COFFEY.

Chlorophyll. I. Ætioporphyrins from plant- and blood-pigment porphyrins. H. FISCHER and A. TREIBS (Annalen, 1928, **466**, 188—242).—Comparisons are made, mainly by spectrum analysis, of the ætioporphyrins obtained from various plant- and blood-pigment porphyrins by thermal decom-

position at 300—350° in a high vacuum. Thus, mesoporphyrin gives *mesoætioporphyrin*, $C_{32}H_{38}N_4$, m. p. 369° (Pregl block), which does not appear to be identical with any of the known ætioporphyrins (crystallisation tests, A., 1926, 1256). Mesophyllin affords ætiophyllin, from which after removal of magnesium with hydrochloric acid meso- and ætio-porphyrins are obtained. Rhodoporphyrin, most probably $C_{32}H_{34}O_4N_4$ (*ester*, m. p. 269°), yields *rhodoætioporphyrin* (I), (or $C_{31}H_{36}N_4$), m. p. 294° (corr.), together with the probably intermediate pyrroporphyrin (II) [*ester*, m. p. 243° (corr.)]. When *rhodohæmin*, $C_{32}H_{32}O_4N_4ClFe$, and rhodoporphyrin are decarboxylated by heating with 5 parts of resorcinol at 200° (cf. Schumm, this vol., 1148), II is produced. Bromination of I in chloroform–acetic acid solution gives a perbromide, which on treatment with acetone passes into *bromorhodoætioporphyrin* (III), $C_{30}H_{33}N_4Br$(?), m. p. 340° (Pregl block). When mesoætioporphyrin and ætioporphyrin I are brominated similarly, the resulting products contain only a small amount of bromine. Treatment of III with zinc dust and acetic acid does not effect elimination of bromine, but affords a zinc complex easily decomposed by acid. Oxidation with chromic anhydride and sulphuric acid gives methylethylmaleinimide and bromocitraconimide (?), whilst reduction with hydrazine in presence of a palladium–calcium carbonate catalyst regenerates I. Deuteroporphyrin and bromoporphyrin I (dibromodeuteroporphyrin) yield *deuteroætioporphyrin*, $C_{28}H_{30}N_4$, m. p. 285° [corr.; m. p. 335° (block), from deuterohæmin], identical spectroscopically with deutero-, pyrro-, and rhodo-ætioporphyrins, and brominated to a *dibromo*-derivative, m. p. 371° (block). 1 : 4 : 6 : 7-Tetramethyl-2 : 3 : 8-triethyl-5-β-carboxyethylporphin affords an *ætioporphyrin*, $C_{32}H_{38}N_4$, m. p. 344° (block), identical with ætioporphyrin IV. Decarboxylation of II gives pyrroætioporphyrin (IV), m. p. 278° (corr.), identical with I. Phylloporphyrin affords, in addition to *phylloætioporphyrin* (V), $C_{30}H_{34}N_4$, m. p. 267° [corr.; *iron* complex; *monobromo*-derivative, m. p. 274° (block)], the three new colouring matters, *phyllorhodin*, $C_{31}H_{32}ON_4$, red, *phyllochlorin*, green, and *phylloverdin*, $C_{31}H_{32}ON_4$, green, probably formed by elimination of water. When V is heated with methyl-alcoholic potassium hydroxide, isomerisation into IV occurs. Synthetic *iso*pyrroporphyrin (1 : 4 : 5 : 8-tetramethyl-3 : 6-diethyl-7-β-carboxyethylporphin) gives iso*pyrroætioporphyrin* (*bromo*-derivative), identical with IV. iso*Uroætio*-, m. p. 356°, and uroætio-porphyrins, m. p. 393—394° (cf. A., 1925, i, 307), are described. The ætioporphyrin, m. p. 341° (block), from hæmoporphyrin is identical (spectrum) with ætioporphyrin I.

When bromoporphyrin I is reduced with hydriodic and acetic acids and subsequently oxidised with lead dioxide and sulphuric acid, citraconimide and hæmopyrrolecarboxylic acid are obtained. Similar treatment of II furnishes methylethylmaleimide and the above acid. Oxidation of bromopyrroporphyrin (Treibs and Wiedemann, this vol., 1384) with chromic oxide and sulphuric acid affords, in addition to the malemide, bromocitraconimide, showing that II, a porphinmonocarboxylic acid, contains a free methene group in which bromination takes place without loss of carbon. Magnesium methyl iodide converts II or its ester into a *porphyrin alcohol*, $C_{33}H_{40}ON_4$, m. p. 260°. Similarly, mesoporphyrin dimethyl ester yields a *carbinol*, $C_{37}H_{46}O_3N_4$ or $C_{38}H_{50}O_2N_4$, m. p. 295° (corr.) from methyl alcohol, 308° from acetic acid.

The *xanthoporphinogen* (cf. A., 1927, 1206) from mesoætioporphyrin crystallises with 1 mol. of benzene easily replaced by 1 mol. of water. Ætioxanthoporphinogen I (*mono*- and *di-potassium* and *disodium* salts) crystallises with $3COMe_2$. *Mesoxanthoporphinogen* (*ethyl* ester) is intensely yellow and very hygroscopic.

Nitration of ætioporphyrin I with cold nitric acid (*d* 1·48) gives a *trinitro*-derivative, m. p. 305° [Pregl block; *nitrate*; *hydrochloride*; *copper*, m. p. 313° (block), and *iron* salts]. *Trinitroætioporphyrin* II [*hydrochloride*; *copper* salt, m. p. 285° (block)] has m. p. 246° (block) and is spectroscopically identical with its isomeride.

Crystallographic data [by Steinmetz] for several ætioporphyrins and the absorption spectra of a large number of the above compounds and those of the *copper* salts and *hæmochromogen* derivatives of meso-, rhodo-, deutero-, and phyllo-ætioporphyrins are given.

H. Burton.

Chlorophyll. II. Rhodins and verdins. H. Fischer, A. Treibs, and H. Helberger (Annalen, 1928, **466**, 243—264).—In an attempt to introduce an acetyl group into the porphin molecule pyrroporphyrin was treated with an excess of acetyl chloride in presence of carbon disulphide and aluminium chloride. The product isolated was *pyrrorhodin*, $C_{31}H_{32}ON_4$, m. p. 280° (block), probably identical with phyllorhodin (cf. following abstract). Similar treatment of mesoporphyrin gives *mesorhodin* (I), $C_{34}H_{36}O_3N_4$, m. p. 297° [block; *methyl* ester, m. p. 268° (corr.), from the *potassium* salt and methyl sulphate; *copper* salt; *iron* complex, $C_{34}H_{34}O_3N_4ClFe$; *magnesium* complex (*phyllin*), by the action of magnesium methyl iodide], together with *mesoverdin*, $C_{34}H_{36}O_3N_4$, m. p. 298° (*hydrochloride*; *copper* salt). Fuming sulphuric acid converts mesoporphyrin into I. The action of concentrated methyl-alcoholic potassium hydroxide on I in pyridine solution yields a mesoverdin, m. p. 308° (block).

Fuming sulphuric acid at 50° converts 1 : 4 : 6 : 7-tetramethyl-2 : 3 : 8-triethyl-5-β-carboxyethylporphin into a *rhodin*, $C_{33}H_{36}ON_4$ (*copper*, *magnesium*, and *iron* complexes), which on oxidation with chromic oxide and sulphuric acid yields methylethylmaleimide. The absorption spectra of the majority of the above compounds are tabulated.

The production of these rhodins from porphincarboxylic acids is due to elimination of water between the β-carboxyethyl group and either the imino- or methene hydrogen in the porphin ring. Thus, monoacidic porphins yield chemically indifferent rhodins (*i.e.*, pyrro-), whilst diacidic porphins give acidic rhodins (meso-).

H. Burton.

Chlorophyll. III. A. Treibs and E. Wiedemann (Annalen, 1928, **466**, 264—291).—Alkaline fission of phæophytin gives a mixture of phytochlorin *e* (I), $C_{35}H_{38 \text{ or } 40}O_7N_4$, and phytorhodin *g* (II),

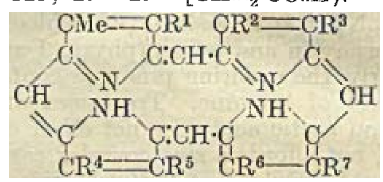
$C_{35}H_{36\,(or\,38)}O_8N_4$ (cf. Willstätter and Stoll, A., 1911, i, 659). Degradation of a mixture of I and II with methyl-alcoholic potassium hydroxide at 155° in presence of pyridine gives a mixture of pyrro- and phyllo-porphyrins; at 145—150° only phyllo-; at 220° only pyrro-. Similarly, I at 155° affords pyrro- (10%) and phyllo- (40%), whilst II at 165° yields a small amount of pyrro-porphyrin (cf. Willstätter, *loc. cit.*).

Pyrroporphyrin (III) [*methyl* ester, m. p. 241° (corr.; *iron* salt); *copper* and *magnesium* salts], when treated with bromine in acetic acid solution, furnishes a perbromide, which on treatment with acetone passes into *bromopyrroporphyrin* [*methyl* ester, m. p. 261° (corr.)]. Willstätter's phylloporphyrin contains pyrroporphyrin. Pure phylloporphyrin (IV), $C_{31}H_{34}O_2N_4$ [*methyl* ester, m. p. 235° (corr.; *iron* salt); *copper* salt], is brominated to *bromophylloporphyrin* (V) (*methyl* ester), which on oxidation with chromic oxide and sulphuric acid yields methylethylmaleimide, bromocitraconimide, and hæmatic anhydride. When IV or V is heated with methyl-alcoholic potassium hydroxide at 190—200° in a sealed tube, III is obtained. Absorption spectra of most of the above compounds are tabulated. Phyllo- and pyrro-rhodins (cf. preceding abstract) are shown to be identical.

H. BURTON.

Porphyrin syntheses. XVIII. Syntheses of coproporphyrins I and II, and mesoporphyrins II, V, and XII. H. FISCHER, H. FRIEDRICH, W. LAMATSCH, and K. MORGENROTH (Annalen, 1928, **466**, 147—178).—When the brominated methene from cryptopyrrolecarboxylic acid (I) (Fischer and Andersag, A., 1926, 1261) is heated with succinic acid at 180—190°, hydrogen bromide is eliminated, and esterification of the resulting product with methyl alcohol gives coproporphyrin tetramethyl ester (II), m. p. 252° [corr.; *manganese* complex, m. p. 267° (corr.); *zinc* compound, m. p. 299° (corr.); *tetrahydrazide* not melted at 320°]. Methyl-alcoholic hydrogen bromide converts I into the *compound* $C_{20}H_{26}O_4N_2Br$, which when treated with succinic or tartaric acids at 180—200° gives 3 or 6% of coproporphyrin. Treatment of coproporphyrin iron salt, m. p. 240° (corr.; *loc. cit.*), with hot 10% sodium hydroxide solution and subsequent treatment of the product obtained after acidification with a mixture of pyridine and acetic acid gives *coproporphyrin iron* salt *acetate*. Similar treatment of coprohæmin tetramethyl ester in presence of hydrochloric acid affords *coprohæmin*, which when crystallised from acetic anhydride loses a part of its halogen. Oxidation of II with lead dioxide in chloroform–acetic acid solution yields *coproxanthoporphinogen tetramethyl* ester, m. p. 315° (uncorr.; decomp.; free *acid*), reduced by sodium amalgam and acetic acid to II. When (4-methyl-3-ethyl-5-carbethoxypyrryl)-(2:4-dimethyl-3-β-carboxyethylpyrrolenyl)methene is heated progressively with sodium methoxide solution at 130—210° a mixture of ammonia-soluble (probably ætio-) and -insoluble, m. p. 204° (corr.), porphyrins is obtained.

When heated with formic and hydrobromic acids ethyl 2:4-dimethyl-3-β-carboxyethylpyrrole-5-carboxylate and cryptopyrrolecarboxylic acid are converted into (3:5-*dimethyl*-4-β-*carboxyethylpyrryl*)-(3:5-*dimethyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, m. p. 214—215° (*hydrochloride*; *picrate*, m. p. 214°). When this is heated with (3-*methyl*-5-*bromomethyl*-4-β-*carboxyethylpyrryl*)-(3-*methyl*-5-*bromomethyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, obtained by bromination of bis-(2:4-dimethyl-3-β-carboxyethylpyrryl)methene hydrobromide, in presence of succinic acid at 140—150°, mesoporphyrin XII [*methyl* ester, m. p. 190—191° (*copper* compound, m. p. 215°; *hæmin* derivative, obtained by the action of ferrous acetate on the ester in presence of acetic acid and sodium chloride); *ethyl* ester, m. p. 195—196° (corr.; *copper* complex, m. p. 203°); *hydrochloride*; *copper* compound; *hæmin* derivative], is obtained. Mesoporphyrin XII has, therefore, the structure A ($R^1=R^2=Et$; $R^3=R^5=R^6=Me$; $R^4=R^7=[CH_2]_2{\cdot}CO_2H$).



(A)

Opsopyrrolecarboxylic acid aldehyde and hæmopyrrolecarboxylic acid react in presence of hydrobromic acid, forming (3-*methyl*-4-β-*carboxyethylpyrryl*)-(4:5-*dimethyl*-3-β-*carboxyethylpyrrolenyl*)-*methene hydrobromide*, m. p. 175° (decomp.) after darkening at 120°, brominated to (5-*bromo*-3-*methyl*-4-β-*carboxylethylpyrryl*)-(4:5-*dimethyl*-3-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*. When this is heated with succinic acid at 220°, coproporphyrin I (tetramethyl ester) is produced. This porphyrin is, therefore, A with $R^1=R^3=R^4=R^6=[CH_2]_2{\cdot}CO_2H$; $R^2=R^5=R^7=Me$.

Opsopyrrolecarboxylic acid and cryptopyrrolecarboxylic acid aldehyde condense in presence of hydrobromic acid, yielding (3:5-*dimethyl*-4-β-*carboxyethylpyrryl*)-(3-*methyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, m. p. 200° (decomp.) after darkening at 150—180°. This is brominated to (3:5-*dimethyl*-4-β-*carboxyethylpyrryl*)-(5-*bromo*-3-*methyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, which when heated with succinic acid at 220° affords 6% of coproporphyrin II [in A, $R^1=R^2=R^5=R^6=[CH_2]_2{\cdot}CO_2H$ and $R^3=R^4=R^7=Me$; tetramethyl ester, m. p. 288°] (cf. this vol., 902).

(5-Bromo-3-methyl-4-β-carboxyethylpyrryl)-(3:5-dimethyl-4-ethylpyrrolenyl)methene hydrobromide, m. p. 251° (decomp.) after darkening at 215°, is converted by heating with succinic acid at 180° into mesoporphyrin V [in A, $R^1=R^6=[CH_2]_2{\cdot}CO_2H$; $R^2=R^5=Et$; $R^3=R^4=R^7=Me$; *dimethyl* ester, m. p. 274°; *copper* salt, m. p. 285—286°; *hæmin* derivative]. (3:5-*Dimethyl*-4-*ethylpyrryl*)-(3-*methyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, m. p. 180—190° (decomp.) after darkening at 140°, prepared from cryptopyrrolealdehyde and opsopyrrolecarboxylic acid, is brominated to (3:5-*dimethyl*-4-*ethylpyrryl*)-(5-*bromo*-3-*methyl*-4-β-*carboxyethylpyrrolenyl*)-*methene hydrobromide*, which also affords mesoporphyrin V.

Hæmopyrrole and opsopyrrolecarboxylic acid alde-

hyde afford (*3-methyl-4-β-carboxyethylpyrryl*)-(*4 : 5-dimethyl-3-ethylpyrrolenyl*)*methene hydrobromide*, brominated to (*5-bromo-3-methyl-4-β-carboxyethylpyrryl*)-(*4 : 5-dimethyl-3-ethylpyrrolenyl*)*methene hydrobromide*, which in turn yields, after fusion with succinic acid at 200°, mesoporphyrin II [in A, $R^1=R^6=[CH_2]_2\cdot CO_2H$; $R^2=R^5=R^7=Me$; $R^3=R^4=Et$; *methyl* ester, m. p. 233°; *copper* salt, m. p. 261°; *hæmin* derivative], also obtained from (*4 : 5-dimethyl-3-ethylpyrryl*)-(*5-bromo-3-methyl-4-β-carboxyethylpyrrolenyl*)*methene hydrobromide* [unbrominated *methene hydrobromide*, m. p. 209° (decomp.) after darkening at 180°].

Ethyl 4-methyl-3-β-carboxyethylpyrrole-5-carboxylate, m. p. 106°, is prepared by decarboxylation of the corresponding -2-carboxylic acid at 250°. 5-Carbethoxyopsopyrrole is converted by hydrocyanic and hydrochloric acids into its 2-*formyl* derivative, m. p. 230°. *4-Methyl-3-β-carboxyethyl-2 : 5-dicarbethoxypyrrole* has m. p. 147—148°.

The absorption spectra of a large number of the above compounds are tabulated. H. BURTON.

Porphyrin syntheses. XIX. Synthesis of deuterohæmin and deuteroporphyrin. H. FISCHER and A. KIRSTAHLER (Annalen, 1928, **466**, 178—188).—2 : 3-Dimethylpyrrole and 2 : 4-dimethylpyrrole-5-aldehyde condense in presence of alcoholic hydrobromic acid to give (*4 : 5-dimethylpyrryl*)-(*2 : 4-dimethylpyrryolenyl*)*methene hydrobromide* (I), m. p. 217° (decomp.) after darkening at 185° [free *base*, m. p. 115° (corr.; *hydrochloride*)], which is brominated in acetic acid solution to a *compound* (II), $C_{13}H_{15}N_2Br_3$, darkens at 220°, not melted at 300°. When a mixture of I and bis-(2-bromo-3-methyl-4-β-carboxyethylpyrryl)methene hydrobromide (III) is heated with succinic acid at 180—190°, deuteroporphyrin [*methyl* ester (IV), m. p. 219—220° (complex *iron* salt, m. p. 250°)], is obtained, and has, therefore, the formula A (preceding abstract) with $R^1=R^3=H$; $R^2=R^4=R^7=Me$; $R^5=R^6=[CH_2]_2\cdot CO_2H$. Similar treatment of a mixture of II and III gives deuteroporphyrin together with another *porphyrin* (*methyl* ester, m. p. 232°). Treatment of deuteroporphyrin with ferrous acetate, acetic acid, sodium chloride, and hydrochloric acid gives deuteroporphyrin iron salt (deuterohæmin), $C_{30}H_{28}O_4N_4ClFe$. Bromination of IV in acetic acid gives a *perbromide*, m. p. 138°, which on treatment with acetone passes into *dibromodeuteroporphyrin dimethyl* ester, m. p. 274°, not depressing the m. p. (267°) of the natural product. The *copper* salt, m. p. 288°, of this ester does not depress the m. p. of the copper salt of bromoporphyrin I ester. The absorption spectra of the synthetic deuteroporphyrin and the above salts are tabulated.

"Pyroporphyrin" (Schumm, this vol., 1263) and deuteroporphyrin are identical. H. BURTON.

So-called bisthiohydantoins of Frerichs, Forster, and Holler. H. W. STEPHEN and F. J. WILSON (J.C.S., 1928, 2826—2827).—The 3 : 3-bis-ψ-thiohydantoins of Frerichs and Forster (A., 1910, i, 190) and of Frerichs and Holler (A., 1913, i, 909) are to be regarded as 2 : 4-diketo-5-alkyltetrahydrothiazole-2-ketazines, $CHR<\begin{matrix}CO\cdot NH\\S-C:N\cdot N:C\end{matrix}\begin{matrix}NH\cdot CO\\-S\end{matrix}>CH_2$, since on hydrolysis with hydrochloric acid hydrazine hydrochloride together with the corresponding 5-alkyl derivatives of 2 : 4-diketotetrahydrothiazole, $CHR<\begin{matrix}CO\cdot NH\\CO.CO\end{matrix}$, are formed (cf. this vol., 904). Thus 2 : 4-diketo-5-methyltetrahydrothiazole-2-ketazine, m. p. 289° (lit. above 280°), yields hydrazine hydrochloride and 2 : 4-diketo-5-methyltetrahydrothiazole, m. p. 46—47°, whilst 2 : 4-diketo-5-ethyltetrahydrothiazole-2-ketazine, m. p. 233° (lit. 225—226°), gives hydrazine hydrochloride and 2 : 4-diketo-5-ethyltetrahydrothiazole, m. p. 64—65°.

A. I. VOGEL.

Oximes of *N*-methyl-2-benzthiazolone and *N*-methyl-2-quinolone. K. FUCHS and E. GRAUAUG (Ber., 1928, **61**, [*B*], 2194—2197; cf. this vol., 430).—1-Chlorobenzthiazole is converted by methyl iodide below 80° into *1-iodobenzthiazole methiodide*, transformed by an excess of hydroxylamine in anhydrous methyl alcohol into *2-methylbenzthiazolone-1-oxime*, $C_6H_4<\begin{matrix}S\\NMe\end{matrix}>C:N\cdot OH$, m. p. 202—203° (decomp.). Similarly, 2-iodoquinoline methiodide gives the oxime of *2-keto-1-methyl-1 : 2-dihydroquinoline*, m. p. 180·5—181·5° (decomp.), which is remarkably stable towards hot acids and alkalis; the *hydrochloride*, m. p. 230—232° (decomp.), *perchlorate*, and *sodium* salt are described. Reduction of the oxime by stannous chloride and hydrochloric acid affords 2-aminoquinoline methochloride. Oxidation by bromine in pyridine, ferric chloride, or hydrogen peroxide does not appear to yield the nitroso-compound.

H. WREN.

Preparation of substituted μ-methylbenzthiazoles and their transformation into new heterocyclic polymethine dyes. W. KONIG [with P. SEIDEL and G. STUHMER] (Ber., 1928, **61**, [*B*], 2065—2074; cf. A., 1912, i, 495).—4 : 4'-Dichloro-2 : 2-dinitrodiphenyl disulphide is converted by zinc dust and boiling acetic anhydride into *4-chloro-1-methylbenzthiazole*, m. p. 62° (*methiodide*, m. p. 212°, and corresponding *perchlorate*, m. p. 192°), from which the *methylene base*, $C_6H_3Cl<\begin{matrix}S\\NMe\end{matrix}>C:CH_2$, m. p. 138°, is derived by the action of sodium hydroxide on the methiodide suspended in acetone. *5-Chloro-1-methylbenzthiazole*, m. p. 81°, is obtained by the action of potassium ferricyanide on a solution of *p*-chlorothioacetanilide in sodium hydroxide or by the successive action of sodium hydroxide and acetic anhydride on an alcoholic solution of the product derived from sulphur chloride and aniline hydrochloride. The corresponding *methiodide*, m. p. 212°, *methoperchlorate*, m. p. 198°, *methobromide*, m. p. 270° (decomp.), and *methylene base*, m. p. 145°, are described. The last substance gives an additive *compound*, $C_9H_8NS_3$, decomp. above 275°, with carbon disulphide. *5-Bromo-1-methylbenzthiazole*, from p-*bromothioacetanilide*, m. p. 153°, gives a *methiodide*, m. p. 208°, *methoperchlorate*, m. p. 216°, and *methylene base*, C_9H_8NSBr, m. p. 148°. *5-Methoxy-1-methylbenzthiazole*, b. p. 170°/20 mm., 284°/760 mm., obtained from thioacet-*p*-anisidide or from the product of the action of sulphur chloride on anisidine hydrochloride, gives a *methiodide*, m. p. 228°, and *methobromide*, m. p. 248° (decomp.); *5-methoxy-1-*

methylene-1 : 2-*dihydrobenzthiazole*, m. p. 135°, and its additive *compound* with carbon disulphide, $C_{11}H_{16}ONS_3$, m. p. 239° (decomp.), are described. 4(?)-*Chloro*-5-*methoxy*-1-*methylbenzthiazole*, m. p. 64° (*methiodide*, m. p. 215°), is obtained as by-product of the preparation of 5-methoxy-1-methylbenzthiazole. *o*-Toluidine hydrochloride and sulphur chloride in water give a *product*, (?)$Cl{\cdot}C_6H_2Me{<}{}^{NH}_{S}{>}S{:}O$ or $Cl{\cdot}C_6H_2Me{<}{}^{N}_{S}{>}S{\cdot}OH$, converted by successive addition of sodium hydroxide and acetic anhydride into 5-*chloro*-1 : 3-*dimethylbenzthiazole*, m. p. 79° (*methiodide*, m. p. 244°).

Chlorodimethylbenzthiazole methobromide is transformed by *p*-dimethylaminobenzaldehyde in presence of boiling acetic anhydride into 5-*chloro*-2-*methyl*-1-p-*dimethylaminobenzylidenemethylbenzthiazolium bromide*,

$$C_6H_4{<}{}^{S}_{\underset{Alk-N-X}{}}{>}C{\cdot}[CH{:}CH]_n{\cdot}C_6H_4{\cdot}NAlk_2,$$

m. p. 249°. 5-*Methoxy*-2-*methyl*-1-p-*dimethylaminobenzylidenemethylbenzthiazolium bromide*, m. p. 255°, 4(?)-*chloro*-5-*methoxy*-2-*methyl*-1-p-*dimethylaminobenzylidenemethylbenzthiazolium iodide*, m. p. 214°, and 5-*chloro*-2 : 3-*dimethyl*-2-p-*dimethylaminobenzylidenemethylbenzthiazolium iodide*, m. p. 234°, are prepared similarly.

4-Chloro-1-methylbenzthiazole methiodide is converted by orthoformic ester in boiling acetic anhydride into 6 : 6′-*dichloro*-1 : 1′-*dimethyl*-2 : 2′-strepto*monovinylenethiocyanine iodide*,

$$C_6H_4{<}{}^{S}_{\underset{Alk-N-X}{}}{>}C{\cdot}\overset{8}{C}H{:}\overset{9}{C}H{\cdot}\overset{10}{C}H{:}C{<}{}^{S}_{\underset{Alk-N}{}}{>}C_6H_4,$$

decomp. above 270°. 5 : 5′-*Dichloro*-1 : 1′-*dimethyl*-2 : 2′-strepto*monovinylenethiocyanine iodide*, decomp. 286°; 6 : 6′-*dimethoxy*-1 : 1′-*dimethyl*-2 : 2′-strepto*monovinylenethiocyamine perchlorate*, decomp. about 290°; 5 : 5′-*dibromo*-1 : 1′-*dimethyl*-2 : 2′-strepto*monovinylenethiocyanine iodide*, decomp. 280°, and 5 : 5′-*dichloro*-1 : 1′ : 7 : 7′-*tetramethyl*-2 : 2′-strepto*monovinylenethiocyanine iodide*, m. p. 243°, are similarly prepared. The absorption curves of the new thiocyanines resemble closely that of thiazole-purple; in the visible spectrum they give a pronounced band which exhibits two sharp maxima for thin layers, the most persistent of which lies towards greater wave-length. The influence of substituents is in the same sense with thiocyanines and the simplest *strepto*monovinylenethioflavines, although not so marked with the latter substances, which give a single, relatively broad, non-resolvable band in the visible spectrum. H. WREN.

1 : 3 : 4-Oxdiazines. II. J. VAN ALPHEN (Rec. trav. chim., 1928, **47**, 909—919; cf. this vol., 780).—5-Keto-1 : 3 : 4-oxdiazines are obtained by the action of chloroacetyl chloride on β-acylphenylhydrazines and subsequent elimination of 1 mol. of hydrogen chloride from the intermediate α-chloroacetyl derivatives by treatment with anhydrous potassium carbonate in acetone:

$$\begin{matrix} CH_2Cl\ HO{\cdot}CR \\ | \\ CO-NPh-N \end{matrix} \longrightarrow \begin{matrix} CH_2-O-CR \\ | \\ CO{\cdot}NPh{\cdot}N \end{matrix}.$$

Th, *α-chloroacetyl-β-acetylphenylhydrazine*, m. p. 131°, affords Δ^2-5-*keto*-4-*phenyl*-2-*methyl*-1 : 3 : 4-*oxdiazine*, m. p. 65°; *α-bromoacetyl*-β-iso*butyrylphenylhydrazine* yields Δ^2-5-*keto*-4-*phenyl*-2-iso*propyl*-1 : 3 : 4-*oxdiazine*, m. p. 40°, and β-*benzoyl*-α-*chloroacetylphenylhydrazine*, m. p. 198°, gives Δ^2-5-*keto*-2 : 4-*diphenyl*-1 : 3 : 4-*oxdiazine*, m. p. 96°, either by treatment with potassium carbonate or by the action of concentrated ammonia solution. The methyl and *iso*propyl derivatives are hydrolysed by aqueous-alcoholic sulphuric acid to phenylhydrazine and β-*iso*butyrylphenylhydrazine, respectively, whilst the diphenyl derivative is unaffected. This last compound is soluble in sodium hydroxide solution, reacting in its enol form.

α-N-*Phenylaminoacetyl*-β-*acetylphenylhydrazine*, m. p. 140°, is hydrolysed by aqueous-alcoholic sulphuric acid to α-N-*phenylaminoacetylphenylhydrazine*, m. p. 157° (*benzylidene* derivative, m. p. 194·5°). β-*Benzoyl*-α-N-*phenylaminoacetylphenylhydrazine* has m. p. 159°. H. BURTON.

Catalytic dehydrogenation of nicotine. J. P. WIBAUT and J. OVERHOFF (Rec. trav. chim., 1928, **47**, 935—939).—When nicotine is passed over platinised asbestos at 320—350° a 72—73% yield of *N*-methyl-2-(3′-pyridyl)pyrrole [picrate, m. p. 168—169° (lit. 163—164°)] is obtained. H. BURTON.

Alkaloids of *Hyoscyamus reticulatus*, L. R. A. KONOVALOVA and O. J. MAGIDSON (Arch. Pharm., 1928, **266**, 449—452).—The root contains about 1% of *s*-tetramethyldiaminobutane, b. p. 166—167° (*picrate*, m. p. 198—200°; *chloroaurate*, m. p. 200—205°; *chloroplatinate*, m. p. 224°), identical with that isolated by Willstätter and Heubner, (A., 1907, i, 959) from *H. muticus*, and a trace of hyoscyamine. No volatile, nitrogenous bases are present in *H. pusillus*, *Datura violaceum*, *D. stramonium*, and mandragora. S. COFFEY.

Chloroarsinosoquinine. III. F. X. ERBEN (Ber., 1928, **61**, [*B*], 2106—2108; cf. A., 1927, 265).—Dissolution of well-dried dehydroquinine in an excess of warm arsenic trichloride and preservation of the solution at the atmospheric temperature for about 6 months leads to the production of *chloroarsinosodiquinine*, $(C_{20}H_{22}O_2N_2)_2AsCl$, distinguished from chloroarsinosoquinine by its solubility in warm nitrobenzene. The *sulphate* of chloroarsinosoquinine is converted by sodium sulphite into *chloroarsinosodiquinine sulphite*. H. WREN.

Tests for morphine and related alkaloids. C. C. FULTON (J. Lab. Clin. Med., 1928, **13**, 750—762).—The "iodic acid–peroxide" test for morphine is described; the Pellagri test is improved. Tests are based on the formation of a dehydration product obtained by heating the alkaloid with concentrated sulphuric acid at 40—50°. CHEMICAL ABSTRACTS.

Cresolarsinic acids. C. FINZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1302—1311; Chem. Zentr., 1928, i, 2173—2174).—Four new cresolarsinic acids are added to the four out of ten already known; Christiansen's compound (A., 1923, i, 500) is 6-hydroxy-2-methylphenylarsinic acid, not 2-hydroxy-4-methylphenylarsinic acid. Bart's method was employed for 2-hydroxy-3-methyl- and 2-hydroxy-5-methyl-phenylarsinic acid with limited success; generally the diazotised aminomethylphenylarsinic acid was heated. The following compounds

are described : 2-hydroxy-3-methylphenylarsinic acid, m. p. (slow heating, froth) 200—205°, (rapid heating) 205°; 3-hydroxy-4-methylphenylarsinic acid, m. p. 174—175° (?-*nitro*-derivative, m. p. 237° [decomp.]); 2-hydroxy-4-methylphenylarsinic acid, m. p. (rapid heating) 125° (?-*nitro*-derivative, m. p. 193°, sinters 120°); 2-hydroxy-5-methylphenylarsinic acid, softens at 90—100°; after solidifying, m. p. 218° (frothing); 5-hydroxy-2-methylphenylarsinic acid, m. p. 184—185° (frothing); 3 : 3′-dihydroxy-4 : 4′-dimethylarsenobenzene, m. p. 192—197°; 2 : 2′-dihydroxy-4 : 4′-dimethylarsenobenzene, decomp. 108—110°; (?)-dinitro-derivative, m. p. 191° (decomp.).

A. A. ELDRIDGE.

Preparation of 4-chaulmoogrylaminobenzenearsinic acid. M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 31—32).—*4-Chaulmoogrylaminobenzenearsinic acid*, from chaulmoogryl chloride and arsanilic acid, decomposes at 230°.

CHEMICAL ABSTRACTS.

Manufacture of new substituted 5 : 5′-[di]acylamido-4 : 4′-dihydroxyarsenobenzenes. I. G. FARBENIND. A.-G.—See B., 1928, 837.

Friedel and Crafts' reaction and the organometallic compounds of aluminium. P. LEONE (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1332—1337; Chem. Zentr., 1928, i, 2174).—The view that organo-metallic compounds are formed on admixture of aromatic hydrocarbons and aluminium chloride is supported; the position of equilibrium is, however, far to one side, so that only traces are formed. Aluminium phenyl iodide reacts with alkyl iodides forming benzene homologues; methyl iodide yields benzene, toluene, and xylene, ethyl iodide yields benzene, ethylbenzene, diethylbenzene, and higher homologues, propyl iodide yields *iso*propylbenzene (not propylbenzene), whilst *iso*amyl iodide yields small quantities of *iso*amylbenzene. Ketone synthesis cannot, however, be effected with aluminium organic compounds.

A. A. ELDRIDGE.

Structure of silk fibroin. E. ABDERHALDEN and H. MAHN (Z. physiol. Chem., 1928, **178**, 253—275).—Silk fibroin dissolved in 50% lithium bromide solution was treated with bromine in chloroform, and thus separated into a soluble and an insoluble portion. The two products were hydrolysed. In the insoluble portion, which had taken up bromine, were found glycine, alanine, serine, and 2 : 5-dibromotyrosine. The smaller soluble portion contained glycine and probably alanine and serine. Silk fibroin in 50% lithium bromide was exposed for varying lengths of time to *N*-alkali. The quantity of bromine absorbed was fairly constant, but the amount of precipitate varied with the time of alkali action.

The breakdown of the protein by alkali was very rapid. Untreated and treated silk fibroin was stable to pepsin; it was hydrolysed by mixed pancreatic enzymes. The fibroin is probably partly broken down on dissolution in lithium bromide.

J. H. BIRKINSHAW.

Structure of proteins. E. ABDERHALDEN and W. KRONER (Z. physiol. Chem., 1928, **178**, 276—290).—An attempt was made to find a general method for the isolation of the polypeptide breakdown products of proteins. Benzoylation of the esters followed by high-vacuum distillation led to decomposition except in the case of benzoyl-*dl*-leucylglycine ethyl ester. An attempted fractionation of the benzoylated polypeptide esters from caseinogen by means of solvents was no more successful. A separation was finally attained by repeated precipitation of the butyl alcohol extract with much water. A solid product was obtained which on hydrolysis gave benzoyl-leucine and glutamic acid in theoretical yield.

J. H. BIRKINSHAW.

Treatment of dipeptide or peptone with sugar, hexosediphosphate, and methylglyoxal. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, **200**, 459—467).—Small changes in optical rotation are obtained on mixing alanylalanine or silk fibroin peptone with solutions of dextrose, lævulose, or methylglyoxal. Mixing magnesium hexosediphosphate with alanylalanine gave practically no change of rotation.

P. W. CLUTTERBUCK.

Degradation of gelatin and gelatin-peptone with acetic anhydride. Isolation of associated polypeptides. A. FODOR and C. EPSTEIN (Biochem. Z., 1928, **200**, 211—222).—The various fractions obtained in the author's previous work with gelatin (this vol., 435) have been analysed and the observations extended to gelatin-peptone.

P. W. CLUTTERBUCK.

Degradation of gelatin by glycerol under various conditions. Isolation of a non-colloidal intermediate product hydrolysable by pepsin. A. FODOR and R. SCHOENFELD (Biochem. Z., 1928, **200**, 223—235).—Gelatin is converted by glycerol at 130° into a product, soluble in water and insoluble in alcohol, which gives the biuret and ninhydrin reactions, which has the same mol. wt. (406) as gelatin-peptone (400), which gives the same value (2/3) for the ratio "amino-N/total-N," and is hydrolysed by both pepsin and trypsin. The process is carried much further by heating at 180°, and fractionation of the product indicates the formation of lower polypeptide anhydrides.

P. W. CLUTTERBUCK.

Products of hydrolysis of proteins. J. TILLMANS, P. HIRSCH, and F. STRACHE (Biochem. Z., 1928, **199**, 399—433; cf. this vol., 436).—The apparent dissociation constants (cf. Bjerrum, A., 1923, i, 444) of various di- and tri-peptides and of asparagine have been determined electrometrically; the values obtained both for acid and basic constants are greater than those obtained in the same way for simple amino-acids, those for tripeptides being a little greater than those for dipeptides. Both acidic and basic groups become progressively stronger as the length of the peptide chain increases, but the strength does not increase indefinitely. The simple diketopiperazines, whether in strongly acid or strongly alkaline solutions, do not combine with alkali or acid. Asparagine in strongly acid solution acts as if it has only one basic group. The hydrolysis of proteins with sodium hydroxide proceeds at first rapidly, then much more slowly, probably because some parts of the protein molecule are much more readily attacked than others. These facts strengthen

the formerly expressed opinion favouring the ring structure of proteins. For characterising and identifying the various proteins it is better to hydrolyse for 4 hrs. at 100° with 0·5*N*-sodium hydroxide or for 24 hrs. at 100° with 0·5*N*-hydrochloric acid than to use the methods of hydrolysis formerly employed. The curves of "molecular binding power" of the chief proteins found in foods have been plotted. These curves show that, in this connexion, there are no great differences between the various proteins. Such differences as are found appear gradually in passing through the series of proteins. A process is described by means of which, from the curve of "molecular binding power" of a mixture, the amounts of the separate constituents can be deduced, provided that the dissociation constants of the separate constituents are known. From such curves it is evident that, in the hydrolysates, a considerable part of the nitrogen present occurs in an "acidimetrically inactive" form. Since the products of alkaline hydrolysis when afterwards treated with acid exhibit decreasing "molecular binding powers," it is possible that diketopiperazines may undergo keto-enol transformations. W. McCartney.

Compounds of albumin and metallic salts. H. Bechhold (Biochem. Z., 1928, **199**, 451—458).—Methods of washing-out and of differential ultrafiltration have been applied to the study of mixtures of solutions of albumin with solutions of salts of heavy metals. It is probable that the complex compound of albumin and the chlorides of calcium, strontium, or barium is decomposed during the washing-out process, for these chlorides are completely removed from the albumin. Salts of nickel and of cobalt are also completely removed, but neither anion nor cation is removed, under the same conditions, from albumin solutions treated with the chlorides of zinc, aluminium, chromium, or iron (ferric) and, in the case of the first three of these metals, a constant ratio of albumin to metallic salt is found. It is not probable, however, that this constant ratio is due to the formation of actual chemical compounds. The product of interaction of ferric chloride and albumin (Liquor ferri albuminati) is a hydrosol of iron oxide dispersed in an exceedingly fine condition in albumin. Gold chloride closely resembles ferric chloride in its behaviour with albumin, but silver, in the form of silver nitrate, seems to form a water-soluble undissociated silver–albumin (1 : 5200) compound. These compounds are all soluble in water and, in aqueous solution, are hydrolytically or electrolytically dissociated. If the metal forms an insoluble hydroxide this may remain with the albumin after the washing-out, so forming an apparent compound containing metal and albumin in constant proportions. W. McCartney.

Investigation of solutions containing albumin and metallic salts by the washing-out method. H. Schorn (Biochem. Z., 1928, **199**, 459—467; cf. preceding abstract).—A method for the preparation, by electro-ultra-filtration, of egg-albumin free from electrolytes is described. The existence of the lower zone of precipitation of albumin by salts of heavy metals is due to the presence in the albumin of calcium salts: in albumin free from calcium this zone is absent. Water-soluble compounds of albumin with silver, zinc, chromium, and aluminium or their salts can be prepared. In these compounds the ratio of metal to albumin is 1 : 5100 to 1 : 5200. The reaction between ferric chloride and albumin is quite different from that between the salts of the other metals and albumin, the difference apparently being due to complications caused by hydrolysis. W. McCartney.

Equilibria between albumin and metallic salts (silver nitrate, ferric chloride, gold chloride). E. Heymann and F. Oppenheimer (Biochem. Z., 1928, **199**, 468—497; cf. preceding abstracts).—In solutions containing metallic salts and albumin in different proportions the amount of uncombined metallic salt which is in equilibrium with the compound of metallic salt and protein has been determined by analysis of the intermicellar liquid, and the curves of combination of silver nitrate, ferric chloride, and gold chloride with highly-purified albumin have been studied. The maximum amounts of combined silver nitrate and ferric chloride are independent of the absolute concentrations of the albumin and of the salt, but the maximum for ferric chloride is greater than that for silver nitrate. With silver nitrate, in mixtures in all proportions, cations and anions are combined with albumin in equivalent amounts, whereas with ferric chloride this occurs only when the ratio is high. When the ratio is low more iron than chlorine is combined, and for gold chloride analogous results are found. The ways in which the metallic salts may be combined with albumin are discussed and the existence of molecular compounds is assumed, although the possible formation of adsorption compounds is not denied. W. McCartney.

Bromine uptake of caseinogen and of caseinogen keratin hydrolysates. F. Lieben and R. Müller (Biochem. Z., 1928, **197**, 119—135).—When caseinogen is treated with a large excess of bromine or of bromine in aqueous or alkaline solution 5—6% of bromine is adsorbed. Tyrosine, histidine, and cystine are chiefly responsible for the bromine consumption of protein hydrolysates, and take up, respectively, per mol. 4, 4, and 10 atoms of bromine, both when treated separately and when present together. Large amounts of bromine partly oxidise tyrosine and produce melanin. Further, tyrosine and cystine react rapidly with bromine, whilst histidine reacts slowly, and hence, according to the amount of bromine added and to the duration of the experiment, the uptake of bromine may deviate from the requirements of the three acids. The distribution of bromine in protein hydrolysates was investigated by means of phosphotungstic acid precipitation. Histidine which has reacted with bromine is no longer precipitated by this acid. In the case of keratin there is increased bromine uptake after reduction of the hydrolysate, corresponding with the conversion of 1 mol. of cystine into 2 mols. of cysteine. Nascent iodine reacts only to a slight extent with protein hydrolysates. W. McCartney.

Effect of *X*-rays on tyrosine and cystine. W. Stenström and A. Lohmann (J. Biol. Chem., 1928,

79, 673—678).—Tyrosine in dilute solution (0·01% or less) is decomposed to a considerable extent by exposure to *X*-rays; cystine is not affected.

C. R. HARINGTON.

Determination of tyrosine in proteins. M. T. HANKE (J. Biol. Chem., 1928, **79**, 587—609).—The value of the author's method (A., 1926, 633) for the determination of tyrosine in protein hydrolysates is confirmed, although the values then obtained were 0·3—0·6% low on account of loss of tyrosine with the silver precipitate of histidine; it is better to precipitate the tyrosine directly from the hydrolysis mixture by the author's method and then to determine it by the method of Folin and Ciocalteu (A., 1927, 892). The criticisms of Looney (A., 1926, 1050) are answered on the ground that he employed too much tyrosine. Slight variations were observed in the tyrosine content of different samples of the same protein, according to the age and the method of drying of the sample.

C. R. HARINGTON.

Micro-determination of halogens and sulphur in organic substances, especially chromium compounds. F. HEIN, K. HOYER, and K. KLAR (Z. anal. Chem., 1928, **75**, 161—164).—For the micro-determination of halogens 20 mg. of substance and 0·18 g. of sucrose are intimately mixed with 2—2·5 g. of sodium peroxide in a Pringsheim crucible and covered with 2 g. of sodium peroxide, and the mixture is ignited by a hot wire etc. The heated and filtered solution of the mass is acidified with nitric acid and heated with sulphurous acid, and hydrogen peroxide solution, followed by nitric acid, is added. After dilution, an excess of 0·02*N*-silver nitrate solution and a few c.c. of ether are added and the excess of silver is titrated with 0·02*N*-thiocyanate solution, using iron alum as indicator.

For the determination of sulphur the alkaline solution is acidified with hydrochloric acid and chromate reduced by heating with alcohol and sodium nitrite. The resulting solution and a faintly ammoniacal solution of barium chloride are added through capillary tubes to a boiling solution of ammonia, which is afterwards acidified with hydrochloric acid.

J. S. CARTER.

Determination of sulphur in organic compounds. E. A. SMITH and J. W. BAIN (Canadian Chem. Met., 1928, **12**, 287—288).—The sulphur content of samples of barium lignosulphonate was determined by the following five methods: Eschka's method, fusion with sodium peroxide followed by gravimetric determination of sulphate, Klason's method in which the oxidation is carried out by the fumes from asbestos soaked in nitric acid in a combustion tube, Apitzsch's method using platinum gauze and oxygen, and Carius' method. The most consistent and highest results were obtained by Carius' method, which was closely approached by Apitzsch's method. Losses evidently occurred in the other methods, which gave very variable results.

C. IRWIN.

Colour reactions of the bile acids. L. CUNY (J. Pharm. Chim., 1928, [viii], **8**, 358—364).—Seven colour reactions of the bile acids have been applied to each of the following substances: cholic, deoxycholic, anthropodeoxycholic, hyoglycodeoxycholic acids and the sodium salts of hyoglycodeoxycholic and hyocholic acids. In each reaction only cholic acid gave an intense colour and these colours have been spectroscopically examined. It is concluded that the colour reactions of the bile acids are due mainly to cholic acid, the accompanying acids having only a weak effect, and as the salts of cholic acid predominate in the human bile, these colour reactions still maintain their importance, but the presence of the related compounds should not be forgotten.

E. H. SHARPLES.

Biochemistry.

Modifications of the Haldane gas-analysis apparatus. V. DU VIGNEAUD (J. Lab. Clin. Med., 1927, **13**, 175—180).

Apparatus for the continuous recording of the oxygen consumption of small animals. A. N. RICHARDS and L. W. COLLISON (J. Physiol., 1928, **66**, 299—306).—The animal is placed in a closed chamber and the carbon dioxide and water which it produces are absorbed by soda-lime. Oxygen is bubbled in through paraffin oil to keep the pressure constant in the chamber. The oxygen consumption is determined and recorded automatically from the rate of formation of the bubbles.

B. A. EAGLES.

Effects of breathing carbon dioxide and oxygen mixtures on the carbon dioxide and oxygen tensions in the tissues. J. A. CAMPBELL (J. Physiol., 1928, **66**, Proc. Physiol. Soc., i—ii).—The presence of carbon dioxide in no way prevents the entry of oxygen into the tissues.

B. A. EAGLES.

Influence of disodium hydrogen phosphate on gaseous exchange. E. SCHMUTZLER (Biochem. Z., 1928, **200**, 407—413).—The effect of addition of phosphate to a carbohydrate diet in decreasing the respiratory quotient of rats and, to a diet of meat, in greatly reducing its specific dynamic action (Abelin, A., 1926, 539; 1927, 276) could not be confirmed with dogs. Addition of phosphate to a carbohydrate diet caused the R.Q. to increase somewhat more slowly at first, but after 1 hr. it attained the same value as the control, whilst addition of phosphate to a diet of meat caused the specific dynamic action of the meat to be slightly increased, but the increase was within experimental error.

P. W. CLUTTERBUCK.

Oxygen capacity of hæmoglobin. M. ABELOOS, J. BARCROFT, N. CORDERO, T. R. HARRISON, and J. SENDROY (J. Physiol., 1928, **66**, 262—266).—The blood-gas pump and the Van Slyke constant-volume apparatus give concordant values, both for nitrogen and oxygen, in the analysis of hæmoglobin solutions.

B. A. EAGLES.

Combination of carbon dioxide in blood. I. Velocity of dehydration and hydration of carbonic

acid components of blood. II. Detection of quickly reacting, fixed carbon dioxide in hæmoglobin. III. Detection of a hæmoglobin–carbon dioxide complex in solutions of carbon dioxide and hæmoglobin. IV. Carbon dioxide combining power of reduced and oxy-hæmoglobin. V. Physiology of carbhæmoglobin. O. M. HENRIQUES (Biochem. Z., 1928, **200**, 1—4, 5—9, 10—17, 18—21, 22—24).—I. The carbon dioxide exchange in the lungs cannot be explained as a simple dehydration of carbonic acid, since this process proceeds much too slowly.

II. Part of the carbon dioxide of blood is combined with hæmoglobin and this part is liberated much more readily than that combined as hydrogen carbonate.

III. The presence of "carbhæmoglobin" in solutions of hæmoglobin and carbon dioxide is detected by determining amounts of hydrogen carbonate and of free and total carbon dioxide.

IV. Up to pressures of about 100 mm., reduced hæmoglobin unites with much more carbon dioxide than does oxyhæmoglobin, but at higher pressures the amounts become equal.

V. Exchange of carbon dioxide proceeds in terms of the carbhæmoglobin content of the blood, and the hydrogen carbonate and carbonic acid play only a subsidiary rôle in respiration similar to that of the chlorine ion. P. W. CLUTTERBUCK.

Gas and electrolyte equilibria in blood. XIV. Base bound by serum-albumin and -globulin. D. D. VAN SLYKE, A. B. HASTINGS, A. HILLER, and J. SENDROY, jun. (J. Biol. Chem., 1928, **79**, 769—780).—Over the range p_H 6·8—7·8 the relationship between the p_H and the base bound by protein is linear for serum-albumin and -globulin, the numerical value of the milliequivalents of base per g. of protein-nitrogen being 0·78 (p_H 5·16) in the first case and 0·48 (p_H 4·89) in the second. C. R. HARINGTON.

Gas and electrolyte equilibria in blood. XV. Line charts for graphic calculations. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1928, **79**, 781—798).—Nomographic charts, based on data previously obtained, are given for the application of the Henderson–Hasselbalch equation to blood-plasma, and for the calculation of the factor for conversion of whole blood carbon dioxide into carbon dioxide of serum or plasma. C. R. HARINGTON.

Colloid-chemistry of hæmoglobin. II. B. JIRGENSONS (Biochem. Z., 1928, **200**, 331—338).—The effect of organic substances on the spectrum and on the colloidal stability of oxyhæmoglobin (this vol., 537) is due to the capillary activity of these substances. Inorganic salts alone have no such influence, but the effect of organic substances is intensified by the presence of salts. Thus with salts and alcohol the bands are displaced towards the violet and the spectrum of cathæmoglobin is obtained. With small concentrations of magnesium chloride and alcohol almost complete coagulation of oxyhæmoglobin sol is obtained, but if both are in high concentration no coagulation occurs. Rise of temperature favours both precipitation and spectroscopic changes. P. W. CLUTTERBUCK.

Basic amino-acids of horse hæmoglobin. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, **79**, 377—388).—From crystalline horse hæmoglobin there have been isolated, by methods described in earlier papers (this vol., 1121), histidine 7·64%, arginine 3·32%, and lysine 8·10%.

C. R. HARINGTON.

Globin and denatured globin. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1928, **5**, 213—222).—Details are given for the preparation of globin from hæmoglobin. By titrating a given weight of hæmatin with varying quantities of globin solution and converting the methæmoglobin formed into oxyhæmoglobin it is calculated that the chemical equivalent of globin is the same as that of globin present in natural oxyhæmoglobin, namely about 16,000. Under conditions limited by the concentration of reagents suitable for the optical instruments used, a weight of denatured ox globin equal to one equivalent weight of ox globin combines with 6 mols. of reduced hæmatin. The observation of Wu and Lin (cf. A., 1927, 688) has been confirmed that if methæmoglobin was converted into acid hæmatin and globin and the solution neutralised at once, almost all the acid hæmatin is reconverted into methæmoglobin, whereas in the case of oxyhæmoglobin only about two thirds reconversion takes place. Oxyhæmoglobin is decomposed into hæmatin and globin more slowly and at a lower p_H than is methæmoglobin. Denatured horse- or ox-globin has a much higher rotation than the corresponding native globin. Denatured globin freshly prepared by the Schulz method often contains a small amount of globin. W. O. KERMACK.

Photochemical dissociation of iron–carbonyl compounds (carbon monoxide–hæmochromogen, carbon monoxide–ferrocysteine) and the law of photochemical equivalence. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, **200**, 414—458).—Continuing the authors' attempt to calculate the absorption spectrum of the respiratory enzyme from the photochemical dissociation of its carbonyl compound (cf. A., 1927, 1221; this vol., 537, 549, 851), a considerable amount of theoretical and experimental work is described in which are investigated the photochemical dissociation of carbon monoxide–hæmochromogen and of carbon monoxide–ferrocysteine and the influence of the pressure of carbon monoxide, of temperature, and of wave-length thereon. The light absorption coefficients of these two compounds are determined and the validity of Einstein's law is tested and the law confirmed.

P. W. CLUTTERBUCK.

Adsorption by erythrocytes. I. Adsorption of alanine. A. KULTJUGIN and N. IVANOVSKI (Biochem. Z., 1928, **200**, 236—243).—Washed erythrocytes of cat, dog, and ox adsorb an amount of alanine, varying with its concentration, from solutions, the process being concluded in 30 min.

P. W. CLUTTERBUCK.

Erythrocyte as a colloidal system. III. Permeability of erythrocytes to electrolytes. IV. Mechanism of hæmolysis in hypotonic solutions. A. P. KONIKOV (Zhur. Exp. Biol. Med., 1928, **8**,

480—487, 488—501).—Erythrocytes are permeable to both anions and cations of neutral salts; the ions also combine with the cell proteins, particularly hæmoglobin. The isoelectric point of erythrocytes is at p_H 6·8, that of hæmoglobin. The essential factor in hæmolysis is the osmotic condition of the hæmoglobin. The osmotic resistance increases with the alkalinity, being maximal at p_H 9·0; it depends on the inner state of the erythrocyte. The erythrocyte is regarded as a two-gel system consisting of stroma and hæmoglobin.

CHEMICAL ABSTRACTS.

Occurrence of lipase in polymorphonuclear leucocytes. W. FLEISCHMANN (Biochem. Z., 1928, **200**, 25—28).—The presence of lipase is detected in the polymorphonuclear leucocytes of sterile peritoneal exudates (rabbit) by means of the manometric method of Rona and Lasnitzki (A., 1926, 866).

P. W. CLUTTERBUCK.

Micro-determination of the p_H of blood using an antimony electrode. R. BRINKMAN and F. J. J. BUYTENDYK (Biochem. Z., 1928, **199**, 387—391).—By means of an antimony-coated platinum wire electrode the p_H of blood can be rapidly determined with sufficient accuracy for clinical purposes, using very small amounts of blood. W. MCCARTNEY.

Relation of p_H and changes in the buffer value of solutions of human serum. M. GEX (Compt. rend. Soc. Biol., 1927, **97**, 1564—1567; Chem. Zentr., 1928, i, 2267).—The $t(=\Delta m/\Delta p_H$, where m is the amount of alkali or acid added)–p_H curves for normal and pathological sera and egg-albumin solutions, determined with the antimony electrode, have the same general character, but differ in the nature and position of the maxima and minima. Serum is a very complex system. Often the minima do not correspond with the principal isoelectric points.

A. A. ELDRIDGE.

Comparative determinations of proteins in horse-serum. D. VON DESEO (Biochem. Z., 1928, **200**, 126—134).—The micro-method for the determination of protein of Howe (A., 1922, ii, 171, 172) in which the proteins are removed by precipitation with sodium sulphate gives results agreeing with those obtained by the gravimetric method after precipitation with saturated ammonium sulphate solution. The values so obtained for total protein agree with those obtained by Robertson's refractometric method (A., 1915, ii, 851), but the values for the albumin and globulin fractions do not agree and Robertson's method cannot be used for fractionation of horse-serum. P. W. CLUTTERBUCK.

Isolation and determination of serum-globulin by means of electrodialysis. L. REINER and H. KOPP (Kolloid-Z., 1928, **46**, 99—107).—The precipitation of globulin during electrodialysis depends on the ratio of protective matter to globulin and on the alterations of hydrogen-ion concentration and the velocity of removal of electrolytes. Among the substances which inhibit coagulation is heparin, which has also the effect of displacing the isoelectric point in the acid direction. Contrary to the assertions of Ettisch and Ewig, membranes coated with albumin are found to serve a useful purpose in electrodialysis. The existence of an electrical polarisation in colloid membranes during electrodialysis is discussed.

E. S. HEDGES.

Determination of blood-calcium. E. M. WATSON (J. Lab. Clin. Med., 1928, **13**, 670—671).—An apparatus for the micro-titration of calcium oxalate is described. CHEMICAL ABSTRACTS.

Serum-calcium content of man. J. H. ROE and B. S. KAHN (J. Lab. Clin. Med., 1928, **13**, 762—763).—Values varying from 9·0 to 11·6 mg. per 100 c.c. of serum (average 10·13 mg.) were obtained.

CHEMICAL ABSTRACTS.

Copper in human blood-serum. H. A. KREBS (Klin. Woch., 1928, **7**, 584—585; Chem. Zentr., 1928, i, 2419).—A mixture of the fluid with cysteine and sodium pyrophosphate buffer is shaken with air, the oxygen used indicating the amount of copper present. Human blood-serum contains 0·62—1·24 (average 0·91)$\times 10^{-3}$ mg. per c.c.; higher values are observed in pregnancy, tuberculosis, and acute infections, and lower values in kidney disease.

A. A. ELDRIDGE.

Modification of the MacLean–Van Slyke method for the determination of chloride in blood. M. I. HANNA (J. Lab. Clin. Med., 1928, **13**, 651—653).—The diluted oxalated blood (1 part with 7 parts of water) is shaken with 10% sodium tungstate solution (1 part) and 0·66N-sulphuric acid (1 part), and filtered; 10 c.c. of the filtrate are mixed with 10 c.c. of water and 5 c.c. of M/29·35 silver nitrate solution and filtered after 5 min.; 10 c.c. of the filtrate, after addition of 2 c.c. of starch–citrate–nitrite solution, are titrated with M/73·1 potassium iodide solution. CHEMICAL ABSTRACTS.

Determination of plasma-chloride. A. E. OSTERBERG and E. V. SCHMIDT (J. Lab. Clin. Med., 1927, **13**, 172—175).—The plasma (1 c.c.) is slowly mixed with nitric acid (1 : 3) with agitation, so that a white, flocculent precipitate of protein is obtained. N/35·46 silver nitrate solution (5 c.c.) is added, followed by ferric indicator, and the excess of silver titrated with N/35·46 thiocyanate.

CHEMICAL ABSTRACTS.

Iodometric micro-method for the determination of chloride. S. PRIKLADOWIZKY and A. APOLLONOV (Biochem. Z., 1928, **200**, 135—144).—The chloride is precipitated with excess of silver nitrate and the excess determined by titration in acid solution with a standard iodine–iodide solution, using starch as indicator. A table is given from which the chloride is read off. The method is used with 0·1 c.c. of blood or plasma. P. W. CLUTTERBUCK.

Determination of inorganic phosphate in blood-serum. S. L. LEIBOFF (J. Biol. Chem., 1928, **79**, 611—619).—Proteins are removed from blood-serum with trichloroacetic acid; the filtrate is neutralised, re-acidified with acetic acid, and the phosphate precipitated as uranyl phosphate; the washed precipitate is dissolved in 20% trichloroacetic acid, treated with potassium ferrocyanide, and the resulting solution compared colorimetrically with one similarly prepared from a standard phosphate solution. The error of the method is $\pm 2{\cdot}5\%$.

C. R. HARINGTON.

Precipitation of phosphorus as strychnine phosphomolybdate (Embden's method). Micro-determination of the various "forms" of phosphorus in blood and of combined phosphorus in various organic substances. J. Roche (Bull. Soc. Chim. biol., 1928, **10**, 1061—1078).—The solution (3 c.c.) containing phosphate ions (about 0·02—0·15 mg.) is treated with a 16% solution of ammonium molybdate in dilute nitric acid and an equal volume of 1% strychnine nitrate in a centrifuge tube for 40 min. After threefold washing, the precipitate is dissolved in 0·025*N*-sodium hydroxide solution containing phenolphthalein. The boiling solution is then neutralised with hydrochloric acid of similar normality, a slight excess added (0·5 c.c.), and finally titrated again with sodium hydroxide. From these titres the weight of phosphorus may be calculated. Blood is first laked and deproteinised with trichloroacetic acid and the phosphorus determined in the filtrate. This gives the "free" phosphorus; the "acid-soluble" and the total phosphorus figures are obtained by oxidising respectively the above filtrate and the original sample with nitric and sulphuric acids.

G. A. C. Gough.

Determination of blood-bilirubin. L. Jendrassik and A. Czike (Deut. med. Woch., 1928, **54**, 430; Chem. Zentr., 1928, i, 2192).—The serum or plasma (2 c.c.) is mixed with 0·5 c.c. of 50% sodium caffeine benzoate and 1 c.c. of diazo-mixture, followed in 5—10 min. by addition of 6·7 c.c. of 96% alcohol; a standard wedge is used for comparison of the filtrate. A. A. Eldridge.

Determination of cholesterol in blood. D. Acél (Deut. med. Woch., 1928, **54**, 431—433; Chem. Zentr., 1928, i, 2192).—Autenrieth and Funk's method is simplified. A. A. Eldridge.

Alcohol content of blood and organs. I. P. Fraenckel (Deut. Z. ges. gerichtl. Med., 1928, **11**, 129—133; Chem. Zentr., 1928, i, 2102).—Introductory. A. A. Eldridge.

Alcohol content of blood and organs. II. H. W. Nicolai (Deut. Z. ges. gerichtl. Med., 1928, **11**, 134—144; Chem. Zentr., 1928, i, 2102).—The alcohol is heated with a large excess of hydrogen iodide, the ethyl iodide collected in alcoholic silver nitrate solution, and the silver iodide weighed.

A. A. Eldridge.

Determination of the reducing substances in blood. A. Baudouin (Bull. Soc. Chim. biol., 1928, **10**, 977—1049).—A critical survey of the more important methods and their modifications.

G. A. C. Gough.

Determination of lævulose in blood. S. van Creveld (Arch. Néerland. Physiol., 1928, **13**, 521—533).—The colour reaction given by lævulose with diphenylamine and hydrochloric acid has been applied to its determination in blood. B. A. Eagles.

Blood-sugar determination and separation of sugars with yeast. A. L. Raymond and J. G. Blanco (J. Biol. Chem., 1928, **79**, 649—655).—The value of the method of Somogyi (A., 1927, 1214) is confirmed; dextrose is adsorbed quantitatively by yeast from its solution in water or in blood; xylose, ribose, arabinose, galactose, and lactose are not adsorbed from water or blood; lævulose, mannose, and sucrose are partly adsorbed; maltose is not adsorbed from water, but is so to the extent of 40% in presence of blood. C. R. Harington.

Micro-determination of free and protein-sugar in blood-plasma. H. Bierry and A. Voskressensky (Compt. rend. Soc. Biol., 1928, **98**, 744—747; Chem. Zentr., 1928, i, 2635).—The deproteinised blood (5 c.c.) is heated on a water-bath for 6 min. with 2 c.c. of alkaline copper salt and the cuprous oxide determined by the Mohr–Bertrand method.

A. A. Eldridge.

Bunsen valve in blood-urea determinations. F. P. Brooks (J. Lab. Clin. Med., 1928, **13**, 668—670).—The simple Bunsen valve is used instead of Johnson's flutter valve, and paraffin is employed to prevent foaming. Chemical Abstracts.

Catalase, anticatalase, and phylocatalase in animal tissue under various physiological and pathological conditions. I. Determination of catalase in blood. E. Gagarina and W. Jankowski (Zhur. exp. Biol. Med., 1926, 33—51).—Maintenance of diluted blood (1 : 25—1 : 50) for 30 min. at 37° with or without the addition of alcohol does not affect the catalase; catalase action is, however, diminished at a dilution of 1 : 500. The diminution can be prevented by ethyl alcohol even at a dilution of 1 : 50,000. Chemical Abstracts.

Coagulation of fibrin as a process of micellar crystallisation and agglutination. E. Hekma (Biochem. Z., 1928, **199**, 333—365).—A review.

W. McCartney.

Hæmolysis by brilliant-green and serum. E. Ponder (Proc. Roy. Soc., 1928, **B 103**, 556—574).—When red blood-cells are sensitised with brilliant-green, a compound is formed between a protein component of the red-cell membrane and the dye. On the subsequent addition of serum, the serum-proteins react with the combined dye to form a hæmolysin which can react with the protein component of the red-cell membrane and thus bring about lysis. The kinetics of the reaction are discussed.

B. A. Eagles.

Quinine hæmolysis; influence of carbon dioxide. W. Weise (Abhandl. Geb. Auslandskunde, 1928, *D*, 26, ii, 5 pp.; Chem. Zentr., 1928, i, 2185).—Promotion of quinine hæmolysis by carbon dioxide takes place, if at all, only under extreme conditions. Inhibition by small acid concentrations, observed by Rusznyak, holds also for carbon dioxide. The intensity of the hæmolysis depends on the amount of quinine brought into contact with a single blood-corpuscle. A. A. Eldridge.

Hæmolytic action of irradiated ergosterol and cholesterol. R. Fischer (Biochem. Z., 1928, **199**, 294—297).—The substances formed from ergosterol and cholesterol when irradiated by sunlight or by ultra-violet radiation in the presence of oxygen act hæmolytically. W. McCartney.

Halogen content of animal tissues. A. T. Cameron and C. H. A. Walton (Trans. Roy. Soc. Canada, 1928, [iii], **22**, V, 1—11).—Results are given

of the determination by Van Slyke's method of the total chloride content of various tissues of man, cow, rat, and dog. No evidence could be obtained of the presence of chlorine in organic combination.

W. O. KERMACK.

Nuclear substance of liver cells. N. ISHIYAMA (Z. physiol. Chem., 1928, **178**, 217—220).—The cell nuclei of fresh calf's liver had a phosphorus : nitrogen ratio of 1 : 4·81. The nucleic acid was isolated; the ratio in this case was 1 : 1·89. By difference the protein component of the nuclei would contain 12·4% of nitrogen, which does not correspond with protamines or histones. J. H. BIRKINSHAW.

Cadmiophile cells of the lung. J. LECLOUX (Bull. Soc. Chim. biol., 1928, **10**, 1091—1099).—The total thiol-compound content and the number of cadmiophile cells (determined by treatment with formaldehyde and cadium chloride; Faure-Frémiet, A., 1921, ii, 228) in the lungs of guinea-pigs and rats is unaffected by alteration of the sulphur content of the diet or by interperitoneal injection of colloidal sulphur. Whilst the number of cells varies greatly from animal to animal, these differences are not accompanied by corresponding variations in the thiol content. Irritation of the lung with chloroacetone causes an increase in the number of cells.

G. A. C. GOUGH.

Applicability of the Schiff reaction to the determination of thymus-nucleic acid. G. WIDSTROM (Biochem. Z., 1928, **199**, 298—306).—The Schiff reaction can be applied to the colorimetric determination of thymus-nucleic acid in preparations containing nucleic acids but free or almost free from albumin. The method is accurate to within about 2% and the most suitable amount of thymus-nucleic acid for the determination is 0·5—2 mg. The preparation and the thymus-nucleic acid for comparison must be hydrolysed simultaneously for the same length of time, the hydrolysates must be of the same degree of acidity, and an equal, accurately measured quantity of the reagent must be added to each hydrolysate. W. McCARTNEY.

Occurrence and detection of a pigment resembling hæmochromogen in suprarenal glands. A. ROSENBOHM (Z. physiol. Chem., 1928, **178**, 250—252).—The suprarenal glands of freshly-killed pigs, cattle, and white rats showed absorption bands corresponding with hæmochromogen. Oxidation with hydrogen peroxide gave a spectrum resembling that of oxyhæmoglobin.

J. H. BIRKINSHAW.

Distribution of creatine-phosphoric acid in various muscles and organs of the animal organism. D. FERDMANN and O. FEINSCHMIDT (Z. physiol. Chem., 1928, **178**, 173—178).—White muscle of the rabbit and cock contains more creatine-phosphoric acid than red muscle. The creatine-phosphoric acid accounts for about 30% of the total creatine of white muscle; the percentage is much less in the case of red muscle. Creatine-phosphoric acid is also found in smooth muscle and in various organs, but not in the kidney. J. H. BIRKINSHAW.

Creatine-phosphoric acid, creatine, and lactacidogen content of white and red muscles of the guinea-pig. A. PALLADIN and S. EPELBAUM (Z. physiol. Chem., 1928, **178**, 179—185).—White muscle (biceps femoris) of the guinea-pig contains more creatine-phosphoric acid, creatine, and lactacidogen than red muscle (semitendinosus), heart-muscle considerably less. The percentage of creatine bound as phosphagen approaches 30% in white muscle, but is much less in red and heart-muscle.

J. H. BIRKINSHAW.

Biocatalyst content of normal and pathological tissues. H. VON EULER and H. JOHANSSON (Z. physiol. Chem., 1928, **178**, 209—216).—Human placenta is shown to contain considerable amounts of co-zymase. The activity coefficient (c.c. CO_2 per hour/g. dried substance) is about 70. The effect of co-zymase and zymophosphate on methylene-blue reduction and respiration of fresh and washed placental tissue and extract is examined.

J. H. BIRKINSHAW.

Amylase in pyloric cæca of *Sariola quinqueradiatas*. T. OYA and K. HARADA (J. Imp. Fish. Inst. Tokyo, 1926, **2**, No. 1, 28—33).—The optimal p_H of the amylase is p_H 7, and optimal temperature 43°; sodium chloride (0·0125 mol.) accelerated its action, but more than 0·05 mol. retarded it.

CHEMICAL ABSTRACTS.

Biochemistry of *Centrina vulpecula*, Rond. M. KOLLMANN, F. VAN GAVER, and J. TIMON-DAVID (Compt. rend. Soc. Biol., 1928, **98**, 776—777; Chem. Zentr., 1928, i, 2624).—Liver- and ovary-oil, respectively, had iodine value 73·4, 113·9; saponif. value 132·3, 133·7; d^{15} 0·9022, 0·9106; n 1·4689, 1·4744.

A. A. ELDRIDGE.

Thiazine dyes as biological stains. II. Influence of buffered solutions on staining properties. R. HAYNES (Stain Tech., 1928, **3**, 131—139).—The intensity of staining fixed sections with thionine, azures-A, -B, and -C, and methylene-blue increases with increase of p_H. It is uncertain as to whether this effect is due to varying the p_H, to the alteration of the salt content of the solution, or to both. Between p_H 5 and 7 there are always more pronounced metachromatic effects than with either more acid or more alkaline buffer solutions.

H. W. DUDLEY.

Secretion of hydrochloric acid into the stomach. J. R. F. RASSERS (Arch. Néerland. Physiol., 1928, **13**, 514—520).—A "lecithalbumin" obtained from the mucosa of pig's stomach is added to a solution of sodium chloride. As shown by titration, free hydrochloric acid is present in the solution. From this observation it is argued that the lecithalbumin of the stomach mucosa is capable of decomposing sodium chloride; the sodium is adsorbed and free hydrochloric acid is secreted into the stomach.

B. A. EAGLES.

Permeability of cells. XIV. Excretion of sugars by the salivary glands. J. JEANGROS (Biochem. Z., 1928, **200**, 367—378).—Intravenous injection of different concentrations of sugar solutions with simultaneously increased secretion of saliva due to injection of pilocarpine did not cause any of the various sugars used to appear in the saliva, even when the condition of hydræmic plethora was also established by injection of warm physiological

saline. As these sugars appeared in the urine, the permeability of the salivary and renal cells must be regarded as quite different. P. W. CLUTTERBUCK.

Detection of dried saliva on cloth. B. MUELLER (Deut. Z. ges. gerichtl. Med., 1928, **11**, 211—224; Chem. Zentr., 1928, i, 2434).—The test depends on the detection of ptyalin by incubation with toluene and neutral starch solution. A. A. ELDRIDGE.

[Determination of] urinary calcium. C. H. COLLINGS (Chem. News, 1928, **137**, 263—265).—The method described is particularly applicable where calcium oxalate is present, but fails in the rare case where sulphate is in evidence. The urine is acidified with hydrochloric and phosphoric acids, the calcium precipitated as phosphate by adding dilute ammonia, and the precipitate is then converted into oxalate, which is determined by titration with 0·05*N*-potassium permanganate solution. S. COFFEY.

Determination of chloride in urine and blood by conductivity titration. L. BUDAY (Biochem. Z., 1928, **200**, 166—175).—The chloride content of urine, serum, and plasma is determined by conductivity titration with silver nitrate after acidification with dilute nitric acid. With whole blood after hæmolysis and acidification, an increase of conductivity is first observed on adding silver nitrate, accompanied by a shift of p_H. P. W. CLUTTERBUCK.

Volhard–Harvey method for determination of chlorides in urine. W. H. JEFFERY (J. Lab. Clin. Med., 1928, **13**, 687).—The ingestion of one aspirin tablet gives a brownish-violet colour characteristic of the reagents employed. CHEMICAL ABSTRACTS.

Urinary colloids and crystalloids as solvents for uric acid. R. ASCOLI (Biochem. Z., 1928, **200**, 95—107).—By determination of the extent to which addition of urine, dialysed urine, and dialysate to solutions of uric acid which had been supersaturated by warming hindered the precipitation of the acid on cooling, it is shown that normal urine and dialysate but not the dialysed urine have considerable solvent power in respect to uric acid, and this is not directly dependent on the reaction of the urine. It is suggested that this power must be ascribed to the crystalloid substances of the urine. P. W. CLUTTERBUCK.

Pernicious anæmia. IV. Relationship between corpuscular hæmoglobin and chloride contents in the anæmias. A. T. CAMERON and M. E. FOSTER (Canad. Med. Assoc. J., 1928, **18**, 673—677).—In pernicious anæmia the hæmoglobin content of a given volume of red blood-corpuscles is increased and the chloride content decreased. In secondary anæmias the chlorine content is usually high, but the hæmoglobin content variable. In anæmia from *Diphyllobotrium latum* high chlorine and low hæmoglobin values were observed.
CHEMICAL ABSTRACTS.

Blood regeneration in severe anæmia. XII. Influence of ash of apricots, liver, kidney, and pineapple. F. S. ROBSCHEIT-ROBBINS, C. A. ELDEN, W. M. SPERRY, and G. H. WHIPPLE. **XIII. Influence of copper salts.** C. A. ELDEN, W. M. SPERRY, F. S. ROBSCHEIT-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1928, **79**, 563—576, 577—586).—XII. The ash of apricots, when added to the diet of dogs rendered anæmic by hæmorrhage, may cause an increased output of hæmoglobin of as much as 45 g. per 14 days; the ash of pineapple has little effect, whilst that of liver and of kidney is active, although only to about half the extent of the whole organ. Copper and iron are relatively abundant in those ashes which are of therapeutic value.

XIII.—Copper salts have a favourable influence on the regeneration of hæmoglobin in anæmic dogs, but the influence is not so marked as that of iron; combinations of the two metals are usually simply additive in effect. C. R. HARINGTON.

Chlorine content of blood. Distribution in hæmopathological, particularly anæmic, conditions. A. EUGSTER (Z. klin. Med., 1928, **107**, 224—255; Chem. Zentr., 1928, i, 2185).—A fall in the hæmoglobin content is often accompanied by a rise in the chlorine content of the whole blood; the relationship in pathological conditions is considered.
A. A. ELDRIDGE.

Blood-phosphorus in health and disease. III. Alleged value of blood-phosphorus determinations in suspected malignant disease. Blood-phosphorus distribution in anæmia, polycythæmia, and leucæmia. F. B. BYROM and H. D. KAY (Brit. J. Exp. Path., 1928, **9**, 72—81).—Changes in the amount of free phosphate, phosphoric esters hydrolysed or not by phosphatases, lipin-phosphate, and total phosphate are attributable to anæmia, and are not specific for cancer. The blood-lipin-phosphorus is increased in severe obstructive jaundice. In pernicious anæmia and anæmia of nephritis, but not in polycythæmia and simple secondary anæmia, the character and amount of the phosphorus compounds of the cell are changed. Leucocytes are relatively rich in phosphorus compounds; hence in leucæmia blood-phosphorus determinations give irregular results. CHEMICAL ABSTRACTS.

Urine of carcinomatous rats. Y. KIMURA (J. Biochem. Japan, 1928, **8**, 469—494).—The fresh urine is acid; the quantity is approximately proportional to the amount of chlorine excreted. With development of the tumour the total nitrogen, ammonia-nitrogen, and uric acid-nitrogen increase, but the percentages of the two fractions decrease. During active growth the amino-nitrogen diminishes but later increases. The allantoin-nitrogen, neutral sulphur, potassium, sodium, calcium, and magnesium increase. The sulphate varies with the ammonia, and the calcium with the sulphate. It is concluded that the tumour causes an increased splitting of body protein, especially of the nucleated cells; the increased protein cleavage is accompanied by insufficient oxidation. The softening of the tumour leads to a great increase in the salt content of the urine. Simultaneous formation of protein is indicated by the diminished excretion of amino-nitrogen.
CHEMICAL ABSTRACTS.

Mineral metabolism in cœliac disease. S. V. TELFER (Glasgow Med. J., 1928, **38**, 306—313).—The existence of a grossly defective absorption of mineral elements and fats is indicated.
CHEMICAL ABSTRACTS.

Degradation of dextrose and lævulose in normal and experimentally diabetic dog's blood. E. S. TURCATTI (Compt. rend. Soc. Biol., 1928, **98**, 175—176; Chem. Zentr., 1928, i, 2512).—In normal blood, 27·59% glycolysis takes place in 6 hrs.; the action is less marked in diabetic blood. The effect of addition of dextrose and of lævulose was examined.
A. A. ELDRIDGE.

Lactacidogen in experimental pancreas diabetes. M. VON FALKENHAUSEN and H. HIRSCH-KAUFFMANN (Z. ges. exp. Med., 1927, **58**, 567—577; Chem. Zentr., 1928, i, 2420).—Lactacidogen metabolism (of dogs) is not disturbed by experimental pancreas diabetes. A. A. ELDRIDGE.

Carbohydrate changes in epilepsy. C. J. MUNCH-PETERSEN (Compt. rend. Soc. Biol., 1928, **98**, 891—893; Chem. Zentr., 1928, i, 2729).—Glycosuria was sometimes observed with a blood-sugar value which normally does not lead to glycosuria; in other cases expected glycosuria was not observed. A. A. ELDRIDGE.

Plasma-chlorides in obstructive jaundice. I. S. RAVDIN and M. E. MORRISON (Arch. Int. Med., 1928, **42**, 491—499).—A consistent reduction of the plasma-chloride of dogs was found in experimental jaundice after ligature of the common duct and cholecystectomy, but not after either of these operations alone. H. R. ING.

Pancreatic fat necrosis. F. K. HERBERT (Brit. J. Exp. Path., 1928, **9**, 57—63).—Soap is formed in the necrotic areas. More than one type of crystal is observed histochemically; possibly neutral fat, fatty acid, and soaps are all present. Analysis indicates acid hydrolysis of the fat, with little formation of soap. CHEMICAL ABSTRACTS.

Significance of electrolytes for the organism. Parturient paresis in cows. B. SJOLLEMA (Biochem. Z., 1928, **200**, 300—308).—The calcium, inorganic phosphorus, potassium, cholesterol, carbamide, chloride, dextrose, total acetone contents, and the alkaline reserve of the serum of cows in milk-fever, of healthy cows in full lactation or freshly calved, and of young animals are tabulated. The calcium and inorganic phosphorus contents of cows in milk-fever are abnormally low, the potassium content is either normal or high, the carbamide and acetone contents are often somewhat higher than normal, whilst the blood-sugar shows no regular variation. P. W. CLUTTERBUCK.

Creatine metabolism in the brain of pigeons in hunger and in polyneuritis. T. LJUBARSKAJA (Pflüger's Archiv, 1928, **218**, 627—634; Chem. Zentr., 1928, i, 2730—2731).—The spastic form of polyneuritis is associated with a diminution of total nitrogen and an increase of creatine in the brain; the paralytic form is associated with a greater diminution and smaller increase, respectively. In the chronic form and in hunger there is a small increase of creatine, the total nitrogen remaining unchanged.
A. A. ELDRIDGE.

Avitaminosis. X. Formation of acetaldehyde in the muscle of normal vitamin-lacking and fasting pigeons. A. PALLADIN and A. UTEVSKI. **XI. Influence of scurvy and fasting on the chemical composition, especially on the creatine content, of brain.** A. PALLADIN and E. SAVRON (Biochem. Z., 1928, **200**, 108—114, 244—249).—X. Acetaldehyde (4—9 mg./100 g. tissue) is formed during autolysis for 18 hrs. of the muscle (pectoral) of normal pigeons. The amount is decreased during avitaminosis and starvation. When boiled tissue of normal animals is added to that of starving or vitamin-lacking pigeons, the formation of aldehyde rises to normal amounts.

XI. The brain of guinea-pigs contains considerable amounts of creatine, the cerebellum being richer than the hemispheres. During scurvy the cerebellum and hemispheres become richer in water and total nitrogen and poorer in phosphorus, but the creatine content remains constant. P. W. CLUTTERBUCK.

***In vitro* respiration of the tissues of beri-beri pigeons.** M. GUGLER (Biochem. Z., 1928, **200**, 340—350).—The respiration, measured by Barcroft's method, of the breast muscle, before and after aqueous extraction, of 13 normal and 13 beri-beri pigeons and the effect of phosphate buffering and of alterations of the interval between the death of the animal and the determination of the respiration of the muscle are investigated. Washed muscle gave more constant results than the fresh tissue. The oxygen consumption of the tissue of the beri-beri animals is less than that of the washed or fresh tissue of normal pigeons, the reduction being with washed muscle about 25% and with fresh muscle about 10%. With phosphate buffering, the respiration values are higher than with hydrogen carbonate buffering and the difference between the respiration of the tissue of normal and beri-beri animals is greater. Washed muscle, however, respires equally well in both buffer solutions. The oxygen consumption is not strictly proportional to the weight of tissue and, to obtain constant results, the proportion of tissue to total fluid is important. The interval between the death of the animal and the beginning of the respiration experiment causes a decrease of respiration, but this is not proportional to the length of the time interval.
P. W. CLUTTERBUCK.

***In vitro* tissue respiration.** E. SENNHAUSER (Biochem. Z., 1928, **200**, 351—355).—The dinitrobenzene method of Lipschitz and the Barcroft method for the determination of tissue respiration are comparatively investigated. Comparable results are obtained by the two methods with fresh tissue of both healthy and beri-beri animals, but with washed muscle the increase of respiration on adding succinate measured by the dinitrobenzene method is only from the low value of washed up to that of fresh tissue, whereas when determined under the same conditions by the Barcroft method it is increased to 3—5 times that of fresh muscle. P. W. CLUTTERBUCK.

Differentiation between normal and syphilitic sera by means of organic colloids. R. DOURIS and J. BECK (Compt. rend., 1928, **187**, 683—686).—When one volume of 2% sodium oleate (limpid solution at 45°) and one of phosphoric acid (0·23%) are added to one volume of normal serum, the mixture

remains perfectly clear. Use of syphilitic serum gives opalescence within five minutes of mixing.

G. A. C. GOUGH.

Intermediate metabolism of rats infected with trypanosomes. G. SCHEFF (Biochem. Z., 1928, **200**, 309—330).—The disturbance of carbohydrate, protein and fat metabolism, and of the acid–base equilibrium in trypanosomiasis are investigated in rats. The chief substances utilised by trypanosomes are carbohydrate and oxygen. The glycogen reserve is therefore gradually used up and a hypoglycæmia results which adrenaline cannot alleviate. Smaller disturbances of protein metabolism also occur, due partly to protein utilisation by the trypanosomes and partly to secondary disturbance of the liver. The utilisation of part of the available oxygen supply by the infecting organisms and the anæmia resulting from infection lead to deficient oxygen supply and a type of asphyxia. Both this and the metabolic changes result in acidosis. P. W. CLUTTERBUCK.

Amino-acids in blood in tuberculosis. L. HANTSCHMANN and M. STEUBE (Klin. Woch., 1928, **7**, 637—638; Chem. Zentr., 1928, i, 2626).

A. A. ELDRIDGE.

Sulphuric acid reaction in deproteinised uræmic serum. K. MACHOLD (Wien. klin. Woch., 1928, **41**, 447—449; Chem. Zentr., 1928, i, 2636).—In the determination of indicanæmia the filtrate (1 c.c.) of a mixture of the serum with 20% trichloroacetic acid solution (1 : 1) is treated, without mixing, with concentrated sulphuric acid (1 c.c.); a reddish-blue coloration at the interface reaches maximal intensity in 2 min. The colour can be extracted with amyl alcohol or chloroform, but not with ether.

A. A. ELDRIDGE.

Metabolism of mammalian tissues in different media. I. Respiration of explantates of rats' hearts, which had grown in the plasma of normal animals and of animals fed on a diet deficient in vitamin. K. BORNSTEIN (Biochem. Z., 1928, **200**, 176—183).—The respiration of explantates of rat's heart grown in the plasma of animals fed on a diet free from vitamin-*B* was found to be decreased to less than one half of that of explantates of hearts of animals receiving a normal diet.

P. W. CLUTTERBUCK.

Development and metabolism of the kidney. P. GYORGY, W. KELLER, and T. BREHME (Biochem. Z., 1928, **200**, 356—366).—The anaerobic glycolysis ($Q_M^{N_2}$) of the cortical tissue of the kidney both in young and adult animals is small but of the medullary tissue is 4—5 times as great, whilst the reverse is true of the respiration, the value Q_{O_2} for the cortical tissue being 4—5 times as great as for the medullary tissue. Warburg's excess fermentation $2Q_{O_2}$ is thus for cortical tissue negative, as is usual for all normal tissue except the retina, but for the medullary tissue is positive.

P. W. CLUTTERBUCK.

Acid–base relationships in the organism. Observations on a human case after removal of the stomach. P. ASCHMARIN and E. MARTINSON (Biochem. Z., 1928, **199**, 307—325).—A woman from whom the stomach had been removed on account of cancer was fed on 3 diets of which the first contained a moderate excess of acid (30 c.c. of *N*-acid), the second an excess of alkali (75 c.c. of *N*-alkali), and the third a large excess of acid (65 c.c. of *N*-acid). On the first diet a reduced ammonia value (Hasselbalch) was observed. On going over to the alkaline diet the p_H of the urine fell, and whilst on this diet very high values for the urinary acid–base difference were noted. After eating, the carbon dioxide tension of the alveolar air fell. These results are discussed in reference to the lack of normal gastric secretion.

H. W. DUDLEY.

Parallelism between creatinine excretion and basal metabolism. TAKAHIRA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551). CHEMICAL ABSTRACTS.

Availability of disulphide acids in replacing cystine of diet. II. α-Dihydroxy-β-dithiodipropionic acid. Oxidation of disulphide acids in animal organism. B. D. WESTERMAN and W. C. ROSE (J. Biol. Chem., 1928, **79**, 413—421, 423—428).—Dithiodiglycollic acid, β-dithiodipropionic acid, and α-dihydroxy-β-dithiodipropionic acid cannot replace cystine in the diet of growing rats, although all these acids are readily oxidised in the organism of the rabbit. C. R. HARINGTON.

Nitrogen metabolism of chicken embryos. H. TARGONSKI (Bull. Acad. Polonaise, 1927, *B*, 1277—1300).—Analyses have been made on the amniotic and allantoic fluids from the chicken embryo with reference to the variation and distribution of the nitrogenous products of metabolism during development. The nitrogen metabolism of the developing embryo differs from that of the adult bird in the relatively small percentages of uric acid present in these two fluids. During the earlier stages of development the products of nitrogen metabolism accumulate in the amniotic fluid. E. A. LUNT.

Detoxication process in the fœtal organism. M. TAKAHASHI (Z. physiol. Chem., 1928, **178**, 291—293).—The elimination of toxic substances by the embryo of the hen's egg was studied. There was a marked increase of ethereal sulphate in the allantoic liquid with the progress of incubation.

J. H. BIRKINSHAW.

Detoxication process in the fœtal organism. II. Synthesis of ornithuric acid in the incubated hen's egg after injection of benzoic acid. M. TAKAHASHI (Z. physiol. Chem., 1928, **178**, 294—297).—Benzoic acid injected into fresh eggs as sodium benzoate (0·005 g. per egg) is shown to be present as ornithuric acid in the allantoic liquid after 14 days' incubation, all the free benzoic acid having disappeared.

J. H. BIRKINSHAW.

Formation of hexone and purine bases during incubation of the hen's egg. J. SAGARA (Z. physiol. Chem., 1928, **178**, 298—301).—Hens' eggs after 14 days' incubation showed a considerable increase in arginine and particularly in lysine content. Purine bases were also formed.

J. H. BIRKINSHAW.

Variations in metabolism during fast and on resumption of feeding. H. TAKAHIRA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment.,

1927, **15**, 481—504, 524—551).—On resumption of feeding a large amount of nitrogen was fixed.

CHEMICAL ABSTRACTS.

Value of small quantities of whole cow's milk when fed to pigs. A. H. BLISSETT and J. GOLDING (J. Agric. Sci., 1928, **18**, 642—648).—The addition of $\frac{1}{2}$ pint of full-cream milk per day to a complete basal diet for pigs increased the live weight of the animals from 8 to 10%, and decreased the ratio of dry matter consumed to live weight increase. When extracted soya-bean meal was included in the basal ration the effect of the added milk was slightly less marked.

A. G. POLLARD.

Digestibility trials with poultry. IV. Digestibility of certain varieties of oats. V. Digestibility and feeding value of Bulrush millet. VI. Influence of the size of the ration on its digestibility. E. T. HALMAN (J. Agric. Sci., 1928, **18**, 634—641, 766—771).—IV. Feeding experiments with fowls show that Grey Winter oats have a better nutrient value than Black Bountiful or Scotch Potato oats. The preference is associated with the fibre content, the thinner-husked varieties giving the better results.

V. Bulrush millet (*Pennisetum typhoideum*) is a suitable feeding-stuff for poultry.

VI. The digestibility of nutrients is not materially affected by variations in the amount of food supplied.

A. G. POLLARD.

Effect of the degree of polishing of rice on its absorption. SUGIMOTO, HIGUCHI, MOMOYDEA, and TANAKA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551).—None of the constituents is completely eliminated; nitrogen decreases slightly, fat, ash, and fibre decrease considerably, whilst the phosphorus varies. The properties of oryzanin from common and glutinous rice are compared. CHEMICAL ABSTRACTS.

Influence of methods of cooking on the absorption of rice. SUGIMOTO, FUJIMAKI, MOMOYEDA, TANAKA, and YASUDA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551). CHEMICAL ABSTRACTS.

Calorific value of soluble carbohydrates in feeding-stuffs. L. A. ALLEN (J. Agric. Sci., 1928, **18**, 691—701).—Considerable variations exist in the calorific values of carbohydrates of feeding-stuffs, and the values are generally higher than those usually assigned to the simpler carbohydrates of known composition. The values obtained varied from 3800 to 4800 g.-cal. per g. with an average of 4310 g.-cal. The values for crude fibre were also higher.

A. G. POLLARD.

Nutritive value of linseed cake. J. STEWART (J. Agric. Sci., 1928, **18**, 702—703).—The starch equivalent of linseed meal, calculated by means of Wood's curves from the experimental data of one lamb fed on linseed meal only, was in close agreement with Kellner's value. A. G. POLLARD.

Effect of variations in vitamins, protein, fat, and mineral matter in the diet on the growth and mortality of eastern brook trout. C. M. McCAY, F. C. BING, and W. E. DILLEY (Trans. Amer. Fish. Soc., 1927, **57**, 240—250). CHEMICAL ABSTRACTS.

Growth of black-beetles (*Periplaneta orientalis*, L.) and of cockroaches (*Blatella germanica*, L.) on artificial and on incomplete diets. J. ZABINSKI (Acta Biol. Exp., Warsaw, 1928, **2**, 123—163).—The length of the normal development cycle of the black-beetle is 12 months; of the cockroach 3 months. More than one third of this time these animals grow equally rapidly whether on a normal or a "synthetic" diet. Black-beetle larvæ fed on synthetic diets attain only one third of their normal weight at the end of the period usually required for full development, and then die. If, however, they are put on an artificial diet at about one half the growth-period, they are able to attain sexual maturity. Cockroaches are able to pass through the entire growth-cycle on a synthetic diet, even when the only source of nitrogen given is glycine. They exhibit, however, symptoms of avitaminosis, such as matt-surfaced chitin, lack of mobility, small size, and sterility. The rate of growth can be controlled by limiting the nitrogen supply, and both of these animals are able to maintain their weight on a nitrogen-free diet over periods of time equal to those of the entire post-embryonic cycle. As soon as nitrogenous food-stuffs are again given, their development recommences at the point at which it was arrested, and normal adult insects are obtained. These animals cannot maintain life on a purely protein diet. R. TRUSZKOWSKI.

Calcium metabolism with diet rich in vitamin but deficient in mineral constituents. H. ZIMMER (Z. ges. exp. Med., 1927, **58**, 362—369; Chem. Zentr., 1928, i, 2420).—A negative calcium balance was observed; no definite relation between excreted calcium and the urinary C : N coefficient was found.

A. A. ELDRIDGE.

Role of calcium in the nutrition and some biological processes of the animal organism. A. POPOV (Arch. Sci. Biol. Moscow, 1927, **27**, 377—391; Chem. Zentr., 1928, i, 2185).—Guinea-pigs deprived of vitamin-*C* show no disturbance of blood-calcium. Experiments with rats indicate the significance of lipoids in calcium assimilation. Administration (oral or subcutaneous) of calcium chloride in milk did not affect the calcium equilibrium in health. A. A. ELDRIDGE.

Formation of glycogen in the wall of the intestine. K. LANG (Biochem. Z., 1928, **200**, 90—94).—The intestinal wall has the power of synthesising glycogen from dextrose and much less readily from lævulose. In the depancreatised dog, the power is retained, but to a much smaller extent. Insulin assists the synthesis. P. W. CLUTTERBUCK.

Metabolism of hearts of cold-blooded animals. Dextrose utilisation with varying amounts of work. G. EISMAYER and H. QUINCKE (Z. Biol., 1928, **88**, 139—144).—A preparation of the frog's ventricle allows simultaneous determination of the work done and the dextrose consumed. The heart uses dextrose in amount increasing with the time, but the large and unknown amounts of reserve glycogen prevent accurate comparison of metabolism with the output of work. E. BOYLAND.

Sugar metabolism. Lactose, galactose, and xylose. J. G. Blanco (J. Biol. Chem., 1928, **79**, 667—672).—After oral administration to normal rabbits, lactose and galactose failed to appear in the blood, whilst xylose was present for a prolonged period; after subcutaneous injection, lactose caused increase in lactose and a more marked and persistent increase in dextrose of the blood, galactose showed an initially high concentration in the blood which steadily fell and was accompanied by little change in the dextrose, and similar, but less uniform results were obtained with xylose. After intravenous injection of all three sugars a simultaneous increase in the dextrose of the blood was observed.

C. R. Harington.

Coefficient of diffusion of lactic acid through muscle. G. P. Eggleton, P. Eggleton, and A. V. Hill (Proc. Roy. Soc., 1928, **B**, **103**, 620—628).—The coefficient of diffusion of lactic acid through muscle is not independent of the state of fatigue of the muscle. This difference is not due simply to concentration of lactic acid; a muscle after heat rigor with a high concentration of lactic acid shows a higher diffusion constant. It is likely that the change in diffusion constant with fatigue is due to an alteration in the lymph inter-spaces of the tissues.

B. A. Eagles.

Concentration and diffusion of phosphate in muscle. G. Stalla (J. Physiol., 1928, **66**, 19—31).—Inorganic phosphate is able to pass freely by diffusion into or out of a muscle immersed in Ringer's solution containing phosphate. The diffusion constant is the same for a resting or a fatigued muscle and is nearly the same for a muscle in rigor. A hypothesis calling for a change in the permeability to phosphate of the muscle fibres is unnecessary.

B. A. Eagles.

Inorganic phosphate content of resting mammalian muscle. J. Sacks and H. A. Davenport (J. Biol. Chem., 1928, **79**, 493—498).—The muscle of the anæsthetised animal was frozen and minced, and the proteins were removed by treatment with trichloroacetic acid at 0°; the inorganic phosphate in the filtrate was precipitated with magnesia mixture and then determined by the method of Fiske and Subbarrov (A., 1926, 443). By this method the inorganic phosphate content of the resting muscle of various mammals was found to be close to 20 mg. %.

C. R. Harington.

Muscular contraction. I. Lactic acid content. H. A. Davenport, H. K. Davenport, and S. W. Ranson (J. Biol. Chem., 1928, **79**, 499—505).—The lactic acid content of muscles in a state of permanent contraction resulting from tetanus intoxication is not markedly different from that of normal muscles.

C. R. Harington.

Lactic acid formation in muscular contraction. O. Meyerhof (Z. physiol. Chem., 1928, **178**, 306—310).—A comment on the work of Embden and Lehnartz (this vol., 1049).

J. H. Birkinshaw.

Lactic acid formation in muscular contraction. G. Embden and E. Lehnartz (Z. physiol. Chem., 1928, **178**, 311—315).—A reply to Meyerhof (preceding abstract).

J. H. Birkinshaw.

Feeding rats with oils and fats. E. Friedberger and S. Seidenberg (Biochem. Z., 1928, **200**, 289—297).—By feeding growing rats with oats and bread mixed with olive and cod-liver oils, considerable inhibition of growth occurs when compared with rats fed on the same diet but without addition of oil. Lard and butter had a similar but smaller effect.

P. W. Clutterbuck.

Action of formaldehyde on lecithin. Formation of methylated compounds in the organism. W. R. Witanowski (Acta Biol. Exp., Warsaw, 1928, **2**, 61—72).—Further quantities of choline are produced by the action of formaldehyde on commercial lecithin containing kephalin, pointing to the partial conversion of the latter into lecithin by methylation of its free amino-group. This increase in choline content varies from 10 to 53% of the original quantity. The optimum of the reaction lies between 5 and 7. The quantity of additional choline produced does not correspond with the number of free amino-groups present in commercial lecithin, indicating either that the reaction does not proceed to completion or that amino-group-containing impurities other than kephalin are present. The addition of calf-liver extract does not increase the yields of choline obtained.

R. Truszkowski.

Relation of bile acids to food cholesterol. K. Loeffler (Z. physiol. Chem., 1928, **178**, 186—191).—Cholic acid when fed to mice and rabbits along with cholesterol produces a much more marked accumulation of cholesterol in the liver than does deoxycholic acid.

J. H. Birkinshaw.

Origin of bile acids. IV. Researches in dogs with complete bile fistula and reversed Eck fistula. E. Enderlen, S. J. Thannhauser, and M. Jenke (Arch. exp. Path. Pharm., 1928, **135**, 131—136).—The technique previously described (this vol., 788, 789) has been modified. A dog is employed having a reversed Eck fistula as well as a complete bile fistula so that cholesterol injected intravenously passes through the liver and is not immediately taken up by the lung, as is the case when the animal has no reversed Eck fistula. Under these conditions it is found that the production of bile acids is not increased by the administration either of cholesterol or of the oxidation product of cholesterol, but that it is very definitely increased after administration of *allo*-cholesterol. It is suggested that *allo*-cholesterol may be an intermediate product between cholesterol and the bile acids and that this compound may be present in animal tissue.

W. O. Kermack.

Origin of bile acids. V. Is there a relation between breakdown of fatty acids and formation of bile acids? E. Enderlen, S. J. Thannhauser, and A. Distl (Arch. exp. Path. Pharm., 1928, **135**, 137—142).—The administration of triolein intraperitoneally or of oleic acid intravenously to a dog with complete bile fistula does not increase the production of bile acids. There is no decrease in the production of bile acids when the spinal column is sectioned in such a way that the mobilisation of fat from the peripheral depots is inhibited.

W. O. Kermack.

Relation between bile and glycogen formation in rabbit's liver. E. FORSGREN (Skand. Arch. Physiol., 1928, **53**, 137—151; Chem. Zentr., 1928, i, 2422).—A high glycogen content of rabbit's liver is associated with a low content of bile constituents. The function of the liver is periodic, with a glycogen maximum in the morning and minimum later. The results are considered in relation to the general problems of metabolism. A. A. ELDRIDGE.

Effect of alcohol on the absorption of dextrose. II. N. EDKINS and M. M. MURRAY (J. Physiol., 1928, **66**, 102—108).—Alcohol accelerates the rate of absorption of dextrose from the alimentary canal into the blood. B. A. EAGLES.

Action of glucosone on animals. P. T. HERRING and A. HYND (J. Physiol., 1928, **66**, 267—273).—The injection of glucosone produces in mice, white rats, rabbits, guinea-pigs, and cats a train of symptoms which closely resemble, but are not identical with, those which follow the injection of insulin. It is suggested that glucosone arises from the action of insulin on the blood-dextrose. Glucosone may be regarded as an important intermediate substance in carbohydrate metabolism. B. A. EAGLES.

Influence of arsenic on the magnitude of the carbon and oxidation quotients of the urine. L. KOROWITSKY (Biochem. Z., 1928, **199**, 366—376).—Oral or subcutaneous administration of therapeutic or toxic doses of arsenic in inorganic or organic combination usually leads to increase of the carbon and oxidation quotients of the urine, but, exceptionally, in the case of toxic doses the quotients sometimes decrease and in the case of therapeutic doses, sometimes remain unaltered. The alterations in the two quotients generally run parallel. Occasionally, although the administration of arsenic continues, the quotients cease to increase or even fall.

W. MCCARTNEY.

Absorption and excretion of boric acid in man. L. KAHLENBERG and N. BARWASSER (J. Biol. Chem., 1928, **79**, 405—408).—Boric acid can be detected in the urine within 1 min. after immersion of the feet in a saturated solution of the acid at 45°.

C. R. HARINGTON.

Effect of administration of iron on the iron reserve. C. S. WILLIAMSON and P. EWING (Arch. Int. Med., 1928, **42**, 600—606; cf. this vol., 199).—96 young rats were fed on a standard caseinogen diet, and an equal number received a similar diet with addition of ferric citrate. The average hæmoglobin concentration of the latter group after 90 days was still equal to that of the former. Ferric citrate was shown not to increase the iron reserve available for hæmoglobin formation by bleeding both groups at this date, when it was found that the hæmoglobin regeneration after 28 days was approximately equal in the two groups. H. R. ING.

Toxicology of lead and its compounds. VI. P. W. DANCKWORTT and E. JURGENS (Arch. Pharm., 1928, **266**, 492—501).—A study has been made of the distribution of lead in the organs, and particularly the bones of the dog. The bones were dissolved in nitric acid, the solution was evaporated, and the residue ashed. The lead was precipitated as chromate. In this way 2 mg. of lead per 100 g. of bone could be accurately determined. The greater part of the lead was found in the bones, flat bones having a higher content than round bones, but where insufficient time had elapsed for all the lead to be carried to the bones, relatively large amounts were also discovered in the liver, heart, and brain. The lead content of ordinary water has no effect on the life of fish. S. COFFEY.

Fatal case of acute lead poisoning. A. BRUNING and B. KRAFT (Arch. Pharm., 1928, **266**, 501—504).—In cases of lead poisoning chemical examination of the organs is essential. When administered orally, lead is found chiefly in the stomach and intestines. Fühner's method of analysis (A., 1918, ii, 240) was employed. S. COFFEY.

[Detection of chronic lead poisoning.] TIMM (Deut. Z. ges. gerichtl. Med., 1928, **11**, 185—188; Chem. Zentr., 1928, i, 2434).—A spectrographic method of examining the constituents of organs is described. Lead is retained for a long time by the living organism. A. A. ELDRIDGE.

Determination of silver in biological fluids and tissues. [Disappearance of silver from, and reappearance in, the blood of dogs.] E. STERKIN (Biochem. Z., 1928, **199**, 392—398).—Organic matter in the material under investigation is destroyed, any chloride present being removed as hydrogen chloride by nascent hydrogen generated from zinc and acid. The silver is then determined volumetrically by the thiocyanate method. When colloidal silver is administered intravenously to dogs the metal at once disappears from the blood and cannot be detected by analysis except when the dose is sufficient to produce poisoning or death. Silver is then always found in the blood. The time at which the symptoms of poisoning appear always coincides exactly with that at which silver can first be detected. In cases where the animal, although poisoned, does not die, the silver again disappears from the blood.

W. MCCARTNEY.

Detection of uranium and localisation of uranium in the animal organism after uranium poisoning. H. EITEL (Arch. exp. Path. Pharm., 1928, **135**, 188—193).—The tissue is incinerated and the residue is then either treated with nitric acid and the liquid evaporated, or heated with borax to 800—900°. Both these methods restore the fluorescence of the uranium present, which is then observed in ultra-violet light. After fatal poisoning with uranium the metal is present in the kidney cortex but not in the medulla or in any other organ. W. O. KERMACK.

Toxicity of anæsthetics containing bromine and chlorine. G. H. W. LUCAS (J. Pharm. Exp. Ther., 1928, **34**, 223—237).—Experiments on rabbits indicate that the administration of anæsthetics containing bromine is followed by the presence of bromides in the liver, and consequent damage to this and other tissues. Experiments *in vitro* have shown that liver pulp can decompose chloroform and bromoform with liberation of the corresponding halogen ion.

E. A. LUNT.

Micro-chemical detection in urine of some derivatives of barbituric acid. O. EHRISMANN and

G JOACHIMOGLU (Biochem. Z., 1928, **199**, 272—275).—The barbituric acid derivative, extracted from urine in the usual way, is heated electrically at 70—130° for 8—20 hrs. in a micro-sublimation apparatus the temperature in which is automatically controlled to within $\pm$ 2·5°. The sublimates are identified by their appearances, which are quite distinct, but the pure substance is always sublimed at the same time and under the same conditions in the same apparatus. For "veronal," "luminal," and "dial" the lowest amount detectable is 0·5 mg. W. MCCARTNEY.

Mechanism of action of hydrocyanic acid; functional significance of glutathione. I. H. HANDOVSKY (Arch. exp. Path. Pharm., 1928, **135**, 143—154).—In the muscles of rabbits poisoned by hydrocyanic acid there is observed an increase of free glutathione and also of lactic acid. At a later stage the total carbohydrate content is increased, but is finally deceased, the decrease occurring in the glycogen fraction, whilst the lower carbohydrates are increased. The glutathione content of the livers of guinea-pigs shows a seasonal variation. W. O. KERMACK.

Action of histamine on the cholesterol content of the blood of normal and splenectomised dogs. A. TANGL and S. RECHT (Biochem. Z., 1928, **200**, 190—193).—The cholesterol content of the blood of normal dogs on injection of histamine at first rises and then falls to the normal value, whereas that of splenectomised dogs at first falls and then rises to normal values. P. W. CLUTTERBUCK.

Chloride, base, and nitrogen content of gastric juice after histamine stimulation. W. S. POLLAND, A. M. ROBERTS, and A. L. BLOOMFIELD (J. Clin. Invest., 1928, **5**, 611—637).—The titratable acid is increased. CHEMICAL ABSTRACTS.

Effect of sympathetic and parasympathetic poisons on the content of creatine in muscle. H. AKATSUKA (J. Biochem. Japan, 1927, **8**, 57—77).—Formation of creatine is increased by adrenaline and decreased by ergotoxin. Physostigmine accelerates the transformation of creatine into creatinine. Curarised animals are not affected. In homœothermic animals cooling causes over-secretion of adrenaline and an increased creatine content of muscle. In poikilothermic animals the muscle-creatine content is not appreciably influenced. CHEMICAL ABSTRACTS.

Myrtillin. F. M. ALLEN (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1927, **81**, 462).—Myrtillin reduces adrenaline hyperglycæmia and accelerates oxygen consumption after carbohydrate ingestion in normal and diabetic subjects. CHEMICAL ABSTRACTS.

Blood-sugar level in nicotine poisoning. A. I. BURSTEIN and J. D. GOLDENBERG (Biochem. Z, 1928, **200**, 115—125).—Acute nicotine poisoning with small, medium, and large doses is accompanied by increase of blood-sugar occurring in 15—30 min. after injection of nicotine, reaching its maximum in the first hour and decreasing to normal again in 3—3·5 hrs. No decrease of glycolysis could be detected. In chronic nicotine poisoning, no permanent increase in blood-sugar occurred. The increase is conditioned by an accompanying increased secretion of adrenaline. P. W. CLUTTERBUCK.

Digitalis uptake and digitalis action in warm-blooded animals. I. Effective dose of various digitalis glucosides for the heart. H. WEESE (Arch. exp. Path. Pharm., 1928, **135**, 228—244).—The ratio of the glucoside taken up by the heart to that taken up by the rest of the body has been determined in the cases of digitoxin, strophanthin, and scillaren (B) and it appears that the heart takes 4—9% of that circulating in the blood. Digitoxin and strophanthin are not destroyed by blood, but scillaren is hydrolysed by the blood and heart. The mammalian heart can accumulate the same amount of glucoside independent of the concentration and quantity used. The rate of action is a simple linear function of the concentration of the glucoside. W. O. KERMACK.

Intensity of the action of quinine salts in relation to their fluorescence. E. MILANESI (Arch. Farm. sperim., 1928, **46**, 29—32, 33—43).—The exposure of solutions of quinine salts to ultra-violet rays has no effect on the paralysing influence of these solutions towards *Paramœcium* and *Vorticella*. That quinine hydrogen sulphate is more active in this respect than the other quinine salts tested may be due to its more marked fluorescence. T. H. POPE.

Cardiovascular action of tropinonesemicarbazone and tropinone and ψ-pelletierine oximes. R. HAZARD and J. LEVY (Compt. rend., 1928, **187**, 676—678).—Whilst tropinonesemicarbazone possesses an enhanced cardiovascular action similar to that of the parent ketone, the corresponding oxime and that of ψ-pelletierine are devoid of such action. G. A. C. GOUGH.

Action of ultra-violet rays on the migration of pigment from the blood of normal and splenectomised dogs. G. FARKAS and H. TANGL (Biochem. Z., 1928, **200**, 184—189).—Irradiation inhibits excretion of pigment by normal animals. Similar inhibition is obtained in splenectomised animals. P. W. CLUTTERBUCK.

Activator of malt amylase. S. NISHIMURA (Biochem. Z., 1928, **200**, 81—89).—The malt amylase complex does not consist of two enzymes but of one enzyme, amylase, which can attack starch slowly, and an activator which accelerates the liquefaction and hydrolysis of starch. The activator is inactivated at p_H 3·0, but regains its activity at 7·4, and, whilst the enzyme is considerably injured at 70°, the activator is quite stable at that temperature. P. W. CLUTTERBUCK.

Invertase. E. CANALS and (MLLE.) P. GOMBERT (Bull. Soc. chim., 1928, [iv], **43**, 1137—1144).—Invertase, after precipitation with alcohol, contains less magnesium and exhibits diminished activity in neutral or acid solution. The activity is partly restored by the addition of magnesium ions (as sulphate). Dialysed invertase, almost entirely free from electropositive magnesium, contains non-dialysable electronegative magnesium, which migrates with and carries the same kind of charge as the enzyme. Magnesium forms an integral part of the invertase micelle. R. BRIGHTMAN.

Stereochemical specificity of ketone-aldehyde mutase. C. NEUBERG and E. SIMON (Biochem. Z.,

1928, 200, 468—472).—Under the same experimental conditions *Mucor javanicus* converts methylglyoxal into *d*-lactic acid, whilst *M. stolonifer* yields *dl*-lactic acid. P. W. CLUTTERBUCK.

Decomposition of β-hydroxybutyric acid by liver enzymes. I. Preparation and properties of the enzyme. Detection of the products of decomposition. II. Oxidation intensity of the system. J. KÜHNAU (Biochem. Z., 1928, 200, 29—60, 61—80).—I. A method is described for the preparation of an enzyme solution free from protein which can oxidise β-hydroxybutyric acid, the action taking place both aerobically and anaerobically and being activated by methylene-blue without decolorisation occurring. *d*-β-Hydroxybutyric acid is oxidised 3 to 4 times as quickly as the *l*-isomeride. The following oxidation products were detected: aldol, acetoacetic acid, $\alpha\gamma$-butylene glycol, acetaldehyde, succinic, fumaric, and malic acids, and traces of acetic and pyruvic acids. The importance of this work in regard to the possible conversion of fat into carbohydrate is discussed.

II. With the help of Clark's indicator method, the intensity of oxidation at 7 of the enzyme system was determined. Under anaerobic conditions, the reduction–oxidation potential is not constant, but decreases in 10—15 hrs. from r_H 23 to a constant final value of r_H 17·6—17·7, the time taken to attain this value being longer the longer is the contact of the enzyme extract with oxygen before the experiment. The influence of aldol on the oxidation intensity is investigated. Methylene-blue is not reduced by the enzyme–hydroxybutyric acid system, since its potential is lower than that of the enzyme system, but the reduction–oxidation intensity of this dye is responsible for an increase in the oxidation of the acid. P. W. CLUTTERBUCK.

Properties of emulsin prepared twenty-three years ago. M. BRIDEL and (MLLE.) M. DESMAREST (Bull. Soc. Chim. biol., 1928, 10, 1056—1060).—See this vol., 1157.

Enzymic proteolysis. II. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, 200, 152—165).—During peptic digestion of caseinogen the breakdown into large fragments without increase of amino-nitrogen previously observed (this vol., 923) during the early stages of tryptic digestion does not occur. More prolonged hydrolysis does result in breakdown, but the amino-nitrogen appearing is entirely present in the non-colloidal fraction. P. W. CLUTTERBUCK.

Specificity of animal proteases. XIV. Structural requirements of the specific fission of proteolytic substrates. Specificity of trypsin, trypsin-kinase, and intestinal erepsin. E. WALDSCHMIDT-LEITZ, W. KLEIN, and A. SCHAFFNER (Ber., 1928, 61, [*B*], 2092—2096; cf. this vol., 673).—Observations are recorded of the action of trypsin, trypsin-kinase, and intestinal erepsin on benzoylglycylglycine, benzoylalanyldecarboxyleucine, bromo*iso*hexoyl-diglycine and -glycyltyrosine, chloroacetylphenylalanine and -tyrosine, carbethoxyglycyltyrosine, benzoylglycyltyrosine, 2-naphthalenesulphonylglycyltyrosine, -tyrosylglycine, and -tyrosine, phenylalanylarginine, and histidylglycine. The previous hypothesis (*loc. cit.*) that a certain electronegative character of the substrate is necessary for its hydrolysis by trypsin and that a free carboxy-group in the former is necessary for addition of the enzyme is confirmed, particularly by the behaviour of the halogenoacyl compounds which are not attacked by erepsin. It is remarkable that the hydrolytic activity of trypsin is greatly increased after activation of the enzyme by enterokinase, the effect depending probably on a change in the mechanism of the reaction. The hypothesis that dipeptides occupy a peculiar position among proteolytically hydrolysable substrates and that they must be regarded as specific substrates of erepsin whatever is the nature of the amino-acids from which they are derived (*loc. cit.*) cannot be completely maintained, since glutamyltyrosine and phenylalanylarginine are appreciably attacked by pancreatic trypsin. H. WREN.

Influence of bile acids on nuclease action in the intestine and liver. T. OKAMURA (J. Biochem. Japan, 1928, 8, 391—396).

Crystalline urease. III. Variations in Jack bean meal. J. B. SUMNER and R. G. HOLLOWAY (J. Biol. Chem., 1928, 79, 489—492).—Crystalline urease cannot be obtained by the author's method (A., 1926, 1061, 1176) unless the dilute acetone extract of the Jack bean meal contains more than 7 units of the enzyme per c.c.; certain samples of meal have been encountered from which dilute acetone and alcohol fail to extract the enzyme in high concentration, and these are useless for the preparation of the crystalline material. C. R. HARINGTON.

Influence of ions on action of urease. E. M. MYSTKOWSKI (Acta Biol. Exp., Warsaw, 1928, 2, 211—224).—The influence of a number of sodium salts on the action of urease on urea was studied. Where inhibition takes place this is proportional to the concentration of salt added, and inversely proportional to the concentration of urease present. Certain salts which at low concentrations accelerate the action of urease in every case retard its action at higher concentrations. In unbuffered solutions the influence of the salts used, at molecular concentrations, is in the order of intensity acetate>sulphate>iodide>thiocyanate>tartrate>citrate>nitrate>chloride, whilst in buffered solutions the order is acetate>sulphate>iodide>thiocyanate>chloride>nitrate>citrate>tartrate. The influence of fluoride is specific, the inhibition curve obtained by adding increasing concentrations of this salt being of the adsorption type, pointing to the inactivation of urease by adsorption of fluoride on its surface. R. TRUSZKOWSKI.

Action of uricase. Properties of uricase. S. J. PRYZLECKI and R. TRUSZKOWSKI (Compt. rend. Soc. Biol., 1928, 98, 789—790, 790—792; Chem. Zentr., 1928, i, 2725).—It is not possible partly to deactivate uricase. It is inactivated by mercurous chloride, sodium fluoride, and alcohol.

Uricase is an oxidising enzyme, probably with a heavy metal as active agent. Colloidal and active substrates are differentiated. Uricase contains sulphur, nitrogen, and traces of phosphorus; it has

no reducing properties. Solutions give faintly the biuret, Millon, xanthoproteic, and Hopkins tryptophan reactions. A. A. Eldridge.

Preparation of uricase. S. Przylecki (Compt. rend. Soc. Biol., 1928, **98**, 787—788; Chem. Zentr., 1928, i, 2725).—Uricase was obtained from frog's tissue, the liver and kidneys of mammals, and from grain. The preparation from tissue by extraction with glycerol, chloroform, and water, precipitation with alcohol, dissolution of the dried residue in sodium chloride solution, filtration, and treatment with acetone, is described. A. A. Eldridge.

Relation of co-zymase to phosphatase activity. A. L. Raymond (J. Biol. Chem., 1928, **79**, 637—648). —Removal of co-zymase from zymin preparations greatly reduced the capacity of the latter to hydrolyse hexosediphosphate, and, to a smaller extent, its capacity to hydrolyse the hexosemonophosphates of Neuberg (A., 1918, i, 423) and of Robison (A., 1923, i, 86), whilst addition of co-zymase to such washed zymins restored their phosphatase activity. The best preparations of co-zymase were obtained by extraction of fresh yeast with cold water and toluene. C. R. Harington.

Hexosephosphates and alcoholic fermentation. A. L. Raymond and P. A. Levene (J. Biol. Chem., 1928, **79**, 621—635).—The effect on a series of hexosemonophosphates and on dihydroxyacetone monophosphate was observed of a preparation of zymin showing an induction period which was completely abolished by the presence of 0·005*M*-hexosediphosphate. No lowering of the induction time was produced by any synthetic ester except lævulose-α-phosphate, which, as also the esters of Neuberg (A., 1913, i, 423) and Robison (A., 1923, i, 86), decreased the induction period, but to a much smaller extent than the diphosphate. During the induction period the rate of hydrolysis of the esters was greater than the rate of fermentation when sufficient ester was present to abolish the induction, whence it is concluded that the esters are first hydrolysed and the hexose is subsequently fermented; the rates of hydrolysis and fermentation were considerably greater with the natural than with the synthetic esters. Arsenate increased the rate of fermentation of the natural esters but had little effect on the synthetic. C. R. Harington.

Phosphorylation and alcoholic fermentation of sugars. C. Neuberg and M. Kobel (Annalen, 1928, **465**, 272—282).—The rate of evolution of carbon dioxide from sugars fermented with dried yeast or maceration juice in presence of potassium phosphate and traces of magnesium hexosediphosphate and of toluene is compared with that from sodium hexosemonophosphate similarly treated. The curves for dextrose, lævulose, and sucrose are very similar, but the induction period is much longer with the first. The fermentation of the hexosemonophosphate, however, begins only slightly more rapidly, and is soon retarded in such a way that after a few hours it has proceeded to a much smaller extent than has that of the uncombined sugars. These results are obtained with yeasts and sugars of varying sources, and show that a hexosemonophosphate cannot be, at least in its normal stable form, an intermediate compound in the fermentation of sugars (cf. Neuberg, A., 1920, i, 582; Meyerhof and Lohmann, A., 1927, 697; Euler and Myrback, *ibid.*, 794). E. W. Wignall.

Mechanism of alcoholic fermentation. A. Lebedev (Biochem. Z., 1928, **200**, 149—151).—Polemical. P. W. Clutterbuck.

Activator *Z*. IV. Specific accelerator of fermentation by fresh yeast. H. von Euler, E. Brunius, and S. Proffe (Z. physiol. Chem., 1928, **178**, 202—208).—Attempts were made to purify "*Z*," which is contained in boiled yeast juice. In the most successful method, precipitation with mercuric nitrate gave a filtrate with eight times the activity of the original juice (comparing the dry weights). J. H. Birkinshaw.

Specificity of carboxylase. C. Neuberg and F. Weinmann (Biochem. Z., 1928, **200**, 473—476).—Samples of top and bottom yeast which were able to break down pyruvic acid in the normal way were unable to decarboxylate trimethylpyruvic acid. P. W. Clutterbuck.

Proteolytic enzymes from bacteria; influence of p_H on proteolysis. Moycho (Compt. rend., 1928, **187**, 681—683).—Filtrates of cultures of *B. prodigiosus* and *B. pyocyaneus* on peptone water are adjusted to varying p_H values and allowed to act on films of sterile gelatin of corresponding p_H. The intensity of the proteolytic activity is measured by the depth of the gelatin liquefied in a given time. The maximum action takes place at p_H 8 in each case; at p_H 4 the former liquid has a very slight action, whilst the latter is inactive. G. A. C. Gough.

Decomposition of olive oil by micro-organisms; conversion of oleic into ketostearic acid. G. Pigulevski and M. Charik (Biochem. Z., 1928, **200**, 201—210).—A ketostearic acid, m. p. 79—80°, has been isolated. P. W. Clutterbuck.

Growth of *Bacterium radicicola*. S. Snieszko (Bull. Acad. Polonaise, 1928, **B**, 55—74).—*B. radicicola* from kidney bean, red clover, cultivated pea, and hairy vetch does not grow on a synthetic medium of p_H above 7·0 or below 4·5. The hydrogen-ion concentration exerts considerable influence on the morphological changes observed in *B. radicicola*. B. A. Eagles.

Mechanism of cellulose digestion in the ruminant organism. II. Transformation of cellulose into dextrose by the agency of cellulose-splitting bacteria. H. E. Woodman and J. Stewart (J. Agric. Sci., 1928, **18**, 713—723).—A cellulose-splitting organism showing optimum activity at 65° was isolated and is described. Little or no dextrose appeared in the media after the normal fermentation process at 65°, but if the fermentation was checked by the addition of toluene when the organisms were in the most active condition, considerable amounts of dextrose accumulated. It is suggested that the production of dextrose is the result of enzymic activity, masked during normal fermentation by the further utilisation of dextrose by the organism as fast as it is formed. A. G. Pollard.

Sulphate reduction by bacteria, with cellulose fermentation products as source of energy. L. RUBENTSCHIK (Zentr. Bakt. Par., 1928, II, **73**, 483—496; Chem. Zentr., 1928, i, 2266).—In the methane fermentation of cellulose on Omelianski's medium a halophilic (opt. 5—7% of sodium chloride) desulphurising *Microspira* was found. Acetic and butyric acids are sources of energy for the organism, which produces up to 83 mg. of hydrogen sulphide per litre. A. A. ELDRIDGE.

Metabolism and distribution of fermentation-sarcina (*S. ventriculi*, Goodsir, and *S. maxima*, Lindner). J. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 421—432).—The limiting p_H values suitable for the cultivation of *S. ventriculi* and *S. maxima* have been determined (cf. Ned. Tijdschr. Hyg., 1927, **1**, 201; **2**, 210). The values vary with the acid. For hydrochloric acid the minimum p_H is 0·8 for pure cultures, for nitric acid 1·5, lactic acid 2·9, and phosphoric acid 1·45. On the alkaline side the limit is p_H 9·8. *S. maxima* differs from *S. ventriculi* only in the cellulose reaction with iodised zinc chloride, which is negative for the former and positive for the latter, and in the products of fermentation. *S. ventriculi* produces, in such substances as egg-white or yeast water, with a little sugar, besides carbon dioxide and hydrogen, a large quantity of ethyl alcohol with a smaller proportion of acetic acid and sometimes formic and lactic acids. *S. maxima*, on the other hand, gives no ethyl alcohol, but considerable quantities of butyric acid, more lactic acid, and some succinic acid, besides similar quantities of acetic and formic acids. A number of samples of soil, sludge, and sand from different parts of the world, not necessarily from cultivated regions, have been found to contain *S. ventriculi*. It is also found in the stomach, but not when this is healthy. It is most easily cultivated from samples of sand. *S. maxima* appears to be found only in clays in which cereals are grown. The life-history and distribution of the sarcina have been studied. M. S. BURR.

Muller's phenomenon. Distant punctate hæmolysis of blood agar by staphylococci. F. M. BURNET (Austral. J. Exp. Biol., 1928, **5**, 205—212).—The conditions have been investigated which favour the appearance of Muller's phenomenon, that is, the occurrence of discrete regions of hæmolysis in a human blood agar medium on which staphylococcus is grown. Some constituent of blood-serum associated with the globulin is an important factor, only human erythrocytes are effective, whilst the strain of staphylococcus and the type of agar used are also of importance. W. O. KERMACK.

Chemical changes accompanying the growth of tubercle bacilli on Long's synthetic medium. T. B. JOHNSON and A. G. RENFREW (Amer. Rev. Tuberculosis, 1928, **17**, 508—519).—During growth the inorganic ammonia content and the p_H of the medium change, constant values being attained when growth ceases. The sudden change in p_H at the end of 4 weeks' growth is accompanied by the appearance of reducing substances, possibly sugars. CHEMICAL ABSTRACTS.

Chemospecific antigens. I. A. KLOPSTOCK and G. E. SELTER (Z. Immunitatsforsch., 1928, **55**, 118—141; Chem. Zentr., 1928, i, 2267—2268).

Reactions of basic dyes with cyclic derivatives of an acid character. W. C. HOLMES and R. M. HANN (Stain Tech., 1928, **3**, 122—130).—The actual staining agent in the Ziehl–Neelson technique is an additive product of the phenol and the basic dye employed. The following phenol–dye complexes were therefore studied: phenol–rosaniline hydrochloride; resorcinol– and quinol–fuchsin hydrochloride; resorcinol–, quinol–, pyrocatechol–, chloroquinol–, pyrogallol–, and phloroglucinol–crystal-violet hydrochloride; β-naphthol–crystal-violet; resorcinol–methylene-blue hydrochloride. Various *salts* of dyes were prepared: rosaniline phenoxide; crystal-violet picrate (insoluble in water), hydrogen phthalate, α-naphthol-4-sulphonate, and 8-amino-α-naphthol-3:6-disulphonate; methylene-blue salicylate, acetylsalicylate, and *o*-toluate; tetraethylthionine acetylsalicylate; azure-C acetylsalicylate. Some of these compounds may be useful as stains for pathological organisms. H. W. DUDLEY.

Wright's stain as a differential spore stain. L. O. DUTTON (Stain Tech., 1928, **3**, 140—142).—A method of differential spore-staining with Wright's stain diluted 5 times in a phosphate buffer of p_H 7·6 is described. Spores are stained a deep blue, whilst the cytoplasm of the sporangium is stained a pinkish-red. H. W. DUDLEY.

Mechanism of action of adrenaline. I. S. EDLBACHER and J. KRAUS (Z. physiol. Chem., 1928, **178**, 239—249).—Adrenaline was found to catalyse the oxidation of glycine to ammonia and carbon dioxide by oxygen or air. From no other amino-acids tested, with the possible exception of cystine, was ammonia evolved in the same manner. The catalytic action seems to be a specific property of two phenolic hydroxyl groups in the *ortho*-position, since pyrocatechol has the same action as adrenaline, but resorcinol, ephedrine, and ephetonine are inactive; quinol has a slight catalytic effect. J. H. BIRKINSHAW.

Isolation of secretin: chemical and physiological properties. J. MELLANBY (J. Physiol., 1928, **66**, 1—18).—Fresh pig's duodenal mucosa is extracted with absolute alcohol. After removal of the alcohol and fats and soaps the secretin is adsorbed from aqueous solution on precipitated bile acids. This precipitate is dissolved in absolute alcohol. Secretin is precipitated on the addition of acetone and is further purified by dissolution in water and reprecipitation by dilute acetic acid. It is a polypeptide containing phosphorus and is rapidly destroyed by pepsin or trypsin. B. A. EAGLES.

Physiological response of rabbits to insulin. M. SAHYUN and N. R. BLATHERWICK (J. Biol. Chem 1928, **79**, 443—460).—A greater dose of insulin is necessary to produce convulsions in rabbits when it is given intravenously than when given subcutaneously or intraperitoneally, although the onset of convulsions is more rapid in the first case; the difference is ascribed to increased mobilisation of the liver-glycogen after administration of insulin intravenously.

The sensitivity of rabbits towards insulin is increased by previous treatment with adrenaline and by section of the splanchnic nerves, and is diminished by feeding with a diet rich in carbohydrate.

C. R. HARINGTON.

Hormonal sterilisation of female animals with insulin. E. VOGT (Vox medica, 1928, 7, 384—388; Chem. Zentr., 1928, i, 2728).—Treatment of rabbits with insulin affects the fertility. Insulin and the female sexual hormone appear to be closely related.

A. A. ELDRIDGE.

Dihydroxyacetone and insulin hypoglycæmia. P. A. LEVENE and J. G. BLANCO (J. Biol. Chem., 1928, 79, 657—666).—Unimolecular dihydroxyacetone was prepared from the commercial product "oxantin" by distillation under diminished pressure; the substance could be determined in blood by application of the method of Hagedorn and Jensen (A., 1923, ii, 265, 440) after removal of dextrose by adsorption with yeast. Dihydroxyacetone showed a reducing power 1·6 times as great as that of dextrose. Injection of dihydroxyacetone into animals suffering from insulin convulsions generally produces temporary recovery; in all cases of recovery there is increased dextrose, and in most cases increased dihydroxyacetone, in the blood. C. R. HARINGTON.

Influence of insulin on the blood-sugar of animals after removal of the kidneys. H. GNOINSKI (Compt. rend. Soc. Biol., 1928, 98, 785—786; Chem. Zentr., 1928, i, 2728).—Nephrectomised animals behave normally towards insulin. Animals ligatured after section of the ureter showed hyperglycæmia 24 hrs. after injection of insulin.

A. A. ELDRIDGE.

Influence of insulin on the blood- and urine-phosphoric acid. A. BOLLIGER (Z. ges. exp. Med., 1928, 59, 717—723; Chem. Zentr., 1928, i, 2419).—Insulin lowers the phosphate value of the blood, but phosphate changes in the blood and urine are not specific for the hormone. A. A. ELDRIDGE.

Action *in vitro* of insulin and of normal and diabetic dog's muscle on dextrose. T. J. C. COMBES (Compt. rend. Soc. Biol., 1928, 98, 174—175; Chem. Zentr., 1928, i, 2511).—Normal dog's muscle diminishes the rotation of dextrose solutions; diabetic muscle reduces it less or not at all. The rotation is diminished by addition of insulin.

A. A. ELDRIDGE.

Insulin does not increase the fixation of blood-sugar by lymphocytes. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1928, 98, 847—849; Chem. Zentr., 1928, i, 2625).

Effect of internal secretions and temperature on the metabolism of amino-acids and simple sugars by animal cells. W. E. BURGE, A. M. ESTES, G. C. WICKWIRE, and M. WILLIAMS (Proc. Amer. Physiol. Soc.. Amer. J. Physiol., 1927, 81, 468).—Cultures of *Paramœcium* utilised (in diminishing order) dextrose, lævulose, and galactose; the rate of utilisation was increased by insulin or pituitrin, but decreased by thyroxine. The utilisation of amino-acids was slightly increased by adrenaline or thyroxine, but unaffected by insulin or pituitrin.

CHEMICAL ABSTRACTS.

Oxidation-promoting action of thyroxine. K. DRESEL (Klin. Woch., 1928, 7, 504—505; Chem. Zentr., 1928, i, 2184).—Thyroxine, on subcutaneous injection into rats, led to increased hepatic, and particularly renal, oxidation. A. A. ELDRIDGE.

Evaluation of thyroid preparations. J. R. MØRCH (Dansk Tidsskr. Farm., 1928, 2, 281—307).—Determination of the iodine content of thyroid preparations does not afford a satisfactory measure of their therapeutic values, a biological method being necessary. If white mice are dosed with thyroid extract an increased production of carbon dioxide results, and a method for computing the values of the different preparations has been based on this. The mice must be fed on a standard diet, and after 8 days have elapsed the normal amount of carbon dioxide produced by respiration during five successive periods of 24 hrs. each is determined. The subsequent increase in carbon dioxide due to the administration of a daily dose of thyroid extract may require 3 weeks to reach a constant value, hence the comparison must not be made until after the lapse of that time. During the whole of the experimental period the animals should be kept at a temperature of 23°. As the weight of the mice frequently alters during this time, small doses of extract leading to an increase in weight, large doses to the reverse, it is necessary to refer the carbon dioxide production to the same unit. In the former case it has been found that the carbon dioxide production is proportional to the superficial area of the animal (which in the case of mice can be calculated from the formula $A=11{\cdot}36\times\text{weight}^{2/3}$) and in the latter case to its weight. The best results are obtained when the quantity of thyroid extract administered is sufficient to cause an increase in carbon dioxide production not exceeding 35%; it is practicable to distinguish with certainty between the effects of two doses differing by 33%. It is suggested that the values of thyroid preparations should be expressed in terms of a unit, which is defined as that amount of a preparation which, when administered in food to white mice daily for 3 weeks, and calculated per 1000 g. weight of animal, is sufficient to cause a 15% increase in carbon dioxide production. Of other biological methods, the acetonitrile process of Hunt and Seidell gives values proportional to the iodine content of the preparations, and is consequently of little value. The axolotl method of Jensen possibly gives values proportional to the content of therapeutically active substances present, but has not yet been compared with the above method.

H. F. HARWOOD.

Bio-assay of preparations of ovarian follicular hormone. E. P. BUGBEE and A. E. SIMOND (J. Amer. Pharm. Assoc., 1928, 17, 962—966).

Preparation of female sexual hormone from urine, particularly in pregnancy. B. ZONDEK (Klin. Woch., 1928, 7, 485—486; Chem. Zentr., 1928, i, 2184).—Urine is extracted with a lipin solvent, the hot residue from the solvent is treated with alkali, the aqueous solution of the residue is extracted with ether, the ethereal residue dissolved in hot water or dilute acetic acid, and the solution containing the hormone is filtered. A. A. ELDRIDGE.

Female sexual hormone, menoformone. IX. Action on the mammary gland. E. Laqueur, E. Borchardt, E. Dingemanse, and S. E. de Jongh (Deut. med. Woch., 1928, **54**, 465—467; Chem. Zentr., 1928, i, 2184).—A study of menoformone as the hormone of the normal development of the mammary gland. A. A. Eldridge.

Colorimetric determination of vitamin-*A*. B. von Euler and H. von Euler (Svensk Kem. Tidskr., 1928, **40**, 242—244).—Ox blood-serum was extracted with twice its volume of ether and the latter distilled off, when an orange-yellow fatty residue was obtained, from which lipochromes crystallised; 0·14 g. of the residue (from 100 g. of serum) was dissolved in 2·5 c.c. of chloroform, and 0·2 c.c. of this solution was mixed with 2 c.c. of a 30% solution of antimony trichloride in chloroform and determined colorimetrically. It gave 7 Lovibond units.

For carrots, 100 g. of the dried pulp were shaken for 3 hrs. with 300 c.c. of ether and the latter was distilled off, leaving a deep red, fatty residue. On dissolving in carbon disulphide and precipitating with alcohol, crystals of carotin were obtained which gave the Carr–Price reaction with antimony trichloride.

These experiments confirm the view that there is a connexion between the carotinoid content of food-stuffs and the presence of vitamin-*A*. S. J. Gregg.

Vitamin-*A* deficiency and calcification of the renal epithelium. E. C. van Leersum (J. Biol. Chem., 1928, **79**, 461—463).—Rats suffering from deficiency of vitamin-*A* frequently show calcification of the renal tubules; this represents the origin of the urinary calculi found in such animals (this vol., 332). C. R. Harington.

Dietary sterility associated with vitamin-*A* deficiency. B. Sure (J. Agric. Res., 1928, **37**, 87—92).—Rats fed on a diet of skim-milk powder, agar-agar, dextrin, ferric citrate, Harris yeast, and wheat oil developed in the second and third generations a sterility characterised by the reabsorption of the fœtus during gestation. It is concluded that this sterility is associated with vitamin-*A* deficiency. E. A. Lunt.

Biochemical relationships of phenols. II. Effect of quinol on vitamin-*A* content of stored oils. R. C. Huston, H. D. Lightbody, and C. D. Ball, jun. (J. Biol. Chem., 1928, **79**, 507—518).—Small amounts of quinol when added to butter and cod-liver oil act as preservatives of the vitamin-*A* in these materials. C. R. Harington.

Vitamin-*A* content of wheat oil. B. Sure (J. Agric. Res., 1928, **37**, 93—99).—A dose of 0·05 c.c. per rat per day maintains good growth for 10—16 weeks. Vitamin-*A* deficiency is accompanied by inanition. E. A. Lunt.

Vitamin-*A* and -*B* content of the pigeon pea (*Cajanus indicus*). C. O. Miller (J. Agric. Sci., 1928, **18**, 569—573).—Meal prepared from the leaves of the pigeon pea proved a good source of vitamin-*A* for rats. The vitamin-*A* content of the seeds was poor. Both leaves and seeds were valuable sources of vitamin-*B*. A. G. Pollard.

Vitamin content of barley germ (malt dust). A. Schittenhelm and B. Eisler (Z. ges. exp. Med., 1928, **58**, 645—661; Chem. Zentr., 1928, i, 2415).—Vitamins-*A*, -*B*, -*D*, and -*E* were detected. A. A. Eldridge.

Complex nature of vitamin-*B*. I. Evidence for a third factor. C. H. Hunt (J. Biol. Chem., 1928, **79**, 723—731).—Vitamins-B_1 and -B_2 were separated by treatment of a yeast autolysate with fuller's earth, which adsorbed the former; the two fractions supplemented each other in maintaining the growth of rats, but failed to produce so good an effect as an equivalent amount of fresh yeast. The existence of a third factor, which appears to be contained in the yeast residue, is deduced. C. R. Harington.

Antineuritic and antipellagric potency of cow's milk. C. H. Hunt and W. E. Krauss (J. Biol. Chem., 1928, **79**, 733—738).—Milk from winter-fed cows is rich in vitamin-B_2 and poor in vitamin-B_1. C. R. Harington.

Concentration of vitamin-*B*. IV. Concentration and separation of the two components of vitamin-*B*. P. A. Levene (J. Biol. Chem., 1928, **79**, 465—470).—Treatment of yeast extract at p_H 3·0 with silica gel (cf. A., 1926, 760, 1279) causes preferential adsorption of vitamin-B_1; preliminary deaminisation followed by adsorption results in a preparation completely free from vitamin-B_2. C. R. Harington.

Excretion of vitamin-*B* in urine. Sugimoto (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551).—The urine of normal men contains a substance which stimulates the growth of yeast, but the presence of vitamin-*B* is doubtful. Chemical Abstracts.

Avitaminosis. IX. Influence of the character of the food on the blood-sugar curve in experimental scurvy and on the sensitivity of guinea-pigs to insulin. A. Palladin and A. Utewski (Biochem. Z., 1928, **199**, 377—386).—The characteristic changes which take place in the sugar content of the blood of guinea-pigs are the same when the food which the animals receive is free from vitamins-*A*, -*B*, and -*C* as when it is free from vitamin-*C* only. When the animals are scorbutic the reaction of the food they receive does not affect the course of these changes, but alkaline food causes the hyperglycæmia to increase more rapidly than does acid food. When scorbutic guinea-pigs are transferred from one vitamin-free diet to another the change from acid to alkaline food causes a second short period of hyperglycæmia. Guinea-pigs which have received alkaline food are much more sensitive to insulin than those which have received acid food. W. McCartney.

Properties of vitamin-*D*. Saiki and Fujimaki (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551).—Vitamin-*D* is not destroyed by heating at 115° for 1·5 hrs., slightly at 140° for 1·5 hrs., 40—50% destroyed in 45 min. at 150—155°, and almost completely in 1·5 hrs. at 165—170°. It is not destroyed in 1 hr. at −60°, but largely destroyed in 1 hr. at 100° in 0·1*N*-acid or alkali. Chemical Abstracts.

Formation and destruction of vitamin-*D* during irradiation of ergosterol. D. van Stolk, E. Dureuil, and Heudebert (Compt. rend., 1928, **187**, 854—856).—An alcoholic solution of pure ergosterol shows absorption maxima at 2932, 2815, 2700, and 2600 Å. Irradiation by the light of a mercury-vapour lamp from which all radiations shorter than 2550 Å. have been removed shows a very slow formation of the vitamin. Irradiation by the total light of a hydrogen lamp in an atmosphere of nitrogen results in the disappearance of the first three bands, an increase in the intensity of the fourth, the appearance of bands at 2503 and 2405 Å., and the formation of much vitamin-*D*. It is suggested that the destruction of the vitamin is due to oxidation and not to deleterious radiations (cf. Morton, Heilbron, and Kamm, A., 1927, 948). G. A. C. Gough.

Physical and biological properties of irradiated sterols. R. Fabre and H. Simonnet (Bull. Soc. Chim. biol., 1928, **10**, 1100—1110).—Chiefly a discussion of work already published. A 0·01% alcoholic solution of ergosterol after 10—30 min. exposure to the light of a mercury-vapour lamp exhibits maximum absorption at 2825 and 2725 Å.: a pronounced general absorption is observed in the shorter waveband. G. A. C. Gough.

Fractionation of the antirachitic vitamin. E. M. Koch and M. H. Cahan (Proc. Inst. Med. Chicago, 1926, 1—4).—Lecithin, oleic acid, stearic acid, and tyrosine, when irradiated with ultra-violet light, did not, like cholesterol, acquire antirachitic properties. These properties were possessed to an important extent by a yellow, resinous material extracted from the irradiated cholesterol, or from the unsaponifiable fraction of cod-liver oil, with liquid ammonia. Chemical Abstracts.

Vitamin effects produced by steryl phosphates and by sterols from erythrocytes. H. von Euler, B. von Euler, and M. Rydbom (Biochem. Z., 1928, **199**, 276—293).—Diergosteryl phosphate (cf. Euler and Bernton, A., 1927, 1066) irradiated in hydrogen or in air has an antirachitic power as great as that of irradiated ergosterol and it also promotes growth in rats in doses of 0·0002 mg. per day. A sterol, or mixture of sterols, isolated from blood-corpuscles and having physical constants very close to those of cholesterol also exhibited antirachitic power, especially when irradiated. Although this material was repeatedly recrystallised, it probably contained about 1% of ergosterol or of a sterol which can be activated by ultra-violet radiation.

W. McCartney.

Hypervitaminosis by large doses of vitamin-*D*. H. Kreitmair (Münch. med. Woch., 1928, **75**, 637—639; Chem. Zentr., 1928, i, 2626).—Hypervitaminosis, caused by overdosing with vitamin-*D*, is associated with increased metabolism, particularly of calcium.

A. A. Eldridge.

Hydrogen-ion concentration of plant-tissues. VII. Buffers of sunflower stem and root. VIII. Buffers of bean stem and root. S. H. Martin (Protoplasma, 1928, **3**, 273—281, 282—301).—VII. The normal reactions of the sap of mature sunflower stems and roots are buffered by a small amount of inorganic phosphate present in solution in the cell sap.

VIII. The sap exhibited a higher buffer capacity than that due to the inorganic phosphate; the buffer value increased with titration to an arbitrary end-point, usually p_H 6·8. The action of oxalates, malates, and carbon dioxide is considered.

Chemical Abstracts.

Hydrogen-ion concentration of plant-tissues. IX. Improved technique for the range indicator method. C. T. Ingold and J. Small (Protoplasma, 1928, **3**, 458—468).—Standard alcoholic indicators are diluted to an alcohol content not greater than 10% with conductivity water; aqueous indicators are preferred, and a minimal immersion period is employed. The indicators are brought as near as possible to their neutral point.

Chemical Abstracts.

Positive, non-, and negative antagonism of binary mixtures of electrolytes [in their toxic action towards plants]. L. Maume and J. Dulac (Compt. rend., 1928, **187**, 668—670).—Binary mixtures of electrolytes containing a common ion and consisting of two salts in which this ion is dissociated to different degrees show an ionic concentration and a toxicity value towards certain plant roots below that indicated by the mixture law (calcium chloride and magnesium chloride; calcium nitrate and sodium nitrate). Mixtures of salts (ammonium, potassium, and sodium chlorides) of approximately the same dissociation constant follow the mixture law in both respects, whilst salts containing no common ion (potassium sulphate and sodium chloride) give enhanced values owing to the formation of the several types of dissociated and undissociated molecules.

G. A. C. Gough.

Correlation between positive antagonism and absorption by plants. L. Maume and J. Dulac (Compt. rend., 1928, **187**, 769—771; cf. preceding abstract).—When wheat was grown in a series of solutions containing calcium chloride and varying amounts of a second salt (sodium chloride, sodium nitrate, or potassium sulphate) it was found that the second salt had an inhibitory effect on the absorption of calcium by the plants which increased with concentration. R. K. Callow.

Influence of the soil reaction on the ionisable constituents of the tomato as determined by electro-dialysis. E. S. Haber (J. Agric. Res., 1928, **37**, 101—114).—Tomato plants have been grown in soils to which varying amounts of acid or basic ions have been added in the form of lime or hydrochloric acid, and the resulting plants have been analysed by the method of electro-dialysis to determine the effect on the ionisable constituents in the plant ash.

E. A. Lunt.

Carbon dioxide nutrition of the forest. II. D. Feher and G. Sommer (Biochem. Z., 1928, **199**, 253—271; cf. A., 1927, 385).—The production of carbon dioxide by the soil in woods directly affects the amount of this gas in the air of the woods. This production, in its turn, is influenced by such factors as the number and activity of the micro-organisms in the soil, the temperature of the soil and of the

air, the respiration of the trees, the atmospheric conditions, and the physical and chemical condition of the soil. The extent of the influence of these and other factors has been measured.

W. McCartney.

Effect of freezing on the respiration of the apple. D. B. Carrick (Cornell Agric. Exp. Sta. Mem., 1928, No. 110, 1—28).—The speed of autolysis varied directly with the degree of freezing. Apples (Winesap, McIntosh, Baldwin) when frozen for 3 or 6 hrs. after ice formation at −7·5° to −8·5° showed an increased respiration at 0° of 85%, the acceleration gradually declining after several days. Apples frozen sufficiently to kill 80% of the cells excreted at 0° only one third of the normal amount of carbon dioxide. The invasion at 20° of frozen apples by *Penicillium* markedly increased the production of carbon dioxide.

Chemical Abstracts.

Nitrogen metabolism of *Pyrus malus*, L. IV. Effect of sodium nitrate applications on the total nitrogen and its partition products in the leaves, new and one-year branch growth. W. Thomas (Plant Physiol., 1927, 2, 245—271).—During the most rapid absorption of nitrate there is a large increase in total water-soluble and non-protein nitrogen, with concomitant increase in amino-, amide, basic, and residual nitrogen. A larger amount of nitrogen is stored in the autumn, as amide nitrogen and residual nitrogen compounds, chiefly in the one-year branch growth.

Chemical Abstracts.

Nitrogen and carbon nutrition of plants. Bornemann (Fortschr. Landwirts., 1928, **3**, 250—252; Chem. Zentr., 1928, i, 2415).—It is considered that plants are unable to utilise urea directly; the urea increases the activity of soil bacteria which, by producing more carbon dioxide, increase assimilation by the plant.

A. A. Eldridge.

Sachs' method applied to the determination of the migration of [nitrogenous] substances [in plants]. R. Combes (Compt. rend., 1928, **187**, 666—668).—After avoiding the sources of error already indicated by Brown and Escombe (A., 1905, ii, 849) and by Thoday (A., 1913, i, 1425), the method of Sachs is still found to yield untrustworthy results when applied to the migration of nitrogenous substances in green and autumnal leaves. The source of error is unknown.

G. A. C. Gough.

Role of iron in the formation of chlorophyll. T. N. Godnev (Bull. polytech. inst. Ivanovo-Vosniesensk, 1927, No. 10, 87—92).—In the absence of iron, magnesium pyrrole-2-carboxylate is harmful to chlorotic leaves (cf. Deuber, Amer. J. Bot., 1926, **13**, 276).

Chemical Abstracts.

Potassium and sodium in sea-weeds. G. Bertrand and M. Rosenblatt (Bull. Soc. chim., 1928, [iv], **43**, 1133—1137).—See this vol., 1059.

Formation of iodine in *Laminaria*. P. Freundler (Bull. Soc. Chim. biol., 1928, **10**, 1123—1128).—Chiefly a reply to Dangeard (this vol., 562, 1061); it is denied that previous figures are invalidated by errors arising from volatilisation of iodine. The volatile iodine is probably evolved in greatest amount in the spring, whilst in the autumn the amount generated is almost negligible.

G. A. C. Gough.

Iodine content of Cape Cod cranberries. F. W. Morse (J. Biol. Chem., 1928, **79**, 409—411).—Three samples of cranberries from the neighbourhood of Cape Cod had iodine contents of 26—35 parts per billion.

C. R. Harington.

Increase of the iodine content of plants after application of iodine. K. Scharrer and A. Strobel (Angew. Bot., Z. Erforsch. Nutzpflanzen, 1927, 9, No. 2, 187—199; Chem. Zentr., 1928, i, 2442).—Application of iodine (0·25—2·5 kg. per hectare) with sodium nitrate to beet markedly increased the iodine content of roots and leaves. Similar increase was observed with lucerne, clover, false-oat-grass, and fox-tail, and the straw, but not seed, of barley, oats, and peas.

A. A. Eldridge.

Iodine as a biogenic element. XVIII. Liberation of iodine by soils. K. Scharrer and J. Schwaibold (Biochem. Z., 1928, **200**, 258—272; cf. this vol., 787).—Acid mineral soils do, but neutral or alkaline soils do not, liberate iodine from added iodide. Moorland soils do not show iodine liberation because any iodine liberated becomes immediately combined with organic matter. Of mineral soils of the same acidity, loam and clay soils show a higher iodine liberation than sandy soil. The power to liberate iodine is lost by drying at 100° and by sterilising for 3 hrs. at 160°, but is increased by treatment with phenol and aluminium chloride solutions. Iodine liberation occurs only at a p_H below 7 and is generally more pronounced the more acid is the soil and the greater is the content of colloids and iron and manganese compounds.

P. W. Clutterbuck.

Phosphorus distribution in grains. J. E. Webster (J. Agric. Res., 1928, **37**, 123—125).—Analyses were made of the phosphorus distribution of a number of seeds. There appears to be no relation between the total phosphorus content of the seeds and that of any of the fractions, nor could any comparable variation be detected among the different fractions.

E. A. Lunt.

Microchemical detection and change of the organic phosphorus in plants. G. Klein (Planta, 1926, 2, 497—506).—Mandel and Neuberg's method has been adapted to micro-chemical determinations. Changes in the form of phosphorus in seedlings of *Phaseolus multiflorus* and *Zea mays* were studied.

Chemical Abstracts.

Variations of water and dry matter in the leaves of Pima and Acala cotton. R. S. Hawkins (Ariz. Agric. Exp. Sta. Tech. Bull., 1927, **17**, 419—444).—Acala cotton leaves contain more water than Pima. The amount of dry matter increased during the day more rapidly in the latter, but during drought in the former.

Chemical Abstracts.

Metabolism of conifer leaves. J. Doyle and P. Clinch (Proc. Roy. Irish Acad., 1928, **B**, **38**, 116—127).—Peroxidase, sometimes accompanied by an alcohol-soluble inhibitor, has been identified as the sole oxidising enzyme in the leaves of conifers.

Experiments have failed to establish a relationship between the p_H and the water-soluble pentosan fraction of the leaves. E. A. LUNT.

Catalase content of conifer leaves. J. DOYLE and P. CLINCH (Proc. Roy. Irish Acad., 1928, B, **38**, 128—147).—The seasonal variation in the catalase content of conifer leaves is described and appears to be associated with the corresponding variation in starch content. The variations of the initial rate of the catalase activity with temperature, enzyme and substrate concentration have also been determined. E. A. LUNT.

Rice; oxidase. HIGUCHI (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, **15**, 481—504, 524—551).—The catalase was determined as follows: 100 grains were ground and suspended in water (100 c.c.) and the mixture was filtered; 25 c.c. were kept for 1 hr. at 25° after admixture with 10 c.c. of neutral 0·05% hydrogen peroxide solution, and the excess was titrated with permanganate after addition of sulphuric acid. The results for catalase and peroxidase are parallel to those for oxidase. Variations with the quality and origin of the rice are described. CHEMICAL ABSTRACTS.

Composition of tobacco leaves. A. I. SMIRNOV [with M. A. DRBOGLAV and L. S. ERYGIN] (U.S.S.R. State Inst. Tobacco Invest., 1928, Bull. **46**, 1—59).—The variation in tobacco leaves with age has been determined with reference to the following: dry weight, rate of respiration, total carbohydrate, sucrose, maltose, starch, dextrin, invertase, amylase, total nitrogen, protein, nicotine, amide nitrogen, and hydroxy-acid contents. E. A. LUNT.

Enzymes of wheat flour. N. NEUENSCHWANDER (Biochem. Z., 1928, **199**, 445—450).—The flour, alone or in the presence of co-zymase, decolorises methylene-blue very slowly. In the presence of zymophosphate there is even a retardation of the decolorising process. The enzymic activity is enormously increased, however, when an activator (co-zymase) and a hydrogen donator (zymophosphate) are present together and decolorisation proceeds very rapidly. Dry flour when heated for 15 min. at 85° does not lose its enzymic activity. The enzyme content of extracts of flour so treated as well as of untreated flour is very low. The greater the degree of fineness of a flour the greater is its apparent content of oxidising–reducing enzymes. The content also varies in flours of the same degree of fineness but derived from different varieties of wheat. No differences are observed in the oxygen consumptions of flours of different degrees of fineness. In addition, the differences in oxygen consumption by flours from different varieties of wheat do not agree qualitatively with the differences in rate of decolorisation of methylene-blue by these varieties. W. McCARTNEY.

Influence of flour on the reaction of liquid in which it is soaked. S. KOEHLER (Bull. Acad. Polonaise, 1927, B, 951—963).—Flour from rye, wheat, barley, and oats was shaken with solutions of dilute hydrochloric acid or sodium hydroxide of varying hydrogen-ion concentration. At first contact with a slightly acid solution there is an immediate increase in acidity, followed by a lessened acidity at the end of 3 hrs. These changes of acidity indicate the presence of two types of compounds in flour: the more acid ones act immediately on the reaction of the liquid and are readily soluble, the other type of compound slowly decreases the acidity produced by the first type and is sparingly soluble in slightly acid solution. B. A. EAGLES.

Colouring matter of cottonseed hulls. A. H. GILL and H. W. GREENUP (Oil and Fat Ind., 1928, **5**, 288—294).—No colouring matter could be isolated from cottonseed soap stock or foots. The hulls afforded no carotin or xanthophyll and only a negligible amount of gossypol. A resinous or pectin-like *substance*, charring at 320°, approximating to $C_{19}H_{33}O_{21}$, which formed an additive *compound* with copper nitrate, was isolated from the aqueous extract. S. COFFEY.

Gum arabic. L. AMY (Bull. Soc. Chim. biol., 1928, **10**, 1079—1090).—Gum arabic contains a water-insoluble substance which remains as a gel when a solution in cold water is filtered, colloidal arabic acid (partly present as salts), and dialysable acids. The last two constituents are separated by dialysis in the middle chamber of a bath which is divided into three portions by cellophane sheets and contains water in the end chambers. In order to avoid acidification of the arabic acid, an electric current is passed through the bath; strips of copper and platinum serve respectively as anode and cathode. By means of electrometric titration the purified, non-crystalline arabic acid is shown to be a strong monobasic acid, mol. wt. about 1600. The titration curve indicates that it is probably homogeneous. Heating at 100° causes it to develop reducing properties, which are originally absent, and to be partly transformed into an insoluble acid. In the anode chamber of the bath a small amount of a non-reducing acid is found. This acid, which is unstable both to anodic oxidation and to heating at 100°, may be obtained by the addition of sodium carbonate to the anode liquid. G. A. C. GOUGH.

Coarse ultra-filters. H. BECHHOLD and K. SILBEREISEN (Biochem. Z., 1928, **199**, 1—7).—An improvement on a previous method (Bechhold and Gutlohn, A., 1924, ii, 621) for the production of collodion ultra-filters when wide pores are desired consists in using aqueous acetic acid up to 82% concentration as coagulant for the collodion–acetic acid solution. With increasing concentration of coagulant acid the size of the pores increases. J. H. BIRKINSHAW.

Electro-dialysis or electro-osmosis. G. LASCH and J. REITSTÖTTER (Biochem. Z., 1928, **199**, 216—217).—A reply to Reiner (this vol., 543). The full advantages of electro-dialysis are gained only when relatively strong currents are used. J. H. BIRKINSHAW.